Energy transfer in luminescence composite materials based on mesogenic europium (III) complexes and some semiconducting polymers according to quantum-chemical simulation

K A Romanova and Yu G Galyametdinov
Kazan National Research Technological University, 68 Karl Marx Street, Kazan, 420015, Russia

E-mail: ksenuya@mail.ru

Abstract. A TDDFT study of energy transfer processes in luminescence composite materials based on mesogenic europium (III) complexes with substituted β-diketones and Lewis bases and some semiconducting polymers is presented. The calculated energies of the lowest singlet and triplet excited states of ligands and polymers were used to construct the energy level diagrams and indentify the main channels of intramolecular energy transfer. A system of a complex and a polymer, which is most preferable for practical application in optoelectronics, was selected. The simulated data agree well with the experiment.

1. Introduction
Polymer composite materials based on lanthanide (Ln) compounds are widely used in the development of various optoelectronic devices, light-emitting diodes, optical fibers, lasers, light sources, luminescent bio-probes and biomarkers [1-3]. Their popularity can be attributed to the remarkable photophysical properties of Ln(III) complexes: narrow emission bands, long lifetimes of the excited states, significant absorption and Stokes shifts. Emission of Ln(III) occurs due to transitions in the 4f inner shell, which is shielded from the environment by the outer shells. Excitation energy is transferred to the Ln(III) ion through the surrounding ligands, which in turn receive energy from the polymer. Therefore luminescence efficiency of Ln-containing composite materials with semiconducting polymers depends on the mutual relative positions of the excited levels of Ln(III), ligand environment and polymer matrix. Selection of polymers that will provide the most efficient energy transfer to ligands can significantly improve the emission properties of such materials. Specifically europium (III) (Eu(III)) complexes with β-diketones and Lewis base ligands, which define their high absorbency and luminescence intensity, are currently being investigated as components of promising light conversion materials [4, 5].

Mesogenic Ln(III) complexes can potentially exhibit liquid-crystalline properties and orient under the influence of external magnetic and electric fields [6-9]. Such behavior allows significantly expand the areas of their practical application, but requires more careful study. Theoretical simulation makes it much easier to select effective and suitable components for optoelectronic devices. Quantum-chemical methods are one of the main instruments for the study of mesogenic Ln(III) complexes due to the complexity and high cost of their experimental study. In this work, quantum-chemical simulation of the lowest triplet and singlet excited states of mesogenic Eu(III) complexes with substituted β-diketone and
Lewis bases (2,2'-bipyridine, 1,10-phenanthroline) and some semiconducting polymers (figure 1), widely used in optoelectronic devices, was performed.

![Chemical structures of the studied Eu(III) mesogenic complexes and polymers.](image)

**Figure 1.** Chemical structures of the studied Eu(III) mesogenic complexes and polymers.

2. **Computational technique**

Quantum-chemical simulation of equilibrium geometries of Eu(III) complexes and the monomer units of polymers in the ground state was performed on the DFT level with the PBE functional using the Prirodа 06 software [10, 11]. The rL11 relativistic basis set was used for Eu(III) ion and the rL1 basis set for other atoms [12], which are analogues to the cc-pVDZ and cc-pCVDZ double-zeta basis sets of Dunning, respectively [13].

The geometries of the coordination polyhedra of Eu(III) complexes with β-diketones and Lewis bases were adopted from the Cambridge Structural Database [14] and experimental data of X-ray diffraction analyses for similar compound without alkyl substituents [15, 16]. In order to prevent steric hindrances caused by alkyl substitues in β-diketones, the isomer with lowest energy and the crosswise arrangement of ligands was chosen [6-8].

The energies of the lowest triplet and singlet excited states were obtained by the TDDFT method with PBE functional using the Firefly 8.2.0 software [17, 18]. The CIS method was applied for the relaxation of the excited state structures, since TDDFT was unable to localize triplet excitation on each of the ligand in Eu(III) complexes. The scalar relativistic 4f-in-core pseudopotential ECP52MWB with the associated valence basis set was used for Eu(III) ion [19, 20] and 6-31G(d,p) basis set for other atoms. On the basis of the optimized monomer unit geometries, polymer chains with three and five units were constructed, optimized and used for TDDFT study. Excited state calculations for chains with five monomer units showed close values within 0.1÷0.2 eV compared with three units but with much higher computational costs [21].

3. **Results and discussion**

Light absorption and energy transfer processes in luminescence composite materials based on Ln(III) complexes and polymers consist of the following stages. Upon photoexcitation, polymer transfers to the singlet excited state. Then molecule can either deactivate by fluorescence, intersystem crossing to the triplet state or energy transfer process to the resonance excited levels of the Ln(III) complex. The presence of ligands between the polymer and the Ln(III) ion prevents direct excitation of the ion by the
polymer. The absence of the resonance between excited states of polymer and Ln(III) ion due to the large energy gap also excludes the efficient intermolecular transfer between them. Consequently, ligand environment of the Ln(III) starts acting as an “antenna” for Ln(III) and receive excitation energy from the polymer by its singlet or triplet excited states. Then, the excitation energy is transferred in intramolecular process from the ligand to the resonance energy levels of the Ln(III) ion, for example, \(^{3}D_0\) and \(^{3}D_1\) multiplets of the Eu(III). Lewis bases and \(\beta\)-diketones in the studied Eu(III) complexes are also characterized by high molar absorption coefficients and can efficiently pump the central ion on their own. Finally, the Ln(III) ion nonradiatively relaxes to the lowest radiative multiplet and emits a photon, but the back energy transfer to ligand can also occur. Thus, the efficiency of inter- and intramolecular energy transfer processes in polymer composite materials with Ln(III) compounds is determined by the relative position of the excited levels in the emitting Ln(III) ion, in the ligands, and in the polymer. Emission properties of such materials can be controlled by the selection of the polymer and suitable ligands.

In this work, three semiconducting polymers (PFO, PF-DMB, PDFP) were chosen because of the similarity of their structures (anisotropy of geometry, long alkyl substituents) with the studied Eu(III) complexes. Their optimized structures in the ground state are shown in figure 2.

![Figure 2](image_url)

**Figure 2.** Optimized ground-state structures of the studied Eu(III) mesogenic complexes and polymer chains with three monomer units.

The calculated values of the lowest singlet and triplet excited states are given in table 1 and agree well with the experimental data. Optimization of the excited state geometries led to the localization of excitation on a particular ligand and was accompanied by geometry changes in this ligand compared to the ground state. The localization of the excitation on the specific ligand in Eu(III) complexes is indicated by symbol «*» in table 1. Most of the changes related to the bond lengths (~0.2 Å). In the case of \(\text{Bpy}_{17-17}\)-localized excitation the C–H bond in pyridine ring came out of the ligand plane by ~15°. In the case of localization of the triplet excitation on \(\beta\)-diketone \(\text{CPDk}_{5-\text{Tio}}\), close values were obtained for \(\text{Eu(}\text{CPDk}_{5-\text{Tio}}\text{)}_{3}\text{Bpy}_{17-17}\) and \(\text{Eu(}\text{CPDk}_{5-\text{Tio}}\text{)}_{3}\text{Phen}\) complexes (table 1). Therefore, ligand-localized excited states are practically independent of the presence of other ligands in the Ln(III) complex especially in
the case of complexes with a filled coordination sphere without water molecules and other harmonic oscillators.

Table 1. Calculated lowest triplet and singlet excited states (eV) of semiconducting polymers and mesogenic Eu(III) complexes with localization of the triplet excitation on different ligands in comparison with experimental data.

| Complex/polymer                  | Multiplet | $\Delta E_{\text{theor.}}, \text{eV}$ | $\Delta E_{\text{exp.}}, \text{eV}$ |
|----------------------------------|-----------|--------------------------------------|-------------------------------------|
| Eu(CPDk$_{5}$-Tio)$(\text{CPDk}_{5}$-Tio)$_{2}$Bpy$_{17}$-17 | 1         | 3.220                                | -                                   |
|                                  | 3         | 2.315                                | 2.258 [6]                           |
| Eu(CPDk$_{5}$-Tio)$_{3}$Bpy$_{17}$-17* | 1         | 3.547                                | -                                   |
|                                  | 3         | 2.887                                | 2.870 [22]                          |
| Eu(CPDk$_{5}$-Tio)*$(\text{CPDk}_{5}$-Tio)$_{2}$Phen | 1         | 3.171                                | -                                   |
|                                  | 3         | 2.322                                | 2.258 [6]                           |
| Eu(CPDk$_{5}$-Tio)$_{3}$Phen*    | 1         | 3.480                                | -                                   |
|                                  | 3         | 2.659                                | 2.684 [22]                          |
| PFO                             | 1         | 2.993                                | 3.031 [23]                          |
|                                  | 3         | 2.363                                | 2.300 [24]                          |
| PF-DMB                          | 1         | 3.245                                | 3.271                               |
|                                  | 3         | 2.760                                | -                                   |
| PDFP                            | 1         | 3.118                                | 3.115 [25]                          |
|                                  | 3         | 2.610                                | -                                   |

Previously we studied blends based on commonly used poly(N-vinylcarbazole) (PVK) host polymer doped by Eu(III) complex [6]. However, the difference in electron and hole mobility in PVK reduces the efficiency of optoelectronic devices. Therefore, in this work we decided to consider systems of Eu(III) mesogenic complexes with other semiconducting polymers. Despite the fact that PFO polymer is widely used as host material for red phosphorescent compounds [24], its calculated triplet energy level is too low for energy transfer involving Bpy$_{17}$-17 and Phen ligands in the studied Eu(III) complexes (table 1) and too close to the triplet level of CPDk$_{5}$-Tio. Similar triplet levels of the polymer and ligand can increase contribution of energy back transfer from ligand to polymer and emission quenching. However, PF-DMB and PDFP have triplet excited states that are located energetically higher than excited states of CPDk$_{5}$-Tio. Consequently, these polymers can intermolecular transfer excitation energy to $\beta$-diketone and enhance luminescence intensity of the Eu(III) ion. However, polymer PF-DMB has energetically more appropriate and higher positions of the excited levels, which reduces the probability of the energy back transfer. Excited levels of PDFP locate closer to the levels of $\beta$-diketone, which significantly increases the energy losses. Excited states of PFO and PDFP have lower energy than Lewis bases (Phen and Bpy$_{17}$-17) and cannot participate in energy transfer process to these ligands (table 1). Meanwhile PF-DMB can intermolecular transfer excitation energy to Phen from its triplet state.

Two examples of intermolecular energy transfer pathways from the PF-DMB and PDFP excited levels to the ligands in the mesogenic Eu(III) complexes and intramolecular energy transfer from the ligand excited states to the resonance multiplets of Eu(III) are shown in figure 3 in the form of energy level diagrams. Excited levels of Eu(III) were taken from experimental data [26, 27] since the inner 4f shell of the Eu(III) ion slightly interacts with ligand environment.

According to experimental and theoretical studies [4-6], it is established that the energy transfer process to the resonance multiplet levels of Ln(III) occurs mostly from the triplet excited states of the ligands. In the studied complexes the triplet level of $\beta$-diketone is located above the $^3D_0$ level of the Eu(III) ion (figure 3). The energy gap between triplet state of CPDk$_{5}$-Tio and $^3D_0$ level of Eu(III) provides sufficient energy transfer and minimizes contribution of the back transfer. In Eu(CPDk$_{5}$-Tio)$_{3}$Phen the excitation energy is transferred from triplet level of Phen to the $^3D_1$ resonance level of Eu(III). Such position of the triplet level is the most energetically favorable since it provides sufficient energy transfer and minimizes contribution of the back transfer due to the fast nonradiative relaxation $^3D_1 \rightarrow ^3D_0$. In
Eu(CPDk$_{5}$-Tio)$_3$Bpy$_{17-17}$ Lewis base Bpy$_{17-17}$ is in resonance with $^5$D$_2$ multiplet of Eu(III) and energy transfer process includes additional stages of energy transfer between different 5D$_1$ multiplets of the Eu(III) ion or interligand energy transfer in the complex, which reduces the efficiency of the process and luminescence intensity of the complex. Therefore composite material based on Eu(CPDk$_{5}$-Tio)$_3$Phen mesogenic complex and PF-DMB polymer can be considered as a promising system for the experimental study and further application in optoelectronic devices.

![Figure 3](image_url)

Figure 3. Calculated lowest triplet and singlet excited states of the studied polymers and mesogenic Eu(III) complexes with localization of the triplet excitation on different ligands relative to the experimental multiplet levels of Eu(III) ion for the systems: (a) - Eu(CPDk$_{5}$-Tio)$_3$Bpy$_{17-17}$ and PDFP, (b) - Eu(CPDk$_{5}$-Tio)$_3$Phen and PF-DMB.

4. Conclusion

The TD-DFT calculations of the lowest singlet and triplet excited states of mesogenic Eu(III) complexes with substituted β-diketones and Lewis bases and some semiconducting polymers were performed. On the basis of the obtained data, the energy level diagrams were constructed, and the main intramolecular energy transfer pathways were defined. The calculated data agree well with experiment. The efficiency of the intermolecular energy transfer from the excited levels of polymers to the ligands in the Ln(III) complexes was discussed. It was found that in the case of β-diketone- and 2,2'-bipyridine-localized excitations, energy transfers from the triplet levels of the ligands to the $^5$D$_0$ and $^5$D$_2$ levels of Eu(III), respectively, 1,10-phenanthroline-localized triplet state participate in the energy transfer process to the energetically efficient $^5$D$_1$ level of Eu(III). It follows from the simulation results that it is very promising to construct luminescence composite material based on the studied mesogenic Eu(III) complexes and PF-DMB polymer due to more effective intermolecular energy transfer and predictably better emission intensity.

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