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Correlation of Calculated Excited-state Energies and Experimental Quantum Yields of Luminescent Tb(III) *β*-diketonates

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Theoretical calculations employing time-dependent density functional theory (TDDFT) are used to characterize the excited states of Tb(III) *β*-diketonate complexes. Calculated results are compared directly with experimental results that together show a correlation between relative quantum yields and the excited-state energies that depend on the electronic properties of the *p,p′*-substituent group associated with the coordinating N-donor neutral ligand. It is found that changes in the electron donating nature of the neutral ligand structure lead to shifts in the lowest triplet energy level of the complex that consequently change the relative quantum yield. This work provides critical direction for the synthesis of high quantum yield terbium complexes.

Lanthanide-based luminescent materials have been identified as promising candidates for use in organic light-emitting diodes (OLEDs), biological imaging, and sensory devices.[1–10] Considerable research efforts have been devoted to the development of stable lanthanide complexes with high quantum yields for OLED applications by us and others[1,11–16] that have led to uncovering the fundamental processes needed to make OLED based materials functional. What is known is that monochromatic emission of lanthanide complexes is a consequence of f−f transitions that retain a narrow line shape owing to the minimal coupling of the metal center with vibrational components of the coordinated organic ligands. Commonly accepted excitation mechanisms of lanthanide ions involve the population of lanthanide f−f emitting states via energy transfer (ET) from the sensitizer ligand triplet states, which themselves are populated by intersystem crossing (ISC) from the ligand singlet states initially excited by photons or electrons.[7,17–19] However, lacking is the specific guidance for selecting ligand(s) to synthesize lanthanide complexes with more efficient luminescent yields because the role of the electronic structure characteristics of the ligands has not been previously characterized for these systems.

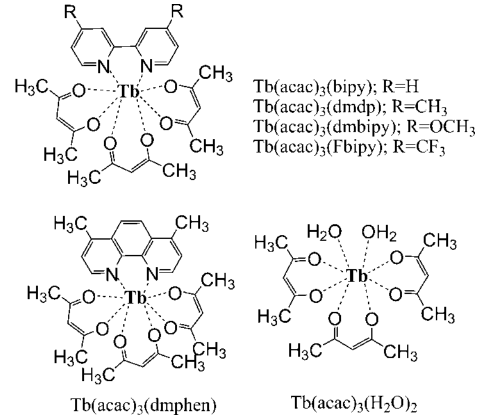

Figure 1. Molecular structures of the Tb(III) *β*-diketonate complexes.

As a means to guide syntheses, theoretical studies can play an essential role in identifying particular metal−ligand candidates with highly desirable luminescent qualities while eliminating those metal−ligand combinations with poor luminescent characteristics. In this work, a theoretical study that probes the singlet and triplet energy levels of Tb(III) *β*-diketonate complexes is carried out using TDDFT from which results are then directly compared with experimental quantum yields. This novel theoretical investigation of the excited electronic structures is based on a systematic series of recently synthesized and experimentally characterized Tb(III) *β*-diketonate complexes possessing desirable luminescent properties. Even though the experimental work has received much attention, the number of theoretical reports considering the spectroscopic properties of such complexes remains, surprisingly, limited.[20–23]

The theoretical work presented here is closely tied to experimental work that together lead to confident predictions of energy transfer efficiency among different lanthanide-ligand systems. Synthesis, purification and characterization of the Tb(III) *β*-diketonate complexes are reported elsewhere in detail.[24] Molecular structures of the Tb(III) *β*-diketonates studied consist of a common *β*-diketonate ligand, 2,4-pentanedione (acac) shown in Figure 1. Central to uncovering the role of the ligands is to alter the substituent group on the *p,p′*-position of the neutral N-donor 2,2′-bipyridine (bipy) ligand, also coordinating the metal center, by using electron donating or withdrawing groups to provide a means of tuning the electronic structure. A phenanthroline type-ligand was chosen while maintaining

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TABLE 1: Experimental and Calculated Bond Distances (Å) of Tb(acac)$_3$(dmdp)

bond label	exp	calc
Tb−O(4)	2.347(5)	2.382
Tb−O(3)	2.314(5)	2.314
Tb−O(2)	2.318(5)	2.341
Tb−O(1)	2.371(5)	2.387
Tb−O(5)	2.386(5)	2.383
Tb−O(6)	2.332(5)	2.387
Tb−N(44)	2.578(5)	2.678
Tb−N(43)	2.557(6)	2.684

similarity of structure of the main bipy ligand. Additionally, O-donor aqua ligands were used to provide a greater contrast as shown below.

All calculations were performed at the level of density functional theory (DFT) using a modified version of the NWChem package developed at the Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory (PNNL).[25] The hybrid B3LYP exchange correlation functional was employed.[26,27] The energy-consistent relativistic effective core potentials (RECPs) developed by the Stuttgart group were used for the Tb(III) center with the optimized valence basis sets supplemented by polarization functions.[28–30] The electrons on the (4s4p4d4f) orbitals were all included in the effective core (large-core RECPs). Standard 6-31G* and 6-311+G* Gaussian basis functions were employed for the C, H, N, F, and O atoms. Geometry optimization of the Tb(III) β-diketonate complexes was carried out without symmetry constraints. The vertical excitation energies and the oscillator strengths at the optimized ground-state geometries were obtained by TDDFT calculations implemented in NWChem 5.0.[31]

The coordination spheres of the DFT-optimized structures are very similar to experimentally determined structures using single crystal X-ray diffraction. The coordination sphere consists of six oxygen atoms (from three negatively charged acac ligands) and two nitrogen or oxygen atoms (from the neutral N-donor or water ligands) forming an octa-coordinated square antiprism geometry. Calculated Tb−O and Tb−N bond distances of Tb(acac)$_3$(dmdp) using the 6-31G* basis set are in good agreement with the experimental bond distances as given in Table 1. The calculated average Tb−O (2.365 Å) and Tb−N (2.568 Å) bond distances change by 0.02 and 0.08 Å from the average experimental values (2.345 and 2.648 Å), respectively. The close agreement of the calculated bond distances using large-core RECPs with the experimental values suggests that the 4f electron participation in Tb−O and Tb−N bonding is negligible as has previously been shown for lanthanide-N/O bonding using model complexes.[32] Our results when compared with the experimental X-ray crystallographic data provide further support that the participation of 4f electrons in the Tb−O/N bonding is negligible.

The energy absorption of the lanthanide complexes occur via the electronic transitions mainly involving coordinated ligand(s).[1,17] All the Tb(III) β-diketonate complexes have strong absorption in the UV region. For example, Tb(acac)$_3$(dmdp) absorbs UV radiation with a $\lambda_{\max}$ of 283 nm as shown in Figure 2. Detailed electronic structures of the Tb-complexes were obtained using TDDFT with the 6−311+G* basis sets and large-core RECPs to explore and identify the ligand(s) responsible for observed absorption characteristics. Figure 2 shows the calculated electronic spectrum of Tb(acac)$_3$(dmdp) with a $\lambda_{\max}$ of 284 nm. The experimental absorption maximum of Tb(acac)$_3$(dmdp) obtained using UV−vis spectroscopy compares well with the calculated vertical exited singlet energy levels applying B3LYP exchange-correlation functional. Comparable results were also obtained among the experimental $\lambda_{\max}$ values of the other complexes [Tb(acac)$_3$(bipy), Tb(acac)$_3$(dmbipy), Tb(acac)$_3$(dmphen), and Tb(acac)$_3$(H$_2$O)$_2$: 284, 280, 267, and 268 nm, respectively] and our calculated values [282, 272, 267, and 261 nm, respectively].

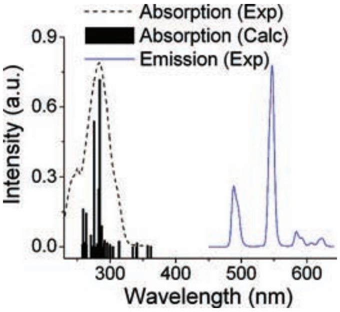

Figure 2. Photophysical studies of Tb(acac)$_3$(dmdp).

To interpret the evolution of the absorption bands, the Kohn−Sham molecular orbitals of Tb(acac)$_3$(dmdp) were analyzed to determine the state-to-state electronic transitions (Supporting Information). The highest occupied molecular orbital (HOMO) mainly involves the acac ligand whereas the lowest unoccupied molecular orbital (LUMO) mainly involves the dmdp ligand. The computational results agree well with the primary features in the UV−vis spectrum, for example, with respect to $\lambda_{\max}$ and spectral line shape. The electronic absorption maximum can be characterized by two primary transitions; (1) a π (HOMO−6) to π^* (LUMO) transition within the dmdp ligand, and (2) a charge transfer-type transition from acac (HOMO−7) ligand to dmdp (LUMO) ligand. Therefore, both acac and dmdp ligands are equally important for the energy absorption. Similar absorption behavior was observed in this work for other Tb(III) β-diketonate complexes with N-donor ligands. In contrast, in Tb(acac)$_3$(H$_2$O)$_2$ the maximum energy absorption occurs via electronic transitions between two acac ligands as evidenced by our computational study, thus, indicating a clear change in the transition mechanism as the ligands are changed to a more electron donating group.

The photoluminescent spectrum of Tb(acac)$_3$(dmdp) is also shown in Figure 2. Upon UV excitation, the complex exhibits vivid green emission both in the solid state and in solution. Four narrow emission peaks, assigned to $^5D_4 \rightarrow {}^7F_n$ (n = 6−3) transitions of Tb(III), are observed, of which the emission originating from the $^5D_4 \rightarrow {}^7F_5$ (547 nm) transition is the strongest.[17] The maximum emission was observed when the complex was excited at its $\lambda_{\max}$ (283 nm). This observation along with the theoretical evaluation of ligand-based excited states show that ligand-to-Tb(III) energy transfer processes are mediated by both acac and dmdp ligands. The experimentally determined relative quantum yields of the complexes are highly influenced by the coordinated N-donor neutral ligand and p,p'-substituent (relative quantum yields of Tb(acac)$_3$(dmphen), Tb(acac)$_3$(dmdp), Tb(acac)$_3$(dmbipy), and Tb(acac)$_3$(H$_2$O)$_2$ are 0.002, 0.035, 0.043, and 0.15, respectively).[24,33,34] Variations in the quantum yields of the above systems are mainly governed by the variations in the ET and ISC sensitization processes. Consequently, a measure of the variations in the quantum yield is provided by the energy differences ΔE_{ET} and ΔE_{ISC} of the Tb(III) β-diketonate complexes as given in Table 2.

The dependence of the luminescent quantum yield of Tb(III) β-diketonate complexes on the triplet state energies (consequently, ΔE_{ET}) is experimentally well documented where a clear

TABLE 2: Calculated B3LYP TDDFT Relative Energy Differences (cm^{-1})

compound	ΔE_{ISC}	ΔE_{ET}
$Tb(acac)_3(bipy)$	187	1829
$Tb(acac)_3(dmdp)$	186	2182
$Tb(acac)_3(dmbipy)$	306	3079
$Tb(acac)_3(Fbipy)$	208	−1786
$Tb(acac)_3(H_2O)_2$	9257	4211
$Tb(acac)_3(dmphen)$	997	1694

correlation is observed between the Tb(III) emitting resonance level $^5D_4$(20400 cm^{-1}) and the lowest triplet state energy of the ligand(s).[35–37] Our calculated ΔE_{ET} values are well correlated with the experimentally observed quantum yields as shown in Figure 3. The relatively low quantum yield of $Tb(acac)_3(dmdp)$ [0.035] compared to that of $Tb(acac)_3(dmbipy)$ [0.043] is due to the relative low ΔE_{ET} value of the former facilitating a back energy transfer from the excited $^5D_4$Tb(III) level to the ligand triplet state. The influence of ΔE_{ET} on the quantum yield is further reflected by comparing structurally similar $Tb(acac)_3(dmphen)$ and $Tb(acac)_3(dmdp)$ complexes. The quantum yield of the former (0.002) is more than ten times lower than that of the latter (0.035) even though the former has a significantly higher ΔE_{ISC} value. The observed low quantum yield of $Tb(acac)_3(dmphen)$ is clearly a result of the low ΔE_{ET} value (1694 cm^{-1}) and is consistent with the fact that experimentally observed quantum yields of Tb(III)-complexes having ΔE_{ET} values below 1850 cm^{-1} dropped dramatically to 0.01 or less due to back energy transfer.[35,36]

The lowest triplet state of the Tb(III) β-diketonate complexes can be mainly described by the transitions involving the HOMO (acac) and LUMO (N-donor neutral ligand) orbitals. By modifying the substituent group on p,p' positions of bipyridine, the lowest triplet energy level of the complex can be fine-tuned leading to a significant change in the ΔE_{ET}values among the complexes. The trend, as determined from our calculations, is that by increasing the electron donating ability of the substituent group present in the coordinated N-donor ligand the lowest triplet state energy of a Tb(III) β-diketonate complex and the ΔE_{ET} value can both be increased. For example, $Tb(acac)_3(dmbipy)$, having electron donating dimethoxy substituted bipyridine, has a relatively higher ΔE_{ET} value compared to that of $Tb(acac)_3(Fbipy)$ with electron withdrawing trifluoromethyl substituted bipyridine. In addition, the energy difference between the lowest ligand singlet and the triplet level (ΔE_{ISC}) also plays a role in energy transfer efficiency. In this context, ΔE_{ISC} should be at least 5000 cm^{-1} to ensure an efficient intersystem crossing.[37,38] Our calculated ΔE $_{ISC}$ values of the $Tb(acac)_3(L)$ [L = N-donor ligands] complexes are less than 5000 cm^{-1}. This observation is consistent with the observed overall low quantum yields of $Tb(acac)_3(L)$ complexes. Finally, $Tb(acac)_3(H_2O)_2$ having relatively higher ΔE_{ICS} (9257 cm^{-1}) and ΔE_{ET} (4211 cm^{-1}) values exhibits the highest relative quantum yield (0.15) among the Tb(III) β-diketonate complexes studied even in the presence of luminescent quenching O−H oscillators.

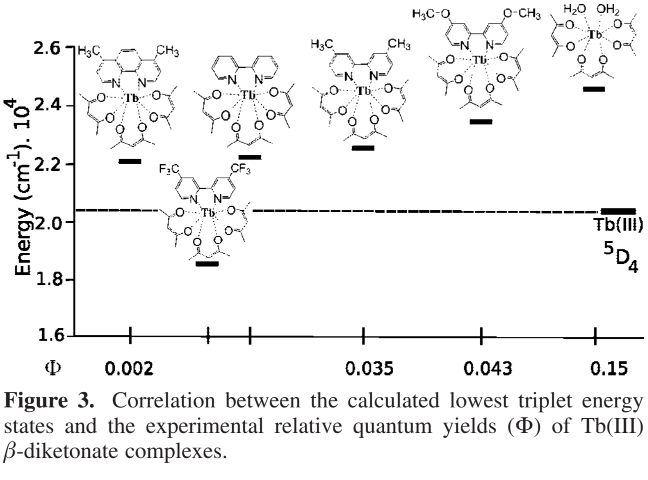

Figure 3. Correlation between the calculated lowest triplet energy states and the experimental relative quantum yields (Φ) of Tb(III) β-diketonate complexes.

In summary, molecular structures and electronic excited-states of a series of Tb(III) β-diketonate complexes were evaluated using DFT and TDDFT level of theory. The calculated bond distances and vertical excitation energies were found to be in good agreement with the experimentally observed X-ray crystal structures and absorption spectra, respectively. A clear correlation between the calculated ΔE_{ET} values and the experimental relative quantum yields was observed where a Tb(III) β-diketonate complex having a relatively higher ΔE_{ET} value exhibited a relatively higher quantum yield. The triplet state energies are highly influenced by the electron donating and withdrawing groups associated with the coordinated N-donor neutral ligand of the complexes. Finally, it is observed that increasing the electron donating ability of the neutral ligand structure increases the ΔE_{ET} value of a Tb(III) β-diketonate complex.

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