

Density-functional study of luminescence in polypyridine ruthenium complexes



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ABSTRACT

A density-functional theory (DFT) study of five ruthenium complexes has been carried out with the goal of gaining deeper insight into factors governing luminescence lifetimes. The five compounds are $[\text{Ru}(\text{bpy})_3]^{2+}$ (**1**), $[\text{Ru}(\text{L1})_2]^{2+}$ (**2**), $[\text{Ru}(\text{tpy})_2]^{2+}$ (**3**), $[\text{Ru}(\text{L1})(\text{tpy})]^{2+}$ (**4**), and $[\text{Ru}(\text{L2})_2]^{2+}$ (**5**), where $\text{bpy} = 2,2'$ -bipyridine, $\text{tpy} = 2,2';6',2''$ -terpyridine, $\text{L1} = 1,1'$ -[2,6-pyridinediylbis(methylene)]bis[3-methylimidazolium] hexafluorophosphate and $\text{L2} = 1,1'$ -[2,6-pyridinediylbis(methylene)]bis[3-methylbenzimidazolium]. Experimental work, including the synthesis and photophysical properties of **5** is also reported in the context of this study. Gas phase geometries optimized using X-ray crystallography geometries as start geometries were found to be close to the start geometries. Gas phase absorption spectra calculated using time-dependent DFT were found to be in good agreement with spectra measured in solution. A partial density of states (PDOS) analysis of the molecular orbitals shows that it is possible to recover a ligand field theory (LFT)-like picture. On the basis of this PDOS-derived LFT-like picture we propose two orbital-based luminescence indices, both motivated by the idea that luminescence quenching results from a low ${}^3\text{MLCT} \rightarrow {}^3\text{MC}$ barrier. The first luminescence index is ΔE , the difference between the e_g^* and lowest energy π^* PDOS bands. The second luminescence index is $d \times \pi$, the product of the amount of π character in the t_{2g} band with the amount of ruthenium d character in the $1\pi^*$ band. These luminescence measures are intended as qualitative rather than quantitative predictors. Low values of ΔE and high values of $d \times \pi$ are shown to correlate with lack of luminescence for the five compounds studied in this paper, while high values of ΔE and low values of $d \times \pi$ correlate well with luminescence.

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1. Introduction

Polypyridine ruthenium complexes have special photophysical properties which make them ideal for use as components in photochemical molecular devices (PMDs) [1], including but by no means limited to dye-sensitized solar cells [2–4]. In an ideal bottom-up molecular electronics approach, ever more elaborate photomolecular devices would be tailor-made to have specific properties designed for specific uses. Of course, it is not that simple since both quantum mechanics and synthesis place their own restrictions [5] on what is currently possible to “engineer.” This paper concerns a particular problem, namely the design of ligands

which would allow the interconnection of ruthenium complexes while still maintaining a long luminescence lifetime. PMD components based upon linking charge-conducting (“molecular wires”) or isolating (“spacers”) chains to bidentate ligands is plagued by the problem of multiple isomers. This is why recent work [6–12] focuses on the synthesis of ruthenium complexes using tridentate ligands, while still attempting to maintain good photophysical properties. Such work [13] could benefit from computational support for testing some of the working hypotheses currently used in ligand design. The computational model should be able (i) to quantitatively reproduce the known X-ray structures and absorption spectra and yet (ii) be interpretable in the ligand field theory (LFT) [14] terminology commonly used by experimentalists working on the problem of PMD ligand design. In this article, we show by explicit calculations on the five compounds shown in Fig. 1 the extent to which density-functional theory (DFT) calculations can meet both of these requirements and hence constitute a valuable part of the PMD ligand designer’s toolbox.

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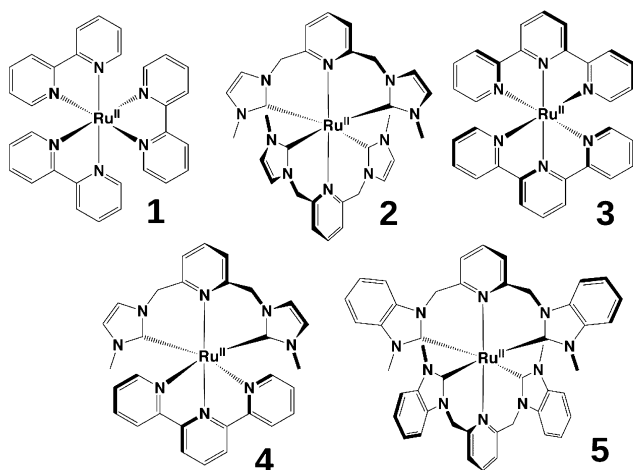


Fig. 1. The five molecules considered in this study: $[\text{Ru}(\text{bpy})_3]^{2+}$ (1), $[\text{Ru}(\text{L}1)_2]^{2+}$ (2), $[\text{Ru}(\text{tpy})_2]^{2+}$ (3), $[\text{Ru}(\text{tpy})(\text{L}1)]^{2+}$ (4), $[\text{Ru}(\text{L}2)_2]^{2+}$ (5), where bpy = 2,2'-bipyridine, tpy = 2,2':6',2''-terpyridine, L1 = 1,1'-[2,6-pyridinediylbis(methylene)]bis[3-methylimidazolium] and L2 = 1,1'-[2,6-pyridinediylbis(methylene)]bis[3-methylbenzimidazolium].

Much of our understanding of luminescence in ruthenium complexes is based upon a long history of studies (see, e.g., Refs. [15–19,6,20,1,21–29]) of the prototypical tris(2,2'-bipyridine)ruthenium(II) cation (compound 1 in Fig. 1), which we shall simply refer to using the common abbreviation $[\text{Ru}(\text{bpy})_3]^{2+}$. The LFT picture which emerges is one of a pseudooctahedral complex with ruthenium-centered filled bonding t_{2g} orbitals and empty antibonding e_g^* orbitals separated by a typically unspecified number of unoccupied ligand π^* orbitals (Fig. 2). This picture has been used and continues to be used as a convenient and serviceable working model for analyzing photophysical properties and designing ligands. However, DFT has proven its value for first-principles quantitative predictions of molecular structure and TD-DFT (TD-DFT, Ref. [30–32] provide recent reviews) has been able to do an excellent job in the quantitative prediction of absorption spectra of ruthenium complexes. As will be seen later in this article, DFT molecular orbitals (MOs) correspond well with the LFT picture of Fig. 2. Assigning the experimental absorption spectrum [33] which shows two broad peaks, one at about $22,500\text{ cm}^{-1}$ and the other at about $35,000\text{ cm}^{-1}$, is much less straightforward as this apparently simple spectral structure hides a number of nearly degenerate ligand-centered (LC) $\pi \rightarrow \pi^*$ and metal-to-ligand charge transfer (MLCT) $d \rightarrow \pi^*$ transitions.

TD-DFT calculations, including spin-orbit coupling, have been performed [27] and analyzed producing the picture shown schematically in Fig. 3. Initial absorption of a photon, possibly followed by radiationless relaxation, leads to a singlet MLCT state ($^1\text{MLCT}$) which rapidly converts through an intersystem-crossing mechanism to the correspondingly energetically slightly lower

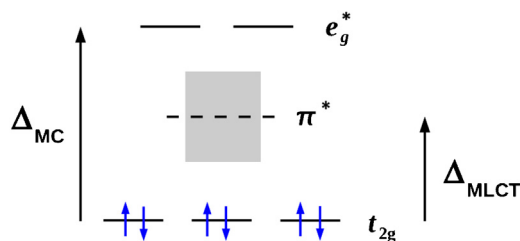


Fig. 2. Generic ligand field theory diagram for octahedral ruthenium(II) polypyridyl complexes. MC refers to metal-centered while MLCT refers to metal-to-ligand charge transfer transitions.

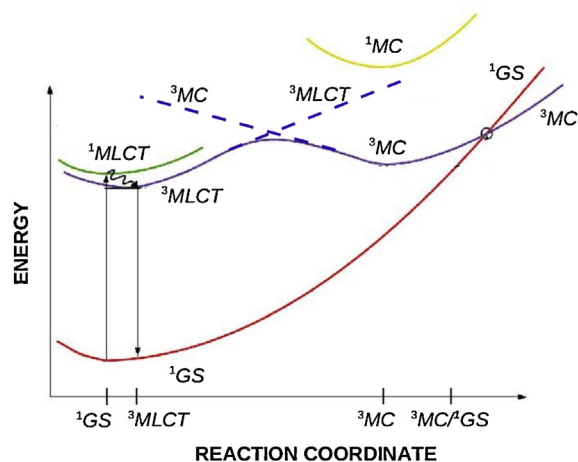


Fig. 3. The diagram shows the principle potential energy curves in our model. The abscissa corresponds roughly to the simultaneous stretching of the Ru–N bonds (breathing mode) while the ordinate represents the state energy. Abbreviations: GS, ground state; MLCT, metal–ligand charge transfer state; MC, metal-centered state. The dashed lines indicate diabatic states whose avoided crossing leads to the energetic barrier on the adiabatic surface between the $^3\text{MLCT}$ and ^3MC minima.

triplet ($^3\text{MLCT}$). Note that spin-orbit coupling due to the presence of ruthenium favors intersystem crossings. The luminescence phenomenon is presumed to be phosphorescence from the $^3\text{MLCT}$ minimum to the singlet ground state (^1GS) since the lifetime is long.

One of the mechanisms for luminescence quenching is provided by nearby electronic states [1,34]. Thus the $^3\text{MLCT}$ undergoes an avoided crossing (shown by the dashed lines in Fig. 3) with the triplet MC (^3MC) $t_{2g} \rightarrow e_g^*$ state whose minimum is at a larger metal–ligand distance than for the $^3\text{MLCT}$ state, leading to the possibility of a reaction barrier for the interconversion,



between the two states. Radiationless relaxation may occur from either the $^3\text{MLCT}$ or ^3MC state, but probably occurs most efficiently from the ^3MC state,



by passing through an intersystem crossing conical intersection to the ground state at still larger metal–ligand distances corresponding to partial ligand dissociation or displacement by the solvent [27]. Simulation of triplet excited state dynamics has been described recently [28] and mixed TD-DFT/surface hopping photo-dynamics simulations of this reaction has also been reported [29].

In contrast to the situation for $[\text{Ru}(\text{bpy})_3]^{2+}$, even a cursory study of the relevant literature shows that working hypotheses for designing new ligands for PMDs rely heavily on the LFT model [35]. This is in part because, while the above-mentioned state-of-the-art calculations are indeed impressive and illuminating, they are too long and costly in computing resources to be useful for PMD ligand design. This is especially true when going to larger ligands with less symmetry. Not only would the calculations be still longer and more costly to perform, especially for routine screening purposes, but there is another problem. This is an interpretational problem due to the fact that the antibonding ruthenium e_g^* orbital is now mixing with an increasingly dense manifold of ligand orbitals, potentially losing all contact with the traditional LFT language. We are thus left with the somewhat unfortunate situation that the working hypotheses are rarely validated by actual MO calculations.

The results indicated in this paper show that appropriate use of TD-DFT may indeed be used to validate working hypotheses and hence have potential value in PMD ligand design. In the results

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