

Teaching Inorganic Photophysics and Photochemistry with Three Ruthenium(II) Polypyridyl Complexes: A Computer-Based Exercise

Claudio Garino,[†] Alessio Terenzi,^{‡,§} Giampaolo Barone,[‡] and Luca Salassa^{*,||}

[†]Department of Chemistry and NIS Centre of Excellence, University of Turin, via P. Giuria 7, 10125 Turin, Italy

[‡]Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Università di Palermo, Viale delle Scienze, Edificio 17, 90128 Palermo, Italy

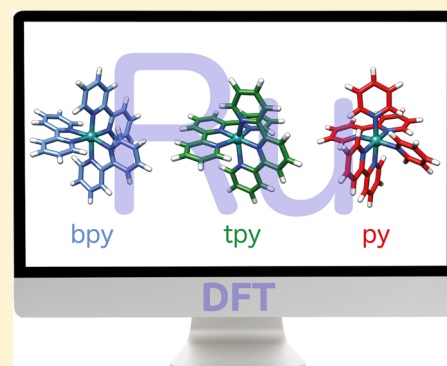
[§]Institute of Inorganic Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria

^{||}CIC biomaGUNE, Paseo de Miramón 182, 20009, Donostia, Spain

Supporting Information

ABSTRACT: Among computational methods, DFT (density functional theory) and TD-DFT (time-dependent DFT) are widely used in research to describe, *inter alia*, the optical properties of transition metal complexes. Inorganic/physical chemistry courses for undergraduate students treat such methods, but quite often only from the theoretical point of view. In the calculation exercise herein described, students are guided step by step through the computational study of the photophysics and photochemistry of polypyridyl Ru(II) d⁶-metal complexes. In particular, by means of DFT and TD-DFT calculations, they are asked to examine and interpret a set of experimental data describing the absorption, emission, and photochemical behavior of three structurally related ruthenium complexes, namely, [Ru(bpy)₃]²⁺ (1), [Ru(tpy)₂]²⁺ (2), and [Ru(bpy)₂(py)₂]²⁺ (3). These complexes are particularly suitable for an educational purpose since they exhibit distinct optical and photochemical properties despite being structurally akin to each other. In the computational chemistry laboratory, the instructor progressively guides students through the preparation of DFT and TD-DFT inputs and the use of software for the analysis of output files, including visualization of optimized geometries, absorption spectra, orbitals, and spin density surfaces. The exercise covers training of students in several key concepts concerning the photophysics and photochemistry of transition metal complexes. These include Franck–Condon transitions and the role of ³MLCT (metal-to-ligand charge transfer) and ³MC (metal-centered or ligand-field) states in luminescence and ligand photodissociation processes. Notably, the mixed character of this exercise allows its integration with theoretical and experimental activities and the design of truly multidisciplinary courses.

KEYWORDS: Upper-Division Undergraduate, Graduate Education/Research, Continuing Education, Inorganic Chemistry, Laboratory Instruction, Physical Chemistry, Calculator-Based Learning, Hands-On Learning/Manipulatives, Photochemistry, Coordination Compounds



INTRODUCTION

The study of the photophysical and photochemical properties of transition metal complexes is pivotal for training undergraduate students in inorganic and physical chemistry. In fact, we base a great variety of new applications on the excited-state chemistry of metal complexes, especially compounds bearing polypyridyl ligands. Among these, Ru(II) complexes have been intensively studied for use in photoredox catalysis,¹ as caging scaffolds for the light-controlled release of neurotransmitters in neurons,² and as effective photoactivatable anticancer prodrugs.³ Such promising advances have been fostered by continuous improvements in the understanding of their excited state dynamics. Ultrafast time-resolved techniques have been fundamental for such evolution, including X-ray based methods, which now capture molecular movies of transition metal complexes in the excited state by portraying their atomic motions.^{4,5}

Likewise, computational methods, in particular those based on density functional theory (DFT), had a strong impact in the study of the optical features of transition metal complexes. They have been employed to characterize absorption and emission properties,⁶ to improve light-induced electron transfer from metal-based dyes to semiconductor materials in dye-sensitized solar cells,⁷ and also to explain photochemical transformation in a range of derivatives.⁸

DFT^{9,10} and TD-DFT (time-dependent DFT)¹¹ are by far the most used methods in the case of systems containing transition metals, as they provide accurate descriptions of several ground- and excited-state properties at a reasonable computational cost.

These computational approaches are widely adopted in research, however their educational use is often limited. Instead, exposing students to DFT and its practical application to

photophysics and photochemistry can provide meaningful learning experiences, such as gaining first-hand knowledge on electronic spectroscopy and chemical reactivity, and visualize abstract concepts or short-lived molecular species (e.g., molecular events and chemical entities), which typically remain elusive for the majority of students. Several articles in this journal have applied similar approaches for teaching various aspects of the chemistry of transition metal complexes.^{12–14} Furthermore, computational chemistry is a powerful tool for students to interpret experimental data they collect in laboratory experiences, and simultaneously train them to handle computer-based research, nowadays a mandatory approach in many fields and work environments.

Herein, we describe a computer-based exercise specifically designed to introduce students to the use of computational methods in coordination chemistry, and particularly in the study of the photophysics and photochemistry of polypyridyl d⁶-ruthenium complexes.

The exercise was carried out at the Chemistry Department of the University of Palermo (Italy) in the framework of an undergraduate course of 25 students on the photochemistry of transition metal complexes. After lecture-only classes, (second and third year) students with no direct experience in computational chemistry and photochemistry were involved in practical sessions, where DFT and TD-DFT calculations were employed to determine key excited-state features of prototypical Ru(II) polypyridyl complexes.

The exercise is derived from state-of-the-art research approaches and aims at stimulating active learning by encouraging students to acquire and analyze their own data, generate hypotheses, and discuss (and present) results with peers and the instructor.

THE PROBLEM TO TACKLE

Three structurally related ruthenium(II) complexes (Figure 1), namely, [Ru(bpy)₃]²⁺ (1), [Ru(tpy)₂]²⁺ (2), and [Ru(bpy)₂(py)₂]²⁺

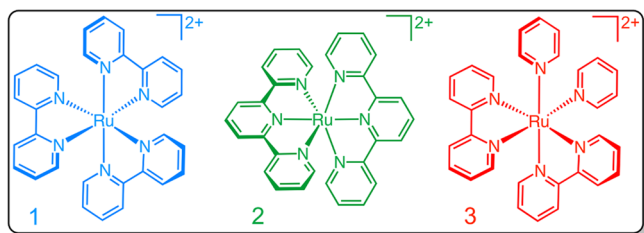


Figure 1. Schematic representation of complexes 1–3.

(3) (bpy = 2,2'-bipyridine, tpy = 2,2':6',2''-terpyridine, py = pyridine), were selected since they display dramatically different excited-state features despite their structures differing only in how the six pyridyl ligands surrounding the Ru²⁺ ion are connected to each other. Complexes 1–3 were specifically chosen among a myriad of derivatives studied in the past few decades because they well exemplify the photophysical and photochemical features of group VIII derivatives, on which still nowadays cutting-edge applications rely.

As summarized in Figure 2 and Table 1, complex 1 emits with a relatively good quantum yield at ca. 620 nm upon excitation of its metal-to-ligand charge transfer (MLCT) band.¹⁵ On the contrary, 2 is a very poor emitter, and radiative decay is observed only at 77 K,¹⁶ whereas 3 is not emissive and undergoes

photodissociation of one pyridyl ligand upon light excitation at room temperature.¹⁷

For the three ruthenium complexes (1–3), students were provided with a set of experimental data retrieved from the literature, including X-ray structures,^{18–20} absorption and emission spectra, emission quantum yield and lifetimes, and photostability data.^{15–17,21}

Using DFT as a tool, students were asked to interpret such experimental results,²² visualizing electronic transitions and specific excited-state geometries and electronic distributions.

As final assignment, students reported and discussed results of their work in a short scientific-like paper (maximum 3 paper sheets), which included introduction, results and discussion, and conclusions.

PRACTICAL IMPLEMENTATION

Under the guidance of the instructor, students prepared input files and ran selected DFT and TD-DFT calculations. Since they had insufficient background in DFT and computational chemistry, the instructor used complex 1 as a model to guide them in the preparation of the various Gaussian 09²⁵ input files needed for the exercise. Precisely, inputs for geometry optimizations and excitation energy (singlet–singlet) calculations of 1 were created step by step by the instructor and projected on-screen, allowing students to be acquainted with the methodology and software. A similar approach was used for visualizing output files, plotting orbital and spin density surfaces, and analyzing the TD-DFT results with the support of the program GaussSum 2.25.²⁶ Calculations on complexes 2 and 3 were then prepared, run, and analyzed independently by students. Details on the computational methodology and step-by-step description of the procedure adopted for 1 are reported in Computational Methodology and the Supporting Information.

All programs were previously installed on computers used by students. Each single calculation was submitted and run only until the first SCF (Self Consistent Field) cycle started in order to verify the correctness of the input file and reduce dead time while keeping students involved. Output and checkpoint files were afterward provided to students for analysis of results.

The instructor asked milestone questions at specific stages of each exercise session to check the understanding and progression of students in both the practical and theoretical aspects of the work. Discussion among students was encouraged, and the instructor could observe how students debated concepts. Representative examples of questions asked are listed below (others are reported in the Supporting Information): (i) Can you assign the character of the lowest-energy absorption band of 1–3 using TD-DFT? (ii) Can you indicate which of the two triplet states optimized for each complex is more likely to cause photochemical instability? Why? (iii) Why is 1 the most luminescent of the three complexes? And why does 3 efficiently photodissociate one of the ligands compared to 1 and 2?

DATA ANALYSIS

Students resolved two major tasks during the exercise, that is, (i) interpreting the absorption spectrum of 1–3 by calculation of singlet–singlet transitions and analysis of their composition and (ii) characterizing the emission and photochemical behavior of the complexes by examining the nature of low-lying triplet states and their relative energy. During theoretical classes, the instructor provided the fundamentals of absorption spectroscopy and underlined the key role of ³MLCT and ³MC states in the

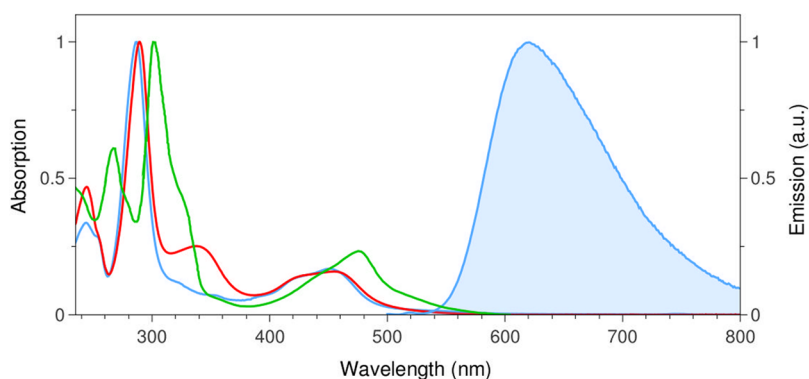


Figure 2. Visible absorption spectra of **1** (blue), **2** (green), and **3** (red) and emission (solid) spectrum of **1**.¹⁵ Absorption spectra were recorded in CH₃CN solution at 298 K; the emission spectrum of **1** was recorded in deaerated CH₃CN solution at 298 K.

Table 1. Emission Spectral Maximum, Emission Quantum Yield, and Emission Lifetime in Deaerated Acetonitrile Solution

	λ_{em} (nm)	Φ (298 K)	τ /ms (298 K)	Φ (77 K)	τ /ms (77 K)
[Ru(bpy) ₃] ²⁺	621 ^a	0.095 ^a	0.86 ^b	0.376 ± 0.036 ^c	5.21 ^c
[Ru(tpy) ₂] ²⁺	602 ^d			0.42 ± 0.04 ^d	10.4 ± 0.2 ^d
[Ru(bpy) ₂ (py) ₂] ²⁺	585 ^e				

^aSee ref 15. ^bSee ref 23. ^cAerated ethanol–methanol glass, see ref 24. ^dDeaerated butyronitrile glass, see ref 16. ^eDeaerated ethanol–methanol glass at 77 K, see ref 17.

emission properties and photochemical behavior of **1–3** and other ruthenium(II) polypyridyl complexes. Undoubtedly, recent advanced computational and spectroscopic studies indicate that the scenario is more intricate (e.g., interplay between ³MLCT and ³MC states),^{27,28} however such details are out of the scope of the present exercise and training.

A concise and highly educative review by Demas and De Graff illustrates the fundamental concepts at the basis of the photochemistry of representative d⁶ metal complexes.²⁹ This article indeed provides a useful theoretical background for both instructors and students.

Although the methodology was not optimized, several studies on **1–3** and related complexes^{5,27,30} confirm that the theory level employed here (i.e., DFT functional and basis set) and the agreement between computational results and experimental values (e.g., absorption and emission) are satisfactory and suitable to extrapolate qualitative information. Good practice in research studies is to benchmark the performance of DFT functionals and basis sets versus experimental data, with the aim of obtaining the best description possible of the system(s) investigated.^{31,32} Nevertheless, such work is generally time-consuming and ultimately out of the scope of this exercise.

Absorption

Following ground-state geometry optimization of **1–3** and analysis of structural parameters (e.g., comparison among complexes and with respect to their X-ray structures), students calculated singlet–singlet electronic transitions using TD-DFT. This method affords vertical excitation energies, their probability in terms of oscillator strength, and their orbital composition. Conveniently the use of programs such as GaussSum facilitates the analysis of output files, and allows plotting theoretical absorption spectra and assignment of their bands by visualization of electron density difference maps (EDDMs).

Table 2 and Figure 3 summarize the work carried out by students in this part of the exercise, that is comparison of structures (Figure 3a), plotting of absorption spectra (Figure 3b), and their assignment by visualization of EDDMs and analysis of

Table 2. Selected TDDFT Singlet Transitions Displaying High Values of Oscillator Strength (*f*) for Complexes **1–3**

Transition	Energy (eV)	Wavelength (nm)	Oscillator Strength	Major Contributions (>10%)
Complex 1				
8	2.99	414	0.1517	H - 2 → LUMO (15%), H - 2 → L + 2 (33%), H - 1 → L + 1 (33%)
18	4.04	307	0.0722	H - 2 → L + 6 (74%), HOMO → L + 7 (14%)
39	4.71	263	1.0108	H - 5 → LUMO (10%), H - 4 → L + 1 (31%), H - 3 → L + 2 (31%)
Complex 2				
7	3.06	405	0.1746	HOMO → L + 2 (82%)
26	4.26	291	0.3334	H - 3 → LUMO (35%), H - 3 → L + 1 (10%), H - 2 → L + 7 (30%)
48	5.25	236	0.4498	H - 6 → LUMO (31%), H - 5 → L + 1 (31%)
Complex 3				
5	2.92	425	0.1313	H - 2 → L + 1 (71%), H - 1 → LUMO (20%)
17	3.91	317	0.1137	HOMO → L + 6 (77%)
36	4.63	268	0.246	H - 3 → L + 1 (82%)

the orbitals giving major contributions to selected transitions (Figure 3c).

For example in the case of **1**, the singlet–singlet transition S8 has the highest oscillator strength value in the 400–500 nm range, hence determining the nature of this low-energy band. After calculation of the EDDM corresponding to S8 (Supporting Information), students assigned a MLCT character to the transition and the band. The EDDM indeed shows that electron density is lost by the Ru center (yellow surface) and is gained by the bpy ligands (red surface).

The described tasks allowed students to improve their understanding of concepts such as Franck–Condon excitation, to visualize with EDDMs the different nature of localized and charge transfer excited states, and to understand population of

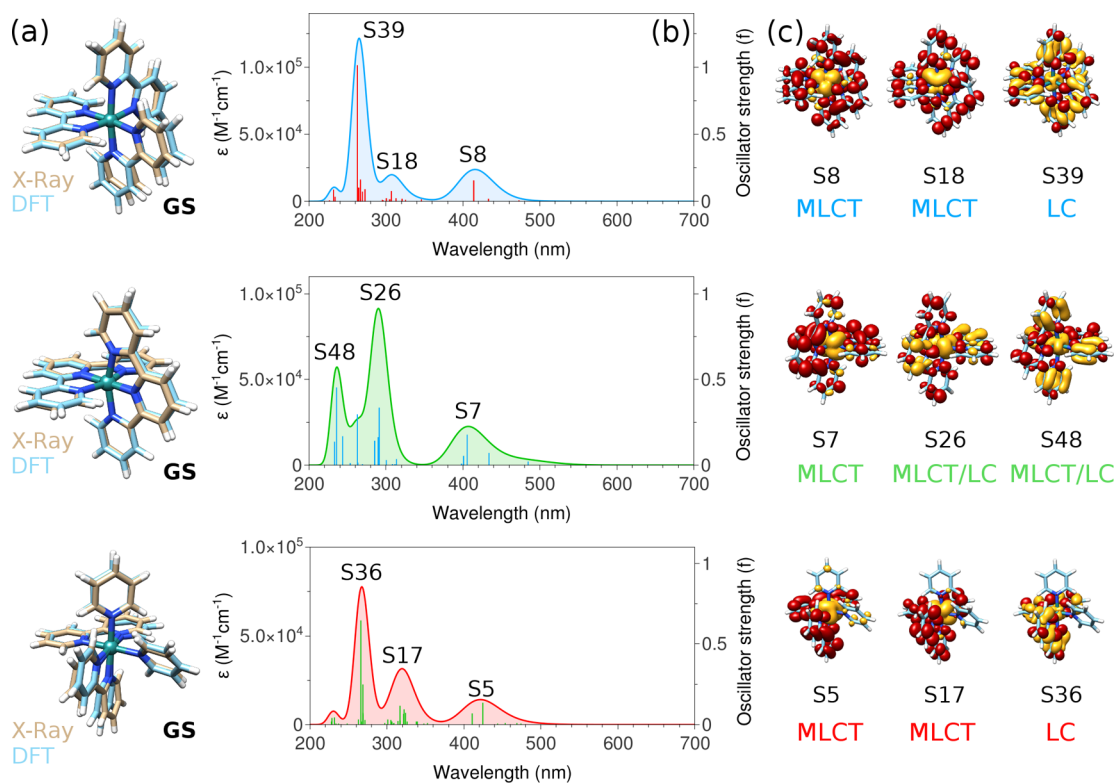


Figure 3. Selected computational results analyzed by students to determine the ground state (GS) and absorption properties of 1–3. These include comparison of X-ray and DFT-optimized structures (a), analysis of singlet–singlet electronic transitions and theoretical absorption spectra (b), and assignment of selected transitions (c) using electron difference density maps (EDDMs, right). In the EDMs, yellow indicates a decrease in electron density, while red indicates an increase.

which states has the potential to cause photochemical instability by analyzing orbital shapes and contributions. Moreover, students acquired a deeper level of comprehension in absorption spectroscopy after building by themselves the absorption spectra of 1–3 from the calculated TD-DFT transitions and assigning the character of each band using the information extrapolated from calculation outputs. The [Supporting Information](#) contains practical details on how to perform such analysis.

Emission and Photochemistry

Emission properties of 1–3 strongly depend on the interplay between $^3\text{MLCT}$ and ^3MC states, as does their intrinsic photostability. Students set up geometry optimizations of these excited states (Figure 4a), and the teacher directly provided resulting structures as output files.³³

After assigning the character of each optimized triplet state using spin density surfaces ([Supporting Information](#)), students depicted the energy diagram for the three complexes (Figure 4b) to rationalize the dramatic difference between the emission yield of 1 and 2 (Table 1) and the remarkable photoinstability of 3 (which dissociates efficiently one pyridine ligand).

Analysis and comparison of the triplet excited state geometries of 1–3 (Figure 4a) with respect to their ground state structure allowed the student to understand why both 1 and 2 display better stability toward ligand dissociation compared to 3. In fact, all ^3MC geometries are significantly distorted, with 3 showing one Ru–N(py) bond elongated to 2.67 Å. Such a dramatic structural change suggests that the ^3MC state is dissociative toward one pyridine ligand in the case of 3. Complexes 1 and 2 also present elongated Ru–N bonds compared to the ground state (ca. 2.10 Å). In the case of 1, two bpy ligands have each one a pyridyl ring at 2.39 Å from the Ru center, while in the case of 2

the two lateral rings of one tpy have Ru–N distances of 2.32 Å. However, the presence of at least one tightly bound N-ring for the bi- and tridentate bpy and tpy ligands prevents (or complicates) their photodissociation in 1 and 2.^{28,30}

On the other hand, the decreased ΔE between the $^3\text{MLCT}$ and ^3MC state fits with the decrease of the emission quantum yield in the order $1 \gg 2 \approx 3$.^{15–17} The markedly reduced emission of 2 with respect to 1 was explained in terms of both a smaller $^3\text{MLCT}$ – ^3MC ΔE and a lower energy gap between its $^3\text{MLCT}$ and GS states, which favor nonradiative decay. Unfortunately, prediction of emission energies by the commonly used ΔSCF method⁶ does not afford satisfactorily accurate results at the level of calculations adopted and was not included in the exercise to avoid confusion.

Therefore, both the proximity of the ^3MC and $^3\text{MLCT}$ states and the dissociative nature of the ^3MC state in 3 consistently explained its high pyridine photodissociation yield under visible light irradiation.

STUDENTS' PERCEPTION AND OUTLOOK

Students responded positively to the tasks designed in the exercise. Step-by-step generation of absorption spectra and 3D representation of electronic transitions/states and transient excited-state species by computational methods appreciably improved their understanding of theoretical concepts, as verified by their performance during the final test.

The molecules chosen for the experiment effectively highlight the richness of the photophysics and photochemistry of transition metal complexes. It was striking to the students that very small structural changes caused such dramatic effects in optical and photochemical properties.

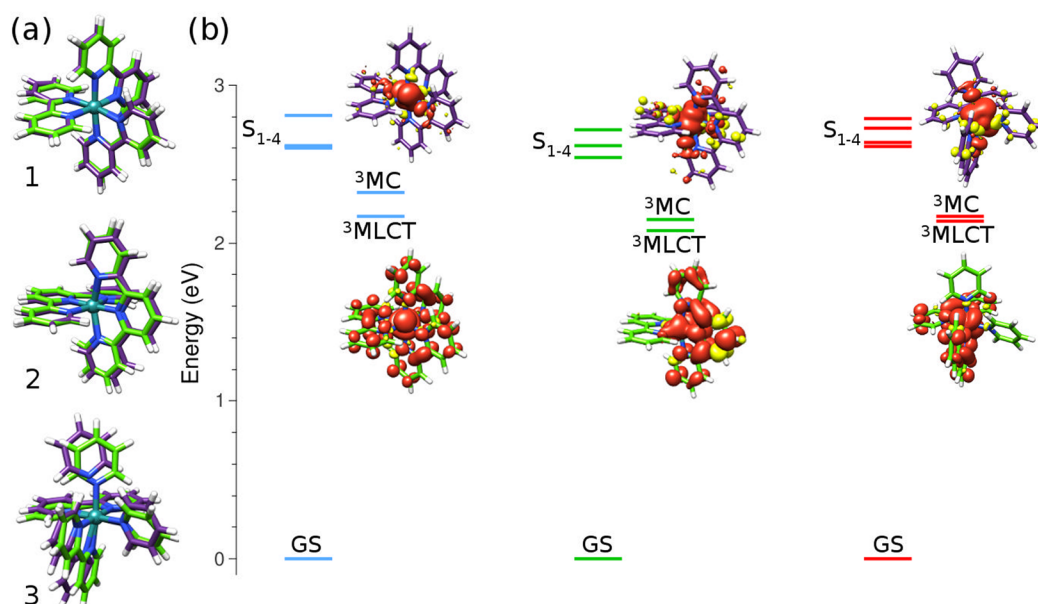


Figure 4. Selected computational results on triplet excited states, including (a) optimized $^3\text{MLCT}$ and ^3MC structures and (b) Jablonski diagram obtained using DFT (triplets) and TD-DFT (singlets) data. Spin density surfaces are plotted (red and yellow) for the two optimized triplet geometries of 1–3.

The preparation of a scientific paper at the end of the training gave them the possibility to train in reporting and presentation skills, as well as the opportunity to discuss among themselves which were the most relevant aspects of their computational work.

Although the instructor adopted a simple hands-on approach to teach and apply DFT and TD-DFT, the skills acquired by the students were notable as they were introduced to aspects of computer-based science, which included managing text editors and terminals, launching calculations, and using visualization software.

Finally, it is worth emphasizing that the present exercise can be complemented, on one hand, with a set of basic lessons on DFT and TD-DFT and, on the other, with selected wet-lab experiments, such as the synthesis and characterization of complexes, measurements of absorption and emission properties (eventually including lifetimes), photolysis, and photoreactivity experiments (e.g., photoredox catalysis with model reactions).¹ In such a truly multidisciplinary course students could be exposed to a wide range of approaches and techniques currently used by inorganic photochemists in their research laboratories.

■ COMPUTATIONAL METHODOLOGY

The program Gaussian 09²⁵ was employed to perform DFT and time-dependent DFT (TD-DFT)^{34,35} calculations on complexes 1–3. These included geometry optimizations of the singlet ground-state and the triplet lowest-lying structures. TD-DFT was used to calculate 50 singlet–singlet transitions. Calculations were run at the PBE0/SDD/6-31G^{36–38} level, using acetonitrile as solvent in the TD-DFT calculations (pcm method³⁹). Geometries were optimized in the gas phase. The program GaussSum 2.2.5²⁶ was adopted to analyze transition contributions, extract electron density difference maps (EDDMs), and simulate theoretical UV–vis spectra.^{40,41} Either AVOGADRO⁴² or CHIMERA⁴³ was used by students to visualize molecules and their electronic features.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00801.

Calculation setup tutorial (PDF)

Gaussian files and absorption spectra (ZIP)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lsalassa@cicbiomagune.es.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Authors acknowledge the Spanish Ministry of Economy and Competitiveness (Grants CTQ2012-39315), the MICINN of Spain for the Ramón y Cajal Fellowship RYC-2011-07787), the Department of Industry of the Basque Country (Grant ETORTEK), and the EU FP7MC CIG fellowship UCnano-mat4iPACT (Grant No. 321791). The Italian MIUR program “Programma Messaggeri della Conoscenza” is acknowledged for supporting the teaching project (ID 132) of L.S. at the University of Palermo (Italy). A.T. received funding from the Mahlke-Obermann Stiftung and the European Union’s Seventh Framework Programme for research, technological development and demonstration under Grant Agreement No. 609431.

■ REFERENCES

- Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113* (7), 5322–5363.
- Fino, E.; Araya, R.; Peterka, D. S.; Salierno, M.; Etchenique, R.; Yuste, R. RuBi-Glutamate: Two-Photon and Visible-Light Photoactivation of Neurons and Dendritic Spines. *Front. Neural Circuits* **2009**, *3*, No. 2, DOI: 10.3389/neuro.04.002.2009.

- (3) Farrer, N. J.; Salassa, L.; Sadler, P. J. Photoactivated Chemotherapy (PACT): The Potential of Excited-State D-Block Metals in Medicine. *Dalton Trans.* **2009**, 10690–10701.
- (4) Bressler, C.; Chergui, M. Ultrafast X-Ray Absorption Spectroscopy. *Chem. Rev.* **2004**, *104* (4), 1781–1812.
- (5) Borfecchia, E.; Garino, C.; Salassa, L.; Ruiu, T.; Gianolio, D.; Zhang, X.; Attenkofer, K.; Chen, L. X.; Gobetto, R.; Sadler, P. J.; Lamberti, C. X-Ray Transient Absorption Structural Characterization of the ³MLCT Triplet Excited State of Cis-[Ru(bpy)₂(py)₂]²⁺. *Dalton Trans.* **2013**, 42 (18), 6564–6571.
- (6) Vlcek, A.; Zalis, S. Modeling of Charge-Transfer Transitions and Excited States in d(6) Transition Metal Complexes by DFT Techniques. *Coord. Chem. Rev.* **2007**, *251* (3–4), 258–287.
- (7) Fantacci, S.; De Angelis, F. A Computational Approach to the Electronic and Optical Properties of Ru(II) and Ir(III) Polypyridyl Complexes: Applications to DSC, OLED and NLO. *Coord. Chem. Rev.* **2011**, *255* (21–22), 2704–2726.
- (8) Garino, C.; Salassa, L. The Photochemistry of Transition Metal Complexes Using Density Functional Theory. *Philos. Trans. R. Soc., A* **2013**, *371* (1995), No. 20120134, DOI: 10.1098/rsta.2012.0134.
- (9) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, NY, 1989.
- (10) Baseden, K. A.; Tye, J. W. Introduction to Density Functional Theory: Calculations by Hand on the Helium Atom. *J. Chem. Educ.* **2014**, *91* (12), 2116–2123.
- (11) *Fundamentals of Time-Dependent Density Functional Theory*; Marques, M. A. L.; Maitra, N. T.; Nogueira, F. M. S., Gross, E. K. U., Rubio, A., Eds.; Lecture Notes in Physics; Springer Berlin Heidelberg: Berlin, Heidelberg, 2012; Vol. 837.
- (12) Freitag, R.; Conradie, J. Understanding the Jahn-Teller Effect in Octahedral Transition-Metal Complexes: A Molecular Orbital View of the Mn(beta-diketonato)₃ Complex. *J. Chem. Educ.* **2013**, *90* (12), 1692–1696.
- (13) Montgomery, C. D. Pi Backbonding in Carbonyl Complexes and Carbon-Oxygen Stretching Frequencies: A Molecular Modeling Exercise. *J. Chem. Educ.* **2007**, *84* (1), 102–105.
- (14) Pernicone, N. C.; Geri, J. B.; York, J. T. Using a Combination of Experimental and Computational Methods to Explore the Impact of Metal Identity and Ligand Field Strength on the Electronic Structure of Metal Ions. *J. Chem. Educ.* **2011**, *88* (9), 1323–1327.
- (15) Ishida, H.; Tobita, S.; Hasegawa, Y.; Katoh, R.; Nozaki, K. Recent Advances in Instrumentation for Absolute Emission Quantum Yield Measurements. *Coord. Chem. Rev.* **2010**, *254* (21–22), 2449–2458.
- (16) Amini, A.; Harriman, A.; Mayeux, A. The Triplet Excited State of ruthenium(II) bis(2,2':6',2'-terpyridine): Comparison between Experiment and Theory. *Phys. Chem. Chem. Phys.* **2004**, *6* (6), 1157–1164.
- (17) Pinnick, D. V.; Durham, B. Photosubstitution Reactions of Ru(bpy)₂XYⁿ⁺ Complexes. *Inorg. Chem.* **1984**, *23* (10), 1440–1445.
- (18) Brey, J.; Domel, H.; Stoll, A. Chiral Recognition among Tris(diimine)-Metal Complexes, 6 - Racemic Compound Formation versus Conglomerate Formation with [M(bpy)₃](PF₆)₂ (M = Ni, Zn, Ru); Molecular and Crystal Structures. *Eur. J. Inorg. Chem.* **2000**, 2000 (11), 2401–2408.
- (19) Craig, D. C.; Scudder, M. L.; McHale, W. A.; Goodwin, H. A. Structural Studies of Complexes of Tridentate Terimine Systems. Crystal Structure of bis(2,2':6',2'-terpyridine)ruthenium(II) Perchlorate Hydrate, bis(2,2':6',2'-terpyridine)osmium(II) Perchlorate Hemihydrate and bis((1,10-Phenanthroline-2-Yl) (pyridin-2-yl)amine)iron(II) Tetrafluoroborate Dihydrate. *Aust. J. Chem.* **1998**, *51* (12), 1131–1139.
- (20) Kolp, B.; Viebrock, H.; von Zelewsky, A.; Abeln, D. Crystal Structure Analysis and Chiral Recognition Study of Delta-[Ru(bpy)₂(py)₂][(+)-O,O'-Dibenzoyl-Dtartrate]·12H₂O and Lambda-[Ru(bpy)₂(py)₂][(-)-O,O'-Dibenzoyl-Ltartrate]·12H₂O. *Inorg. Chem.* **2001**, *40* (6), 1196–1198.
- (21) Sauvage, J.; Collin, J.; Chambron, J.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelli, F.; Decola, L.; Flamigni, L. Ruthenium(ii) and Osmium(ii) Bis(terpyridine) Complexes in Covalently-Linked Multi-component Systems: Synthesis, Electrochemical Behavior, Absorption Spectra, and Photochemical and Photophysical Properties. *Chem. Rev.* **1994**, *94* (4), 993–1019.
- (22) Wagenknecht, P. S.; Ford, P. C. Metal Centered Ligand Field Excited States: Their Roles in the Design and Performance of Transition Metal Based Photochemical Molecular Devices. *Coord. Chem. Rev.* **2011**, *255* (5–6), 591–616.
- (23) Durham, B.; Caspar, J. V.; Nagle, J. K.; Meyer, T. J. Photochemistry of tris(2,2'-bipyridine)ruthenium(2+) Ion. *J. Am. Chem. Soc.* **1982**, *104* (18), 4803–4810.
- (24) Crosby, G. A.; Demas, J. N. Quantum Efficiencies on Transition Metal Complexes. II. Charge-Transfer Luminescence. *J. Am. Chem. Soc.* **1971**, *93* (12), 2841–2847.
- (25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, 2009.
- (26) O'Boyle, N. M.; Tenderholt, A. L.; Langner, K. M. Cclib: A Library for Package-Independent Computational Chemistry Algorithms. *J. Comput. Chem.* **2008**, *29* (5), 839–845.
- (27) Osterman, T.; Abrahamsson, M.; Becker, H.-C.; Hammarstrom, L.; Persson, P. Influence of Triplet State Multidimensionality on Excited State Lifetimes of Bis-Tridentate Ru-II Complexes: A Computational Study. *J. Phys. Chem. A* **2012**, *116* (3), 1041–1050.
- (28) Camilo, M. R.; Cardoso, C. R.; Carlos, R. M.; Lever, A. B. P. Photosolvolytic of Cis-[Ru(α-diimine)₂(4-aminopyridine)₂]²⁺ Complexes: Photophysical, Spectroscopic, and Density Functional Theory Analysis. *Inorg. Chem.* **2014**, *53* (7), 3694–3708.
- (29) Demas, J.; DeGraff, B. Design and Applications of Highly Luminescent Transition Metal Complexes. *Anal. Chem.* **1991**, *63* (17), A829–A837.
- (30) Salassa, L.; Garino, C.; Salassa, G.; Gobetto, R.; Nervi, C. Mechanism of Ligand Photodissociation in Photoactivable [Ru(bpy)₂-L₂]²⁺ Complexes: A Density Functional Theory Study. *J. Am. Chem. Soc.* **2008**, *130* (29), 9590–9597.
- (31) Jacquemin, D.; Wathélet, V.; Perpète, E. A.; Adamo, C. Extensive TD-DFT Benchmark: Singlet-Excited States of Organic Molecules. *J. Chem. Theory Comput.* **2009**, *5* (9), 2420–2435.
- (32) Jacquemin, D.; Brémond, E.; Planchat, A.; Ciofini, I.; Adamo, C. TD-DFT Vibronic Couplings in Anthraquinones: From Basis Set and Functional Benchmarks to Applications for Industrial Dyes. *J. Chem. Theory Comput.* **2011**, *7* (6), 1882–1892.
- (33) We adopted the following common approach to optimize the two types of triplet geometries: (i) the ground-state DFT structure of each complex was used as guess geometry for running an optimization calculation with multiplicity “3” and obtain the structure correspondent to the lowest-lying triplet ³MCLT; (ii) the so-obtained ³MLCT geometry was then used to perform a second optimization calculation with multiplicity “3” after selective elongation of two Ru–N bonds, affording the structure correspondent to the ³MC excited state.
- (34) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. Molecular Excitation Energies to High-Lying Bound States from Time-Dependent Density-Functional Response Theory: Characterization and Correction of the Time-Dependent Local Density Approximation Ionization Threshold. *J. Chem. Phys.* **1998**, *108* (11), 4439–4449.
- (35) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. An Efficient Implementation of Time-Dependent Density-Functional Theory for the Calculation of Excitation Energies of Large Molecules. *J. Chem. Phys.* **1998**, *109* (19), 8218–8224.
- (36) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(37) Fuentealba, P.; Preuss, H.; Stoll, H.; Von Szentpály, L. A Proper Account of Core-Polarization with Pseudopotentials: Single Valence-Electron Alkali Compounds. *Chem. Phys. Lett.* **1982**, *89* (5), 418–422.

(38) McLean, A. D.; Chandler, G. S. Contracted Gaussian Basis Sets for Molecular Calculations. I. Second Row Atoms, $Z = 11-18$. *J. Chem. Phys.* **1980**, *72* (10), 5639–5648.

(39) Cossi, M.; Scalmani, G.; Rega, N.; Barone, V. New Developments in the Polarizable Continuum Model for Quantum Mechanical and Classical Calculations on Molecules in Solution. *J. Chem. Phys.* **2002**, *117*, 43–54.

(40) Browne, W. R.; O'Boyle, N. M.; McGarvey, J. J.; Vos, J. G. Elucidating Excited State Electronic Structure and Intercomponent Interactions in Multicomponent and Supramolecular Systems. *Chem. Soc. Rev.* **2005**, *34* (8), 641–663.

(41) Headgordon, M.; Grana, A. M.; Maurice, D.; White, C. A. Analysis of Electronic-Transitions as the Difference of Electron-Attachment and Detachment Densities. *J. Phys. Chem.* **1995**, *99* (39), 14261–14270.

(42) Hanwell, M. D.; Curtis, D. E.; Lonie, D. C.; Vandermeersch, T.; Zurek, E.; Hutchison, G. R. Avogadro: An Advanced Semantic Chemical Editor, Visualization, and Analysis Platform. *J. Cheminf.* **2012**, *4*, 17.

(43) Pettersen, E. F.; Goddard, T. D.; Huang, C. C.; Couch, G. S.; Greenblatt, D. M.; Meng, E. C.; Ferrin, T. E. UCSF Chimera - A Visualization System for Exploratory Research and Analysis. *J. Comput. Chem.* **2004**, *25*, 1605–1612.