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PHOTOPHYSICOCHEMISTRY OF PORPHYRINS AND RUTHENIUM COMPLEXES
ADSORBED ON MESOPOROUS TiO₂ THIN FILMS

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ABSTRACT

For many years, the search of new organic, organometallic and inorganic molecules has been attracting considerable interest in science due their potential applications in technology, medicine and fundamental science. Among these new materials, porphyrins and ruthenium complexes have called special attention to the scientific community due to its versatile structural manipulation through molecular engineering, and their unique photophysical and photochemical properties. To estimate the perspectives of such classes of compounds to potential applications, it is imperative to systematically carry out characterizations of their molecular properties, especially those involving its excited state formation and possible interactions with the surrounding quantities.

A topic of extensive work during the last ten years is the application of dye molecules, such as porphyrin and ruthenium compounds, as sensitizers in dye sensitized solar cells (DSSCs). DSSCs represent an attractive technology to addressing the world's demand for renewable energy. Such devices are composed of mesoporous thin films of nanometer sized metal oxide spheres, most commonly titanium dioxide (TiO_2), and a molecular sensitizer anchored to the surface of the metal oxide nanoparticles. The most recent works reported the efficiency of a porphyrin based DSSC to be 13%.¹ Although still lower in efficiency when compared with the mostly used photovoltaic systems based on silicon, DSSC represents a promising alternative for solar energy conversion devices of low cost and ease of manufacturing.

In the first part of this dissertation, PART I, the conventional spectroscopic characterization of two classes of free base porphyrins is presented as a start up investigation. Chapter 1 investigates the UV-vis absorption spectrum of a free base cationic porphyrin derivative [5,10,15,20-tetrakis (1,3-dimethylimidazolium-2-yl) porphyrin tetraiodide], abbreviated to H_2TDMImP , in polar solvents. Our results showed that, for diluted solutions ($< 14 \mu\text{M}$), the outlying cationic groups linked to the porphyrin ring mesocarbons triggers strong interactions with the polar solvent molecules, leading to significant changes in the spectral features of the porphyrin moiety. When the porphyrin concentration is increased, spectral changes suggested that H-type porphyrin aggregates were formed, preventing the outlying cationic groups of the porphyrin to interact with solvent molecules. Chapter 2 is focused on the comparison of steady state and time-resolved photophysical properties of the [5,10,15,20-tetra(pyridyl)-21H,23H-porphyrin], or H_2TPyP , when an ruthenium complex,

[Ru(terpy)(PPh₃)Cl], is bounded to the peripheral pyridine groups of the H₂TPyP. The systematic spectral study showed that the porphyrin ring and the peripheral ruthenium complexes have weak electronic interaction due to the absence of favorable driving force for intermolecular electron transfer between the porphyrin and the ruthenium moieties. Also, time-resolved photoluminescence and transient absorption studies showed that the radiative singlet relaxation was quenched after complexation with external ruthenium groups, which is thought to arise from new faster non-radiative decay channels from the S₁ state.

The PART II of this dissertation composed by Chapter 3, tries to create a coherent “bridge” between what was done prior to the experience at JHU, and what ended up being the convergence to a possible new research line adopted by Prof. Newton group – the observation of photodriven charge and energy transfer in organic and inorganic system. In PART II is introduced the concepts and the working mechanism of the DSSCs, as a preparation to following Chapters 3, 4 and 5 of this dissertation. Chapter 3 is focused on a new free base tetrapyrrolyl porphyrin *meso*-substituted with a ruthenium complex, Ru(dmb)₂NO₂. The said molecule, although absent of functional binding groups, was suitable for sensitization of TiO₂ through what is believed to be electrostatic interactions with the nanocrystallite surface. The limited number of experiments performed in this chapter couldn't precisely inform the possibility of photoinduced electron injection. Although not achieved the desired success in these experiments, Chapter 3 led to substantial contributions to the understanding of how DSSC should operate with porphyrin sensitizers.

In PART III, it is proposed a work focused on ruthenium complexes used as sensitizers to DSSC. More specifically, it offers a discussion on a particular effect that arises after photoinduced electron injection, the Stark effect. This effect is the response of the ground state molecules and the other chemical components to the surface electric fields originated from injected electrons into the TiO₂ and/or adsorbed cations on the TiO₂ surface. In Chapter 4, it is proposed the analysis of a heteroleptic ruthenium complex adsorbed on TiO₂ thin films that have its absorption spectrum perturbed by electric fields from either electrochemically accumulation of electrons or injected electrons right after pulsed laser excitation. The Stark effect is systematically studied as a function of four different types of cations adsorbed on the TiO₂ surface: Na⁺, Li⁺, Mg²⁺ and Ca²⁺. The nature of each cation critically defines the strength of the electric field at the ‘TiO₂ – dye molecule’ interface based on screening mechanisms. Chapter 5 gives an approach in which a ruthenium compound composed by a mono-pyridine ligand is adsorbed to the TiO₂ surface. Critical insights, which concerns about charge motion and screening the high TiO₂ permittivity, were satisfactorily

obtained. Finally, Chapter 5 proposes a new model to report the time evolution of the Stark effect, under restrict conditions.

Keywords: Porphyrins, Ruthenium, TiO_2 , dye sensitized solar cells, Stark effect.

RESUMO

Durante muitos anos, a busca por novos compostos, orgânicos, organometálicos e inorgânicos tem atraído considerável interesse no meio científico devido às suas potenciais aplicações na tecnologia, medicina e no desenvolvimento de ciência básica e aplicada. Dentre estes novos materiais, se destacam as porfirinas e complexos de rutênio por sua versátil manipulação estrutural via engenharia molecular e suas propriedades foto-físicas e foto-químicas. Para que viabilize a estimativa de perspectivas dessa classe de compostos para potenciais aplicações, torna-se imperativo desenvolver caracterizações sistemáticas de suas propriedades moleculares, principalmente aquelas envolvendo a formação de seus estados excitados e as possíveis interações com as entidades presentes no meio.

Um tópico vigente de intenso interesse de pesquisa científica nos últimos dez anos é a aplicação de moléculas altamente absorvedoras de luz visível, tais como porfirinas e complexos de rutênio, como corantes sensibilizadores em células solares sensibilizadas por corantes (CSSCs). As CSSCs representam uma atrativa tecnologia para suprir a demanda mundial por energia renovável. Tais dispositivos são compostos por filmes finos mesoporosos de óxidos metálicos esféricos de escala nanométrica, mais comumente o dióxido de titânio (TiO_2), e por moléculas sensibilizantes ancoradas à superfície das nanopartículas de óxido metálico. O mais recente recorde de eficiência em CSSCs registrou um valor de 13%, para um dispositivo contendo porfirinas como corantes absorvedores de luz. Embora ainda menos eficientes do que os dispositivos fotovoltaicos feitos de sílica, as CSSCs representam uma promissora alternativa de baixo custo e facilidade de fabricação.

Na primeira parte desta Tese, PARTE I, é apresentado uma caracterização espectroscópica convencional de duas classes de porfirinas base livres. No Capítulo 1, é investigado o espectro de absorção UV-vis de uma porfirina base livre catiônica, abreviada H_2TDMImP . Os resultados mostraram que os grupos periféricos catiônicos ligados aos mesocarbonos do anel porfirínico são responsáveis por gerar fortes interações com moléculas de solventes específicos, induzindo alterações significativas na forma do espectro de absorção da porfirina em função da concentração da solução. Ao aumentar a concentração da solução, é formado agregados de porfirinas do tipo-H, os quais impedem que os grupos catiônicos interajam com as moléculas de solvente. O Capítulo 2 foca na comparação de propriedades foto-físicas em estado estacionário e resolvidas no tempo de uma porfirina base livre H_2TPyP antes e depois da anexação de quatro grupos periféricos de rutênio, $[\text{Ru}(\text{terpy})(\text{PPh}_3)\text{Cl}]$, aos

mesocarbonos do anel porfirínico. O estudo sistemático mostrou que ambos anel porfirínico e os grupos de rutênio são fracamente perturbados a níveis eletrônicos. Ainda, não foi observado potenciais energéticos favoráveis à transferência de elétrons entre os grupos. Experimentos de fotoluminescência resolvida no tempo e de absorção transiente mostraram que a relaxação por canais de decaimento radiativo do estado excitado singlete são suprimidos após a complexação dos grupos de rutênio, fruto do surgimento de novos e rápidos níveis vibracionais e canais de decaimento não-radiativos a partir do estado excitado S_1 .

A PARTE II desta Tese, composta pelo Capítulo 3, é uma tentativa de coerentemente conectar os trabalhos realizados em momentos que antecedem ao meu doutorado sanduíche na Johns Hopkins University (JHU), e os trabalhos provenientes enquanto estudante visitante nos laboratórios do professor Gerald Meyer, na JHU. Trabalhos estes que vieram a se tornar uma potencial nova área de pesquisa para os laboratórios do grupo do professor Newton – a observação de processos de transferência de carga e energia induzidos por luz em sistemas orgânicos e inorgânicos. Na PARTE II, é introduzido uma breve discussão a cerca dos conceitos e mecanismos de funcionamento das CSCSs, como uma preparação para os Capítulos 3, 4 e 5, que se seguem. O Capítulo 3 aborda a sensibilização do TiO_2 observada por interações eletrostáticas entre as nanopartículas de TiO_2 e uma porfirina base livre com grupos periféricos de rutênio, $Ru(dmb)_2NO_2$, na ausência de grupos funcionais para ancoramento à superfície do semiconductor. O número restrito de experimentos realizados neste capítulo inviabiliza uma definição se há a ocorrência de cargas foto-injetadas no TiO_2 . Embora o Capítulo 3 não tenha experimentalmente apresentado o sucesso desejado, ele forneceu contribuições substanciais para o entendimento de como CSCSs devem operar via sensibilização por moléculas de porfirinas.

Na ultima etapa desta tese, a PARTE III, é proposto um trabalho focado em complexos de rutênio usados como corantes sensibilizadores em CSCSs. Mais especificamente, esta parte do trabalho discute um efeito particular que surge após a injeção de elétron foto-induzida, o chamado Efeito Stark. Este efeito quantifica a resposta das moléculas no estado fundamental e dos componentes químicos presentes na interface ‘ TiO_2 – molécula’ à presença de campos elétricos superficiais originados de elétrons injetados no TiO_2 e/ou devida à presença cátions adsorvidos na superfície do TiO_2 . No Capítulo 4, é proposto a análise de um complexo heteroléptico de rutênio adsorvido em filmes finos de TiO_2 o qual tem seu espectro de absorção perturbado pela presença de campos elétricos superficiais tanto induzidos pela acumulação eletroquímica de elétrons ou pela injeção de elétrons imediatamente após a excitação por um pulso laser. O efeito Stark é sistematicamente

estudado em função quatro diferentes cátion adsorvidos na superfície do TiO_2 : Na^+ , Li^+ , Mg^{2+} e Ca^{2+} . A natureza de cada cátion criticamente define a força do campo elétrico na interface baseado em mecanismos de blindagem de carga/campo pelos cátions. No Capítulo 5, uma nova abordagem do efeito Stark é apresentada por um composto de rutênio contendo apenas um ligante mono-piridínico, adsorvido na superfície de TiO_2 . Observações cruciais no que diz respeito à dinâmica de movimento e processos de blindagem de carga/campo dos elétrons dentro do TiO_2 foram satisfatoriamente obtidos. Finalmente, no Capítulo 5, é proposto um novo modelo para descrever a evolução temporal do efeito Stark, sob condições específicas.

Palavras-chave: porfirina, rutênio, TiO_2 , célula solar sensibilizada por corante, efeito Stark.

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PART I:

Photophysical and Photochemical Properties of Porphyrins.

INTRODUCTION

Porphyrins

Porphyrins have been, for decades, widely studied due its very interesting photophysical and photochemical properties. The basis for the understanding of their spectral properties was first introduced by Gouterman, at the sixties, through a theoretical analysis about the porphyrins absorption spectra.²⁻⁴

In fact, porphyrins comprise a class of important molecules that serve nature in several ways. They are present in many biological processes, such as oxygen and electrons transport and energy transfer in photosynthesis.⁵ Furthermore, porphyrins have been highlighted as efficient sensitizers and catalyst in chemical and photochemical processes, such as in photodynamic therapy (PDT) applied in cancer treatment.⁶⁻⁷ In addition, porphyrins have shown great capability to be employed in photonic devices.⁸⁻⁹ At the 90's, porphyrins were by Kay and Grätzel as light-harvesting material in dye sensitized solar cells,¹⁰⁻¹¹ being today a major focus of research. Recent work have reported efficiencies of 13%.¹

In general, porphyrins have their basic structure constituted of a macrocyclic ring, which is composed by pyrrole groups connected through methylene bridges with mesocarbon atoms, which give them the high π -conjugated character. Finally, porphyrins must be stabilized with central substituents linked to the nitrogen atoms of the pyrrole groups, which could be hydrogen atoms or metal ions, Figure I-1.¹² The strongly π -conjugated system of the porphyrins associated with their structural manipulation versatility, either with center or peripheral substituents, provide them several interesting photophysical and photochemical properties such as good photostability, a wide absorption range in the UV-vis, photoluminescence and long-lived singlet and triplet excited states, two photon absorption, non-linear refraction and absorption, among others.¹³⁻¹⁷

Relative to their photophysical properties, porphyrins can be defined as regular or irregular.¹² The regular ones have their UV-vis and photoluminescence spectra essentially determined by the π -electrons of the porphyrin ring, showing small perturbative interactions by the central substituent. This type of porphyrin can have two hydrogens ($2H^+$), also known as free base porphyrins, or metals ions with closed shell configuration (d^0 or d^{10}). The

irregular porphyrins are composed by transition metal ions with *d* or *f* open shells. For these cases, the metal ions strongly interact with the porphyrin π -electrons, via spin-orbit coupling, generating significant perturbations on the porphyrin ring photophysical properties.¹⁸ It can be seen clear changes in their absorption and emission spectra and also excited state quenching processes.

Particularly in this work, regular porphyrins were used regular in which hydrogen atoms, 2H^+ , were placed as central substituents, the so called free base porphyrins.

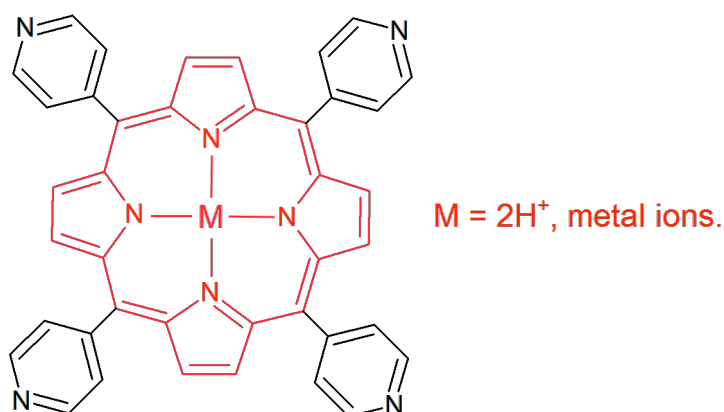


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The absorption spectra of porphyrins are characterized by two major features, a absorption band between 350 nm and 450 nm known as the Soret band that has extinction coefficient typically greater than $100,000 \text{ M}^{-1} \text{ cm}^{-1}$ and a set of up to four absorption bands (typically two for metalloporphyrins) known as the Q bands that have extinction coefficient on the order of $10,000 \text{ M}^{-1} \text{ cm}^{-1}$, Figure I-2A.³ The first one involves a transition to the second singlet excited state, $\text{S}_0 \rightarrow \text{S}_2$, while the Q bands are assigned to transitions to the first singlet excited state, $\text{S}_0 \rightarrow \text{S}_1$. Both types of absorption are $\pi - \pi^*$ in character, and localized at orbitals of to the porphyrin ring, which have been understood by the four orbital model described by Gouterman.¹⁹

The presence of hydrogen atoms as the central substituents to the porphyrin ring, decreases the molecule's symmetry, from the D_{4h} symmetry to D_{2h} . As a consequence, the Q band region will show four absorption bands, whereas metalloporphyrins shows only two bands. Thus, for free base species the $\text{Q}(0,0)$ transition is splitted into $\text{Q}_x(0,0)$ and $\text{Q}_y(0,0)$

while the $Q(1,0)$ transition is divided into $Q_x(1,0)$ and $Q_y(1,0)$, Figure I-2B. The loss in symmetry causes then the transitions to split into specific polarized transitions along the planar porphyrin ring.^{2, 20}

Generally, porphyrins show photoluminescence activity from their less energetic singlet excited state, $S_0 \leftarrow S_1$, since more energetic excited states, S_n , have very fast radiationless decay dynamics through internal conversions. Excited state relaxation from S_2 in metalloporphyrins may take from hundreds of femtoseconds to tens of picoseconds,²¹⁻²² while for free base porphyrins it is faster than 100 fs.²²⁻²⁵ Fluorescence from the higher energy excited state, S_2 , was also reported but will not be discussed herein.²⁶⁻²⁷ Although fluorescence emission of porphyrins is more common to observe, phosphorescence was also observed, mainly at low temperatures, but with much lower quantum yields. Phosphorescence emissions are often triggered by heavy atoms perturbations via spin-orbit coupling.^{2, 4, 28}

In all works presented in this dissertation, Chapters 1, 2 and 3, every porphyrin used was regular and free base porphyrins, *i. e.* had two hydrogen atoms, $2H^+$, as the central substituents. More specifically, the porphyrins had pyridine groups linked to the four mesocarbons of the porphyrins ring. The generated porphyrin molecule is the 5,10,15,20-tetra(pyridyl)-21H,23H-porphyrin, abbreviated to H_2TPyP , Figure I-1.

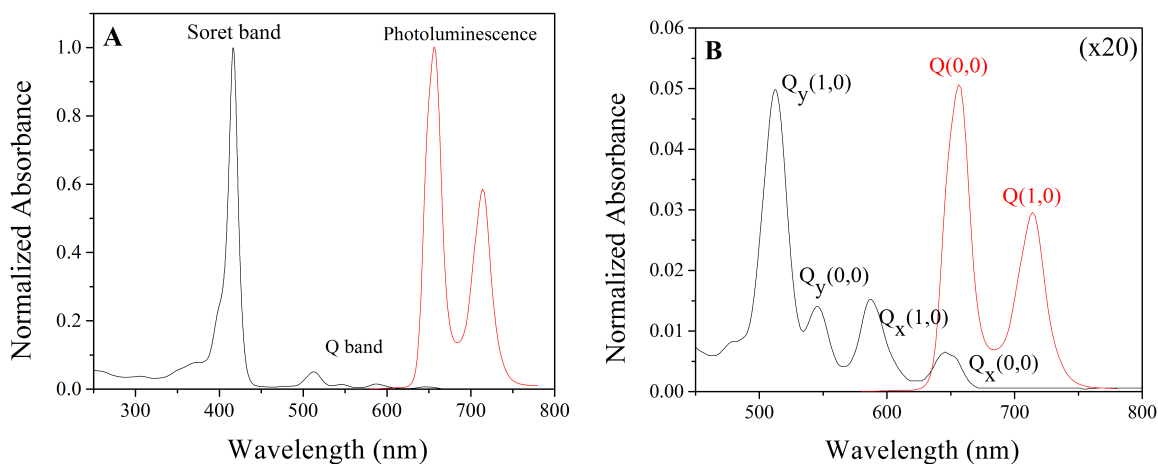


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Porphyrin photoluminescence spectra display very small Stokes shifts and exhibits two peaks due to transition from the S_1 excited state back to different vibronic levels of the S_0 ground state. Porphyrin emission spectra are located around 650 and 800 nm, showing a

characteristic red emission, Figures I-2A and B. In particular, H₂TPyP presents two well defined peaks centered at 647 nm (the stronger one) and 709 nm,^{13, 29} associated with transitions from the lowest energetic vibronic state of S₁ to two vibronic levels of the S₀ ground state ($\nu_0 \leftarrow \nu_0$ and $\nu_1 \leftarrow \nu_0$). These transitions are respectively related with the Q bands Q_x(0,0) e Q_x(0,1).

As discussed above, porphyrins have strong light harvesting character in the visible light range, and its photostability enable researcher to use several spectroscopic techniques to study photophysics and photochemistry of the excited states of porphyrins. For such reasons, porphyrins have been a promising target of research for a wide field of research, from biological system, photonic devices to cancer therapy and solar cells.

In the first part of this dissertation, PART I, the conventional spectroscopic characterization of two classes of free base porphyrins is presented as the start up investigation.

Chapter 1 investigates the UV-vis absorption spectrum of a free base cationic porphyrin derivative [5,10,15,20-tetrakis (1,3-dimethylimidazolium-2-yl) porphyrin tetraiodide], abbreviated to H₂TDMI⁺P, in polar solvents. Our results showed that, for the present sample, the less energetic transitions belonging to Soret band were favored when compared to other ionic porphyrins and that the Q-band presents a rhodo type structure¹². Quantum chemical calculations have shown that the outlying cationic groups linked to the porphyrin ring mesocarbons triggers strong interactions with the polar solvent molecules, leading to significant changes in the spectral features of the porphyrin moiety, at low concentrations of the solution. Increasing the porphyrin concentration, the spectral changes suggested that H-type porphyrin aggregates were formed, preventing the outlying cationic groups of the porphyrin to interact with solvent molecules.

Chapter 2 is focused on the comparison of steady state and time-resolved photophysical properties of the [5,10,15,20-tetra(pyridyl)-21H,23H-porphyrin], or H₂TPyP, when an ruthenium complex, [Ru(terpy)(PPh₃)Cl], is bounded to the peripheral pyridine groups of the H₂TPyP. The systematic study comprises to characterize of each compound individually, and after complexation. The steady state analysis shows that the porphyrin Soret band has expressive spectral features changes while the Q band are completely unaffected by the external ruthenium groups. Electrochemistry and quantum chemical calculations associated with the steady state absorption spectra enabled the construction of the energy diagram for electron transfer of the investigated compounds. It was observed no favorable

driving force for intermolecular electron transfer between the porphyrin and the ruthenium moieties. Time-resolved photoluminescence and transient absorption showed that the radiative singlet relaxation was quenched after complexation with external ruthenium groups. Such quenching is thought to arise from new faster non-radiative decay channels from the S_1 state, which is also deleterious to the triple state population build up.

Transient Absorption Experiments

Introduced by G. Porter and R. G. W. Norrish, the laser flash photolysis technique is an experimental method to investigate and characterize photophysical and photochemical properties of molecular systems (organic, inorganic and organometallic materials) based on the observations of transient states formed upon pulsed light excitation.³⁰ Among its diversity of applications it's noteworthy to mention use of the technique in the observation of excited states formation^{13-15, 31}, photochemical reactions³²⁻³³, electron transfer processes³⁴⁻⁴¹, which are processes frequently seen in many research areas such as artificial photosynthesis¹⁰⁻¹¹, photodynamic therapy⁴² and solar cells⁴³⁻⁴⁵.

The intense technological development in electronics and pulsed lasers achieving such small pulse time width (nanoseconds to femtoseconds) provided the transient absorption technique to observe transient species at time resolutions from picoseconds to nanoseconds.

The transient absorption system is basically composed by two different channels, the excitation and the probe channel. The first one is consisted of a pulsed laser, which critically defines the experiment time resolution. The probe channel is mostly composed by a Xenon lamp as source of continuous light to probe the changes in absorbance of the molecular system right after pulsed laser excitation.

The working mechanism of the transient absorption technique is briefly discussed as follows. The excitation pulsed laser has to be absorbed by the molecule which gives energy to the system to be excited from its ground state configuration to highly energetic excited states. Once excited, molecules are strongly susceptible to undergo many photophysical and photochemical processes described previously above, or the molecule may find radiative or non-radiative pathway decays back to its ground state. The probe lamp is responsible for

monitoring any change in absorbance while the system is in the so called transient state, until It completely resets its initial conditions of the ground state.

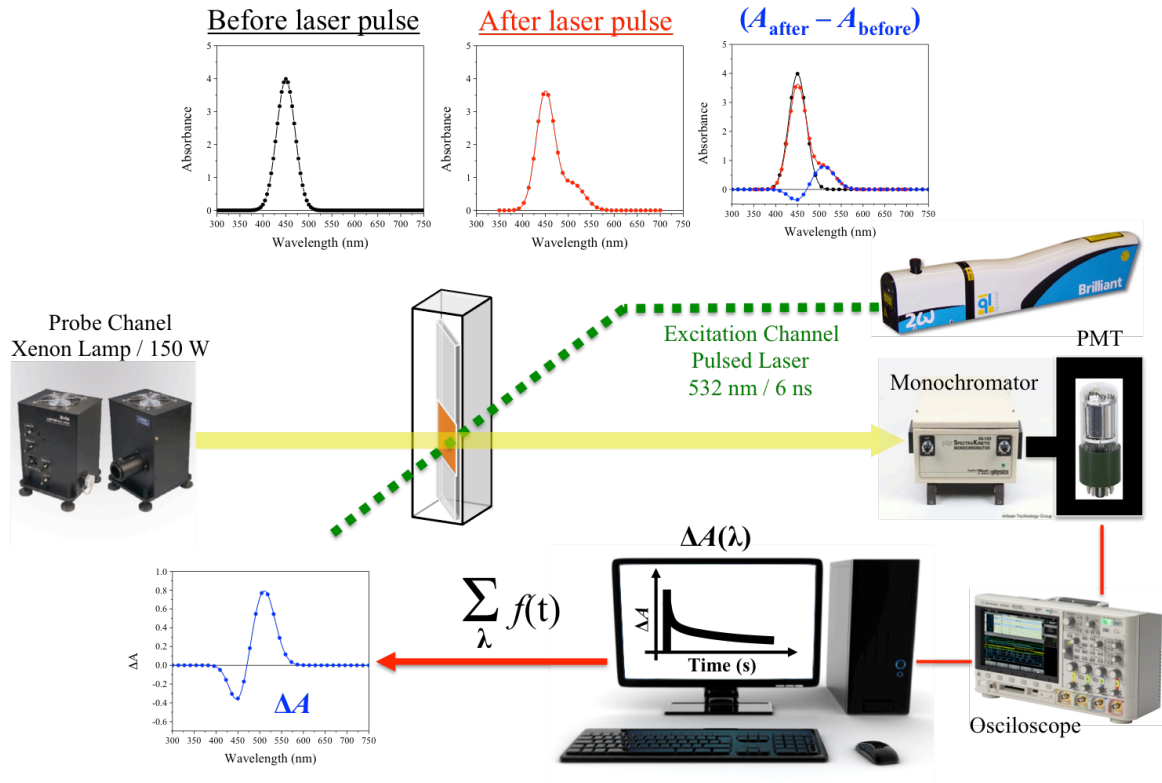


Figure I-3. Typical experimental structure of the transient absorption experiments.

Mathematically speaking, the transient absorption kinetics can be derived from the conventional Beer-Lambert Law. Assuming two cases, Figure I-4, on before and another after pulsed laser excitation, A), $I_1 = I_0 e^{-A_1}$ and B), $I_2 = I_0 e^{-A_2}$, respectively. Where I is the intensity of the transmitted light and A is the absorbance of the system at each condition.

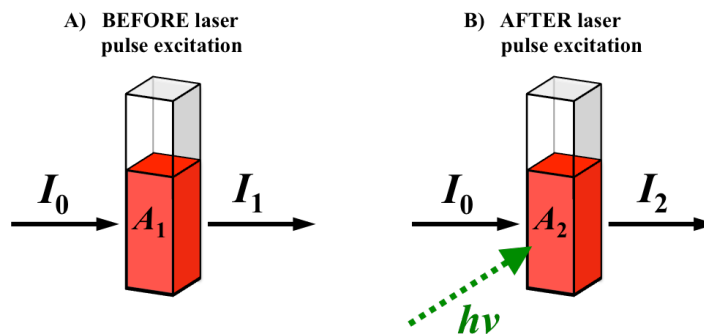


Figure I-4. Illustration of the system conditions before and after pulsed laser excitation.

Connecting both situation by doing the division I_1/I_2 :

$$\frac{I_1}{I_2} = e^{(A_2 - A_1)} = e^{\Delta A} \quad (\text{I-1})$$

where quantities A are directly related to the concentration of species in conditions created before and after laser pulse excitation: $A_1 = \varepsilon_1 N_0(t)$ and $A_2 = \varepsilon_1 N_1(t) - \varepsilon_2 N_2(t)$. Where the concentration are time-dependent and $N_0(t)$, $N_1(t)$, $N_2(t)$ are respectively the initial concentration of molecules in their initial condition or ground state (before laser pulse excitation), the concentration of molecules left in the initial condition and those that went any kind of photo-reaction process after laser pulse excitation. Concentration, N , is usually given in Mol/L while ε is the molar extinction coefficient and is commonly given in $\text{M}^{-1}\text{cm}^{-1}$. The absorbances in Equation I-1 can then be rearranged, knowing that $N_0(t) = N_1(t) + N_2(t)$, to finally give what is measured in the experiment:

$$\Delta A = (\varepsilon_2 - \varepsilon_1) N_2(t) \quad (\text{I-2})$$

where $N_2(t)$ express the concentration of molecules in a specific transient state formed the after light excitation. The extinction coefficient of the species is a constant quantity while their concentration changes over time. The Equation I-2 mathematically express the kinetic traces observed in transient absorption experiments.

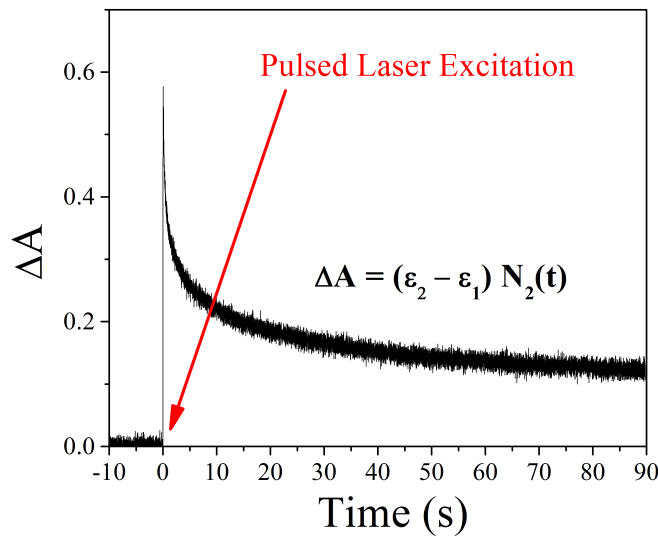


Figure I-5. Example of a transient kinetics observed in transient absorption experiments.

It is noteworthy to say that each transient kinetic is associated with a specific probed wavelength. In many works authors might refer to plots called the transient spectrum. The transient spectrum can be build by plotting the change in absorbance, ΔA , of several wavelength of interest in the electromagnetic spectrum from a specific time delay (t). When ΔA is expressed as a multiple plots, in a single graph window, for many time delays, it's possible to observe the time evolution of ΔA associated with the formation and/or disappearance of a transient specie.

CHAPTER 1: Influence of the Solvent-Porphyrin Interaction on the UV-Vis Absorption of Free Base Imidazol Cationic Porphyrin.

1.1. INTRODUCTION

Porphyrins are highly conjugated compounds formed by four pyrrole rings connected at the α position of the ring by unsaturated methine bridges completing the macrocycle. Besides their excellent photostability and intense absorption in the UV-Vis spectral region, they also present great potential for application in a huge amount of fields, varying from photomedicine⁴⁶ to photonics⁴⁷. Mainly due to such applications, porphyrins and derivatives are focus of a large amount of investigations over the past decades. Particularly, due to the direct correlation with the electronic structure of the macrocycle, the investigation of the optical absorption features at UV-Vis region, and how external factors are able to affect them, is, even nowadays, an important research field with great impact on: (i) fundamental understanding of light-matter interaction processes^{47,48} and (ii) development of new devices, as for instance, optical limiters⁸. It is known that solvent polarity has great influence on the UV-Vis spectrum of porphyrin, as also has the presence of outlying groups that can distort the ring, directly or through hydrogen bonding with solvent, generating spectral shifts and changes in the absorption intensity and bandwidths.^{13, 49-51} The most common observation about the effect of substituents on the UV-Vis spectral features of porphyrins is the change of the two protons by a metal ion, at the center of the macrocycle. Such modification changes dramatically the structuration of the Q band, mainly due to the changes in the ring symmetry.¹⁹

In the present work we performed a systematic investigation on the UV-Vis absorption spectra of a cationic free base 5,10,15,20-tetrakis (1,3-dimethylimidazolium-2-yl) porphyrin tetraiodide ($H_2TDMI\text{mP}$) in polar solvents at different porphyrin concentrations. $H_2TDMI\text{mP}$ is a porphyrin-type molecule formed by the presence of cationic imidazolium group linked to the mesocarbon of the structure, as depicted in Figure 1.1.

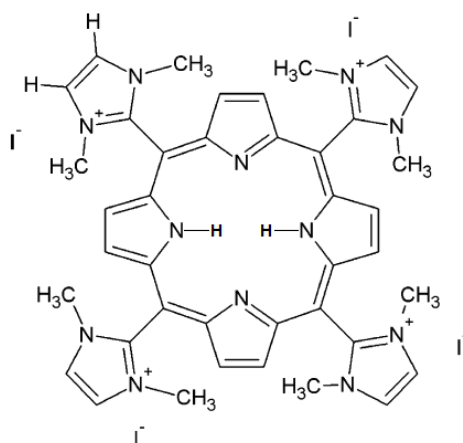


Figure 1.1. Representation of the molecular structure of the free base 5,10,15,20-tetrakis (1,3-dimethylimidazolium-2-yl) porphyrin tetraiodide).

Our data showed that H₂TDMImP presents an unconventional absorption spectrum in both Soret and Q-band regions when dissolved in polar solvents at low concentration. We observed that the shape of the Q-band is formed by two, Q_y(0,0) and Q_x(1,0), stronger sub-bands, contrary to what is observed for other monomeric ionic porphyrins, like free base tetrasulphonatophenyl (H₂TPPS₄)⁵² and tetramethylpyridil (H₂TMPyP)⁵³ that present *phyllo* type spectra^{12,54}. Moreover, the Soret band presented a small shoulder at low energy portion of the spectrum. Quantum chemical calculations suggested that such spectral features were caused by the interaction between the cationic imidazolium group, linked to the mesocarbon, and solvent molecules. Finally, since the formation of molecular aggregates allows us to understand the processes of intermolecular interactions^{48,55}, we acquired different UV-Vis spectra increasing the porphyrin concentration. Spectroscopic signatures indicated that increasing the porphyrin concentration H-type aggregates were formed, as observed for other cationic porphyrins.^{55,56} Furthermore, the results also suggest that the H-type aggregates were shielding the cationic outlying group from solvent interaction, restoring the Q and Soret band usual structuration.

1.2. Experimental Methods

1.2.1 – Spectroscopic Measurements

The free base 5,10,15,20-tetrakis(1,3-dimethylimidazolium-2-yl) porphyrin tetraiodide was synthesized following the procedure previously described, by professor Rodrigo de Paula from Universidade Federal do Recôncavo da Bahia.⁵⁷

The UV-Vis spectra were acquired through the use of a UV-Vis spectrophotometer Shimadzu model 1650, for solutions prepared in different solvents and with distinct concentrations, in order to observe the possible formation of porphyrin aggregates.

Moreover, this porphyrin is not soluble in apolar solvents, which is expected due to its cationic nature. Consequently, a set of polar, protic (ethanol, methanol and water) and aprotic (acetone, acetonitrile, dimethylformamide, dimethylsulfoxide) solvents were employed to prepare the solutions. The H₂TDMI_{Im}P has good solubility in all solvents employed, for all investigated concentrations. In all experiments, solutions containing the cationic porphyrins were prepared in different solvents with concentrations varying from $\approx 2.7 \mu\text{M}$ to about $\approx 14.5 \mu\text{M}$.

1.2.2 – Quantum Chemical Calculations

Quantum chemical calculations were performed using the Gaussian 09 software⁵⁸, in collaboration with Prof. Antônio Eduardo da Hora Machado from the Instituto de Química - UFU. Briefly, the singlet ground state structure of associations involving the combination between H₂TDMI_{Im}P and different amounts of explicit molecules of ethanol was optimized using the global hybrid meta-GGA (DFT) M06 functional and the 6-31G(d,p) basis set⁵⁸, under a self-consistent reaction field approach (SCRF) based on the application of the integral equation formalism polarizable continuum model (IEFPCM) to build a continuum of uniform dielectric constant simulating the solvation of this compound in ethanol.^{59,60} All calculations were done without any symmetry constraints, and geometries were confirmed as stationary structures by the presence of only real vibrational frequencies. The lowest 30 singlet-singlet excitations and the corresponding oscillator strengths were calculated from the optimized

structures, in a TD-DFT and self-consistent reaction field approaches, using the same functional and the 6-311G(d,p) basis set.

1.3. RESULTS AND DISCUSSIONS

1.3.1 – Electronic Absorption Spectrum

The electronic absorption spectrum at the UV-Vis region acquired for H₂TDMImP in ethanol, with concentration of 2.7 μ M, is presented in Figure 1.2. It is basically composed by a strong Soret band, around 416 nm (Figure 1.2A), and a structured Q band, with four sub-bands, located between 479 nm and 650 nm (Figure 1.2B).

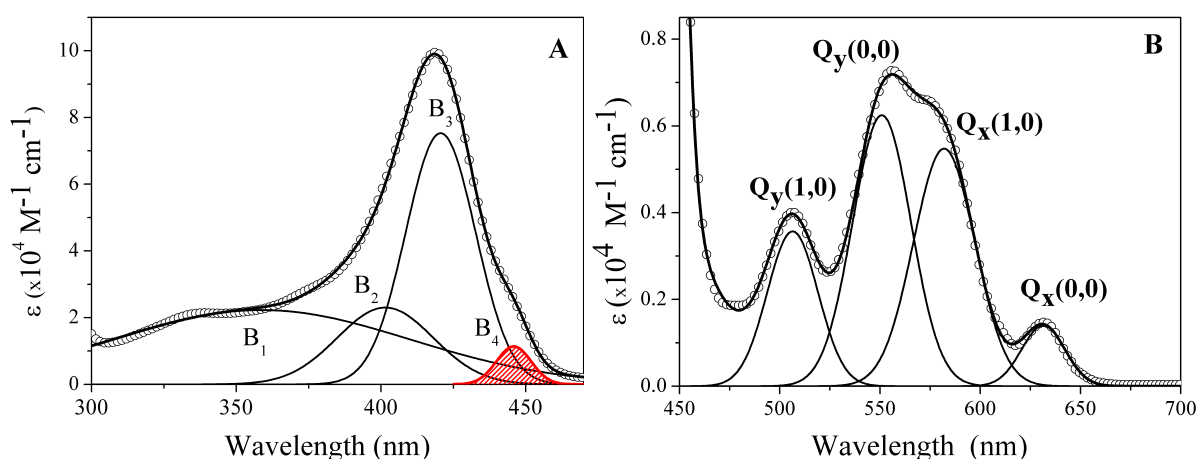


Figure 1.2. Gaussian deconvolution for H₂TDMImP in ethanol, with a concentration around 2.7 μ M, for the (A) Soret band and (B) Q-band regions. The open circles are the experimental data, the solid black lines are the theoretical curves obtained from Gaussian deconvolution and the red solid band is the Gaussian curve assigned to the new unusual shoulder at low energy region.

The Gaussian deconvolution shows that Soret band was composed by four sub-bands, the more energetic and broader one named as B₁, two of intermediate energy, named B₂ and B₃, responsible for the characteristic peak of Soret band, and a less energetic and intense one located around 446 nm (see sub-band in red at Figure 1.2A), assigned to the shoulder observed at the low-energy portion of Soret band. The observation of this shoulder is not usual since, typically, the UV-Vis spectrum observed for free base ionic porphyrins in

solution, presents a Soret band formed by three sub-bands assigned to vibrational transitions from the ground state to the second excited singlet state.^{14, 52-53}

Concerning to the Q-band, Figure 1.2B, H₂TDMImP presented a structuration in which the Q_y(0,0) and Q_x(1,0) sub-bands are the stronger ones, depicting a pronounced *rhodo* type spectrum^{12,54}. Except for water, acetone and acetonitrile, the observed structuration of Q-band was observed for all polar solvents employed in this investigation, see Figure 1.3.

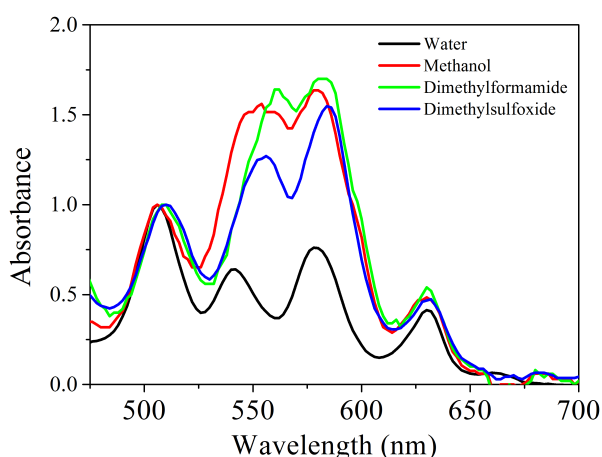


Figure 1.3. Absorption spectra at the Q-band region for H₂TDMImP, in different polar solvents. The concentration of H₂TDMImP employed was around 3 μ M for all samples.

Aiming a deeper understanding of the H₂TDMImP absorption spectrum we carried out quantum chemical calculations, performed in three different environments: free base isolated (gas-phase), solvated in ethanol by a continuum dielectric, and finally using the combination of a continuum dielectric and explicit ethanol molecules, as explained in Section 1.2. It was noted from these calculations a small angular distortion of the porphyrin ring, due to the presence of ethanol explicit molecules, with respect to the plane containing the ring without explicit molecules, as depicted in Figure 1.4.

The calculations showed that such distortions were caused by the interaction between ethanol molecules and imidazolium outlying moieties, changing the overlap between vibronic states in transitions attributed to Q-band, magnifying some of them, e.g. Q_x(1,0) and Q_y(0,0), and being deleterious for other ones. It is worth mentioning that the distortion of the ring increased as the number of ethanol molecules was increased. Moreover, the magnification of Q-band vibrational modes assigned to transitions at y- and x-directions strongly suggests that this effect was caused by interactions occurring at the diagonal direction of the ring,^{2,3} at the mesocarbon positions, where dimethylimidazolium groups are located.

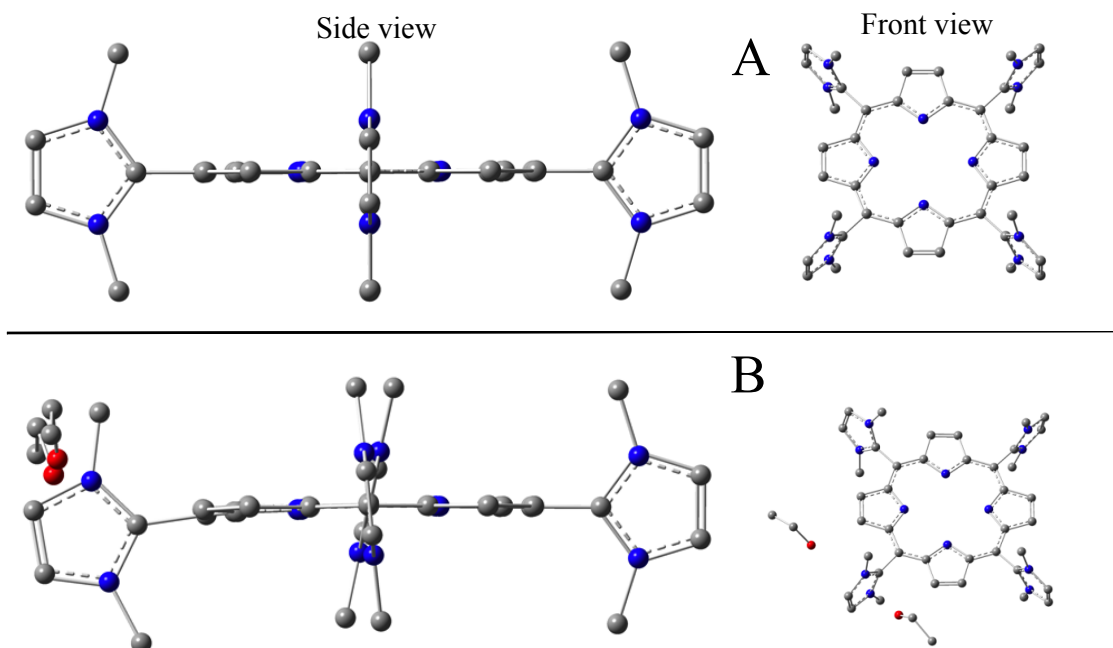


Figure 1.4. Structure of $H_2TDMIImP$ in (A) continuum dielectric environment and (B) continuum dielectric plus two ethanol molecules. The distortion of the ring generated by the presence of explicit ethanol molecules can be clearly seen. The hydrogen atoms were excluded for sake of clarity.

By the comparison of transitions obtained from experiments and calculations, it was also concluded that the Q bands were essentially composed by the combination of the following molecular orbitals: HOMO-1, HOMO, LUMO and LUMO+1, while the Soret band (the most energetic transitions) was composed by more internal orbitals (below HOMO-1) and the LUMO and LUMO+1. In Figure 1.5 is plotted the calculated transition energies obtained for the isolated porphyrin, under the continuum dielectric solvation and after the addition of explicit molecules of ethanol. The graphic shown in Figure 1.5 were built just considering transitions with significant values of oscillator strength (higher than 0.005).

It was seen that the energies attributed to both, Q and B band transitions, remained almost unchanged, suggesting that the HOMO-LUMO energy gap was not influenced by interactions between this porphyrin and ethanol molecules. In fact, from the calculated state energies it was verified that the increase in the number of explicit molecules of ethanol magnifies the energy of both HOMO and LUMO by almost the same amount, which explains the unchanged HOMO-LUMO energy gap.

It is also noted that, differently of the Q-band, for the Soret band, the number of possible transitions increases (see Figure 1.5) with the presence of ethanol molecules.

Furthermore, the calculations suggested that the oscillator strengths attributed to lower energy transitions, at B-band, were enhanced by the increase of the number of explicit ethanol molecules, increasing the participation of these transitions in the observed final spectrum. For instance, for the transition at ~ 3.26 eV the oscillator strength varied from 0.701, in the presence of one explicit molecule of EtOH, to 0.979 in the presence of four explicit EtOH molecules. This observation perfectly matches with the observed shoulder located at the lower energy region of Soret band for H₂TDMIImP (446 nm). For the Q-band, the calculations indicated that although expressive changes have not been observed in the HOMO-LUMO gap, there was a intensification of the oscillator strength of transitions located in the central part of the band.

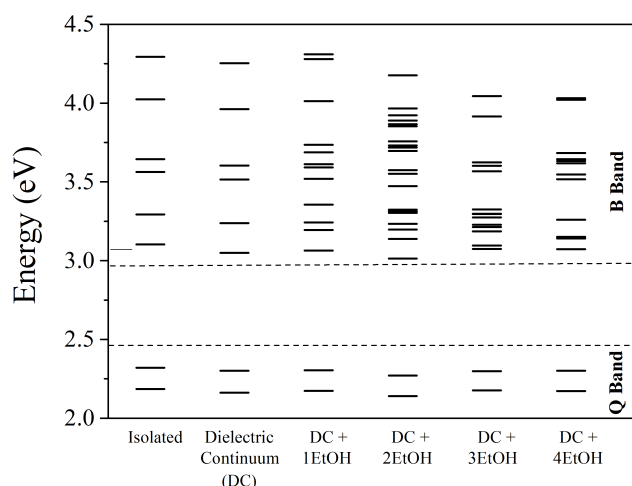


Figure 1.5. Energy for possible singlet-singlet transitions calculated for H₂TDMIImP, in different environments. Transitions with oscillator strength lower than 0.005 were disregarded in the analysis.

In Figure 1.6 is plotted the orbitals assigned to transitions located at Soret Band, HOMO-3 and LUMO orbitals. It was observed that in the presence of explicit solvent molecules, the HOMO-3 orbital was comprised by the solvent and the imidazolium group while the LUMO was located at porphyrin ring. However, in the absence of explicit solvent molecules, even the more internal orbitals, were always located at porphyrin ring.

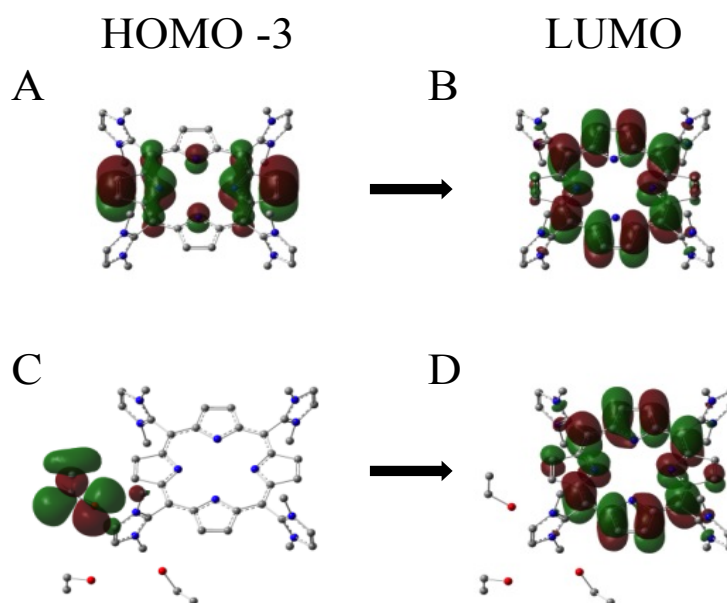


Figure 1.6. HOMO-3 and LUMO molecular orbitals for H₂TDMImP solvated by a continuum dielectric (A and B) and in a continuum dielectric combined with three explicit ethanol molecules (C and D). The hydrogen atoms were excluded for the sake of clarity.

In fact, from the calculations it was also observed that, in the presence of explicit ethanol molecules, the orbitals assigned to transitions at the region of Q-bands (HOMO, HOMO-1) were only located at porphyrin ring. On the other hand, the more internal orbitals assigned to transitions in the Soret band were located mostly on ethanol molecules and cationic peripheral groups, see Figure 1.7.

As the unoccupied orbitals were located in the porphyrin ring, we conclude that some transitions assigned to Soret Band were mainly from orbitals located in the ethanol molecules and imidazolium groups, to orbitals at porphyrin ring. Such combination of orbitals characterized charge transfer from solvent molecules to porphyrin ring, suggesting a strong solvent-porphyrin interaction. Figure A1.2 shows all calculated orbitals for different number of explicit ethanol molecules.

In fact, it is known that porphyrin structures with outlying ruthenium complexes linked to pyridyl moieties of H₂TPyP, also located at mesocarbon, present a red shift of Soret band caused by the enhancement of low energy transitions.¹³ Such similarity in the observed behavior of the Soret band, corroborates with the idea that the interaction of solvent and imidazolium ring, located at meso positions, was responsible by the shoulder observed at 446 nm.

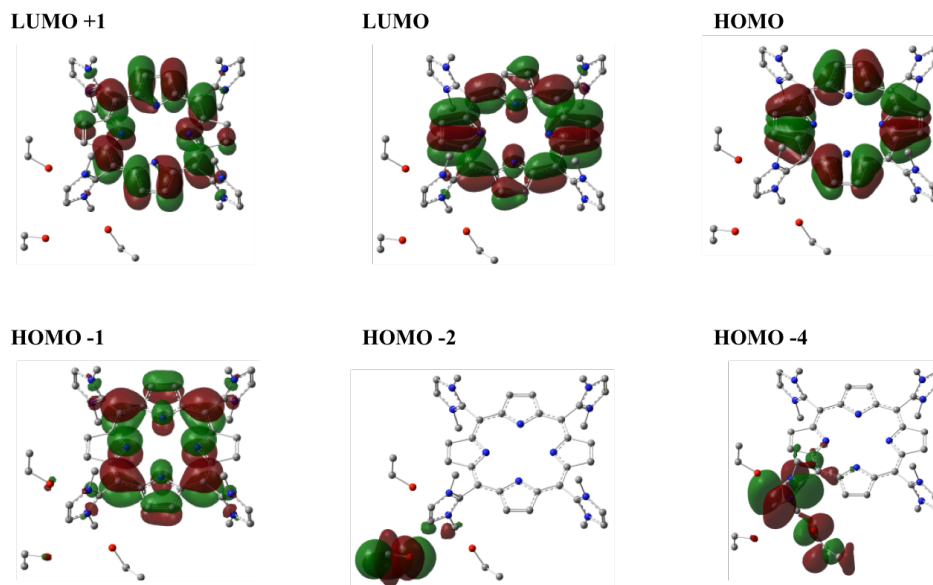


Figure 1.7. Molecular orbitals of H₂TDMImP in presence of three ethanol explicit molecules. The hydrogen atoms were excluded for the sake of clarity. A more detailed picture is also presented in Figure A.1.1, in the chapter Appendix.

1.3.2 – *H*-aggregate Formation

As it is well known ionic porphyrins tends to form aggregates in concentrated solutions, and since molecular aggregates furnish valuable information to understand the processes of intermolecular interactions,^{48,55} UV-Vis spectra measurements were performed increasing the H₂TDMImP concentration.

In Figure 1.8A, it is presented the electronic spectra for H₂TDMImP in ethanol acquired for different concentrations, varying from ~2.7 μ M (initial concentration) to ~14.5 μ M. In this titration experiment, the absorbances were monitored via Beer-Lambert Law, $A = \epsilon \cdot N \cdot L$, where N is concentration, L is the optical path and ϵ , specifically here, did not represent the real extinction coefficient of the molecule but instead, it means a proportionality constant for further comparison between the spectra in different concentrations of the monomers (N).

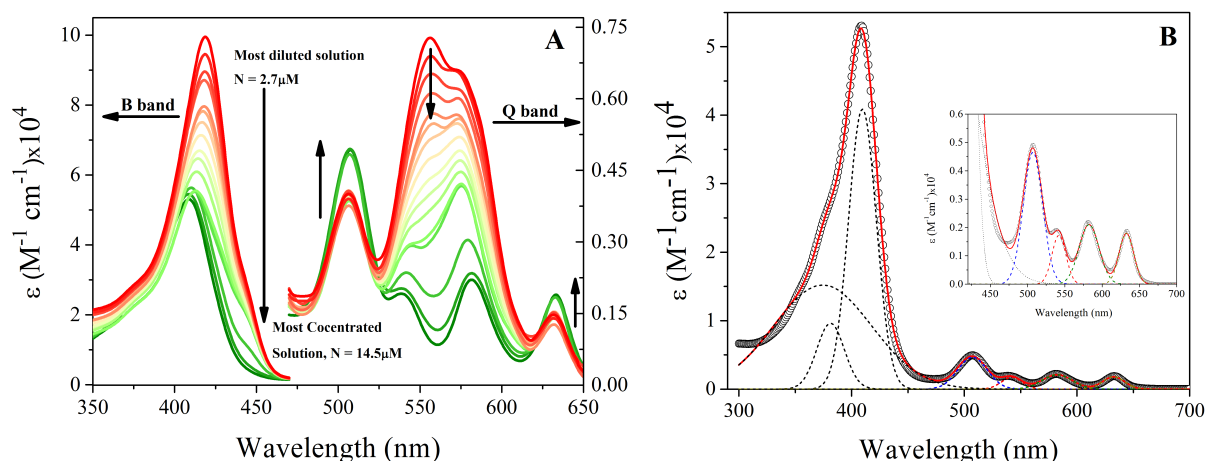


Figure 1.8. (A) UV-Vis absorption spectra for H₂TDMImP in ethanol, acquired at different concentrations and (B) Gaussian deconvolution for H₂TDMImP spectrum, in ethanol at a concentration around 15 μ M. The open circles are the experimental data, the solid red line is the theoretical curve obtained from Gaussian deconvolution (dashed black line). The inset, in Figure 1.8B, presents the highlighted Q-band region.

It was observed that for concentrations of $\sim 14.5 \mu\text{M}$ the magnitude of the Soret band was reduced to 50% of its initial amplitude, being such band blue-shifted in about 10 nm. Moreover the *phyllo* type structure of the Q-band was completely recovered (see Figure 1.8B) and the shoulder at 446 nm completely disappeared.

As expected, an increase in the concentration of H₂TDMImP caused a well-known spectroscopic behavior attributed to the formation of H-type aggregates (decrease of the magnitude of the Soret Band as well as its blue shift), strongly suggesting that aggregates were formed by porphyrin moieties.^{55,56,61,62} Furthermore, changes in fluorescence spectrum, with the increase of the H₂TDMImP concentration corroborate with the hypothesis of aggregate formation. In Figure 1.9 is shown the fluorescence spectra, corrected to the changes in the solution absorbance according to reference [55] and acquired for the lower and higher investigated concentrations.⁵⁵

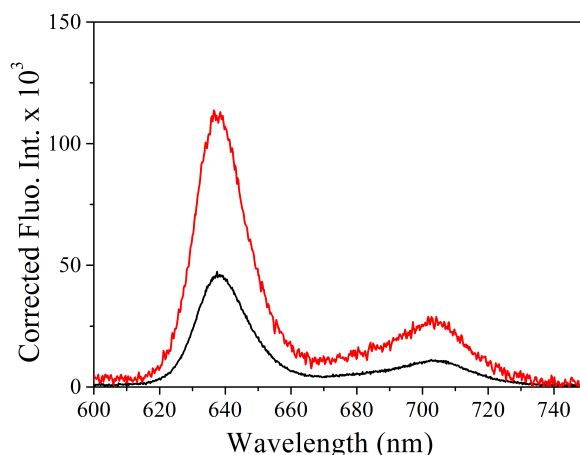


Figure 1.9. Corrected fluorescence spectra of H₂TDMImP in ethanol acquired for concentrations of $\approx 3 \mu\text{M}$ (red solid curve) and $\approx 15 \mu\text{M}$ (black solid curve), with excitation wavelength at 514 nm.

It was observed that the increase of porphyrin concentration reduces the fluorescence intensity but did not change the spectral shape of the fluorescence spectrum, a clear evidence for aggregate formation.

H-type aggregates are face-to-face aggregates generally formed by ionic porphyrins due to many kinds of environment features such as: increase in the porphyrin concentration,^{56,62} increase of the ionic strength,⁵⁵ combination of porphyrins with metal nanoparticles in hybrid solutions⁵⁶ and many others.

Accompanying the spectra behavior shown in Figure 1.8A it became clear that the formation of H-type aggregates was responsible by the drastic changes observed in the Q-band structuration and by the disappearance of the shoulder at 446 nm. In fact previous work have reported H-type aggregates of cationic porphyrin presenting the *Phyllo* structuration type for Q-bands.⁵⁶ Thus, since the spectral features assigned to the interaction between cationic imidazolium groups and solvent molecules disappeared due to the formation of H-type aggregates, our results strongly suggested that the formation of aggregates shielded the interactions between outlying groups and solvent molecules. The same behavior was also observed for other solvents, including the aprotic solvents dimethylformamide and dimethylsulfoxide, supporting that the aggregate formation was responsible by the shielding of the porphyrin against the solvent interaction.

1.4. CONCLUSIONS

In conclusion, the combination of experimental and theoretical data strongly suggested the influence of the solvent-porphyrin interactions on the absorption spectra of the free base cationic porphyrin derivative, 5,10,15,20-tetrakis (1,3-dimethylimidazolium-2-yl) porphyrin tetraiodide, in polar solvents. Quantum chemical calculations showed that the interaction between polar solvent molecules and imidazolium cationic groups should distort the porphyrin ring, which explains the changes in the shape of the Q-band. Moreover, the calculations revealed that the low energy electronic transitions at the Soret band region had their oscillator strengths magnified by the interaction with ethanol molecules, what explains the behavior experimentally observed. Finally, the changes observed in the UV-Vis spectrum, mainly at Q-band region, due to the formation of H-type aggregates, strongly suggested that the aggregates were shielding the interaction between imidazolium groups and solvent molecules.

1.5. APPENDIX

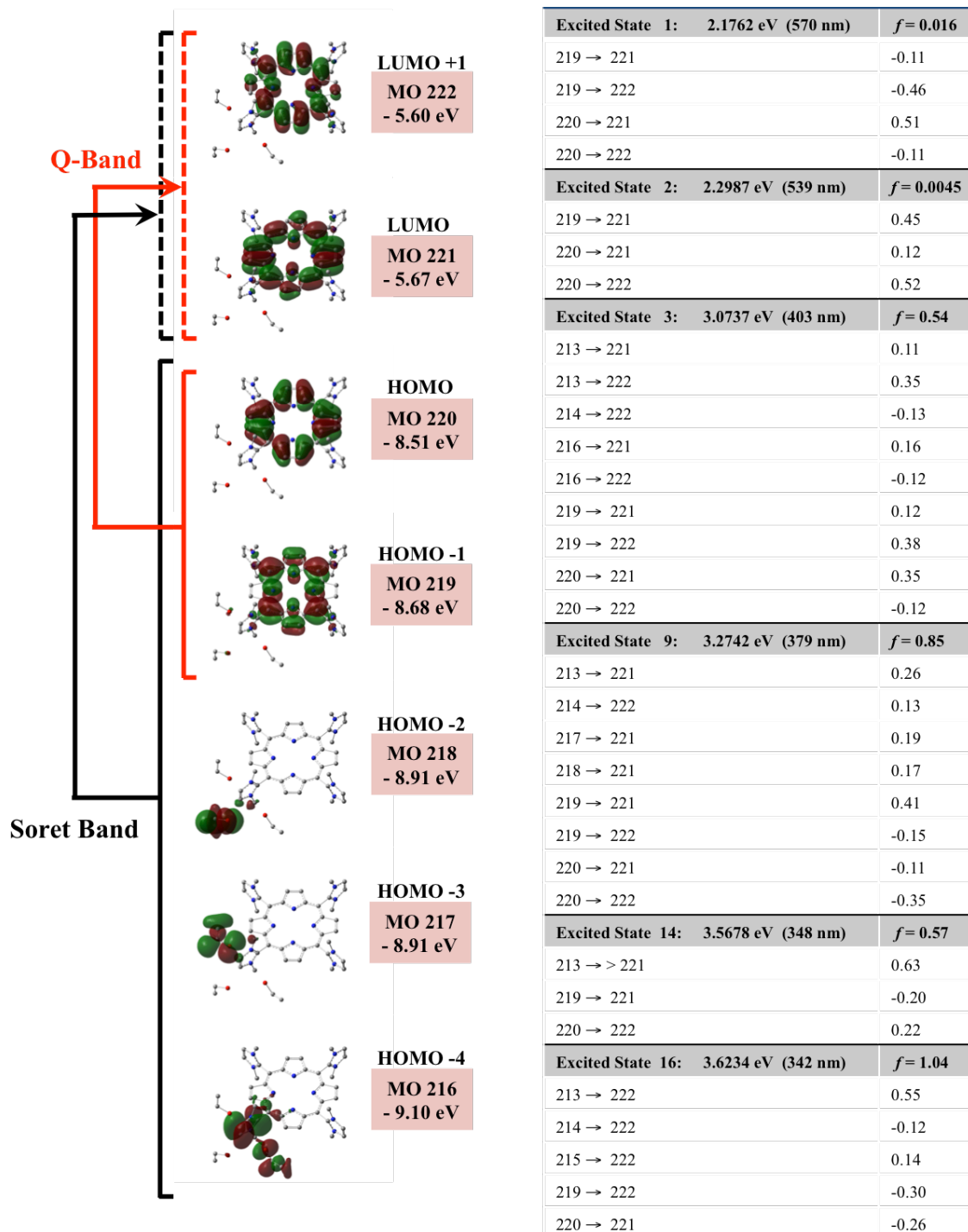


Figure A1.1. Calculated molecular orbitals and the resultant excited states of H₂TDMImP solvated with a dielectric continuum (ethanol) and in the presence of three ethanol molecules.

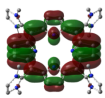
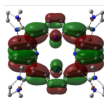
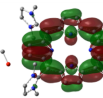
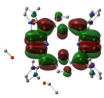
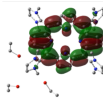
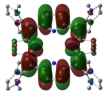
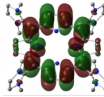
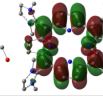
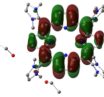
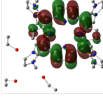
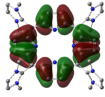
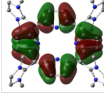
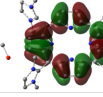
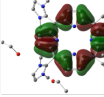
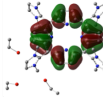
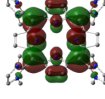
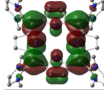
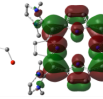
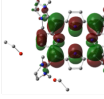
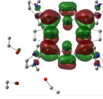
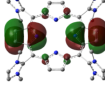
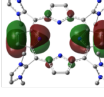
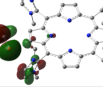
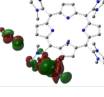
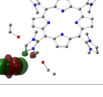
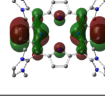
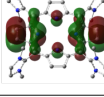
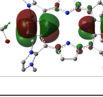
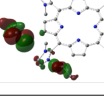
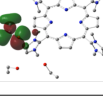
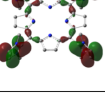
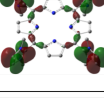
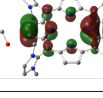
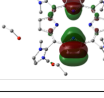
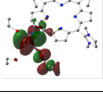
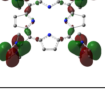
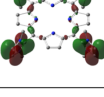
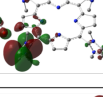
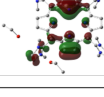
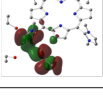
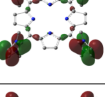
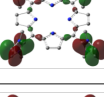
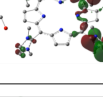
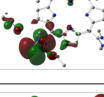
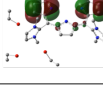
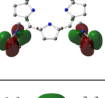
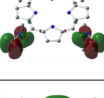
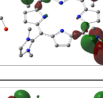
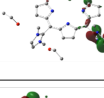
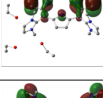
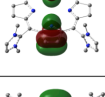
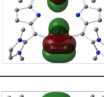
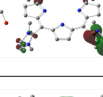
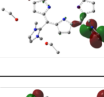
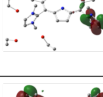
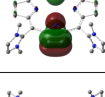
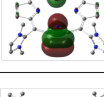
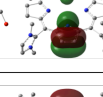
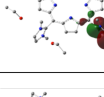
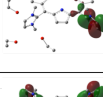
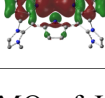
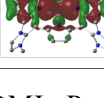
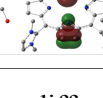
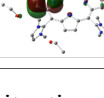
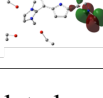
MO	Solvent Configuration				
	ISOLATED	DC	DC + 1EtOH	DC + 2EtOH	DC + 3EtOH
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LUMO					
HOMO					
HOMO -1					
HOMO -2					
HOMO -3					
HOMO -4					
HOMO -5					
HOMO -6					
HOMO -7					
HOMO -8					
HOMO -9					
HOMO -10					

Figure A1.2. Calculated MO of H₂TDMIImP at five different situations: isolated, solvated with a dielectric continuum and with one, two and three explicit ethanol molecules.

CHAPTER 2: Comparison of the Photophysical and Photochemical Properties of a Free Base Tetrapyrrolic Porphyrin With External Ruthenium(II) Groups.

2.1. INTRODUCTION

Porphyrins are aromatic macrocyclic molecules formed by four pyrrole rings linked by unsaturated methylene bridges.¹² This class of compounds is present in a great variety of natural processes such as photosynthesis (Mg porphyrins), oxygen transport and storage (iron porphyrins), and in many others.⁵ Besides the interest in understanding these natural processes, porphyrins are also widely studied because of their potential applications in fields such as photonics,⁶³ medicine (e.g., cancer therapy),^{46, 64} gas sensors,⁶⁵ molecular devices,^{9, 66} energy conversion, and solar cells.⁶⁷ In free-base types, two central protons are linked to the nitrogen atoms of the porphyrin ring to assure structural stability.¹² In particular, 5,10,15,20-tetra(pyrrolic)-21H,23H-porphyrin, herein abbreviated H₂TPyP, is formed by four pyrrolic groups attached to the mesocarbons of the macrocycle, as shown in Figure 2.1.

A major advantage of this class of compounds is the possibility of carrying out structural modifications that can tune some specific property with the aim of improving its behavior. Efforts in this direction have been made through changes of the central ion,¹⁶⁻¹⁷ aggregate formation,^{31, 68-69} insertion of lateral and axial ligands,⁷⁰⁻⁷¹ oligomers,⁷² isomeric structures,⁷³ cationic porphyrins,^{14, 53} and others. Systematic studies on the relation between photophysical properties and molecular structure are necessary to understand these modifications.

Due to the electronic similarity between ruthenium and iron, the role of ruthenium placed at the center of the macrocycle and the influence of different types of ligands on the photophysical and photochemical properties of porphyrins has been exhaustively investigated in the past decades.⁷⁴⁻⁷⁷ It is known that when Ru²⁺ is inserted at the center of the macrocycle,

the resulting irregular porphyrin gives rise to a strong quenching of the emission due to the intense interaction between the central ion and the π electrons of the macrocycle ring.^{12, 74} Moreover, a strong dependence between the nature of the axial ligand and the photophysical characteristics, mainly for the lowest excited-state, is also observed.⁷⁵

Concerning about ruthenium outlying groups, great interest arises owing to its potential to form supramolecular porphyrin structures,⁷⁸ which have great influence on the photophysical properties of these molecules.^{71, 78-80} Moreover, it is largely known that ruthenium compounds, similar to that used here as outlying group attached to the H₂TPyP molecule, are one of the most employed structures in dye sensitized solar cells (DSSCs) devices. The combination of such structures with porphyrin rings can expand the spectral range for light harvesting, which could lead to the increase in the cell efficiency. However, to hint such target, photophysical investigations are imperative as a starting point. One desired objective of such investigations is to probe the potential these molecules have to be employed as sensitizers in DSSCs.

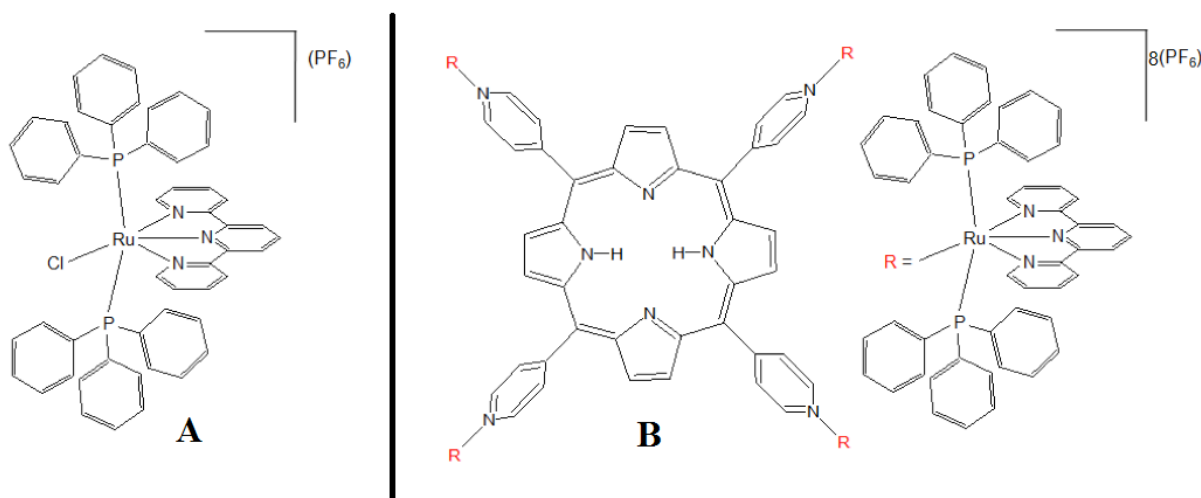


Figure 2.1. Molecular structures of (A) $[\text{Ru}(\text{terpy})(\text{PPh}_3)_2\text{Cl}]\text{PF}_6$ and (B) $\{\text{H}_2\text{TPyP}[\text{Ru}(\text{terpy})(\text{PPh}_3)_2]_4\}8\text{PF}_6$, where $\text{R} = [\text{Ru}(\text{terpy})(\text{PPh}_3)_2]\text{PF}_6$. The absence of the external ligands R gives the unsubstituted free base tetrapyrrolic porphyrin, H₂TPyP.

Here, we study a regular type of porphyrin having external ruthenium groups interacting with the electrons of the porphyrin ring via a pyridine bridge, as depicted in Figure 2.1, and the isolated ruthenium substituent for comparisons. The ruthenium complex, $[\text{RuCl}(\text{terpy})(\text{PPh}_3)_2]\text{PF}_6$, simplified to $\text{Ru}(\text{terpy})\text{PPh}_3$ has one 2,2';6',2''-terpyridine ligand (terpy) and two triphenylphosphine groups (PPh_3) linked to the ruthenium(II) metal, and a

chloride. The complexation of four Ru(terpy)PPh₃ at the pyridines of the porphyrin ring originates the {H₂TPyP[Ru(terpy)(PPh₃)₂]₄}8PF₆ porphyrin, abbreviated to H₂TPyP-Ru(terpy)PPh₃.

2.2. EXPERIMENTAL METHODS

2.2.1 – Materials and Preparations

Materials. The following reagents were used as received from the indicated commercial suppliers: dichloromethane (CH₂Cl₂; Sigma Aldrich); tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆; Sigma Aldrich, ≥99.0%); Rhodamine B (Sigma Aldrich, ≥95.0%); argon gas (Airgas, >99.998%).

Preparation. The compounds were synthesized by the group of Prof. Alzir Batista from the Departamento de Química of the Universidade Federal de São Carlos (UFSCar). In brief, the [RuCl(terpy)(PPh₃)₂]PF₆ [terpy= 2,2':6',2''-Terpyridine, PPh₃= Triphenylphosphine] complex was synthesized following the published procedures.⁸¹ The H₂TPyP[Ru(terpy)(PPh₃)₂]₄4PF₆ was synthesized from 15 mg (2.24x10⁻⁵ mol) of TPyP (5,10,15,20-tetra(4-pyridyl)porphyrin) and 106 mg (1.01x10⁻⁴ mol) of [RuCl(terpy)(PPh₃)₂]PF₆ in 10 mL of a mixture of chloroform (95%) and methanol (5%). The solution was stirred for 12 h, the volume was reduced to at about 10 mL and ether was added to give a brown powder. The excess of [RuCl(terpy)(PPh₃)₂]PF₆ was removed by dissolution of the product in CH₃OH followed by filtration. The filtrate was reduced to 1 mL, and ether was added to give the desired compound. Yield: 70 mg (93,5 %). Anal. calcd for C₂₄₄H₁₉₀F₂₄N₂₀P₁₂Ru₄.H₂O: C, 62.99; H, 4.16; N, 6.02%. Found: C, 62.64; H, 4.19; N, 5.86%. IR (1% KBr solution) $\nu_{\text{max}}/\text{cm}^{-1}$: 1592 ($\nu_{\text{C=N}}$), 1437, 1086 and 979 ($\nu_{\text{P-C}}$), 841 (PF₆), 740 ($\delta_{\text{C-H}}$), 692 ($\delta_{\text{C-H}}$), 562(PF₆) 513 ($\nu_{\text{Ru-P}}$); cyclic voltammetry: redox pair Ru^(II)/Ru^(III), E_{1/2} = 1003.5 mV, E_{ap}/cp = 0,89; ³¹P{¹H} NMR: (Singlet) 20.6 (ppm); molar conductivity (CH₂Cl₂): 332 $\mu\text{S}/\text{cm} - 1:4$.

2.2.2 – Spectroscopy and Electrochemistry

UV-Vis Absorption. Steady-state UV-visible absorption spectra were obtained on a Varian Cary 50 spectrophotometer at room temperature in 1.0 cm path length quartz cuvette. The solutions were prepared in dichloromethane with concentrations of 4.3 μM and 3.2 μM for $\text{H}_2\text{TPyP-Ru(terpy)PPh}_3$ and Ru(terpy)PPh_3 respectively, from which was obtained their extinction coefficient, ϵ , using Beer-Lambert's Law. For further studies of photoluminescence and transient absorption the solutions were purged with argon gas for a minimum of 20 minutes.

Photoluminescence. Steady-state photoluminescence (PL) spectra and excitation spectra (ES) were obtained with a Spex Fluorolog spectrophotometer equipped with a 450 W Xe lamp for the excitation source, with samples dissolved in dichloromethane, argon gas purged, and placed in a 1.0 cm thick quartz cell. Was used a 90° configuration for detection of the signal. The excitation wavelengths were adjusted using a monochromator placed between the light source and the sample. The concentrations employed in these PL measurements were controlled via absorption measurements such that the absorption at the excitation wavelength did not exceed 0.2, in order to avoid reabsorption effects.

Photoluminescence quantum yield was calculated using the actinometry method where Rhodamine B was the reference standard.

Time-resolved photoluminescence. Photoluminescence decay times were obtained with an apparatus based on the time-correlated single photon counting method. The experiments were performed in collaboration with the laboratories of professor Iouri Borissevitch from the Universidade Federal de São Paulo – Ribeirão Preto. The excitation source was a titanium – sapphire laser (Tsunami 3950 – Spectra Physics), pumped by the second harmonic of a diode-pumped Nd:YVO₄ laser (Millenia – Spectra Physics), and frequency doubled to 465 nm in a LBO crystal (GWN-23PL – Spectra Physics).

Transient absorption. Nanosecond transient absorption measurements were obtained with an apparatus similar to that which has been previously described in the literature.⁸² Briefly, samples were excited by a Q-switched, pulsed Nd:YAG laser (Quantel U.S.A. (BigSky) Brilliant B; 5–6 ns full width at half-maximum (fwhm), 1 Hz, ~ 10 mm in diameter) tuned to

532 nm with the appropriate nonlinear optics. The excitation energy was measured by a thermopile power meter (Molelectron) and was typically 1–5 mJ/pulse so that the absorbed energy was typically <1 mJ/pulse. A 150 W xenon arc lamp served as the probe beam and was aligned orthogonal to the laser excitation light. The lamp was pulsed with 100 V for detection at sub-100 μ s time scales. Detection was achieved with a monochromator (Spex 1702/04) optically coupled to an R928 photomultiplier tube (Hamamatsu). Appropriate glass filters were positioned between the probe lamp/sample and the sample/detection monochromator. Transient data was acquired with a computer-interfaced digital oscilloscope (LeCroy 9450, Dual 350 MHz) with an overall instrument response time of $\sim$ 10 ns. Typically, 30 laser pulses were averaged at each observation wavelength over the range 400–750 nm, at 3 or 5 nm intervals. Full spectra were generated by averaging 2–10 points on either side of the desired time value to reduce noise in the raw data. For single wavelength measurements, 90–180 laser pulses were typically averaged to achieve satisfactory signal-to-noise ratios.

Electrochemistry. A potentiostat (Bioanalytical Scientific Instrument, Inc. (BAS) model CV-50W or EC Epsilon electrochemical analyzer) was employed for electrochemical measurements in a standard three-electrode arrangement with a glassy carbon working electrode (BAS), a Pt gauze counter electrode (BAS), and a nonaqueous silver reference electrode (BAS). The ferrocenium/ferrocene ($\text{Fc}^{+/0}$) half-wave potential was measured both before and after experiments in a 100 mM TBAPF₆/dichloromethane electrolyte that was used as an external standard to calibrate the reference electrode. All potentials are reported versus the normal hydrogen electrode (NHE) through the use of a conversion constant of -630 mV from NHE to $\text{Fc}^{+/0}$ in acetonitrile at 25°C.⁸³

2.3. RESULTS AND DISCUSSIONS

2.3.1 – Steady State Characterization.

The electronic spectra of the porphyrin $\text{H}_2\text{TPyP-Ru(terpy)PPh}_3$, the ruthenium complex Ru(terpy)PPh_3 and the H_2TPyP are present in Figure 2.2A. The $\text{H}_2\text{TPyP-Ru(terpy)PPh}_3$ UV-Vis absorption spectrum presented strong peaks at the UV spectral region,