ULTRAFAST EXCITED STATE RELAXATION DYNAMICS OF ELECTRON DEFICIENT PORPHYRINS: CONFORMATIONAL AND ELECTRONIC FACTORS

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ABSTRACT

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Metallo-tetrapyrroles (MTP) are highly stable macrocyclic π -systems that display interesting properties that make them potential candidates for various applications. Among these applications are optoelectronics, magnetic materials, photoconductive materials, non-linear optical materials and photo tumor therapeutic drugs. These applications are generally related to their high stability and efficient light absorption ability in the visible and near-infrared region of the optical spectrum. Metallo porphyrins are well known and widely studied representatives of metallotetrapyrroles.

Electron deficient substituents in the meso positions are well known to greatly influence the interaction between the metal d-orbitals and the nitrogen orbitals of the tetrapyrrole macrocycle. In this work, a series of electron deficient porphyrins has been studied to gain some knowledge about the change in the excited state dynamics with structural and electronic modifications. Among these porphyrins is nickel and iron modified species bearing perfluoro-, perprotio-, p-nitrophenyl- and perfluorophenyl- meso substituents. Ultrafast transient absorption spectrometry has been used as the main research instrument along with other spectroscopic and electrochemical methods.

A new technique has been employed to study the photophysical properties of zinc (II) tetraphenylporphine cation radical. It employs a combination of controlled potential coulometry and femtosecond absorption spectrometry. The fast transient lifetime of 17 ps of the π -cation species originates in very efficient mixing of the a_{2u} HOMO cation orbital that places electronic density mainly on pyrrolic nitrogens and metal d-orbitals. That explains the lack of any emission of the cationic species. This non-radiative decay process might elucidate the processes taking place in photosynthetic systems when electron is removed from porphyrinic moiety and the hole is produced. In this work zinc(II) meso-tetraphenylporphine radial cation species has been formed electrochemically *in situ* and studied by means of femtosecond absorption spectrometry to prove that this new technique could be used to elucidate the photophysical behavior of open shell species.

To my mom, dad, brothers and all others who helped me through all these years

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CHAPTER 1: INTRODUCTION

Tetrapyrrole Macrocycles: Background

Metallo-tetrapyrroles (MTP) are highly stable macrocyclic π -systems that display interesting properties that make them potential candidates for various applications. Among these applications are optoelectronics, magnetic materials,^{1,2} photoconductive materials, non-linear optical materials³ and photo tumor therapeutic drugs⁴. These applications are generally related to their high stability and efficient light absorption ability in the visible and near-infrared region of the optical spectrum. Metallo porphyrins are well known and widely studied representatives of metallotetrapyrroles.⁵⁻⁸

Typical ground electronic state absorption spectrum of a metalloporphyrin is shown in Figure 1.1:



Figure 1.1. A typical spectrum of a metalloporphyrin.

The spectrum of a metalloporphyrin has a characteristic very intense (ε >10⁵ M⁻¹*cm⁻¹) UV-vis transition in the range of 390-430 nm called Soret or B band and several weaker transitions in the vis-NIR region called Q bands.⁹ These spectra are well explained by Gouterman's four orbital model.⁹ In this model, the four orbitals are porphyrin π and π * orbitals; the two highest occupied molecular orbitals (HOMOs) of a_{1u} and a_{2u} symmetry, and the two lowest unoccupied molecular orbitals (LUMOs) of e_g symmetry (Figure 1.2):





Figure 1.2. The highest occupied molecular orbitals (a_{1u} and a_{2u} symmetry) and the lowest unoccupied molecular orbital (e_g symmetry) of metalloporphyrins⁹.

The two major absorbances arise from coupling of the two transitions between the HOMOs and LUMOs ($\pi \rightarrow \pi^*$) (Figure 1.3):



Figure 1.3. Molecular orbital diagram for the four-orbital model of metalloporphyrin absorbances.¹⁰

The Q bands are the result of the transition dipoles nearly canceling each other out, therefore resulting in a weaker absorbance. The higher energy Soret transition results from a linear combination of the two transitions with reinforcing transition dipoles and is therefore very intense. Some shifts in the positions of the bands as a function of metal are due to weak interaction of the metal with the a_{2u} and e_g orbitals.¹⁰ As shown in Figure 1.2, the a_{1u} orbital has nodes at the pyrrole nitrogens and therefore remains relatively unaffected by metal.¹¹

Properties of tetrapyrrole (TP) macrocycles, their derivatives and assemblies have been characterized using a variety of optical spectroscopic techniques.⁵⁻⁸ Most photophysical studies

that have been performed on macrocyclic π -systems to date have focused on porphyrin and its derivatives and Kalyanasundaram has reviewed these reports.⁵ The excited state dynamics depends on the nature of the central metal atom and significant effects on the excited state lifetimes have been observed. Thus, excited state characterization is important in determining possible applications of these compounds.

Photothermal Therapy

When it come to high peak power laser irradiation, the thermal effects, which are considered to be an energy wasting event in photodynamic therapy, become significant and opens another path for tumor phototherapy. A study by Ara et al.¹² indicates that pulses in nanosecond timescale can create the conditions for acoustic shock wave propagation through biological milieu causing significant mechanical damage. The process with these characteristics has been defined as photothermal sensitization.¹³ An ideal photothermal sensitizer should possess features including a very short lifetime of its electronically excited state and high photostability.¹⁴ The other important feature of a potential photothermal sensitizer is that the higher absorption between 600 nm to 1000 nm optical region, so called "phototherapeutic window" and is characterized by maximum light penetration into tissues.

Basic Photophysics

To understand excited state dynamics one needs a knowledge of basic photophysics that can be outlined with the aid of a diagram that was first introduced by Jabloński in 1935^{15} , and is depicted in the Figure 1.4^{16} :



Figure 1.4. Jabloński's diagram describing molecular photophysics.¹⁶

In this diagram, dark horizontal lines represent electronic states and are labeled according to their spin multiplicity (singlet or triplet). The first singlet state is labeled as S_1 , the second S_2 and other excited states exist with higher energies. Triplet states are labeled with T in the same manner. The light colored horizontal lines represent the vibrational states associated with each electronic state. The vertical solid lines with upward arrows represent light absorption of the ground state molecules (ground state absorption) or excited state molecules (ESA). A molecule that is in its ground singlet state can be excited to any number of singlet excited states (S_1 , S_2 , etc.). The excitation to the first excited state (S_1) of a porphyrin generates the Q-band in the ground state absorption spectrum and excitation to the S_2 state generates the Soret or B-band. The electronically excited molecule can relax radiatively (fluorescence and phosphorescence) or non-radiatively (internal conversion - IC and intersystem crossing - ISC). The optical absorptions originating from the excited states (singlet or triplet) allow probing of the concentrations of these states and their temporal profiles.

Zinc Porphyrins

Photosynthesis is a fascinating process which has attracted formidable interest from various fields of science over several decades.¹⁷⁻²² To synthesize compounds expected to mimic the structural and geometrical properties of photosynthesis a number of zinc(II) porphyrins has been employed to serve as electron donating center participating in electron transfer process that is one of the crucial steps in photosynthetic cycle.¹⁷⁻²⁴ Recently zinc(II) porphyrins (e.g. zinc(II) meso-tetraphenylporphine) have found their application in molecular photonics.²⁵ Existing capacitor technologies include the miniaturization of capacitor devices and the incorporation of thin film polymer dielectrics.²⁵ High polarizability and suitable dielectric properties make porphyrin small molecules very attractive candidates for such devices.

Zinc porphyrins represent the group of *normal* porphyrins. The electronic configuration of zinc atom is d¹⁰ and the interactions between the porphyrin π -system and the metal are somewhat small⁹. Recent fluorescence up-conversion experiments suggest that the S₂ excited state of zinc(II) meso-tetraphenylporphine [Zn(II)TPP] in ethanol deactivates with the lifetime of 2.35 ps via internal conversion into the S₁ state and fluorescent transition into the ground state²⁶. The deactivation of zinc(II) porphyrins S₁ singlet excited state predominantly occurs through the T₁ triplet state. Thus, the quantum yield of triplet state for Zn(II)TPP is 0.96²⁷. In deaerated toluene at 298K the triplet state deactivates with the lifetime 1.2 ms for $Zn(II)TPP^{27}$. Similarly to their free-base archetypes, zinc(II) porphyrins show distinct fluorescence in many solvents. The fluorescence lifetime was reported to be 2.7 ns for $Zn(II)TPP^{27}$. The phosphorescence quantum yields for these compounds are $<10^{-4}$ at 298 K due to efficient non-radiative relaxation of the triplet state.²⁷

Owing to their large triplet-triplet extinction coefficients, zinc(II) porphyrins have found their use in various biological and chemical sensing devices.²⁸ Furuto et al.²⁹ have used triplet-triplet absorption quenching of Zn(II)TPP doped film for measuring oxygen concentration. High quantum yield of triplet state of zinc (II) porphyrins allowed for using them as efficient singlet oxygen photosensitizers in photodynamics therapy (PDT).^{13,30} Yamamoto et al.³¹ reported that zinc-coproporphyrin III (Zincphyrin) acted efficiently as a photodynamic therapy agent in mice.

Nickel Porphyrins

Nickel has been shown to be an integral component of a number of redox enzymes.³² Many hydrogenases contain nickel in addition to iron-sulfur clusters, and it appears that it is a common constituent of those hydrogenases whose function is to oxidize rather than to evolve hydrogen. The nickel centre can undergo facile changes in oxidation number. Evidence has been presented that hydrogen atom, as well as the competitive inhibitor carbon monoxide, can bind directly to nickel^{32,33}, implying that the nickel centre might be the active site of these enzymes. A nickel-tetrapyrrole coenzyme, Co-F430, is present in the methyl CoM reductase and in methanogenic bacteria; the tetrapyrrole is classed as a tetrahydrocorphinoid, being intermediate in structure between porphyrin and corrin.³⁴ Porphyrins can truly be referred to as the energy collector of life even the methanogenic bacteria in the stomach of most mammals (including humans) contain an unusual nickel porphyrin.³⁵ Nickel porphyrins have found their application as in vitro nitric oxide (NO) sensors to electrochemically measure nitric oxide production in human polymorphonuclear neutrophil leukocytes.³⁶

Nickel porphyrins are typical representatives of the *hypso* porphyrins class.¹⁰ They display complex photophysical behavior, due to a combination of interconnected conformational, electronic and vibrational changes that take place upon excitation. These molecules have a very low quantum yield of fluorescence (Φ <10⁻⁵)^{6,9}. One of the most important properties of the nickel porphyrins is the d⁸ electronic configuration of the central metal ion. The electronic transitions involving the metal atom can be strongly affected by ligands, which can change the spin of nickel from S=0 to S=1.⁹ Therefore, when there are no axial ligands attached, the highest occupied orbital of the metal is d_{z2} and the lowest unoccupied orbital is d_{x2-y2}. The results of the extended Hückel calculations and the lack of luminescence supported the suggestion that the normally emissive (π , π *) excited state of the porphyrin macrocycle deactivates to produce the lower lying singlet or/and triplet metal centered (d_{z2}, d_{x2-y2}) excited state ^{6,9}. The mechanism of a d,d state formation is presented on Scheme 1.1:





Holten et al. have shown that common nickel porphyrins such as Ni(II)TPP and Ni(II)OEP have a (π,π^*) excited state that forms a (d,d) state within 1 ps $^{6,9,37-40}$, and the (d,d) state repopulates the ground state in 200-500 ps⁴¹⁻⁴⁶. An interesting feature of nickel porphyrins is the formation of the vibrationally hot transients upon excitation. Holten observed the transient positive absorption bands corresponding to the (d,d) excited state in non-coordinating solvents, that displayed a blue-shift and wavelength-dependent kinetics on the 5-25 ps time scale ³⁷⁻⁴⁰. This complex behavior of the transients has been explained in terms of excess vibrational energy in the metal-centered (d,d) excited state that was formed through the fast (<1ps) deactivation of the (π,π^*) excited state of the tetrapyrrolic macrocycle. The excess energy dissipates into the environment as the excited molecules travel down the vibrational cascade to form the cool (d.d) state in 5-25 ps $^{37-40}$. At this time the π system of tetrapyrrole macrocycle has already returned to its ground state configuration and all excitation is centered on metal. The excess of vibrational energy in the excited metal center affects the ground state electronic structure of porphyrin ligand and results in a shift of its ground state absorption spectrum producing a characteristic derivative shape difference spectrum of a d,d state (Figure 1.5)³⁷⁻⁴⁰, as opposed to the featureless diffuse spectra of the ring (π,π^*) and metal-to-ligand charge transfer excited states⁴⁷⁻⁴⁹.



Figure 1.5. Absorption difference spectrum characteristic of a d,d metal centered excited state of a nickel (II) porphyrin.

The property of nickel(II) complexes to have distinctive derivative shaped spectra in the d,d excited state provides an excellent opportunity for examining deactivation dynamics of photoexcited porphyrin and its interaction with environment that may accompany a transition from an electronic excited state of the macrocycle to an electronic excited state of the metal. As reported by Eom et al.⁵⁰, during this process nickel(II) complexes then return to their thermal equilibrium via intramolecular vibrational energy redistribution among porphyrin normal modes and intermolecular vibrational redistribution to the surrounding solvent molecular system via solvent/solute interaction.⁵⁰ Thus, short excited state lifetime of the excited state of nickel(II) porphyrins and its non-radiative decay pathway make this class of porphyrins possible candidates as photothermal therapeutic agents.¹²⁻¹⁴

Iron Porphyrins

Heme (or haeme) is an important biochemical structure.⁵¹⁻⁵⁷ It is, indeed, present in hemoglobin, and cytochromes.⁵⁵⁻⁵⁷ It can be found in mitochondria, chloroplasts, and other places in the cell. The electrochemistry of the metal present in the protein is critical to its function. The tremendous value is the ability to interact in oxidation-reduction reactions and transport oxygen, both between tissues and within cells. Redox reactions and the biological transfer of electrons are essential for energy production in living organisms. Interest in the structure of heme is the reason that myoglobin was the first protein whose structure was described. These configurations give the molecule three-dimensional shape and allow the molecule to twist and turn to provide access to the heme groups.

Hemes are present in every Kingdom, bacteria, protists, fungi and plants and animal.⁵¹⁻⁵⁴ Prevalence of this pathway suggests that the gene that encodes the protein is ancient. The different functions are probably new uses for a protein structure whose gene was already present. Biosynthesis of the heme of hemoglobin and chlorophyll both start with the porphyrin ring structure.⁵¹⁻⁵⁴ Iron porphyrins have also found their application as catalysts for oxidation hydrocarbons in both synthetic chemistry and industrial processes⁵⁸⁻⁶⁰, and third order non-linear optical materials⁶¹⁻⁶⁵.

Iron porphyrins belong to the *d-type hyper* porphyrin group.¹⁰ These porphyrins have vacancies in the $e_g(d_{\pi})$ orbitals⁹ which make a porphyrin ligand-to-metal charge transfer transition possible. There is also considerable mixing of the metal d_{π} orbitals with the LUMO of the porphyrin, since they are of the same symmetry (e_g) .⁶⁶ The extensive mixing then accounts for the complex spectra often observed in the *d-type hyper* porphyrins.¹⁰ The metal and ligand orbital interactions produce additional peaks to the blue of Soret band and make Q-band region

look broad and featureless. This mixing occurs more readily when the porphyrin LUMO is close in energy to the metal orbitals. It is extensive mixing of metal and porphyrin orbitals that makes iron porphyrins of great interest for photophysical and photochemical studies.⁶⁶

Electron Deficient Porphyrins

The tetrapyrrolic porphyrin ring is implicated as a ligand in a wide variety of metalcatalyzed redox reactions of considerable biological importance, *inter alia*, those involving hemes and chlorophylls. Moreover, a useful chemistry has been developed around these catalytic systems *e.g.* activation of hydrocarbons using mimics of cytochrome P-450.⁶⁷ A variety of experimental and theoretical studies^{6,25,68,69} predict that extremely electron deficient porphyrins will find particular utility in the development of catalysts for the activation of small molecules. Moore et al.⁶⁹ successfully used iron (III) meso-tetra(pentafluorophenyl)porphine as a catalytic moiety for oxidation of isobutene, in which hydrocarbon oxidizing equivalents were derived from dioxygen. Electron deficient macrocyclic ligands impart exceptional electronic characteristics to the porphyrin central metal ion; such metalloporphyrin systems may serve as a platform for the development of Co, Fe, and Ni catalysts that mimic cytochrome P450's ability to utilize dioxygen for the selective oxidation of hydrocarbons. It has been established⁷⁰ that the redox properties of the ligand vary with the incorporated metal while in turn the metal redox properties can be controlled by the peripheral substituents of the porphyrin placed at the meso positions. Meso-tetra(heptafluoropropyl)porphine is virtually impossible to oxidize electrochemically while zinc (II) porphyrin with the same ligand produces cation radical upon oxidation at $E_{1/2 (ZnP/ZnP+)} = 1460 \text{ mV}.^{71}$

From this point of view, electron-withdrawing substituents are particularly interesting since they lead to electron-deficient porphyrins which are generally less easily oxidized than the parent compound. These substituents can affect the conformation of the macrocycle and hence the redox potentials.^{25,72} As strong electron-withdrawing substituents with pure negative inductive effect (a neat *-I*) character, the perfluoroalkyl groups have received great attention. Kaesler and LeGoff prepared the first porphyrins bearing eight perfluoroalkyl chains on the pyrrole rings by acid-catalyzed self-condensation of functionalized derivatives of 2,5-dimethyl-3,4-bis(polyfluoroalkyl) pyrroles.⁷³ Since then, porphyrins bearing electron deficient substituents have been receiving increasing attention.^{6,25,68,69}

Electron deficient substituents in the meso positions are well known⁷¹ to greatly influence the interaction between the metal d-orbitals and the nitrogen orbitals of the tetrapyrrole macrocycle. The lack of electron density on the meso groups is directly conveyed to the tetrapyrrole macrocycle and consequently to the central metal making the whole molecule highly electron deficient.^{25,71} In contrast to the above studies, electron-deficient 5,10,15,20tetrakis(perfluoroalkyl)porphyrins²⁵ are nonplanar, but exhibit hypsochromic absorption spectra, sharp emission bands, and small Stokes shifts typical of normal planar porphyrins, such as mesotetraphenylporphine.⁷¹ The fluorescence quantum yields of these molecules are reduced by a factor of 3 compared to meso-tetraphenylporphine, and the S₁ lifetimes are reduced by a factor of only 7. Thus, the photophysics of two classes of sterically encumbered, nonplanar porphyrins, the electron-rich meso-tetrabutylporphine, dodecaphenylporphine, and octaethyl-mesotetraphenylporphine and the electron-poor meso-perfluoroalkylporphines, are dramatically different: the former class exhibits highly "perturbed" optoelectronic behavior, while the latter does not. The current understanding of the stereoelectronic consequences of porphyrin ring distortion is unable to explain the disparity in these spectroscopic studies. It is important to be able to reconcile these data if one is to understand the photophysics of protein-bound porphyrinderived pigments and how macrocycle structure modulates the electronic properties in the panoply of heme protein active sites in biology.⁷⁴

Theoretical Methods

Metalloporphyrins have been studied by a variety of quantum chemical methods including Extended Hückel (EH)⁷⁵, semiempirical CNDO (Complete Neglect of Differential Overlap), INDO (Intermediate Neglect of Differential Overlap) and ZINDO (Zerner's INDO)⁷⁶⁻ ⁷⁹, and *ab-initio* methods⁷⁹. CNDO does not do geometry optimizations. This method is known as semi-empirical because it is based on a mixture of first principles of chemistry and physics with experimental results that are used to determine the Hamiltonians.⁷⁸ Quantum chemistry calculations based only on first principles are known as 'ab-initio' methods. CNDO uses two main approximations that deviate from *ab-initio*: a) a core approximation and b) the zerodifferential overlap approximation. CNDO, INDO and ZINDO are examples of "Self consistent field theory", which obtain the results by solving simultaneous non-linear equations iteratively until the results between two iterations are close. CNDO knows nothing of bonds and calculates pure wave functions based on atom location and atom type. CNDO is primarily used for calculation of partial atomic charge and dipole moment, for which it is known to give fairly good answers.⁷⁷ The "closed" shell method is faster than the "open" shell method for calculating CNDO results, but the mathematics is less rigorous. CNDO also reports the total energy and binding energy of a molecule. If the closed shell method is chosen it reports the eigenvalues from which HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels can be determined.⁷⁶

The semiempirical Hartree-Fock calculations do not provide satisfactory results. HF computations yield inaccurate ionization potentials of porphyrins.⁸⁰ In addition, the transition metal porphyrins and excited states require high-correlated *ab-initio* methods, which are hardly available considering the size of porphyrinic molecules.⁷⁹ Vangberg et al⁸¹ reported that the semiempirical calculations are not able to provide "correct" ordering of the relative stability of different metalloporphyrin isomers.

Compared to ab-initio molecular orbital methods Density Functional Theory (DFT) method provides more accurate results.⁸⁰ DFT is an exact reformulation of the Schrödinger equation and is based on Hohenberg-Kohn theorem⁸² according to which the ground state energy of an electronic system is uniquely determined by the electronic density functional $\rho(r)$. This allows for using electron density as basic variable and allows one to replace the complicated Nelectron wave function Ψ (x₁, x₂, ...x_N) by the much simpler electron density $\rho(r)$. This made it possible to compute the ground state geometries and electronic structures for such big and complex molecules as metalloporphyrins.⁸³

In order to properly assign the mechanisms and dynamics of the radiationless deactivation of the Q-state of a metalloporphyrin, it is necessary to know the nature and energies of the silent states existing in the $S_1 \rightarrow S_0$ gap.⁸⁰ The Time-Dependent DFT (TDDFT) calculation of excitation energies provides accurate results and combined with experimental methods it can provide a full analysis of the ground state electronic structure of studied system.⁸³ TDDFT methods used for calculation of excited states are very suitable for large molecule calculation and provide accurate excitation energies.⁸⁴ TDDFT is a rigorous and useful method for calculating

the properties of many-atom systems in time-dependent external fields, and is an extension of DFT, which allows for the description of the dynamic evolution of electronic systems.^{80,84} The excited state characteristics, such as excitation energies, and the oscillator strengths are computed by TDDFT.^{80,84} All TDDFT chemical applications are based on the same theoretical background, *viz.* the Runge and Gross theorem.⁸⁰ This theorem states that evolution of the electron density of a many electron system determines the "external potential uniquely up to an additive purely time-dependent fuction".^{83,84} TDDFT is an extension of the Hohenberg-Kohn theorem to systems in a time-varying field. The energy calculations are simple and straightforward to execute because the symmetry aspects are taken into account so the excited states belong to a particular irreducible representation.^{83,84}

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CHAPTER 2: MATERIALS AND METHODS

2.1 MATERIALS

Toluene (99.5+%, Aldrich, Spectrophotometric grade), acetonitrile (99.9%, Sigma, HPLC grade), butyronitrile (99.9%, Sigma, HPLC grade), benzonitrile (99.9%, Sigma, HPLC grade), ethyl alcohol (99.9%, Sigma, HPLC grade), ethyl ether (99.9%, Sigma, HPLC grade), acetone (99.9%, Sigma, HPLC grade), methyl alcohol (99.93%, Aldrich, HPLC grade), dichloromethane (99.9%, Aldrich, HPLC grade), tetrabutylammonium hexafluorophosphate (Sigma), were used without further purification. Argon gas was obtained from AGA industries. Pt wire electrode (99.99%, CH Instruments, Inc.), Pt wire (0.1 mm, Aldrich) and Pt gauze (woven from 0.07 mm wire, Aldrich) were used as auxiliary and working electrodes respectively in electrochemistry and spectroelectrochemistry.

Nickel(II) meso-tetra(pentafluorophenyl)porphine, nickel(II) meso-tetra(pnitrophenyl)porphine, nickel(II) meso-tetra(heptafluoropropyl)porphine, iron(III) mesotetra(heptafluoropropyl)porphine, nickel(II) meso-tetra(n-propyl)porphine, zinc(II) mesotetraphenylporphine, meso-tetraphenylporphine, were synthesized by Frontier Scientific, Inc. and used as received.

2.2 INSTRUMENTATION AND METHODS

UV-visible Absorption Spectroscopy

The ground state electronic absorption UV-visible spectra were recorded using Varian Cary 50 Bio (Varian Corporation) Single beam spectrophotometer. All spectra were recorded at room temperature (295K) using 10 mm or 2 mm path lengths quartz cuvettes.

Electrochemistry and Spectroelectrochemistry

Cyclic voltammetry measurements were carried out by using a BAS Epsilon (Bioanalytical System) electrochemical system. A standard three-electrode system was employed. A platinum electrode functioned as the working electrode and a CHI platinum wire electrode served as an auxiliary electrode. For the reference electrode, an SCE electrode was used as standard. The advantage of this approach is the minimization of the liquid junction potential.

Electrochemical oxidations and reductions (controlled-potential coulometry) were also carried out using the same system. A homemade spectroelectrochemical cell was used in the experiments (See Figure 2.1). The cell consists of a 0.5 mm rectangular screw cap spectrophotometric cuvette that is fitted into a bottom of a Teflon beaker. A piece of platinum gauze, 100 mesh, woven from 0.07 mm diameter wire was used as a semi-transparent working electrode. The electrode was placed in a 0.5 mm spectrophotometric cell and connected to the potentiostat output by a platinum wire. The potential applied to the electrode produced reduced or oxidized species that diffuse away from the semi-transparent Pt electrode to saturate the 0.5 mm layer of the solution inside the spectrophotometric cell. The absorption spectra of the sample were taken as a function of time until the potential induced spectral evolution was complete. Typically 1 or 2 minutes were necessary for the equilibrium to establish. This time could vary with the solvent. The spectroelectrochemical cell filled with pure solvent was used as a reference.



Figure 2.1 Schematics diagram of the spectroelectrochemical cell

Femtosecond Transient Absorption Spectroscopy

The ultrafast transient (pump-probe) absorption spectrophotometer has been described previously¹ and the recent modification have been communicated elsewhere.² Transient absorption experiments were performed in the Ohio Laboratory for Kinetic Spectrometry at

Bowling Green State University. A Spectra-Physics Hurricane system was used as the laser source. This system (Figure 2.2) includes a seed laser (Mai Tai, cw diode pumped laser and a mode-locked Ti:sapphire pulsed laser), a pump laser (Evolution, diode-pumped Q-switched Nd:YLF laser), a pulse stretcher, a Ti:sapphire regenerative amplifier, and a pulse compressor. The output of the system consisted of pulses of 800 nm, 1 mJ, 100 fs (fwhm) at a repetition rate of 1 kHz. The Hurricane output was divided into two parts: 95% was used for sample excitation by sending it through a second-harmonic generator (for 400 nm excitation) or an optical parametric amplifier (Spectra-Physics OPA 800). The remaining 5% was sent through a computer-controlled delay line (1.6 ns) and then focused on a 3 mm thick sapphire plate (Crystal Systems, Inc., HEMLUX grade) to generate a white light continuum used to probe the absorption of the excited sample.

An optical chopper was used to modulate the excitation beam in order to switch the sample between excited and ground states at a frequency of 100 Hz. The second-harmonic generator consisted of a x3 telescope and 1 mm length BBO crystal. The angle between pump and probe beams was 5° .



Figure 2.2 The schematic diagram of the ultrafast transient absorption spectrometer.

The linear polarization of the probe beam was set at an angle 54.7° with respect to that of the pump beam, in order to eliminate the influence of molecular reorientation on the observed dynamics. The sample flow-through cell had an optical path of 2 mm and was connected to a solution reservoir and flow system. The continuum was coupled into a 400 micron fiber optic cable after the sample cell and thereafter input into the CCD spectrograph (Ocean Optics, PC) for time-resolved spectral information (380-750 nm). The light at 400 nm passed through the chopper. The CCD spectrograph was externally triggered by the chopper in order to distinguish between the continuum spectra corresponding to the ground and excited states of the sample. Typically, 500 transient spectra were averaged at a particular delay time. The CCD spectrograph,

the delay line were driven by a computer-controlled system. In-house LabVIEW (National Instruments) software routines allowed automatic spectral acquisition over a series of delay line settings. The instrument rise time of the ultrafast spectrometer was ca. 130 fs. The absorption spectra of the solutions were measured before and after the experiment to check for possible sample decomposition.

Potentiostatic Transient Absorption Spectroscopy

The controlled potential transient absorption technique is a combination of the wellknown spectroelectrochemical method and a femtosecond transient absorption. The chemical species are generated *in situ* either by oxidation or reduction in the cell used for spectroelectrochemistry as described above. Then after equilibrium is established the photophysical behavior of the excited state species is investigated by means of traditional pumpprobe transient absorption spectrometry.

Quantum Chemical Calculations

The quantum chemical computations have been performed by Codruta-Alexandrina Simioanca and Alexandra Soldatova in a collaborative agreement. The ADF (Amsterdam Density Functional) suite of programs, release 2004.01 have been employed to carry out calculations.³ The local density approximation (LDA) functional of Vosko-Wilk-Nusair (VWN),⁴ and the generalized gradient approximation (GGA), utilizing Becke's⁵ gradient approximation for exchange and Perdew's⁶ for correlation (BP) have been used for calculations. Time-dependent density functional theory (TDDFT) yielded excitation energies as a result of computations. In the ADF realization^{7,8}, the solution of the TDDFT response equations is obtained as a result of iterations starting from the usual ground state or zeroth-order Kohn-Sham (KS) equations.⁷ An approximation to the usual static exchange-correlation (xc) potential v_{xc} (**r**) is necessary for that. After the solution to ordinary KS equations has been obtained, one has to compute the first order density change from an iterative solution to the first order KS equations. An approximation to the first functional derivative of the time-dependent xc potential v_{xc} (**r**, t) with respect to the time-dependent density ρ (**r**', t'), the xc kernel, is necessary in these first order equations. The Adiabatic Local Density Approximation (ALDA) has been employed for that purpose. In this approximation the time dependence (or frequency dependence referring to the Fourier-transformed kernel) is omitted, so that the differentiated static LDA expression can be used. The Vosko-Wilk-Nusair parameterization was utilized in this work.⁴ For the exchange correlation potentials that are the part of the zeroth-order KS equations, the same GGA as in the DFT calculations has been made use of. The all electron ADF TZ2P uncontracted triple-E STO basis set was used in all DFT and TDDFT calculations. It contained one 3d and one 4f polarization function for C, N and F atoms, one 2p and one 3d polarization function for H, and a triple- ξ 3d, 4s basis with one 4p and one 4f function for Ni.

Ground state optimized geometry was used to compute vertical absorption energies, E_{va} . The following expression has been used to get adiabatic energies, E_{adia} :

$$E_{adia} = E_{ve} + \Delta E$$

where E_{ve} is the vertical emission energy, which is calculated at TDDFT level using the relaxed excited state geometry. The ΔE is the change in energy of the ground state when it is deformed to the relaxed geometry of the excited state⁹.

Ni(II)T(n-Pr)P and Ni(II)TPrF₇P have been optimized in geometry for the selected triplet excited states. A spin-unrestricted method for open-shell DFT calculations for the triplet states was used. Spin contamination, monitored by the expectation value of S², was discovered to be negligible. The true minima of optimized ground and excited state triplet conformations were verified by frequency computations. These calculations were performed at DFT/B88P86/6-31G(d) level of theory using the PQS 3.1 suite of programs.¹⁰

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CHAPTER 3: NICKEL(II) MESO-TETRA(p-NITROPHENYL), NICKEL(II) MESO-TETRA(PENTAFLUOROPHENYL), AND NICKEL(II) MESO-TETRA(HEPTAFLUOROPROPYL) PORPHYRINS

3.1 INTRODUCTION

The study of the physical properties and the reactivity of synthetic porphyrinic compounds to understand the mode of action of naturally occurring porphyrinic cofactors continues to provide valuable insights into the processes that determine functionality of natural systems.¹ Nickel(II) tetrapyrroles, which have d⁸ electronic configuration of the central metal ion and contain no axial ligands, possess a low energy metal excited state corresponding to a change of configuration $(d_{z2})^2 \rightarrow (d_{z2}, d_{x2-y2})$. This state is simply referred to as the (d,d) state² and is formed very rapidly after photoexcitation into Soret band or Q band.³⁻⁵ It is known that nickel (II) porphyrins exhibit ultrafast excited state relaxation dynamics owing to the central metal, which provides additional pathways for the deactivation of the tetrapyrrole ring excited states. The lack of luminescence ($\Phi < 10^{-5}$) together with the results of extended Hückel calculations⁶ led to the proposal that the ground state is rapidly repopulated via metal centered excited (d,d) state. Drain et al. proposed that nickel porphyrins excited states deactivate by the pathway $(\pi,\pi^*) \rightarrow$ $^{1,3}(d,d) \rightarrow \text{ground state.}^7$ Nickel(II) porphyrins have rich photophysical behavior that can be exploited to probe the relationships among conformational, electronic and vibrational properties.⁸ Non-planar nickel porphyrins such as nickel (II) dodecaphenylporphine⁹ provide a unique opportunity to address fundamental issues concerning vibrational relaxation and conformational

dynamics in large molecules, as well as the mechanisms by which different non-planar distortions of porphyrin macrocycle can lead to altered photophysical properties.

The chemical and photochemical reactivity of metalloporphyrins may be tuned by distortions in the otherwise planar geometry of the porphyrin ligand.¹⁰ The central metal is usually responsible for the catalytic activity of metalloporphyrins, thus by introducing substantial distortions to the tetrapyrrole macrocycle the chemical reactivity could be decreased because the metal is now protected with bulky ligand and cannot therefore be exposed to the substrate from axial position. On the contrary, more planar porphyrins are easily subjected to axial ligation and exhibit higher catalytic activity. Such distortions of the porphyrin ring can be accomplished in several ways, such as addition of exocyclic rings, reduction in one or more of the pyrrole subunits, axial ligation, and constraints exerted by surrounding protein.^{11,12} The effects on chemical activity are nicely illustrated by an enzymatic system in methanogenic bacteria. The final step in methane formation by methanogenic bacteria requires an unusual, highly reduced nickel tetrapyrrole cofactor, F₄₃₀, to catalyze reduction of a methyl sulfide to methane and disulfide.¹³ F₄₃₀ cofactor has partially reduced macrocycle and exhibits higher flexibility than more conjugated tetrapyrroles. In its highly ruffled conformation, it is capable of undergoing metal reduction producing nickel (I) unlike other nickel (II) porphyrins, which undergo ring reduction instead.

Out-of-plane macrocyclic ring distortions also significantly perturb the electronic properties of porphyrinic chromophores.¹⁴ There are numerous examples of nonplanar metallotetrapyrroles in a variety of biological systems^{1,7,15} ranging from photosynthetic reaction centers¹⁶ to vitamin B_{12}^{17} . Synthetically, saddling or ruffling distortions may be accomplished by steric interactions of exo ring substituents such as alkyl substitution.¹⁸

Besides changing the geometry of the macrocycle to alter photophysical behavior of metalloporphyrins, it is possible to alter the electronic density on the tetrapyrrolic ring by introducing different electron withdrawing groups into meso positions. ¹⁸ Electron deficient substituents in meso positions are well known¹⁹ to greatly influence the interaction between the metal d-orbitals and the nitrogen orbitals of tetrapyrrole macrocycle. In this work a series of electron deficient nickel porphyrins bearing p-nitrophenyl- [Ni(II)TNPP], pentafluorophenyl- [Ni(II)TPPF], and perfluoropropyl- [Ni(II)TPrF₇P] substituents in meso positions have been studied to ascertain their photophysical behavior. Hammett σ_p constants have been used to estimate the electron withdrawing propensity of the meso substituents.

3.2 RESULTS

Ground Electronic State Absorption Spectra

The ground electronic state absorption spectrum of meso-tetra(p-nitrophenyl)porphine [Ni(II)TNPP] in benzonitrile exhibited a strong near-UV Soret band at around 425 nm and weaker visible Q bands at 532 nm and 560 nm (the latter appearing as a shoulder) (Figure 3.1):



Figure 3.1. Ground-state absorption spectrum of Ni(II)TNPP in benzonitrile.

In non coordinating toluene the meso-tetra(pentafluorophenyl)porphine [Ni(II)TPPF] ground state absorption spectrum had a strong narrow near-UV Soret band with a maximum at 406 nm and two weaker visible Q-bands at 524 nm and 558 nm respectively of almost equal intensity (Figure 3.2):



Figure 3.2. Ground state absorption spectrum of Ni(II)TPPF in toluene.

The absorption spectrum of Ni(II)TPrF₇P was weakly solvent dependent, when weakly coordinating media such as acetone and non coordinating toluene (Figure 3.3) were used. The maximum of the Soret band absorption was shifted from 406 nm in acetone to 412 nm in toluene. These solvents can be considered both non coordinating because when strongly coordinating solvent (i.e. pyridine) is used there is a considerable (ca. 50 nm) red shift of both Soret and Q bands and a substantial broadening of the B band. In our case the spectral shift of 6 nm in the Soret region and 2 nm in the Q band suggest that there is no coordination of a solvent molecule into an axial position of the metalloporphyrin.



Figure 3.3. Ground state absorption spectra of Ni(II)TPrF₇P in acetone (black line) and toluene (red line) at the same concentration and experimental conditions.

Time-Resolved Transient Absorption Spectroscopy

Visible region transient absorption changes and kinetic data with ~130 fs time resolution were acquired for all porphyrins at the same experimental conditions, using different excitation wavelengths. In each case the time evolution of the spectra was quite complex and revealed two or more kinetic components, with time constants ranging from subpicoseconds to hundreds of picoseconds before complete ground state recovery was observed. The photophysical behavior had both notable similarities and striking differences for porphyrins bearing aromatic or aliphatic substituents in meso-positions, and so the results for aryl- and alkyl-substituted porphyrins are presented separately.

Ni(II)TNPP. Figure 3.1 shows time-resolved absorption data in the Q band region for NiTNPP in benzonitrile at 298 K, acquired using 130-fs excitation flashes at 400 nm.



Figure 3.4. Transient absorption difference spectra in the Q band region of Ni(II)TNPP in benzonitrile acquired following a 130 fs excitation pulse at 400 nm: S_1 state at 1 ps (black line), relaxed ³(d,d) state at 25 ps (red line).

Over the first 1 ps after excitation, bleaching of the ground state at 532 nm was accompanied by the growth of the positive absorption over the whole visible range of the spectrum (Figure 3.4(black line)). Over the next 40 ps or so, the difference spectrum continued to evolve into one having a derivative-like shape (Figure 3.4 (red line)). Over the following several hundred picoseconds, the derivative-shaped spectrum decayed uniformly to the baseline, reflecting complete ground-state recovery.

Representative Q band region kinetic data are shown in Figures 3.5 and 3.6.



Figure 3.5. Representative kinetic trace and the fit of the time evolution of the absorption at 490 nm of Ni(II)TNPP in benzonitrile from Figure 3.4. The arrow indicates the first kinetic phase.



Figure 3.6. Representative kinetic data and the fits of the evolution of the absorption difference of Ni(II)TNPP in benzonitrile from Figure 3.4: (A) ground-state bleaching and (B) transient absorption. The arrows indicate the three kinetic phases of the transient evolution. The insets show the early time of the transients evolution.

Visual inspection of these data, like the spectral data in Figure 3.4, indicated that there were three major domains of the time evolution, and the kinetics was analyzed using a triple-exponential function. These domains are indicated by the arrows in Figures 3.5 and 3.6. The kinetic component 2 was not ground state recovery although it appeared such in Figure 3.6(A). There was an additional kinetic component that preceded the other three, which was responsible

for the time evolution of the spectra in Figure 3.4 (black line), but the time constant of this process (c.a. 300 fs) approached the instrument response and was omitted from the fitting procedure. The three phases had average time constants of 0.87, 15 and 450 ps over the 465 - 650 nm region (Table 3.1).

Although the values of the first and the third time constants were essentially wavelength independent, the second component changed from 10 to 20 ps across the red-edge of the Q band region. The transient kinetics presented in Figure 3.5 contains all three components, but due to the low amplitude of the second and the third ones they are not shown.

Ni(II)TPPF. Figure 3.7 shows time-resolved absorption data in the Q band region for NiTPPF in toluene at 298 K, acquired using 130-fs excitation flashes at 400 nm.



Figure 3.7. Transient absorption difference spectra in the Q band region of Ni(II)TPPF in toluene acquired following a 130 fs excitation pulse at 400 nm: S_1 state at 1 ps (black line), relaxed ³(d,d) state at 25 ps (red line).

Over the first 1.2 ps after excitation, bleaching of the ground state at 524 nm and at 558 nm increased accompanied by the growth of the positive absorption over the whole visible range of the spectrum (Figure 3.7 (black line)). Over the next 20 ps or so, the difference spectrum continued to evolve into one having a derivative-like shape (Figure 3.7 (red line)). Over the following several hundred picoseconds, the derivative-shaped spectrum decayed uniformly to the baseline, reflecting complete ground-state recovery.

Representative Q band region kinetics data are shown in Figures 3.8 and 3.9.



Figure 3.8. Representative kinetic trace and the fit of the time evolution of the absorption at 480 nm of Ni(II)TPPF in toluene from Figure 3.7. The arrow indicates the first two kinetic phases.



Figure 3.9. Representative kinetic data and the fits of the evolution of the absorption difference of Ni(II)TPPF in toluene from Figure 3.7: (A) ground-state bleaching and (B) transient absorption. The arrows indicate the three kinetic phases of the transient evolution. Insets show the early time of the transients evolution.

Visual inspection of these data, like the spectral data in Figure 3.7, indicated that there were three major domains of the time evolution, and the kinetics was analyzed using a triple-exponential function. These domains are indicated by the arrows in Figures 3.8 and 3.9. The kinetic component 2 was not ground state recovery although it appeared such in Figure 3.9(A). There was an additional kinetic component that preceded the other three, which was responsible for the time evolution of the spectra in Figure 3.7 (black line), but the time constant

of this process (c.a. 300 fs) approached the instrument response and was omitted from the fitting procedure. The three phases have average time constants of 1.0, 10 and 690 ps over the 465 – 650 nm region (Table 3.1). Although the values of the first and the third time constants were essentially wavelength independent, the second component changes from 5 to 15 ps across the red-edge of the Q band region.

As it would be expected for nickel (II) porphyrins the early time kinetics exhibited wavelength dependence and the transient difference spectra shifted to the blue within the first 50 ps (Figure 3.10)



Figure 3.10. A series of spectral cuts from the optical dynamic surface of Ni(II)TPPF in the time range $1 \rightarrow 50$ ps, normalized at 545 nm maximum to clearly show the time-dependent blue shift.

The fitted data of the temporal decay profiles indicated that, as the probe wavelength moved to the blue, the time constants the fast processes 1 and 2 (Figure 3.9) became larger and their contribution to the decay processes became smaller. The slow component 3 with lifetime of about 690 ps was measured for all the decay profiles and remained the same regardless of the probe wavelengths. This process has been well established to be an electronic deactivation from the metal ${}^{3}(d,d)$ excited state to the $(d_{z2})^{2}$ ground state.²⁰⁻²² thus, the time constant of 690 ps for the slow component was fixed in the curve fitting procedure to extract the time constant of the decay component in the temporal profiles of the transient absorption signals (Figure 3.11):



Figure 3.11. Temporal profiles of transient absorption signals at various probe wavelengths of Ni(II)TPPF in toluene after photoexcitation at 400 nm.

The observation of the kinetic traces in Figure 3.11 clearly indicates the greater contribution of the fast component 1 to the overall kinetics when the probe wavelength moves to the blue. The data presented in Figure 3.10 and 3.11 suggest that the 1 and 2 components (Figure 3.9) correspond to the vibrational relaxation processes as it has been observed for a number of large molecules.²⁰⁻²²

Ni(II)TPrF₇P. Figure 3.12 shows time-resolved absorption data in the Q band region for NiTPrF₇P in toluene at 298 K, acquired using 130-fs excitation flashes at 400 nm.



Figure 3.12. Transient absorption difference spectra in the Q band region of Ni(II)TPrF₇P in toluene acquired following a 130 fs excitation pulse at 400 nm: S_1 state at 1 ps (black line), relaxed ³(d,d) state at 6 ps (red line).

Over the first picosecond after excitation, bleaching of the ground state at 540 nm and at 591 nm was accompanied by the growth of the positive absorption over the whole visible range of the spectrum (Figure 3.12 (black line)). Over the next 5 ps or so, the difference spectrum continued to evolve into one having a derivative-like shape (Figure 3.12 (black line)). The negative absorption over 575 - 600 nm region decreased in amplitude, which might arise from substantial overlap of opposing Q band ground-state bleaching and excited-state absorption. Over the 50 picoseconds, the derivative-shaped spectrum slightly shifted to the blue and then decayed uniformly within 22 ps to the baseline, reflecting complete ground state recovery.

Representative Q band region kinetics data are shown in Figures 3.13 and 3.14.



Figure 3.13. Representative kinetic trace and the fit of the time evolution of the absorption at 484 nm of Ni(II)TPrF₇P in toluene from Figure 3.12. The arrows indicate the two kinetic phases.



Figure 3.14. Representative kinetic data and the fits of the evolution of the absorption difference of Ni(II)TPrF₇P in toluene from Figure 3.12: (A) ground-state bleaching and (B) transient absorption. The arrows indicate the two kinetic phases of the transient evolution.

Visual inspection of these data, like the spectral data in Figure 3.12, indicated that there were two major domains of the time evolution, and the kinetics was analyzed using a double exponential function. These domains are indicated by the arrows in Figures 3.13 and 3.14. There was an additional kinetic component that preceded the other three, which was responsible for the time evolution of the spectra in Figure 3.12 (black line), but the time constant of this process (c.a. 300 fs) approached the instrument response and was omitted from the fitting procedure. The three phases had average time constants of 1 and 22 ps over the 465 – 650 nm region (Table 1).

Although the value of the second time constants was essentially wavelength independent, the first component changed from 0.8 to 1.2 ps across the red-edge of the Q band region. There was a long lived component appearing as an offset due to the small presence of zinc and free base porphyrins derivatives in the sample.

Table 3.1. Summary of Femtosecond Kinetic Data for Ni(II)TPPF, Ni(II)TNPP, and Ni(II)TPrF₇P

Solvent	λ _{ex} (nm)	$(\pi\pi^*) \rightarrow (d,d) (ps)$	(d,d) relaxn (ps) ^a	$(\mathbf{d},\mathbf{d}) \rightarrow \mathbf{ground} \ (\mathbf{ps})^{\mathbf{b}}$
Ni(II)TPPF	400	1.02 ±0.01	10 ±1	690 ± 5
toluene				
Ni(II)TNPP	400	0.87 ±0.01	15 ±1	450 ±6
benzonitrile				
Ni(II)TPrF7P	400	1.2 ±0.1	-	22 ± 1

toluene

^aThe time constant attributed to vibrational/conformational dynamics in the (d,d) excited state normally shows a variation with the detection wavelength (i.e., the time constant decreases with increasing wavelength across the red side of the spectrum.

^bThe deactivation of the (d,d) state often shows a slight variation with detection wavelength near one or both edges of the spectral region investigated.

3.3 DISCUSSION

Ground Electronic State Absorption Spectra

The most prominent change in the spectrum of Ni(II)TPrF₇P compared to Ni(II)TNPP and Ni(II)TPPF is that the Q bands are considerably red shifted, even in non-coordinating solvents (Figures 3.1-3.3). The bigger red shift in the Ni(II)TNPP Soret band can be attributed to the solvent influence. Benzonitrile is capable of coordinating with the peripheral nitro groups inducing additional deformation of a macrocycle to the saddled geometry. This deformation mostly affects $S_0 \rightarrow S_2$ transition and consequently shifts Soret band to the lower energy transitions.²³ Red shifts of the Q bands have been previously reported to be characteristic of the highly peripherally crowded non-planar porphyrins.^{2,7,24} The Q-bands red shift results from the reduced Ni-N distance that causes in-plane nuclear reorganization (IPNR), which is defined as changes in the porphyrin bond lengths and bond angles induced by strong electronic effects of the substituent on macrocycle.²³ Considering the small size of nickel (II) ion it is reasonable to suggest that such macrocyclic core contraction is taking place. For the flexible alkyl-substituted porphyrins that have their peripheral groups in meso positions it is quite common to exhibit substantial ruffling of the tetrapyrrole ring.²⁵ The out-of-plane distortions in Ni(II)TPrF₇P affect the interaction of the metal d_{z2} and d_{x2-y2} orbitals with the a_{1u} and $a_{2u}(\pi)$ HOMOs.⁷ As a result, the a_{2u} orbital is stabilized and lowered in energy while a_{1u} is destabilized and raised in energy causing red shift in absorption spectra.

The gradual spectral shift to the red for the discussed porphyrins could also be wellcorrelated with the increasing electron withdrawing ability of the meso substituents in the studied molecules. The substituent electron withdrawing effect decreases the size of nickel (II) ion by displacing its electronic density towards the ligand which in turn decreases the Ni-N bond length. The resulting IPNR effect is responsible for the red shifts in the absorption spectra. An estimation of the electronic effect of the peripheral substituents has been done by summing the Hammett constants σ_p for the individual electron withdrawing substituents.²³ The cumulative constants were 1.92, 1.08 and 1.04 for Ni(II)TPrF₇P, Ni(II)TPPF, and Ni(II)TNPP respectively. The redmost spectral shift for the Ni(II)TPrF₇P was consistent with the highest value of the summed Hammett constant of 1.92 indicating the highly electron deficient species. The lack of electron density on the meso groups is directly conveyed to the tetrapyrrole macrocycle and consequently to the central metal displacing electron density towards the meso substituents.

Time-Resolved Transient Absorption Spectroscopy

The 400 nm pulse generated first the ${}^{1}(\pi,\pi^{*})$ state designated S₂. This state underwent rapid radiationless deactivation during the instrument response time to form another state that had a spectrum (e.g. 1 ps in Figure 3.4) identified as the first observed transient (FOT). The assignment of this FOT to a particular state was not straightforward.

There are two proposed deactivation pathways of nickel porphyrins proposed by Drain⁷ and Eom²⁰ so we should discuss them separately. They mainly differ in terms of the FOT assignment. Drain et al.⁷, assigned the first observed transient of nickel (II) dodecaphenylporphine [NiDPP] to the lowest ${}^{1}(\pi,\pi^{*})$ excited state. They based their conclusions on the broad and featureless transient absorption which is characteristic of the lowest singlet excited state of a porphyrin. Thus, 1 ps spectra presented in Figures 3.4, 3.7, and 3.10 could also be assigned to the S₁ state. The lack of one or more distinct absorption peaks in the 600 – 800 nm region (not shown in Figures) evidenced that the FOT was due to ${}^{1}(\pi,\pi^{*})$ state rather than a $^{3}(\pi,\pi^{*})$ state.^{21,26} For the studied porphyrins the O states decayed with time constants ranging from 0.9 ps to 1.2 ps at 295 K. This process accounted for the kinetic component 1 for all studied compounds (e.g. Figures 3.5 and 3.6). The (π,π^*) lifetime largely reflected formation of the (d,d) excited state^{6,27}, without significant deactivation to the ${}^{3}(\pi,\pi^{*})$ state. There were several factors suggesting that the intersystem crossing pathway was not significant. Subpicosecond intersystem crossing from ${}^{1}(\pi,\pi^{*})$ to ${}^{3}(\pi,\pi^{*})$ was not expected for a porphyrin containing a firstrow diamagnetic metal ion,^{7,14} due to insufficient spin-orbit coupling and an absence of mixing involving unpaired metal and ring electrons. The (π,π^*) lifetime was not significantly perturbed by addition of 10% methyl iodide to the toluene and benzonitrile solutions of all three studied porphyrins. There was also no evidence for ${}^{3}(\pi,\pi^{*})$, based on the lack of near-infrared absorptions as noted above.²⁸ Therefore, Holten²⁹ suggested that the metal centered excited state formed directly from the (π,π^*) state and, thus, it was a singlet (d,d) state. The transient difference spectrum had a derivative-like shape (Figures 3.4, 3.7 and 3.10 (red spectra)) which is characteristic to the Ni porphyrins with the excited metal center.^{26,30} Within the next 5-15 ps the metal centered excited state continued to evolve with transient spectra narrowing and slightly shifting to the blue²² (kinetic component 2, e.g. Figure 3.9). This phenomenon has been accounted for by conformational/vibrational relaxation process.^{31,32}

However, considering the fact that stimulated emission has not been detected even at shortest time delay between pump and probe pulses, it is also possible to conclude that lifetime of the lowest porphyrin ring $S_1(\pi,\pi^*)$ state is shorter than the instrument response. The normally emissive S_2 or S_1 states of porphyrins can undergo stimulated emission when a photon from a probe beam excites corresponding emissive transition to the ground state. Therefore, if there had been any of S_1 state formed as FOT in our experiments, it would have been observed by

stimulated emission which takes place within probe pulse duration (~ 130 fs) and therefore can effectively compete with other deactivation pathways of S₁ state. Thus, by analogy with Ni(II)TPP studied by Eom et al.²⁰ the FOT is assigned to highly vibrationally excited species in the upper vibrational modes of the d,d manifold. The same vibronic transitions present in these hot species could be responsible for the spectral similarities between a hot porphyrinic ligand and singlet state spectra.²⁰ Nickel(II) complexes then returned to their thermal equilibrium via intramolecular vibrational energy redistribution among porphyrin normal modes (the fast kinetic component 1, e.g. Figures 3.5 and 3.6) and intermolecular vibrational redistribution to the surrounding solvent molecular system via solvent/solute interaction (the kinetic component 2, e.g. Figure 3.9). The transient optical bands of the (d,d) excited state in non coordinating media narrow and blue shift with wavelength dependent kinetics on the 1-25 ps timescale (Figure 3.10). This is characteristic to the vibrational/conformational relaxation process. Additionally, we have observed the different contribution of the fast component 1 to the temporal profiles of the transient evolution depending on the monitoring wavelength (Figure 3.11). That clearly indicates that the FOT in our case is "super hot" (d,d) state which then undergoes intramolecular relaxation process (kinetic component 1 in Figure 3.9) within 1-3 ps and intermolecular vibrational cooling process involving solvent molecules participation within 3-25 ps (kinetic component 2 in Figure 3.9) to produce vibrationally/conformationally relaxed (d,d) state (component 3 in Figure 3.9).

The kinetic component 3 has been established to be an electronic deactivation from the metal ${}^{3}B_{1g}(d_{z2}, d_{x2-y2})$ excited state to the ${}^{1}A_{1g}(d_{z2})^{2}$ ground state, similar to Ni(II)TPP deactivation dynamics.^{20,30} The slowest time constants for all three studied porphyrins did not exhibit dependence on the monitoring wavelength indicating the electronic transition to repopulate the

ground state. The d,d state deactivation proceeded via triplet metal centered excited state 3 (d,d). Our own quantum chemical calculations for nickel (II) meso tetra(heptafluoropropyl)porphine and those done by Rosa et. al 33 on Ni(II) octakis methylthio porphyrinate indicated that singlet d,d states lie well above the S₁ ligand state and cannot participate in deactivation pathway.

The ${}^{3}(d,d)$ excited state is likely to be below the first triplet excited state T₁ because the triplet energy estimated from the free base porphyrins phosphorescence measurements was higher than 1eV where (d,d) state was expected to be.^{21,26,34} Such estimation holds true because as reported by Kalyanasundaram et al²⁸ the lowest triplet state energy of porphyrins depends weakly on the nature of the peripheral substituents and increases upon insertion of metal into the tetrapyrrole ring. So for nickel porphyrins the energy of the triplet state would be around 1.8 eV as has been calculated³⁵ for Ni(II)TPrF₇P.

Ni(II)TPrF₇P bearing highly electron deficient peripheral meso substituents exhibited significantly short d,d state lifetime of 22 ps as opposed to the 690 ps and 450 ps for Ni(II)TPPF and Ni(II)TNPP respectively. This suggested that tetrapyrrole ring of nickel porphyrins bearing aromatic substituents in meso positions was not affected by the electron withdrawing ability of nitro- and fluoro-groups to the same extent as it was in the case of perfluoroalkyl substituted moiety.^{7,36} The π -donating effect of aromatic meso substituents considerably compensates the overall electron withdrawing effect as predicted by Hammett σ_p -constants.¹⁴ Moreover, flexible alkyl meso substituents may induce a substantial degree of distortion on tetrapyrrole macrocycle changing the ground state geometry from nominally planar (Ni(II)TPPF and Ni(II)TNPP) to highly ruffled (Ni(II)TPrF₇P).^{2,29,36,37} Therefore, the d,d state lifetime proved to be dependent on both conformational and electronic factors and could be effectively modulated by changing the nature of the peripheral substituents in meso positions. Ni(II)TPrF₇P demonstrated impressive
electron-withdrawing effects modulated through the macrocycle σ network.³⁶ Chapter 4 of this manuscript contains comparative study of Ni(II)TPrF₇P and its perprotio Ni(II)T(n-Pr)P analog including both experimental work and quantum mechanical calculations. That will help understand the individual contributions of conformational and electronic factors to excited state deactivation dynamics for two alkyl meso substituted nickel porphyrins.

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CHAPTER 4: NICKEL (II) MESO-TETRA(n-PROPYL) AND NICKEL (II) MESO-TETRA(HEPTAFLUOROPROPYL) PORPHYRINS

4.1 INTRODUCTION

Nickel(II) porphyrins have been shown to exhibit ultrafast excited state relaxation dynamics because they possess low-lying metal-related states that provide effective deactivation pathways of the tetrapyrrole ring π -localized excited states.¹⁻³ Drain et al. showed that nickel porphyrin excited states deactivate by the pathway: $(\pi,\pi^*) \rightarrow (d,d) \rightarrow$ ground state.⁴ However, our own experiments (Chapter 3) evidenced that the deactivation pathway is: "super hot" ³(d,d) state \rightarrow relaxed ³(d,d) \rightarrow ground state. The latter proposal is consistent with the observations by Eom for the nickel (II) meso-tetraphenylporphine.⁵

Nickel(II) porphyrins have rich photophysical behavior that can be exploited to probe the relationships among conformational, electronic and vibrational properties.⁶ Electron deficient substituents in the meso positions are known⁷ to greatly influence the interaction between the metal d-orbitals and the nitrogen orbitals of the tetrapyrrole macrocycle. Reduced electron density at the meso positions is directly conveyed to the tetrapyrrole macrocycle and thence to the central metal. Moreover, Renner et al⁸ have noted that porphyrins having flexible alkyl substituents in the meso positions often exhibit substantial ruffling of the tetrapyrrole ring. Since the central metal plays the primary role in the excited state deactivation dynamics of the nickel (II) porphyrins it is expected that the fast vibrational relaxation process lifetime and the relaxed d,d state lifetime will be affected by the peripheral substituents.

Studies of the photophysical behavior of tetracoordinated nickel porphyrins are ubiquitous¹⁻³ but the cooperative conformational and electronic factors contribution into the excited state deactivation dynamics are still not completely understood. As evidenced from the literature⁹, the Ni porphyrins are divided into two main groups: one being highly conformationally distorted (ruffled, saddled, etc.) and one being nominally planar. The former exhibit a blue shift of the (d,d) excited state spectral maximum and demonstrate excited state lifetime dependence on solvent; the latter exhibit red shifts and show no lifetime dependence on solvents. The shifted excited state Q bands for both classes are connected to some extent with the population of the d_{x2-y2} orbital in the ligand-field excited state. Population of this orbital and increased repulsion with the ring a_{2u} HOMO causes a shift in the HOMO-LUMO gap and the (π,π^*) transition energies. The blue shift in the transient Q band of the nonplanar porphyrins relative to the ground state of these complexes is easily explained if a less-distorted geometry is assumed in the ligand-field excited state. This new geometry displaces nickel (II) ion out-ofplane, and with the increased dipole moment the porphyrin excited state relaxation dynamics becomes sensitive to the solvent. The ground state of the porphyrin is usually symmetric and the dipole and quadruple moments are cancelled.^{4,9} Furthermore, the core size is expected to be larger the more planar the macrocycle, relieving electronic repulsion between the metal d_{x2-y2} and the ring a_{2u} electrons. The electron deficient substituents such as heptafluoropropyl help relieve the repulsion between the metal LUMO and porphyrin HOMO orbitals. Therefore, the combination of electron withdrawing propensity of meso-substituents and the ruffled geometry might induce some unique d,d excited state behavior.

To further elucidate the effect of electron withdrawing and conformational factors exerted by meso substituents on the d,d state deactivation dynamics we have investigated the relaxation dynamics of alkyl-substituted nickel porphyrins by placing electron withdrawing C_3F_7 residues at the four meso positions of an Ni(II) porphyrin, viz., Ni(II) mesotetra(heptafluoropropyl)porphine [Ni(II)TPrF₇P]. The electron rich but non-planar perprotiopropyl derivative, (Ni(II) meso-tetra(n-propyl)porphine [Ni(II)T(n-Pr)P]) was examined for comparison purposes. All experimental studies have been performed in non-coordinating solvents for the purpose of keeping the nickel ion in its tetracoordinated and low spin state. An important question to be addressed is whether the excited state behavior of Ni(II)TPrF₇P is more similar to the nominally planar nickel porphyrins or to the distorted ones.

Density Functional Theory (DFT) theoretical methods have proved to be useful for computing the ground state geometries and electronic structures of large, complex molecules such as metalloporphyrins.¹⁰ In order to properly assign the mechanisms and dynamics of the radiationless deactivation of the Q-state of a metalloporphyrin, it is necessary to know the nature and energies of the silent states existing in the $S_1 \rightarrow S_0$ gap.¹¹ Time-Dependent DFT (TDDFT) has been employed for calculation of excitation energies so when combined with experimental methods it provided a full analysis of the ground state electronic structure of studied system.¹⁰ TDDFT is a rigorous and useful method for calculating the properties of many-atom systems in time-dependent external fields, and is an extension of DFT, which allows for the description of the dynamic evolution of electronic systems.^{11,12} The excited state characteristics, such as excitation energies, and the oscillator strengths have been computed by TDDFT.^{11,12}

4.2 RESULTS

Ground Electronic State Absorption Spectra

Figure 4.1 shows the ground state absorption spectra of Ni(II)T(n-Pr)P (black solid line) and Ni(II)TPrF₇P (red dashed line) in toluene at room temperature.



Figure 4.1. Ground state optical absorption spectra of Ni(II)TPrF₇P (red dashed line) and Ni(II)T(n-Pr)P (black solid line) in toluene. Spectra are normalized at their Soret bands maxima for comparison purposes.

The spectra in Figure 4.1 are characterized by two clear vibrational progression peaks of sizable intensity in the visible region corresponding to the Q (0,0) (for Ni(II)T(n-Pr)P appearing as a shoulder) and Q (1,0) bands. The Q (0,0) peak of Ni(II)TPrF₇P is centered at 591 nm, and Q (1,0) peaks are at 539 nm and 550 nm for Ni(II)T(n-Pr)P and Ni(II)TPrF₇P respectively. Also there is an intense absorption in the near UV, the Soret (B) band, and weak continuum absorption

in between. The spectrum of Ni(II)TPrF₇P has an additional broad absorption centered at 358 nm presumably arising from the additional transitions due to the perfluoropropyl substituents.

Time-resolved Transient Absorption Spectroscopy

Photo-excitation studies were carried out using excitation wavelengths of 400 nm on the blue side of the Soret band, and in the Q-band envelope 591 or 539 nm for Ni(II)TPrF₇P and Ni(II)T(n-Pr)P respectively. Since excitation to the Q band region produced similar transient spectral and kinetic behavior, only 400 nm excitation data are presented in this chapter. Both compounds were promoted to their S_2 ligand centered excited states using 400 nm laser pulses of ca 130 fs duration. In each case the time evolution of the spectra was quite complex and reveals two or more kinetic components, with time constants ranging from subpicoseconds to tens of picoseconds before complete ground state recovery was observed.

Figure 4.2 shows time-resolved absorption data in the Q band region for Ni(II)TPrF₇P (Figure 4.2(A)) and Ni(II)T(n-Pr)P (Figure 4.2(B)) in toluene at 298 K.



Figure 4.2. Transient evolution spectra and decay kinetics of Ni(II)TPrF₇P (A) and Ni(II)TnPrP (B) in toluene. Red dotted lines were recorded 1 ps after the excitation pulse; black solid lines were recorded 5 ps after the excitation pulse. Insets: time profiles at the Q-band bleaching: (A) at 591 nm and (B) 539 nm.

Upon photo-excitation, the first observed transient (FOT), showed a broad absorption throughout the visible region superimposed on which were prominent negative bands due to bleaching of the ground state. It should be the lowest $S_1(\pi,\pi^*)$ that is rapidly formed from the

initially formed $S_2(\pi,\pi^*)$. However, we did not detect any stimulated emission even at the shortest time delay between pump and probe pulses, thus allowing the conclusion that the lifetime of a $S_1(\pi,\pi^*)$ is shorter than our instrument response. The normally emissive S_2 or S_1 states of porphyrins can undergo stimulated emission when a photon from a probe beam excites corresponding emissive transition to the ground state. Therefore, if there had been any of S₁ state formed as FOT in our experiments, it would have been observed by stimulated emission which takes place within probe pulse duration (~ 130 fs) and therefore can effectively compete with other deactivation pathways of S₁ state. The lack of broad absorption in Vis-NIR region^{13,14} allowed us to rule out another possible FOT, *viz.* the ${}^{3}T(\pi,\pi^{*})$. As reported by Eom et al.⁵, the possible FOT is a (d,d) state having an excess of vibrational energy. The transient spectrum (red dashed lines in Figure 4.2) has a broad and intense absorption over the visible spectral region superimposed on which there is a negative absorption corresponding to the Q band bleaching of the ground state. The similarity of this transient spectrum to that of the $S_1(\pi,\pi^*)$ arises from the fact that the most intense vibronic transitions of a (d,d) state are those of a ground state macrocycle π -system when the excitation has been transferred to the central Ni ion. The formation of the relaxed (d,d) state was complete within 2 ps or so for both studied compounds. For Ni(II)T(n-Pr)P this lifetime appeared as a growth of a negative absorption. These derivativelike spectra shown at 5 ps post pulse are identified as arising from the relaxed (d,d) states. Over the next 3 ps or so, the difference spectrum continued to evolve into one having a derivative-like shape (black lines in Figures 4.2(A) and 4.2(B)). For both compounds the derivative-shaped spectra slightly shifted to the blue and then decayed uniformly to the baseline indicating complete ground state recovery. The early blue shift is identified as arising from vibrational cooling in the d-manifold (Figure 4.3):



Figure 4.3. A series of spectral cuts from the optical dynamic surface of Ni(II)TPrF₇P in the time range $1 \rightarrow 3$ ps, normalized at the red-most maximum to clearly show the time-dependent blue shift.

The absorption of highly vibrationally excited species denotes a very broad spectral feature in the entire visible region at shorter time delays. The transitions from higher vibrational levels appear at lower energy with respect to the main electronic transition from the lowest vibrational level. As the molecules start to cool and relax to the excited potential well, the absorption of transient species in the red region disappears quickly while the absorption of cooled species, more to the blue, increases. This is a characteristic vibrational relaxation process of metalloporphyrins and many large molecules.

The perfluorinated compound showed a d,d state lifetime of 22 ps and the d,d state of the perprotiated compound had a 85 ps lifetime (Figure 4.2 (insets)). Neither complex showed any

excited state lifetime dependence on solvent properties since additional experiments in acetone, ethyl alcohol/ethyl ether mixtures, and benzonitrile revealed 17, 21, 20 ps lifetimes for Ni(II)TPrF₇P and 79, 75, 76 ps lifetimes for Ni(II)T(n-Pr)P respectively.

4.3 DISCUSSION

Alkyl-substituted nickel porphyrins are characterized by high conformational flexibility exhibiting substantial ruffling of the tetrapyrrole ring⁸. Therefore it was reasonable to assume that both Ni(II)TPrF₇P and Ni(II)T(n-Pr)P would have distorted structure in their ground states since crystallographic data of cobalt¹⁵ and zinc⁷ porphyrins bearing the same perfluoroalkyl ligand indicated that the overall geometry of molecules exhibited considerable distortions. Taking into account the small size of nickel(II) ion that contracts the tetrapyrrole core inducing ruffling⁴ and the similar size of perfluoro- and perprotio-alkyl substituents, the porphyrins ground state geometries have been optimized imposing D_{2d} symmetry using DFT molecular structure calculations (Table 4.1).

Table 4.1. Selected bond lengths (Å) and bond angles (deg) for Ni(II)TPrF₇P and Ni(II)T(n-Pr)P in the D_{2d} ruffled conformation

parameter	Ni(II)TPrF7P	Ni(II)T(n-Pr)P
Ni – N	1.899	1.910
C_{α} - N	1.379	1.381
$\mathrm{C}_\alpha-\mathrm{C}_\beta$	1.444	1.440
$C_\beta - C_\beta$	1.357	1.364
$\mathrm{C}_{\alpha}\!\!-\mathrm{C}_{m}$	1.402	1.397
$C_m - C_{1pr}$	1.522	1.515
$\mathrm{C_{1pr}-C_{2pr}}$	1.583	1.543
$\angle \operatorname{C}_{\alpha} NC_{\alpha}$	106.5°	106.4°
∠ <u>CaCmC</u> a	121.2°	120°
$\angle N C_{\alpha} C_{\beta}$	109.5°	109.6°
$\angle \ C_{\alpha} C_{\beta} C_{\beta}$	107.1°	107.1°
$\angle C_{\alpha}C_mC_{1pr}$	119.4°	119.8°
$\angle (C_{\alpha} \underbrace{N_p N_p C_{\alpha}}_{ad})_{ad}$	0°	0°
∠ (C _a N _p N _p C _a) _{op}	51.1°	43.6°

The computed dihedral angle between the opposite pyrrolic nitrogens of 51.1° for Ni(II)TPrF₇P supported the assumption of highly ruffled ground state molecular structure for this compound. The distortion angle happened to be smaller (43.6°) for Ni(II)T(n-Pr)P but large enough to consider the porphyrin to be substantially ruffled⁹. As expected, the enhancement of the ruffling distortion correlates with the shortening of the Ni-N distance from 1.910 Å for Ni(II)T(n-Pr)P to 1.899 Å for Ni(II)TPrF₇P (Table 4.1).

The highest occupied and lowest unoccupied ground state one-electron levels calculated for Ni(II)T(n-Pr)P and Ni(II)TPrF₇P are shown in Figure 4.4, and an atomic orbital population analysis is given in Tables 4.2 and 4.3.



Figure 4.4. Energy level scheme for Ni(II)T(n-Pr)P and Ni(II)TPrF₇P. The highest occupied MO is indicated by the pair of vertical arrows.

MO	E(eV)	Ni	Ν	Cα	Cβ	C_m	C_1	F_1
				unoccupi	ed			
28a1	-3.062	-	-	19 (2p _{z,y})	40 (2p _{z,y})	33 (2р _{д,х})	2 (2p _z)	2 (2p _x)
21b ₁	-3.724	51 (d _x 2-y2)	25 (2p _x) 10 (2s)	1 (2py)	2 (2p _x)	-	-	-
47e	-4.235	3 (d _π)	9 (2р _{з,х/у})	27 (2p _{z,x/y}) occupie	22 (2p _{z,x/y}) d	28 (2p _{z,y,x})	1 (2p _z)	-
27a1	-5.862	88 (d _z 2); 9 (4s)	1 (2p _x)	-	-	-	-	-
46e	-5.942	67 (d _n)	7 (2p _{z,x/y})	3 (2p _z)	15(2p _{z,x/y})	-	-	-
20Ъ1	-6.141	-	-	73 (2p _{z,y})	21 (2p _{z,y})	-	-	-
27b ₂	-6.376	15 (d _{xx})	23 (2p _{z,y})	-	2 (2p _z)	48 (2p _{z,x})	1 (2p _z)	2 (2p _x)
26b ₂	-6.971	49 (d _{xx})	1 (2p _z)	2 (2p _z)	30 (2p _{z,y})	10 (2p _{z,x})	-	-
19a ₂	-7.004	-	36 (2p _{z,y})	-	59 (2p _{z,y})	-	-	-
45e	-7.561	25 (d _π)	25 (2p _{z,x/y})	-	45 (2р _{з,х/у})	-	-	-
25b2	-7.723	28 (d _n)	232 (2p _{z,y})	1 (2p _z)	41 (2p _{z,y})	-	-	-

Table 4.2. Energies and percent composition of the highest occupied and lowest unoccupied molecular orbitals of Ni(II)TPrF₇P expressed in terms of individual atoms

Table 4.3. Energies and percent composition of the highest occupied and lowest unoccupied

molecular orbitals of N	T(II)	(n-Pr)P expressed	in terms of inc	dividual atoms
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3							
MO	E(eV)	Ni	N	C_{α}	Cβ	C_m	H_l
			ur	noccupied			
17a ₁	-1.647	-	-	6 (2p _z)	59 (2p _{z,y})	29 (2р _{д,х})	3.50(1s)
11b ₁	-2.490	51 (d _x 2-y2) 4(d _x 2-y2)	25 (2p _x) 10 (2s)	1 (2s)	2 (2p _x) 2(2s)	-	-
26e	-2.731	3 (d _π)	12 (2pz,y/x)	21 (2p _{z,x/y}) occupied	27 (2p _{z,x/y})	30 (2p _{z,y,x})	1(1s)
16a1	-4.585	88 (d _z 2) 10 (4s)	1 (2p _x)	-	-	-	-
16b ₂	-4.610	5 (d _{xx})	24 (2p _{z,x})	3 (2p _z)	3(2p _z)	51 (2p _{z,x})	-
25e	-4.680	69(d _π)	5(2p _z)	6 (2p _{z,y/x})	14 (2p _{z,y/x})	-	-
10b ₁	-4.889	-	-	69(2p _{z,y})	25 (2p _{z,y})	-	-
15b ₂	-5.702	72 (d _{xy})	1 (2p _z)	4 (2p _{z,x})	13 (2p _{z,y})	4 (2p _{z,x})	-
9a2	-5.863	-	38 (2p _{z,y})	1 (2p _z)	56 (2p _{z,y})	-	-
24e	-6.320	21 (d _{n})	27 (2p _{z,y/x})	12 (2p _{z,x/x})	23 (2p _{z,y/x})	7 (2p _z)	-
14b ₂	-6.499	15 (d _{xy}) 1 (4s) 1(4p _z)	23 (2p _{z,y})	-	55 (2p _{z,y})	-	-

Among the one-electron levels in Figure 4.4 it is possible to recognize the occupied a_{1u} and a_{2u} Gouterman HOMO (G-HOMO) and unoccupied e_g Gouterman LUMO G-LUMO), and the metal 3d orbitals. For Ni(II)T(n-Pr)P a_{1u} (10b₁) is G-HOMO₋₁ and a_{2u} (16b₂) is G-HOMO while in Ni(II)TPrF₇P the order is reversed such as a_{2u} (27b₂) becomes G-HOMO₋₁ and a_{1u} (20b₁) is G-HOMO. As for the G-LUMO orbitals, they are both of e_g symmetry represented by 26e and 47e for Ni(II)T(n-Pr)P and Ni(II)TPrF₇P respectively. Introduction of highly electron deficient substituents into meso positions substantially stabilizes the a_{2u} orbital of Ni(II)TPrF₇P. See 27b₂ in Figure 4.5.



Figure 4.5. Energy level scheme for Ni(II)T(n-Pr)P and Ni(II)TPrF₇P with energies normalized for comparison purposes with respect to d_{z2} orbital to show the shifting of levels.

That orbital places electron density mainly on the meso carbons and pyrrolic nitrogens (Figure 4.6) while a_{1u} is localized mainly on α and β carbons.



Figure 4.6. Contour plots of G-HOMO, G-LUMO and metal HOMO and LUMO orbitals of Ni(II)TPrF₇P.

The LUMO orbital is stabilized to almost the same extent (Figure 4.5) therefore the HOMO-LUMO energy gap is maintained constant. It is worth noting that metal LUMO d_{x2-y2} orbital is raised in energy in the perfluoropropyl porphyrin due to increased antibonding character arising from better overlap between lone electron pairs on pyrrolic nitrogens and nickel d-orbitals. The smaller cavity size for perfluoropropyl porphyrin facilitates this process. The enhanced mixing of metal and ligand orbitals in electron deficient Ni(II)TPrF₇P produces additional broadening of the Soret peak (Figure 4.1) and results in O bands red shift.⁶ Here the configuration interactions should be taken into consideration as the computed HOMO-LUMO gap does not account for the origin of the red shift. The Q-bands red shift results from the reduced Ni-N distance that causes in-plane nuclear reorganization (IPNR), which is defined as changes in the porphyrin bond lengths and bond angles induced by strong electronic effects of the substituent on macrocycle.¹⁶ The one electron optically allowed transitions presented in Tables 4.4 and 4.5 identify the transitions responsible for the origin of the Soret and Q bands. DFT calculations produce the oscillator strengths corresponding to the strongest Franck-Condon transitions therefore for comparison purposes the experimental absorption maxima are presented for the peak values and not for the (0,0) transitions. It can be seen from Tables 4.2 and 4.4 that fluorine atom participation accounts for the additional peak in Figure 4.1 (red dashed line) centered at around 358 nm. The spectral features did not show any appreciable solvatochromism either for Ni(II)TPrF₇P or Ni(II)T(n-Pr)P. Even in relatively polar medium, such as benzonitrile, the Soret and Q band absorptions only shifted by several nanometers compared to the slightly polar toluene. It is quite common for nominally planar porphyrins to lack the dependence on solvent dielectric properties⁹ because the planar structure of the porphyrinic macrocycle does not have a dipole moment but it is quite unusual to exhibit this behavior for the molecules of such high

distortion¹⁵ as Ni(II)T(n-Pr)P and Ni(II)TPrF₇P. This could be explained by the fact that nickel ion is small enough to be accommodated by the tetrapyrrolic cavity so nickel stays in plane thus not inducing appreciable dipole moment.

Table 4.4. Vertical excitation energies and oscillator strengths (*f*) computed for the optically allowed ¹E and ¹B₂ excited states of Ni(II)TPrF₇P in the D_{2d} conformation and compared to the experimental data.

state	composition (%)	$E_{\nu a} \; ({\rm eV/nm})$	f	$E_{\rm exp}~({\rm eV/nm})^{\rm a}$
2 ¹ E	20b ₁ → 47e (56) 27b ₂ → 47e (42)	2.185 (567)	0.011	2.100 (591) Q
3 ¹ E	46e → 21b ₁ (46) 26b ₂ → 47e (27) 27b ₂ → 47e (14)	2.574 (482)	0.086	
4 ¹ E	46e → 21b ₁ (50) 26b ₂ → 47e (23) 27b ₂ → 47e (14)	2.725 (455)	0.106	
5 ¹ E	46e → 28a ₁ (60) 19a ₂ → 47e (30)	2.865 (433)	0.0051	
6 ¹ E	19a ₂ → 47e (66) 46e → 28a ₁ (19) 26b ₂ → 47e (9)	2.894 (428)	0.071	
7 ¹ E	26b ₂ → 47e (31) 27b ₂ → 47e (24) 20b ₁ → 47e (19) 46e → 28a ₁ (17)	3.243 (382)	1.24	3.010 (412) B
3^1B_2	45e → 47e (81) 27b ₂ → 28a _l (14)	3.434 (362)	0.0017	
$4^{1}\mathrm{B}_{2}$	27b ₂ → 28a ₁ (73) 45e → 47e (16) 44e → 47e (10)	3.469 (358)	0.0034	
81E	$25b_2 \rightarrow 47e (97)$	3.587 (346)	0.01	
91E	$45e \rightarrow 21b_1 \ (94)$	4.066 (305)	0.008	

^a Spectrum of Ni(II)TPrF7P in toluene, this work

Table 4.5. Vertical excitation energies and oscillator strengths (*f*) computed for the optically allowed ¹E and ¹B₂ excited states of Ni(II)T(n-Pr)P in the D_{2d} conformation and compared to the experimental data.

state	composition (%)	$E_{\nu a}~({\rm eV/nm})$	f	$E_{exp}({ m eV/nm})^{ m a}$
2 ¹ E	16b2→26e (66) 10b1→26e (32)	2.157 (575)	0.027	2.340 (530) Q
31E	25e→11b1 (81) 15b2→26e (8)	2.643 (469)	0.036	
4 ¹ E	10b1→26e (40) 16b2→ 26e (18)	2.838 (437)	0.497	
2^1B_2	16b ₂ →17a ₁ (90)	3.135 (396)	0.0041	
6 ¹ E	9a ₂ →26e (46) 15b ₂ → 26e (20) 25e→17a ₁ (17) 10b ₁ →26e (10)	3.212 (386)	0.441	
7 ¹ E	9a2→26e (52) 25e→17a1 (17) 15b2→26e (12)	3.337 (372)	0.483	2.918 (425) B
81E	14b ₂ →26e (94)	3.885 (319)	0.0515	
91E	24e→11b1 (70) 23e→11b1 (26)	4.021 (308)	0.0072	
6^1B_2	23e→26e (58) 15b ₂ →17a ₁ (13)	4.397 (282)	0.031	
7 ¹ B ₂	16b ₂ →18a ₁ (100)	4.713 (263)	0.0017	

^a Spectrum of Ni(II)T(n-Pr)P in toluene, this work

According to ultrafast transient absorption measurements performed in toluene and other non-coordinating solvents and to the results of quantum chemical calculations, the Q state of both Ni(II)T(n-Pr)P and Ni(II)TPrF₇P deactivate by the pathway ${}^{1}(\pi,\pi^{*}) \rightarrow {}^{3}(d,d) \rightarrow$ ground state. Our calculations have shown that the lowest $(d_{z2}d_{x2-y2})$ singlet states $(2^{1}B_{1})$ for both Ni(II)T(n-Pr)P and Ni(II)TPrF₇P have the energies of 2.36 eV and 2.39 eV respectively and are located above the ${}^{1}(\pi,\pi^{*})$ and therefore cannot be populated by the relaxation from the ligand lowest singlet state (2¹E) (Tables 4.6 and 4.7). The similar behavior has been observed by Rosa et al.¹⁷ for Ni(II) meso-tetra(methylthio)porphine as well. A number of low lying excited states located between the lowest singlet π,π^{*} state (2¹E) and the 3 (d,d) state (2³B₁) (Tables 4.6 and 4.7) facilitates ultrafast intersystem crossing.

Table 4.6. Excitation energies (eV), composition and character of the low-lying excited states of Ni(II)TPrF₇P in the D_{2d} conformation.

state	composition (%)	character	$E_{\nu a}$	E _{adia}
$2^{1}E$	20b ₁ → 47e (56) 27b ₂ → 47e (42)	ππ*	2.185 (Q)	
1^1A_1	46e → 47e (96)	MLCT	2.120	
3 ³ E	$46e \rightarrow 21b_1 \ (99)$	$d_{\pi}d_{x}2_{y}2$	1.868	
1^1B_2	46e → 47e (100)	MLCT	1.818	
2 ³ E	$20b_1 \rightarrow 47e (99)$	ππ*	1.792	
$1^1 B_1$	46e → 47e (100)	MLCT	1.779	
1^1A_2	46e → 47e (100)	MLCT	1.738	
$2^{3}B_{1}$	27a1 → 21b1 (94) 46e → 47e (6)	dz2dx2.y2/MLCT	1.679	1.165 ^b
$1^{3}A_{2}$	46e → 47e (100)	MLCT	1.678	
$1^3\mathrm{B}_1$	46e → 47e (94)	MLCT	1.656	
1 ¹ E	$27a_1 \rightarrow 47e~(100)$	MLCT	1.646	
$1^{3}B_{2}$	46e → 47e (100)	MLCT	1.632	
$1^{3}A_{1}$	46e → 47e (100)	MLCT	1.606	
1 ³ E	27a ₁ → 47e (100)	MLCT	1.605	

^a Computed at the optimized geometry of the corresponding triplet.

^b Relaxation has been performed with respect to d,d excited state

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state	composition (%)	character	$E_{\nu a}$	E _{adia}
$2^{1}E_{1}$	$\begin{array}{c} 16b_2 \rightarrow 26e \ (66) \\ 10b_1 \rightarrow 26e \ (32) \end{array}$	ππ*	2.157(Q)	
$4^{3}E_{1}$	$10b_1 \rightarrow 26e$ (100)	$\pi\pi^*$	2.068	
1^1B_2	$25e \rightarrow 26e (100)$	MLCT	2.056	
$2^{3}A_{2}$	$16b_2 \rightarrow 11b_1 (99)$	LMCT	2.056	
1^1B_1	25e ightarrow 26e (96)	MLCT	2.018	
1^1A_2	$25e \rightarrow 26e (100)$	MLCT	1.976	
$1^{3}A_{2}$	$25e \rightarrow 26e (100)$	MLCT	1.925	
$2^{3}B_{1}$	$25e \rightarrow 26e (100)$	MLCT	1.894	
1^1E_1	16a ₁ → 26e (100)	MLCT	1.873	
$1^{3}B_{2}$	$25e \rightarrow 26e (100)$	MLCT	1.871	
$1^{3}A_{1}$	25e → 26e (100)	MLCT	1.840	
3 ³ E1	25e →11b ₁ (81) 16a _l → 26e (18)	d _π d _{x2y2} /MLCT	1.836	
$2^{3}E_{1}$	16a1 → 26e (82) 25e →11b1 (18)	$\mathrm{MLCT}/\mathrm{d}_{\pi}\mathrm{d}_{\mathrm{x}2\text{-y}2}$	1.829	
$1^{3}E_{1}$	$16b_2 \rightarrow 26e (99)$	ππ*	1.733	
$1^{3}\mathrm{B}_{1}$	$16a_1 \rightarrow 11b_1 \; (100)$	d _{z2} d _{x2-y2}	1.653	1.040

Table 4.7. Excitation energies (eV), composition and character of the low-lying excited states of Ni(II)T(n-Pr)P in the D_{2d} conformation.

The vertical absorption energies (Eva) have been computed at the ground state optimized geometry. The adiabatic energies have been obtained according to the expression¹⁸

$$E_{adia} = E_{ve} + \Delta E$$

 E_{ve} is the vertical emission energy that has been calculated at the TDDFT level using the relaxed excited state geometry. The ΔE term accounts for the ground state energy change upon deformation to the relaxed excited state geometry (Figure 4.7)¹⁸



Figure 4.7. Schematic definition of the computed excitation energies (from ref. 18).

The (d,d) state exhibits complex spectral evolution over ca. 3 ps for both compounds, interpreted in terms of vibrational relaxation and cooling (Figure 4.3). The difference arises in the cold ligand-field excited state lifetime which was unusually short (22 ps) for Ni(II)TPrF₇P compared to 85 ps for Ni(II)T(n-Pr)P. Based on the energy gap law⁵, the lifetime of Ni(II)T(n-Pr)P should be shorter than the one of Ni(II)TPrF₇P since the energies of the lowest ³(d,d) excited states are 1.04 eV and 1.17 eV respectively (Tables 4.6 and 4.7). However, this is not the case and perfluoropropyl porphyrin deactivates faster to the ground state due to the small amount of metal-to-ligand charge transfer state (MLCT) mixed into the ³(d,d) excited state (Table 4.6). The high electron withdrawing ability of the meso-perfluoroalkyl substituents thus modulates the relaxation dynamics of Ni(II)TPrF₇P.

Both Ni(II)TPrF₇P and Ni(II)T(n-Pr)P remain considerably ruffled in their lowest metal centered excited states (Tables 4.8 and 4.9) although they both adopt more planar structures with degrees of ruffling of 38.3° and 25.2° respectively.

	Ni(II) TPrF7P		
parameter	$^{1}A_{1}$	$2^{3}B_{1}$	
Ni – N	1.899	1.995	
C_{α} -N	1.379	1.378	
$\mathrm{C}_\alpha-\mathrm{C}_\beta$	1.444	1.445	
$\mathrm{C}_{\beta} \mathrm{-} \mathrm{C}_{\beta}$	1.357	1.357	
$\mathrm{C}_{\alpha}\!\!-\!\mathrm{C}_m$	1.402	1.412	
$\mathrm{C}_{\mathfrak{m}}\!-\!\mathrm{C}_{\mathtt{lpr}}$	1.522	1.522	
$\mathrm{C}_{1\mathrm{pr}}\!-\!F_1$	1.372	1.372	
$\mathrm{C}_{1\mathrm{pr}}\!-\!\mathrm{C}_{2\mathrm{pr}}$	1.583	1.582	
$\mathrm{C}_{2pr}\!-\!F_2$	1.358	1.358	
$\angle C_{\alpha} NC_{\alpha}$	106.5 ⁰	107.3 ⁰	
$\angle C_{\alpha}C_{m}C_{\alpha}$	121.2 ⁰	124.1 ⁰	
$\angle \operatorname{NC}_{\alpha} C_{\beta}$	109.5 ⁰	109.1 ⁰	
$\angle C_{\alpha}C_{\beta}C_{\beta}$	107.1 ⁰	107.2 ⁰	
$\angle \operatorname{C}_{\alpha} \operatorname{C}_m \operatorname{C}_{\operatorname{lpr}}$	119.4 ⁰	117.20	
$\angle (\mathrm{C}_{\alpha}\mathrm{N}_p\mathrm{N}_p\mathrm{C}_{\alpha})_{\mathrm{ad}}$	00	00	
$\angle \left(\mathrm{C}_{\alpha}\mathrm{N}_{p}\mathrm{N}_{p}\mathrm{C}_{\alpha} \right)_{op}$	51.1 ⁰	38.3 ⁰	

Table 4.8. Optimized geometrical parameters (Å, deg) for Ni(II)TPrF₇P in the D_{2d} ground state (¹A₁) and in the lowest triplet excited state (2³B₂ for d,d state).

	Ni(II) T(n-Pr)P		
parameter	¹ A1	$1^{3}B_{1}$	
Ni – N	1.910	2.011	
C_{α} -N	1.381	1.378	
$\mathrm{C}_\alpha-\mathrm{C}_\beta$	1.440	1.444	
$C_\beta - C_\beta$	1.364	1.364	
$C_{\alpha} - C_{m}$	1.397	1.405	
$C_m - C_{lpr}$	1.515	1.518	
$\rm C_{1pr}-C_{2pr}$	1.543	1.543	
$\angle \operatorname{C}_{\alpha} \operatorname{NC}_{\alpha}$	106.4°	107.1°	
$\angle \operatorname{C}_{\alpha}\operatorname{C}_{m}\operatorname{C}_{\alpha}$	120°	123.2°	
$\angle \operatorname{NC}_{\alpha} C_{\beta}$	109.6°	109.3°	
$\angle \operatorname{C}_{\alpha} \operatorname{C}_{\beta} \operatorname{C}_{\beta}$	107.1°	107.2°	
$\angle \operatorname{C}_{\alpha} \operatorname{C}_{\mathfrak{m}} \operatorname{C}_{\operatorname{lpr}}$	119.8°	118.3°	
$\angle (\mathrm{C}_{\alpha}\mathrm{N}_p\mathrm{N}_p\mathrm{C}_{\alpha})_{ad}$	00	0°	
$\angle \left(\mathrm{C}_{\alpha}\mathrm{N}_{p}\mathrm{N}_{p}\mathrm{C}_{\alpha}\right)_{op}$	43.6°	25.2°	

Table 4.9. Optimized geometrical parameters (Å, deg) for Ni(II)T(n-Pr)P in the D_{2d} ground state (¹A₁) and in the lowest triplet excited state (2³B₂ for dd state)

The lack of excited state lifetime dependence on solvent dielectric properties suggests that the ground and excited state dipole moments are similar because the small nickel ion stays in the plane of the tetrapyrrole ligand as manifested by D_{2d} symmetry constraints.^{4,9} This behavior is in great contrast to the one that would normally be expected for the highly ruffled porphyrins, such as Ni(II) tetra(tert-butyl)porphine and Ni(II) tetra-adamantylporphine.^{4,9} These species relieve their steric strain by changing the excited stated geometry which stabilizes the HOMO

and shifts the transitions to the higher energy. This is evidenced by the fact that the (d,d) state derivative-like spectrum has a positive absorption peak immediately to the blue of the ground state bleaching. Despite being highly ruffled in the ground state (Table 4.8), both Ni(II)T(n-Pr)P and Ni(II)TPrF₇P exhibit a red shift in the (d,d) excited state spectrum (Figure 4.2), not the blue one as expected for the molecules with such a degree of distortion. Such behavior is characteristic for the nominally planar nickel porphyrins such as NiT(n-Pe)P when the repulsion between the a_{2u} orbital and the filled d_{x2-y2} is increased in the excited state spectrum to the lower energy transitions.¹⁹

The electronic rather than conformational factors play significant role in excited state deactivation dynamics. Comparing the energy level diagrams of the ground and ³(d,d) excited state (Figures 4.8 and 4.9) on can see the changes responsible for the transient difference absorption spectra presented in Figure 4.2.



Figure 4.8. Comparison of the ground electronic and ³(d,d) excited states energy diagram of Ni(II)T(n-Pr)P.



Figure 4.9. Comparison of the ground electronic and ³(d,d) excited states energy diagram of Ni(II)TPrF₇P.

The G-LUMO e_g orbitals (26e and 47e) of both Ni(II)T(n-Pr)P and Ni(II)TPrF₇P are stabilized in the ³(d,d) excited state. However, the G-HOMOs experience different degrees of uplift for the porphyrins mentioned above. The G-HOMO a_{2u} (16b₂) of Ni(II)T(n-Pr)P goes up in energy decreasing the HOMO-LUMO gap by 0.034 eV which corresponds to the red shift of 8 nm in the transient difference spectrum. It accounts for the derivative shape spectrum which is symmetric unlike the one of Ni(II)TPrF₇P (Figure 4.2). The smaller decrease in HOMO-LUMO gap of 0.005 eV for fluorinated porphyrin results in smaller red shift of $a_{1u} \rightarrow e_g$ (20b₁ \rightarrow 47e) transition corresponding to 1 nm. Therefore, in the excited state difference spectrum of Ni(II)TPrF₇P bleaching dominates over the positive absorption peak to the red.

The unusual excited state behavior exhibited by Ni(II)TPrF₇P presumably originates in cooperative contribution of structural distortions of tetrapyrrolic macrocycle and electron withdrawing ability of perfluoropropyl meso-substituents modulated through σ network. Highly electron deficient perfluoroalkyl porphyrin demonstrated excited state properties of both planar and highly ruffled porphyrinic moieties making this molecule a very attractive candidate for studying conformational and electronic factors that govern the excited state behavior of many natural systems containing porphyrin macrocycle.

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CHAPTER 5: IRON (III) MESO-TETRAPHENYL AND IRON (III) MESO-TETRA(HEPTAFLUOROPROPYL) PORPHYRINS

5.1 INTRODUCTION

Artificial iron porphyrinato complexes are suitable models of native biologically active enzymes (e.g. cytochromes), since they mimic the structure of the site governing physiological function of naturally occurring compounds.¹ They are very important as they form active centers of electron transfer, ligand binding and catalytic proteins.² The third order non-linear properties of porphyrins, porphyrin polymers, and porphyrin coordination compounds have been extensively studied³⁻⁶, and iron porphyrins have been viewed as prospective candidates for possible application in molecular photonics.^{3,4} Humphrey et al.⁷ have discovered that Fe(III) tetrakis(p-hydroxyphenyl)porphyrin could be effectively used as third-order nonlinear optical material and iron charge transfer states play the important role in determining high non-linear response. The efficiency of processes related to two-photon absorption is described by the imaginary part of the material's third-order nonlinear susceptibility, $\chi^{(3)}$, and molecular second hyperpolarizability, γ . Nonlinear refraction is described by the real part of coefficients $\chi^{(3)}$ and γ . The time response of non-resonant electronic third-order nonlinearity in porphyrin films was found to be faster than 120 fs.⁷

The selective oxidations of hydrocarbons are of importance in both synthetic chemistry and industrial processes, therefore biomimetic oxidation reactions by iron(III) porphyrin complexes have attracted much attention.⁸ Lim and coworkers⁹ reported that a simple iron porphyrin complex (e.g. iron(III) meso-tetraphenylporphine [Fe(III)TPP]) catalyzes the

epoxidation and hydroxylation of hydrocarbons by iodosylbenzene. Bartoli et al.¹⁰ noted that introduction of electron withdrawing groups into the meso positions of the porphyrin ring enhanced the reactivity of the iron porphyrins greatly and diminished the oxidative degradation of porphyrin ligands dramatically. Moore et al.¹¹ have demonstrated that iron (III) mesotetra(heptafluoropropyl)porphine chloride [Fe(III)TPrF₇P·Cl] species exhibit considerably reduced electron density in the porphyrin π system, as well as significantly augmented electrostatic potential at the nitrogen core orbitals.^{12,13} The X-ray Photoelectron Spectroscopy (XPS) data showed^{11,12} 1.4 eV increase in 1s ionization potential of N atom compared to pentafluorophenyl substituted porphyrin. The lack of heavy atom substituents at the macrocycle periphery coupled with the fact that non- π -conjugating, σ -electron withdrawing perfluoroalkyl moieties stabilize to the same degree both HOMO and LUMO orbitals of the porphyrin π system endow these species with novel photophysical properties.¹² In iron porphyrins the effective mixing of d metal orbitals and π system is responsible for the multitude of the excited states that take part in the deactivation dynamics, therefore the electron withdrawing effect should be conveyed to the central metal opening the alternative routes for excited state deactivation.

In this work ultrafast transient absorption spectrometry has been employed to elucidate the influence of highly electron deficient perfluoroalkyl substituents on the photophysical behavior of iron(III) porphyrin and establish a relationship between conformational and electronic factors responsible for the excited state relaxation dynamics. Iron(III) mesotetra(heptafluoropropyl)porphine [Fe(III)TPrF₇P·Cl] and iron(III) meso-tetraphenylporphine [Fe(III)TPP·Cl] have been chosen as model compounds.

5.2 RESULTS

Ground Electronic State Absorption Spectra

The ground electronic state absorption spectra of Fe(III)TPP·Cl and Fe(III)TPrF₇P·Cl in toluene showed similarities. The Q-band region extending from 470 to 700 nm exhibited a broad and featureless vibronic progression for both compounds. Strong near-UV Soret bands appeared at 357 and 412 nm for Fe(III)TPrF₇P·Cl and at 370 and 423 nm for Fe(III)TPP·Cl (Figure 5.1):



Figure 5.1. Ground electronic state normalized absorption spectra of Fe(III)TPP·Cl (black solid line) and Fe(III)TPrF₇P·Cl (dashed red line) recorded at room temperature in air saturated toluene.

Time-resolved Transient Absorption Spectroscopy

Visible region transient absorption changes and kinetic data with ~130 fs time resolution were acquired for all porphyrins under the same experimental conditions (295K, toluene, 2µJ/pulse, 10µM solutions), using 400 nm light as excitation pulse. In each case the time evolution of the spectra was quite complex and revealed two or more kinetic components, with time constants ranging from subpicoseconds to tens of picoseconds before complete ground state recovery was observed. The photophysical behavior had both notable similarities and striking differences for porphyrins bearing aromatic or aliphatic substituents in meso-positions, and so the results for aryl- and alkyl-substituted porphyrins are presented separately.

Fe(III)TPP·Cl. Figure 5.2 shows time-resolved absorption data in the Q band region for Fe(III)TPP·Cl in toluene at 298 K, acquired using 130-fs excitation flashes at 400 nm:



Figure 5.2. Transient absorption difference spectra in the Q band region of Fe(III)TPP·Cl in toluene acquired at different delay times after the excitation event.
At ca. 1 ps after excitation of the iron porphyrin, bleaching of the ground state band at 507 nm was accompanied by the appearance of a positive absorption over the 525-750 nm range of the spectrum (Figure 5.2 (black line)). Over the next 1 or 2 ps, the difference spectrum continued to evolve with a blue shift over a wide spectral range (Figure 5.2 (red line)). Over the following several picoseconds, the spectrum decayed uniformly to the baseline, reflecting complete ground-state recovery, with an apparent isosbestic point near 527 nm.

Representative Q band region kinetic data are shown in Figures 5.3 and 5.4.



Figure 5.3. Representative kinetic trace and the fit of the time evolution of the absorption at 465 nm of Fe(III)TPP·Cl in toluene from Figure 5.2.



Figure 5.4. Representative kinetic trace and the fit of the time evolution of the absorption at 545 nm of Fe(III)TPP·Cl in toluene from Figure 5.2.

At all wavelengths the transient signals were fully developed with the instrument response function (ca. 300 fs) and the resulting temporal change was fitted with a double exponential function added to a very minor constant component (probably arising from an excited state of a small fraction of the free base porphyrin impurity). The fast component had a lifetime of 1.5 ps and the slower kinetic component had a lifetime of about 10 ps independent of a monitoring wavelength.

Fe(III)TPrF₇P·Cl. Figure 5.5 shows time-resolved absorption data in the Q band region for Fe(III)**TPrF₇P·Cl** in toluene at 298 K, acquired using 130-fs excitation flashes at 400 nm:



Figure 5.5. Transient absorption difference spectra in the Q band region of Fe(III)TPrF₇P·Cl in toluene acquired at different delay times after the excitation event.

Over ca. 800 fs after the excitation event, bleaching of the ground state bands in the range of 485 nm - 570 nm was accompanied by the appearance of a positive absorption over the 650-750 nm range of the spectrum (Figure 5.5). The transient spectrum had a very broad and intense absorption band above 650 nm. Over the following several picoseconds, the spectrum decayed uniformly to the baseline, reflecting complete ground-state recovery, with an apparent isosbestic point near 485 nm.

Representative Q band region kinetic data are shown in Figures 5.6 and 5.7.



Figure 5.6. Representative kinetic trace and the fit of the time evolution of the absorption at 512 nm of Fe(III)TPrF₇P·Cl in toluene from Figure 5.5.



Figure 5.7. Representative kinetic trace and the fit of the time evolution of the absorption at 712 nm of Fe(III)TPrF₇P·Cl in toluene from Figure 5.5.

At all wavelengths the transient signals were fully developed with the instrument response function (ca. 300 fs) and the resulting temporal change was fitted with a single exponential function added to a very minor constant component (probably arising from an excited state of a small fraction of the free base porphyrin impurity). The only kinetic component had a lifetime of about 4 ps independent of a monitoring wavelength.

5.3 DISCUSSION

Ground Electronic State Absorption Spectra

Both Fe(III)TPP·Cl and Fe(III)TPrF₇P·Cl ground state absorption spectra are quite characteristic of a d-type hyperporphyrin species when iron is in its +3 oxidative state (Figure 5.1).¹⁴ For these species the metal d-orbitals are uniquely situated in energy so extensive mixing of d_{π} orbitals and LUMO orbitals of the porphyrin ring can occur.² This accounts for the complex nature of the ground state absorption spectra. The featureless broad absorption in the range of 470 - 700 nm is produced by vibronic transitions in the porphyrin macrocycle and low energy metal-to-ligand charge transfer states which result from that mixing.¹¹ The region between 470 – 550 nm could be assigned to the vibronic Q bands of the porphyrin, and additional vibronic progression above 550 nm results from low energy charge transfer transitions $(a_{1u}(\pi), a_{2u}(\pi) \rightarrow$ $e_g (d_{vz}, d_{xz})$).⁷ In the case of highly electron deficient Fe(III)TPrF₇P·Cl there is a small blue shift of the Soret band from 423 nm to 412 nm and the Soret vibronic side-band from 370 nm to 350 nm compared to the spectrum of electron rich Fe(III)TPP·Cl. This phenomenon can be explained by the substantial distortions of the pyrrolic ring induced by the aliphatic electron withdrawing substituents which change the geometry from saddled (Fe(III)TPP·Cl) to ruffled (Fe(III)TPrF₇P·Cl).^{13,15} By the same reason the relative intensities of the Soret and the side bands are different for the two studied compounds.¹⁶ The Q-band region of the Fe(III)TPrF₇P·Cl appears to be more diffuse perhaps indicating the greater contribution of low lying charge transfer states into those transitions, while the spectrum of Fe(III)TPP·Cl has a detectible peak centered at 505 nm as observed for regular porphyrins, e.g. Zn(II)TPP.^{17,18}

Time-resolved Transient Absorption Spectroscopy

The deactivation dynamics of the high spin iron(III) porphyrins are quite complex due to the abundance of the low lying charge transfer states and metal centered d,d states which take an active part in relaxation pathway. The spectral features observed for the transient difference spectra are usually overlapping and diffuse. On the basis of work done by White Dixon, et al.² it is reasonable to assign the first observed transient (FOT) for Fe(III)TPP·Cl (Figure 5.2 (black line)) as the ${}^{3}T(\pi,\pi^{*})$. The paramagnetic ferric ion make effective spin-orbit coupling possible which is responsible for effective intersystem crossing from singlet to triplet state of the π system. The lack of fluorescence ($\Phi < 10^{-6}$) implies that the ${}^{1}Q(\pi,\pi^{*})$ state lifetime is less than 1 ps. This assignment is consistent with the (π,π^*) excited state difference spectra reported for other metallo-TPP complexes, which exhibit a strong absorption band centered at 460 nm and broad and weak absorption in the visible region.^{17,19-22} This state is produced after a very rapid radiationless deactivation of a ${}^{1}Q(\pi,\pi^{*})$ state formed upon excitation with 400 nm light. The porphyrin triplet state rapidly deactivates to the metal centered d,d state (Figure 5.2 (blue line)), which then repopulates the ground electronic state within 10 ps. On the contrary, the FOT for Fe(III)TPrF₇P·Cl is the metal-to-ligand charge transfer state. Indeed, the FOT spectrum presented in Figure 5.5 (black line) is consistent with the one of porphyrin radical anion¹⁸ evidenced by a very strong and broad absorption in the 650 - 750 nm range. This charge separated state very rapidly repopulates ground state with a time constant of 4 ps.

The lack of electron density on the meso groups is directly conveyed to the tetrapyrrole macrocycle and consequently to the central metal displacing the electron density towards electron deficient meso substituents.^{11,13,15} The electron withdrawing ability of the perfluoropropyl substituents favors the formation of the metal-to-ligand charge transfer state

withdrawing groups to the meso positions of porphyrin macrocycle.¹³

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CHAPTER 6: IRON (III) AND IRON (II) MESO-TETRA(HEPTAFLUOROPROPYL) PORPHYRINS

6.1 INTRODUCTION

Iron porphyrins are of considerable biological importance, forming the active centers of chromoproteins that carry out electron transfer (cytochromes), ligand binding (globin), and catalytic (oxidase, peroxidase, catalase) reactions.^{1,2} Understanding of the mechanisms and rates of the processes in hemes and heme proteins comes from flash photolysis studies.³⁻⁵ However, a lot remains to be learned about the excited state dynamics of iron porphyrin complexes themselves.⁶ Due to the propensity of porphyrinic moieties containing an iron(II) metal center to undergo rapid oxidation to the iron(III) species⁷⁻⁹ it appeared to be difficult to study the excited state dynamics of hemes unless the low spin¹⁰ Fe(II) metal center was stabilized by strong axial ligands, such as pyridine, piperidine, histidine, which form hexacoordinate complexes with hemes.⁶ Spectroelectrochemical and cyclic voltammetric studies carried out on the low spin, sixcoordinate $Fe(II)TPrF_7P(py)_2$ reveal an extremely large positive shift in the $Fe^{II/III}$ redox couple $[E_{\frac{1}{2}}(Fe^{II/III}) = 510 \text{ mV}]$ relative to that observed for Fe(III)TPrF₇P(Cl) $[E_{\frac{1}{2}}(Fe^{II/III}) = -10 \text{ mV}]$.¹⁰ Highly electron deficient heptafluoropropyl meso-substituents proved to be good candidates to stabilize the iron(II) oxidative state⁷⁻⁹, therefore Fe(III) meso-tetra(heptafluoropropyl) porphine [Fe(III)TPrF₇P] was chosen to generate *in situ* iron (II) species as it undergoes a very easy reduction in acetonitrile when TBAP is used as a supporting electrolyte.¹⁰ The Fe(II)TPrF₇P species generated electrochemically is only weakly coordinated to the perchlorate ion¹⁰ making it a very good model system for studying ultrafast intramolecular excited state deactivation processes without influence of strong σ -bonding axial ligands.

6.2 RESULTS

Spectroelectrochemical Studies of Fe(III)TPrF₇P Reduction

The one electron reduction of $Fe(III)TPrF_7P$ in acetonitrile proceeded to completion at applied voltage of -0.3 V vs SCE with the appearance of several isosbestic points in the optical spectra taken during electrolysis (Figure 6.1).



Figure 6.1. Electronic spectra obtained at 1 min intervals for the $Fe(II)TPrF_7P$ species generated upon bulk reduction of $Fe(III)TPrF_7P$ chloride that shows $PFe^{II/III}$ redox couple. Experimental conditions: [TBAP] = 0.5 M; applied voltage = -300 mV vs SCE; solvent = acetonitrile.

The The ground electronic state absorption spectra of $Fe(III)TPrF_7P$ and $Fe(II)TPrF_7P$ in acetonitrile with TBAP as a supporting electrolyte are presented in Figure 6.2.



Figure 6.2. Ground electronic state normalized absorption spectra of Fe(III)TPrF₇P (black solid line) and Fe(II)TPrF₇P (dashed red line) recorded at room temperature in acetonitrile/TBAP at 0 and -0.3 V vs SCE potential respectively.

The formation of reduced Fe(II) species was accompanied by decrease in intensity of Soret band peaks (at 350 nm and 415 nm) for the parent Fe(III) porphyrin and significant broadening of the reduced species spectrum. The Q-band region extending from 470 to 700 nm exhibited a very broad and featureless vibronic progression for both compounds. In general it is worth noting the overall red shift of the Fe(II) porphyrin spectrum compared to the one of starting Fe(III) porphyrin.

Time-resolved Transient Absorption Spectroscopy

Visible region transient absorption changes with ~130 fs time resolution were acquired for all porphyrins under the same experimental conditions, using 400 nm light as excitation

pulse. In each case the time evolution of the spectra was quite complex and revealed two or more kinetic components, with time constants ranging from subpicoseconds to hundreds of picoseconds before complete ground state recovery was observed. The photophysical behavior had both notable similarities and striking differences for porphyrins having Fe(III) or Fe(II) as central metal, and so the results for Fe(III)TPrF₇P and Fe(II)TPrF₇P are presented separately.

Fe(III)TPrF₇P. Figure 6.3 shows time-resolved absorption data in the Q band region for Fe(III)TPrF₇P in acetonitrile/TBAP solution at 298 K, acquired using 130-fs excitation flashes at 400 nm:



Figure 6.3. Transient absorption difference spectra in the Q band region of Fe(III)TPrF₇P in acetonitrile/TBAP at 0 V vs SCE potential acquired at different delay times after the excitation event.

Over ca. 800 fs after the excitation event, the prominent bleaching of the ground state in the range of 500-570 nm increased with the substantial increase of the positive absorption over the whole visible range of the spectrum (Figure 6.3). The transient spectrum had a very broad and intensive absorption band in the Vis-NIR region above 650 nm. Over the following several picoseconds, the new spectral feature at around 525 nm appeared revealing a new transient species (Figure 6.3 (blue line)). The new species proved to be long lived with a lifetime exceeding 1 ns and probably are due to small amount of a porphyrin without axial chloride ligand.



Representative Q band region kinetic data are shown in Figures 6.4 and 6.5.

Figure 6.4. Representative kinetic trace and the fit of the time evolution of the absorption at 710 nm of Fe(III)TPrF₇P in acetonitrile/TBAP at 0 V vs SCE potential from Figure 6.3.



Figure 6.5. Representative kinetic trace and the fit of the time evolution of the absorption at 480 nm of Fe(III)TPrF₇P in acetonitrile/TBAP at 0 V vs SCE potential from Figure 6.3.

At all wavelengths the transient signals were fully developed within the instrument response function (ca. 300 fs) and the resulting temporal change was fitted with a single exponential function added to a very minor long lived component (probably arising from an excited state of a small fraction of porphyrin without axial chloride ligand). The only kinetic component had a lifetime of about 3 ps and did not depend on a monitoring wavelength.

Fe(II)TPrF₇P. Figure 6.6 shows time-resolved absorption data in the Q band region for Fe(II)TPrF₇P in acetonitrile/TBAP solution at 298 K, acquired using 130-fs excitation flashes at 400 nm:



Figure 6.6. Transient absorption difference spectra in the Q band region of Fe(II)TPrF₇P in acetonitrile/TBAP at -0.3 V vs SCE potential acquired at different delay times after the excitation event.

Over ca. 800 fs after the excitation event, the prominent increase of the positive absorption over the whole visible range of the spectrum (Figure 6.6) is observed with a trough at around 560 nm corresponding to ground state Q-bands bleaching. The transient spectrum had a very broad and intense absorption band in the Vis-NIR region above 650 nm. Over the following several picoseconds, the spectrum evolved into the one represented with a blue line in Figure 6.6. The latter decayed completely to the baseline within several hundred picoseconds indicating a complete ground state recovery.

Representative Q band region kinetic data are shown in Figures 6.7 and 6.8.



Figure 6.7. Representative kinetic trace and the fit of the time evolution of the absorption at 710 nm of Fe(II)TPrF₇P in acetonitrile/TBAP at -0.3 V vs SCE potential from Figure 6.6.



Figure 6.8. Representative kinetic trace and the fit of the time evolution of the absorption at 480 nm of Fe(II)TPrF₇P in acetonitrile/TBAP at 0 V vs SCE potential from Figure 6.6. Inset: the same kinetic trace on a longer timescale.

At all wavelengths the transient signals were fully developed within the instrument response function (ca. 300 fs) and the resulting temporal change was fitted with a double exponential function for most of the kinetic traces. However, there were found to be three different lifetimes of 1, 10 and 250 ps. Due to varying amplitudes of those components it was not always possible to fully resolve all three kinetic components for particular sets of wavelengths, therefore a double exponential function was used for fitting.

6.3 DISCUSSION

Spectroelectrochemical Studies of Fe(III)TPrF₇P Reduction

Thin-layer electronic absorption spectral data were taken at controlled potential of -300 mV vs SCE that exceeds the $E_{1/2}$ value of -10 mV for the Fe^{II/III} redox process¹⁰ of the Fe(III)TPrF₇P·Cl complex. The value of -300 mV applied potential is above the maximum value of cathodic potential E_{pc} which corresponds to the complete reduction of Fe^{III} to Fe^{II} species. This value were taken from the work by Moore¹⁰ based on the Cyclic Voltammetry (CV) data presented and the reduction process was monitored spectroelectrochemically. Non-isosbestic behavior is observed at around 425 nm (Figure 6.1) in the time-dependent electronic spectra that chronicle the initial Fe(III)TPrF₇P-to-Fe(II)TPrF₇P reduction (Figure 6.1). Such non-isosbestic behavior has been observed by Moore et al¹⁰ in their spectroelectrochemical studies of the same iron (III) porphyrin complex. In their experiments, the electrogenerated iron (III) porphyrin species observed in the thin-layer spectroelectrochemical experiments possessed an optical spectrum distinct from that of Fe(III)TPrF₇P·Cl complex¹⁰. This non-isosbestic behavior suggests that perchlorate-metal interactions play a significant role in the electrochemistry at the high electrolyte concentrations employed in this experiments.¹¹⁻¹⁴ In solution with high concentration of perchlorate ion the partial ligand exchange reaction has been previously observed¹¹, so it is possible that Cl^{-} is replaced with ClO_4^{-} for some porphyrinic moleties. Equations 1-3 summarize the electrode-coupled reactions relevant to potentiostatic reduction of Fe(III)TPrF₇P·Cl complex when large concentrations of perchlorate ion are present.^{10,11}

$$Fe(III)TPrF_7P \cdot Cl + e^{-} \leftrightarrow [Fe(III)TPrF_7P \cdot Cl]^{-}$$
(1)

 $[Fe(III)TPrF_7P \cdot Cl]^- \leftrightarrow Fe(II)TPrF_7P + Cl^-$ (2)

$$Fe(II)TPrF_7P + ClO_4^{-} \leftrightarrow [Fe(II)TPrF_7P \cdot ClO4]^{-}$$
(3)

Consistent with this, because electrochemically generated $Fe(II)TPrF_7P$ species have drastically reduced affinity for both chloride and perchlorate axial ligands with respect to their $Fe(III)TPrF_7P$ counterparts² and the ratio of $[CIO_4]^-$ to $[CI]^-$ in this studies is on the order of 10³, it is reasonable that non-isosbestic behavior is observed in the bulk reduction of $Fe(III)TPrF_7P$ ·Cl (eq 1-3). The control experiment with sodium chloride as a supporting electrolyte did not work due to the low solubility of this salt in acetonitrile. As a matter of fact TBAP was the only suitable electrolyte for this experiment; the similar electrolytes with PF^{6-} and BF^{4-} counterions made the reduction process difficult due to the release of F^- ions in the course of dissociation process. The fluoride ions coordinate to the iron (III) center and the resulting reduced species exist in the form of a complex rather than reduced free iron (II) porphyrin.

The resulting spectrum of Fe(II)TPrF₇P porphyrin showed an extensive broadening in the Soret band region (Figure 6.2) compared to the more structured B-band for Fe(III)TPrF₇P·Cl with peak maxima at 350 and 415 nm. Also the Soret and Q-band peaks are red shifted for the reduced iron(II) porphyrin species indicating a improved vibronic coupling and appearance of low lying charge transfer states as reported previously by Huang et al.¹⁵ The reduced Fe(II)TPrF₇P species was stable for several hours, which was evidenced by the absence of any spectral changes, at -300 mV vs SCE potential making this molecule suitable for further femtosecond transient absorption experiments.

Time-resolved Transient Absorption Spectroscopy

An extensive body of research conducted largely over the last 40 years has attempted to place the optical spectroscopy of porphyrins into an orderly framework.¹ Spectral features manifest by these compounds are often diffuse and overlapping, with the mere qualitative assignment for electronic configuration of a particular transition being the legitimate subject of both theoretical and experimental research. This holds particularly true for the iron porphyrins, where strong metal-porphyrin interactions mix excited triplet and singlet porphyrin (π , π *) states with charge transfer transitions.¹⁶

For both Fe(III)TPrF₇P·Cl and Fe(II)TPrF₇P the highly electron deficient mesosubstituents favor very efficient d, π and d, π^* mixing even in the ground state electronic configuration as evidenced by a very broad and featureless absorption in the 500 – 700 nm region (Figure 6.2). This suggests that the first observed transient (FOT) for both iron porphyrins is the metal-to-ligand charge transfer state, produced after a very rapid radiationless deactivation of a ¹Q(π , π^*) state formed upon excitation with 400 nm light. Indeed, the FOT spectra presented in Figures 6.3 and 6.6 (black lines) are consistent with the one of porphyrin radical anion¹⁷ evidenced by a very strong and broad absorption in the 600 – 780 nm range. Subsequently the deactivation dynamics are quite different for Fe(III) and Fe(II) species, therefore their kinetic behavior will be discussed separately.

A possible mechanism for Fe(III)TPrF₇P·Cl excited state relaxation is presented in Scheme 6.1:



Scheme 6.1. Suggested mechanism of the excited state relaxation dynamics of Fe(III)TPrF₇P·Cl after 400 nm excitation.

The charge transfer (CT) state is produced within the instrument response function (ca. 300 fs). This state deactivates very rapidly with a lifetime of 3 ps (Figures 6.4 and 6.5) producing a new excited state capable of ligand dissociation (LD) which has a transient spectrum represented with a blue line in Figure 6.3. Concomitantly, the CT state might deactivate directly into the ground state; in this case 3 ps lifetime is the combined constant for repopulating the ground state and populating the LD state. Considering the strong affinity of Fe(III) species toward the chloride ligand¹⁰ the ligand dissociation process might not involve the full bond breaking and only the formation of charge transfer state with an axial chloride ligand. The LD state has a lifetime exceeding the delay line time span (> 1.6 ns).

In the case of Fe(II)TPrF₇P the deactivation dynamics are more complex than those of its oxidized counterpart. Scrutinizing the transient absorption data suggested that two possible mechanisms might be responsible for the complexity of the relaxation process. These are presented in Schemes 6.2 and 6.3:



Scheme 6.2. Suggested mechanism of the excited state relaxation dynamics of Fe(II)TPrF₇P after 400 nm excitation.



Scheme 6.3. Alternative suggested mechanism of the excited state relaxation dynamics of Fe(II)TPrF₇P after 400 nm excitation.

According to the Equation 3, the Fe(II)TPrF₇P species are weakly coordinated to the perchlorate ions which are known to be weak σ -coordinating ligands with minor electron accepting character.¹⁰ Therefore the transient species with a lifetime of 250 ps could be assigned

to the charge transfer state between the axial perchlorate ligand and the porphyrinic moiety (CT (d,σ_L)) (Figure 6.6 (blue line)). This lifetime corresponds to the charge recombination process when the electron density is returned to the metal center with complete ground state recovery of the porphyrinic moiety. The formation of this state is however unclear.

The kinetic data and transient spectral features presented in Figures 6.6-6.8 could be explained with mechanisms shown in Schemes 6.2 and 6.3. The first mechanism (Scheme 6.2) suggests involvement of a triplet ${}^{3}T(\pi,\pi^{*})$ state which is formed concomitantly with the CT (d,σ_{L}) within 1 ps from the CT (d,π) state (Figure 6.6 (black line)). The transient spectrum represented with a red line in Figure 6.6 is therefore a sum of the CT (d,σ_{L}) and ${}^{3}T(\pi,\pi^{*})$ transient spectra. The decreased intensity of the NIR absorption and stronger visible band at around 480 nm (Figure 6.6) are indicative of a porphyrinic ligand triplet state spectrum. The ${}^{3}T(\pi,\pi^{*})$ is non-dissociative state with respect to the axial ligands and repopulates ground electronic state with a lifetime of 10 ps.

The second alternative excited state deactivation pathway is presented in Scheme 6.3. This mechanism does not involve formation of a ${}^{3}T(\pi,\pi^{*})$ state and suggests that the ground state repopulation proceeds only via charge transfer states with $CT(d,\sigma_{L})$ being the closest to the ground state. Thus, the FOT spectrum presented in Figure 6.6 (black line) is the spectrum of the hot charge transfer state ($CT(d,\pi)_{hot}$) which relaxes within 1 ps into the cooled charge transfer state ($CT(d,\pi)_{cooled}$) with the transient difference spectrum slightly shifting to the blue (Figure 6.6 (red line)). Ultimately, this relaxed $CT(d,\pi)_{cooled}$ state within 10 ps populates axial ligand dissociative $CT(d,\sigma_{L})$ state which deactivates back to the ground state with a 250 ps lifetime.

The potentiostatic femtosecond transient absorption technique proved to be very useful for studying the compounds that are not stable enough to be studied by using conventional

transient absorption methods. It has made it possible to elucidate some processes responsible for the complex ultrafast dynamics of iron porphyrins. Using highly electron deficient porphyrinic ligands with highly ruffled ground state geometry¹⁰ it was possible to investigate the importance of electronic and conformational factor in the photophysical processes of iron porphyrins. Just by simply changing the oxidation state of a central iron it is possible to open new pathways for relaxation of the excited states.

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CHAPTER 7: ZINC (II) TETRAPHENYLPORPHINE CATION RADICAL

7.1 INTRODUCTION

Porphyrin π radical cations are known to play a crucial role in biological electron-transfer systems such as respiration and photosynthesis.¹⁻³ In the natural photosynthetic systems as reported by Barkigia, et al.⁴ chlorophylls, that are closely related to porphyrins, are the main chromophoric moieties that undergo one electron oxidation that starts the photosynthetic cycle.^{5,6} A number of electron donor-acceptor linked systems have been designed and their photodynamics have been examined to mimic photosynthetic charge separation.⁷⁻¹⁴ Zinc(II) tetrapyrroles, which have d¹⁰ electronic configuration of the central metal ion and contain no axial ligands, easily undergo one electron oxidation forming stable π -system radical cation species.¹⁵ Based on the electronic ground state configuration, the π -cation radicals have been categorized into those possessing a ${}^{2}A_{1u}$ or a ${}^{2}A_{2u}$ ground state.^{2,16} The two highest occupied molecular orbitals of metalloporphyrins $(a_{1u} \text{ and } a_{2u})$ are nearly degenerate and their relative energies are dictated by many factors, including the nature and position of the porphyrin peripheral substitution, the central metal ion, the identity and disposition of the axial ligand, environment, temperature and symmetry of the molecule.^{17,18} For zinc(II) mesotetraphenylporphine one electron oxidation proceeds with an electron removal from an $a_{2\mu}$ orbital. This has direct influence on the interaction between the metal d-orbitals and the nitrogen orbitals of the tetrapyrrole macrocycle.¹⁹ In this work zinc(II) meso-tetraphenylporphine radial cation species has been formed electrochemically in situ and studied by means of femtosecond

absorption spectrometry to prove that this new technique could be used to elucidate the photophysical behavior of open shell species.

7.2 RESULTS

Spectroelectrochemical Studies of Zn(II)TPP Oxidation

The one electron oxidation of Zn(II)TPP in acetonitrile proceeded to completion at 0.8 V vs SCE with the appearance of several isosbestic points in the optical spectra taken during electrolysis (Figure 7.1).



Figure 7.1. Oxidation of zinc (II) meso-tetraphenylporphine in acetonitrile. TBAHP was used as a supporting electrolyte.

The optical spectrum of oxidized porphyrin exhibited a sharp Soret band transition at 409 nm and a broad and featureless absorption in the 500-700 nm region showing the π -cation radical formation. The final (olive line in Figure 7.1) spectrum showed no indication of the 425 nm peak

characteristic of the parent compound indicating >99% conversion. The final spectrum was stable at room temperature at the applied potential. When the resulting greenish solution of the cation radical was electrochemically reduced, all of the starting material was recovered indicating complete reversibility of the process.

Femtosecond Time-Resolved Potentiostatic Transient Absorption Spectrometry

Time-resolved absorption spectra in the Soret and Q band regions for zinc(II) mesotetraphenylporphine cation radical and its neutral counterpart in acetonitrile at 298 K, acquired using 130-fs excitation flashes at 400 nm are shown in 7.2:



Figure 7.2. Absorption difference spectra in the visible region of (A) Zn(II)TPP^{+.} and (B) Zn(II)TPP in acetonitrile/TBAHP acquired following a 130 fs excitation pulse at 400 nm. The pulse energy was 2µJ.

At ca. 1 ps after excitation of the cation, bleaching of the ground state bands at 409 and 445 nm was accompanied by the appearance of a positive absorption over the 460-650 nm range of the spectrum (black line in Figure 7.2(A)). Over the following several tens of picoseconds, the

derivative-shaped spectrum shifted slightly to the blue and decayed uniformly to the baseline, reflecting complete ground-state recovery, with an isosbestic point near 470 nm (Figure 7.2(A)). The obscured features around 409 nm possibly result from pump beam interference. For comparison purposes Figure 7.2(B) presents the transient spectral evolution of the neutral Zn(II)TPP species under the same experimental conditions prior to the application of positive potential. The spectral profiles of the two species and their temporal behaviors are clearly different in the presence and absence of applied voltage. The 30 ps spectrum of the neutral remained unchanged in intensity over the instrumental time window (1.5 ns).



Representative Soret and Q band regions kinetic data are shown in Figure 7.3.

Figure 7.3. Representative kinetic data and the fits of the evolution of the absorption difference spectra of Zn(II)TPP^{+.} in acetonitrile/TBAHP from Figure 7.2(A).

At all wavelengths the transient signals were fully developed within the instrument response function (ca. 250 fs) and the resulting temporal change was fitted with a single exponential function added to a minor constant component (probably arising from an excited state of a small fraction of the parent porphyrin). The lifetimes of the transient signals shown in Figure 7.3 were 16.5 ps (445 nm) and 17.6 ps (495 nm). The lifetimes in the 470 – 650 nm band showed weak wavelength dependence ranging from 12 ps at the red edge to 18 ps at the blue.

7.3 DISCUSSION

The spectrum of zinc meso-tetraphenylporphine cation radical (Figure 7.1) displayed features consonant with a π -cation species.^{3,20} The Soret band was slightly blue shifted and weakened in intensity and the Q band region was featureless and broadened (Figure 7.1). These bands arise from those transitions that are responsible for the Soret and Q bands transitions of the neutral species as reported by Fajer, et al.¹ Extensive ESR and EPR studies of oxidized zinc porphyrin species^{16,20-22} have shown that the ground electronic state has a ²A_{2u} configuration after one electron has been removed from the a_{2u}(π) HOMO, an orbital that places electron density mainly on the central nitrogens and the meso carbons.²³ However the central metal remained indifferent to the oxidized ligand²⁴ and does not contribute to the ground electronic absorption spectrum. The lack of broad bands in the 800-950 nm region suggested the absence of any dimeric forms of the cationic species and excluded possible interference from the supporting electrolyte PF₆⁻ anion.¹⁹

The 400 nm excitation beam presumably populates a higher-lying ${}^{2}(\pi,\pi^{*})$ excited state, which apparently undergoes rapid radiationless deactivation to the ${}^{2}(\pi,\pi^{*})$ (D₁) state within the instrument response.²⁵ The D₁ excited state decayed with a lifetime of ca. 17 ps during which the transient spectra narrowed and slightly shifted to the blue (Figure 7.2(A)) indicating a conformational/vibrational relaxation process.²⁶ Thus, the major excited-state deactivation pathway for excited radical cation states examined here appears to be internal conversion from the lowest excited doublet state (D₁) to the doublet ground state (D₀). The lack of luminescence and the efficiency of the non-radiative deactivation mode presumably arise from the small energy gaps between the ground and excited states, evidenced by broad absorption bands in the
Q band region.²⁷ As reported by Yu et al.²⁸ the neutral form of zinc (II) tetraphenylporphine exhibits some early time picosecond kinetics which were assigned to vibrational/conformational relaxation processes. Our own observations (Figure 7.2(B)) of Zn(II)TPP showed small contributions of early time decays of 1.2 ps and 10 ps lifetime at wavelengths beyond 600 nm essentially in agreement with Yu et al.²⁸ However, since the conversion to the radical cation was >99% (Figure 7.1) and comparing the spectral features of Zn(II)TPP and Zn(II)TPP^{+.} in Figures 7.2(A) and 7.2(B), it is clear that any contribution of the neutral species is small and appears only as a small residual offset signal. The analysis of the bleaching peaks at 409 and 425 nm revealed similar kinetics as for the negative absorption signal presented in Figure 3 at 445 nm, except that the offset at 425 nm is greater since that bleaching corresponds to the very intense Soret band transition of the neutral porphyrin. The vibrational relaxation process in the 470 - 650 nm band for the radical cation showed wavelength dependence of the time constants similar to that observed for the neutral species, though the analysis of the kinetics in the 600 - 650 nm region did not reveal any fast 1 ps component as in the case of parent porphyrin²⁸, supporting the conclusion that the contribution of unoxidized porphyrin into the overall kinetics of the cationic species was negligible.

The central metal plays an important role in the deactivation of the excited state. Despite the fact that zinc has completely filled d-orbitals, it provides an efficient mixing of its orbitals with the π -system of the tetrapyrrole ring. Since the electron is removed from the a_{2u} orbital that has electronic density on the pyrrolic nitrogens directly attached to the central metal the mixing is facilitated.²³ The ultrafast relaxation process proves to be a very effective mechanism for the protection of the active chromophore in the photosynthetic center against the photo damage.

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APPENDIX A. GLOSSARY OF COMPOUNDS





Zn(II)TPP



Fe(III) 5,10,15,20-meso-tetraphenylporphine chloride

Fe(III)TPP·Cl



Ni(II) 5,10,15,20-meso-tetra(pentafluorophenyl)porphine

Ni(II)TPPF



Ni(II) 5,10,15,20-meso-tetra(p-nitrophenyl)porphine

Ni(II)TNPP



Ni(II) 5,10,15,20-meso-tetra(heptafluoropropyl)porphine

Ni(II)TPrF7P



Ni(II) 5,10,15,20-meso-tetra(n-propyl)porphine

Ni(II)T(n-Pr)P



Fe(III) 5,10,15,20-meso-tetra(heptafluoropropyl)porphine chloride

Fe(III)TPrF7P·Cl