A Photophysical Investigation of Nickel Tetrapyrrole Macrocycles

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The porphyrins are an important class of chromophores with high stability and efficient light absorption ability in the visible and near-infrared regions of the optical spectrum. They find uses in optoelectronics, magnetic materials, photoconductive materials, non-linear optical materials and photo tumor therapeutic drugs. Porphyrins have a set of highly delocalized $\pi$-orbitals situated on the carbon-nitrogen framework. When such a ligand is coordinated to a centrally-located metal atom of the transition series, having incompletely filled d-orbitals (Ni, Co, Fe, Cu, etc.), the $\pi$- and d-manifolds can interact. As a result the excited state deactivation dynamics becomes very dependent on the electronic nature of the central metal.

This work has two major parts. The first part focuses on the investigation of dual excited states of some Ni(II) porphyrins. Dual excited states are molecular entities that have absorbed two successive photons to generate molecular states with electronic excitation in two distinct regions of the metalloporphyrin. The dual excited states were studied by means of femtosecond two-pump-one-probe transient absorption spectroscopy. Two successive pulses of 400 nm and 550 nm were used for excitation. The first pulse (400 nm) produced an $S_2$ state of the porphyrin $\pi$-system, which deactivated to give rise to an $S_1$ state and subsequently produce a metal-centered (d,d) state. The second (550 nm) pulse selectively targeted an $S_0 \rightarrow S_1$ transition of those molecules having an excited metal center and was delivered to the sample approximately 40 ps after the first excitation event. At this time the ground state of the tetapyrrole $\pi$-system was already regenerated and the excitation was localized at the metal center. Based on the kinetic
and spectral information of the observed transients we propose a mechanism for the Ni(II) porphyrin dual excited state deactivation involving formation of an intramolecular charge transfer state.

The second part concerns the photophysical studies of Ni(II) meso-tetraphenyl tetrabenzoporphyrin (NiTPTBP). The excited states metal-ligand dynamics of Ni(II)TPTBP have been investigated using time-resolved absorption spectroscopy in different solvents. Unusual excited state behavior of Ni(II)TPTBP has been observed that presumably originates in cooperative contribution of structural distortions of tetrapyrrolic macrocycle induced by extended conjugation and electron rich and bulky meso-substituents. This species has demonstrated very interesting excited state properties that can be tuned by altering the solvent polarity. The DFT computations revealed the presence of two ligand-to-metal charge transfer states located close in energy to the 3(d,d) state. These LMCT states are responsible for the lifetime dependence on solvent polarity. Upon photoexcitation two competing processes depopulate the porphyrin lowest singlet excited state S1. One involves the charge transfer states manifold and another involves the metal excited state manifold.
To my parents and all others who helped me through all these years
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TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION.................................................................................................................................................1

Tetrapyrrole Macrocycles: Background .........................................................................................................................1
Relaxation mechanism for excited state molecules ...........................................................................................................4
Photoproperties of metalloporphyrins excited states .......................................................................................................5
Nickel Porphyrins ..............................................................................................................................................................7
Tetrabenzoporphyrins .........................................................................................................................................................8
References ..................................................................................................................................................................11

CHAPTER 2: MATERIALS AND METHODS ..........................................................................................................................15

2.1 Materials ..............................................................................................................................................................................15
2.2 Instrumentation and Methods ........................................................................................................................................15
    UV-visible Absorption Spectroscopy ..........................................................................................................................15
    Femtosecond Transient Absorption Spectroscopy ........................................................................................................16
    Some aspects of multiple pulse excitation techniques ..............................................................................................18
    Quantum Chemical Calculations ................................................................................................................................21
2.3 References ............................................................................................................................................................................23

CHAPTER 3: TWO-PUMP ONE PROBE FEMTOSECOND STUDIES OF Ni(II) PORPHYRINS EXCITED STATES .........................................................................................................................24

3.1 Introduction ...........................................................................................................................................................................24
3.2 Results ..................................................................................................................................................................................27
<table>
<thead>
<tr>
<th>Ground State Absorption Spectrometry</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-Pump-One-Probe Transient Absorption Spectroscopy</td>
<td>28</td>
</tr>
<tr>
<td>Two-Pump-One-Probe Transient Absorption Spectroscopy</td>
<td>30</td>
</tr>
<tr>
<td>3.3 Discussion</td>
<td>38</td>
</tr>
<tr>
<td>3.4 References</td>
<td>44</td>
</tr>
</tbody>
</table>

**CHAPTER 4: PHOTOPHYSICAL INVESTIGATION OF Ni (II) MESO-TETRAPHENYLBENZOPORPHYRIN** ................................................. 46

<table>
<thead>
<tr>
<th>4.1 Introduction</th>
<th>46</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 Results</td>
<td>48</td>
</tr>
<tr>
<td>Ground State Absorption Spectroscopy</td>
<td>48</td>
</tr>
<tr>
<td>Ultrafast Transient Absorption Spectroscopy</td>
<td>49</td>
</tr>
<tr>
<td>DFT/TDDFT computational studies</td>
<td>59</td>
</tr>
<tr>
<td>4.3 Discussion</td>
<td>64</td>
</tr>
<tr>
<td>4.4 References</td>
<td>71</td>
</tr>
</tbody>
</table>

**APPENDIX A: GLOSSARY OF COMPOUNDS** .......................................................... 73
LIST OF FIGURES

1.1 The basic structure of the porphyrin macrocycle................................................................. 1
1.2 Porphyrin HOMOs and LUMOs orbitals.................................................................................. 2
1.3 Molecular orbital diagram for the four orbital model of metalloporphyrin absorbances ........ 3
1.4 Jabłoński’s diagram describing molecular photophysics...................................................... 4
1.5 The mechanism of excited state deactivation of Ni(II)TPP..................................................... 8
1.6 Structural formula of tetrabenzoporphyrin. .......................................................................... 9
1.7 Ground state spectra of Ni(II)TBP and Ni(II)TPTBP in dimethylformamide......................... 10
2.1 A schematic representation of ultrafast absorption spectrometer ......................................... 17
2.2 The schematic representation of double-pulse pump-probe experiment. ............................... 20
2.3 Energy diagram for detecting the triplet quantum yield. ......................................................... 20
2.4 Schematic definition of the computed excitation energies. .................................................... 22
3.1 The ground-state absorption spectra. a) Nickel(II) meso-tetraphenylporphyrine (NiTPP) in toluene; b) Nickel(II) meso-tetra(4-sulfonatophenyl) porphine (NiTPPS).......................... 27
3.2 Three-dimensional representation of the Ni(II)TPPS transients produced via excitation at 400 nm......................................................................................................................... 28
3.3 Transient spectra of Ni(II)TPPS in DMSO at two times after excitation into the Soret band at 400 nm.................................................. ................................................................. 29
3.4 Dynamics surface of Ni(II)TPPS in DMSO after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps................................................. 30
3.5 Transient spectra of the Ni(II)TPPS in DMSO after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps................................................. 31
3.6 Kinetics profiles of the Ni(II)TPPS transient absorption at different probe wavelengths. Solvent: DMSO .................................................................32

3.7 Transient spectra of the Ni(II)TPPS in water after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps ..............................................................33

3.8 Kinetics profiles of the Ni(II)TPPS transient absorption at different probe wavelengths. Solvent: water .................................................................34

3.9 Transient spectra of the Ni(II)TPP in toluene after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps ..............................................................36

3.10 Kinetics profiles of the Ni(II)TPP transient absorption at 475 probe wavelengths. Solvent: toluene .................................................................36

3.11 Kinetic profile of the Ni(II)TPP transient absorption at 575 nm probe wavelength. Solvent: toluene .................................................................37

3.12 The proposed scheme for doubly excited states generation. Left side: the black line is the ground state absorption spectra of Ni(II)TPPS in DMSO; Middle: the dotted line is a red-shifted spectrum after excitation event. Right side: transient spectra of Ni(II)TPPS in DMSO .................................................................39

3.13 Energy diagram for Cobalt(II) porphyrin (Charge transfer) ..............................................41

3.14 Electronic configuration of Ni(II) porphyrin d,d state. After one pulse (400 nm), the excitation is localized at the Ni(II) center. The area enclosed by the dotted line indicates similarity to the Co(II) porphyrin ground state .............................................42

3.15 A mechanism of deactivation of Ni(II) porphyrin excited state. After second pulse (550nm) .........................................................................................43
4.1 The ground absorption spectra of Ni(II) meso-tetraphenyltetrazenzoporphyrin in four solvents .................................................................................................................................................48

4.2 Dynamic surface of the Ni(II)TPTBP recorded in toluene after excitation at 400 nm ..................................................................................................................................................................................50

4.3 Transient spectra of Ni(II)TPTBP in toluene at three times after excitation into Soret band at 400 nm ..........................................................................................................................................................................................50

4.4 Kinetics profiles of the Ni(II)TPTBP transient absorption at different probe wavelengths. Solvent: toluene ..................................................................................................................................................52

4.5 Dynamic surface of the Ni(II)TPTBP recorded in butyronitrile after excitation at 400 nm ..................................................................................................................................................................................54

4.6 Transient spectra of Ni(II)TPTBP in butyronitrile after excitation at 400 nm ..................................................................................................................................................55

4.7 Kinetics profiles of the Ni(II)TPTBP transient absorption at 475 nm probe wavelengths. Solvent: butyronitrile ..................................................................................................................................................55

4.8 Kinetics profiles of the Ni(II)TPTBP transient absorption at different probe wavelengths. Solvent: butyronitrile ..................................................................................................................................................56

4.9 Transient spectra of Ni(II)TPTBP in dimethylformamide after excitation at 400 nm ..................................................................................................................................................58

4.10 The structure of Ni(II)TPTBP. Left: representation of D$_{2d}$ saddled configuration. Right: notation of carbon atoms ..................................................................................................................................................59

4.11 Contour plots of G-HOMO, G-LUMO and metal HOMO and LUMO orbitals of Ni(II)TPTBP ..................................................................................................................................................63

4.12 A series of spectral cuts from the optical dynamic surface of Ni(II)TPTBP in the time range 1 → 40 ps, normalized at 665 nm maximum to clearly show the time-dependent blue shift ..................................................................................................................................................65
4.13 Kinetic profiles of the transient absorption signal at 475 nm for Ni(II)TPTBP in different solvents after photoexcitation at 400 nm .................................................................66

4.14 Proposed mechanisms of deactivation of Ni(II)TPTBP excited state: A. in nonpolar toluene and lutidine; B. in polar butyronitrile and DMF ..............................................................68
LIST OF TABLES

3.1 Lifetimes and relative amplitudes of the two-pump-one-probe transient absorption dynamics of Ni(II)TPPS in DMSO and water .................................................................35

3.2 Lifetimes and relative amplitudes of the two-pump-one-probe transient absorption dynamics of Ni(II)TPP in toluene ...............................................................................37

4.1 Lifetimes and relative amplitudes of Ni(II)TPTBP in toluene .............................................53

4.2 Lifetimes and relative amplitudes of Ni(II)TPTBP in butyronitrile ......................................57

4.3 Lifetimes and relative amplitudes of Ni(II)TPTBP in dimethylformamide ..........................58

4.4 Selected bond lengths (Å) and bond angles (deg) for Ni(II)TPTBP in $D_{2d}$ saddle configuration ..........................................................................................................................60

4.5 Energies and percent composition of the highest occupied and lowest unoccupied molecular orbitals of Ni(II)TPTBP expressed in terms of individual atoms ......................61

4.6 Vertical excitation energies and oscillator strengths ($f$) computed for the optically allowed $^1E$ and $^1B_2$ excited states of Ni(II)TPTBP in the $D_{2d}$ conformation and compared to the experimental data .................................................................................................................62

4.7 Summary of kinetic data for Ni(II)TPTBP acquired in different solvents; $\varepsilon$- the dielectric constant ..................................................................................................................65

4.8 Energies of optically silent states responsible for Ni(II)TPTBP excited state deactivation .................................................................................................................................67
CHAPTER 1: INTRODUCTION

Tetrapyrrole Macrocycles: Background

Metallo-tetrapyrroles (MTP) are highly stable macrocyclic \( \pi \)-systems that demonstrate interesting properties that make them potential candidates for various applications. Among these applications are optoelectronics, magnetic materials,\(^1,2\) photoconductive materials, non-linear optical materials\(^3\) and tumor photo therapeutic drugs.\(^4\) 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.

The simplest form of these porphyrins is called porphine and various porphyrin systems are derived from this porphine framework.\(^5-8\) The basic structure of the porphyrin macrocycle consists of four pyrrolic subunits linked by four methane bridges, Figure 1.1.

\[\text{Figure 1.1. The basic structure of the porphyrin macrocycle. M- central metal. The peripheral positions on the pyrrole units are numbered 1 to 8.}\]
In order to quantitatively assess the metal ion-porphyrin interaction, Gouterman proposed the four-orbital model to explain the absorption spectra of porphyrins.\textsuperscript{9} According to this theory, the absorption bands in porphyrin systems arise from transitions between two HOMO and two LUMOs, and it is the identities of the metal center and substituents on the ring that affect the relative energies of these transitions.\textsuperscript{9} The HOMOs were calculated to be an $a_{1u}$ and $a_{2u}$ orbital, while the LUMOs were calculated to be a degenerate set of $e_g$ orbitals, Figure 1.2.

![Figure 1.2. Porphyrin HOMOs (bottom row) and LUMOs (top row), modified from ref. 9](image)

The two lowest-energy transitions, $a_{2u} \rightarrow e_g(\pi^*)$ and $a_{1u} \rightarrow e_g(\pi^*)$, yield resonances which are assigned to the Q and Soret bands, Figure 1.3. The weaker of the two bands, the Q-band, is ascribed to the phenomenon in which the transition dipoles of the two configurations nearly
cancel. The resonance in which the two transitions dipoles of the two configurations are additive is demonstrated in the intense Soret band. The intensity of the Q(0,0) band is directly related to how close to degeneracy are the two electronic configurations, \(^1(a_{2u}, e_g)\) and \(^1(a_{1u}, e_g)\).\(^{10}\) When transitions metals with unfilled d-orbitals are incorporated into the \(\pi\)-macrocycle, the \(\pi-\pi^*\) transitions can be perturbed, leading to spectral shifts and to new spectral bands. These can arise because of the \(d \rightarrow \pi^*, \pi \rightarrow d,\) and \(d \rightarrow d\) interactions as indicated in Figure 1.3 for a \(d^6\) metal. The mixed system transitions are of charge transfer (CT) type, and are traditionally named metal-to-ligand CT (MLCT) or ligand-to-metal CT (LMCT).\(^{11}\) In cases where the metals are absent or where the metal has filled d-orbitals, the absorption and emission spectra are determined solely by the \(\pi-\pi^*\) transitions as indicated on the left side of Figure 3.\(^5\)

**Figure 1.3.** Molecular orbital diagram for the four orbital model of metalloporphyrin absorbances\(^5\)
Properties of tetrapyrrrole (TP) macrocycles, their derivatives and assemblies have been characterized using a variety of optical spectroscopic techniques.\textsuperscript{5-8} The majority of photophysical studies that have been performed on macrocyclic $\pi$-systems to date have focused on porphyrine and its derivatives. The excited state dynamics of metalloporphyrins depends on the nature of the central metal atom which significantly effects the excited state lifetimes. Therefore, it becomes clear that the excited state characterization is important in determining possible applications of these compounds.

\textit{Relaxation mechanism for excited state molecules}

Once a molecule has absorbed energy in the form of electromagnetic radiation, there are a number of routes by which it can return to ground state. The Jablonski diagram clearly shows a few of these processes, Figure 1.4.\textsuperscript{12}

\textbf{Figure 1.4.} Jabłoński’s diagram describing molecular photophysics. Modified from ref. 12
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 arrow represent light absorption of the ground state molecules (ground state absorption) or excited state molecules (ESA). A molecule that is in its ground state can be excited to one of several singlet excited states ($S_1$, $S_2$, etc.). The excitation to the first excited state ($S_1$) 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 the probing of the concentrations of these states and their temporal profiles.

**Photoproperties of metalloporphyrins excited states**

Metal-centered tetrapyrrole macrocycles contain highly delocalized $\pi$-orbitals situated on the carbon-nitrogen framework, and corresponding central metal orbitals. The metal ion to which the tetrapyrrole macrocycle is ligated plays a decisive role in the excited state deactivation. The d-orbital occupancy is critical and p-block metals, such as Zn, Al, Si, Ge, Ga have completely filled d-orbitals and no possibility exists for these orbitals to interact with molecular orbitals (MO) of porphyrin macrocycle and thus influence the rate of $S_1$ decay. For example, Zinc(II) porphyrins have $d^{10}$ electronic configuration and the interactions between the porphyrin $\pi$-system
and the metal are somewhat small.\(^9\) The deactivation of Zn(II) porphyrins \(S_1\) singlet excited state predominantly occurs through the \(T_1\) triplet state, which is produced with high quantum efficiency. For example, the quantum yield of triplet state for Zn(II)TMPyP was found to be 0.98 and for Zn(II)TPPS and Zn(II)TPP it was 0.96.\(^{13}\) The triplet state deactivates with the lifetime of 1.3 ms for Zn(II)TMPyP, 1.4 ms for Zn(II)TPPS and 1.2 ms for Zn(II)TPP.\(^{13}\) The phosphorescence quantum yields for these compounds are \(<10^{-4}\) at 298 K due to efficient non-radiative relaxation of the triplet state. Zn(II) porphyrins also show distinct fluorescence in many solvents. The fluorescence lifetimes were reported to be 1.3 ns for ZnTMPyP, 1.8 ns for ZnTPPS and 2.7 ns for ZnTPP.\(^{13}\) Thus, their \(S_1\) states have lifetimes on nanosecond time scale and the deactivation occurs by fluorescence and intersystem crossing (ISC). To summarize, the ISC process in p-block metal MTPs produce triplet states with high quantum efficiency and these often have lifetimes in the multi-microsecond timescale.

When the central metal is a transition metal having vacant d-orbitals, such as Ni, Co, Fe, Pd, etc., the excited state deactivation changes dramatically. Now, the \(S_1\) excited state can be deactivated by interactions between \(\pi^*\) orbital and the metal d-orbital manifold. Most of these transition metal porphyrins have inherently short excited-state lifetimes, because the coupling of the vacant d-orbitals with the \(\pi\) orbitals of the porphyrin forms states of intermediate energy, the LMCT and MLCT states, which facilitate rapid deactivation of the \((\pi,\pi^*)\) states of the porphyrin.

However, even though Pd(II) porphyrins have \(d^8\) electronic configuration of the central atom, as do Ni(II) complexes, their deactivation pathways differ dramatically, when comparing with those for Ni(II) porphyrins. Pd(II) porphyrins have a very low quantum yield of fluorescence \(\Phi_F < 10^{-4}\).\(^{14-17}\) The low \(\Phi_F\) values are due to extremely short lifetime of about 20 ps for the lowest singlet state, \(^1Q(\pi-\pi^*)\), which is mainly deactivated by ISC to the \(^3T(\pi\pi^*)\) due to
heavy-metal effect.\textsuperscript{18, 19} For the same reason, the triplet lifetimes of these molecules are shorter (several hundred microseconds) compared to those of regular porphyrins,\textsuperscript{16, 20} such as Zn(II) porphyrins. Gouterman et al.\textsuperscript{21} calculated that there are no charge transfer or d-d excited states lying below $^1Q(\pi-\pi^*)$ state. Hence the shorter lifetimes of the triplet state compared to those regular porphyrins are attributed purely to spin orbit coupling.

**Nickel porphyrins**

Nickel porphyrins 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 (\(\Phi<10^{-5}\)).\textsuperscript{9, 22, 23} One of the most important properties of the Ni(II) porphyrins is the $d^8$ electronic configuration of the central metal ion. The electronic transitions involving the metal atom are strongly affected by the nature of ligands, which can change the spin of Ni(II) from $S=0$ to $S=1$.\textsuperscript{9} Therefore, when no axial ligands are attached, the highest occupied orbital of the metal is $d_z^2$ and the lowest unoccupied orbital is $d_x^2 - y^2$. The results of extended Hückel calculations and the lack of luminescence supports the suggestion that the normally emissive $(\pi,\pi^*)$ excited state of the porphyrin macrocycle deactivates to produce the lower lying singlet or/and triplet metal centered $(d_z^2, d_x^2 - y^2)$ excited state.\textsuperscript{6, 23}

Holten et al. showed that common nickel porphyrins such as Ni(II)TPP and Ni(II)OEP have a $(\pi,\pi^*)$ excited state that forms a $(d,d)$ state less than 1 ps,\textsuperscript{24-26} and the $(d,d)$ state repopulates the ground state in 200-500 ps,\textsuperscript{27-31} Figure 1.5
Figure 1.5 The mechanism of excited state deactivation of Ni(II)TPP.

An interesting feature of nickel porphyrins is the formation of vibrationally hot transients upon excitation. Holten et al. 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.\textsuperscript{24-26} This complex behavior of the transients has been explained in terms of excess of vibrational energy in the metal-centered (d,d) excited state that was formed through the fast (< 1ps) deactivation of the (\pi,\pi^*) state of the tetrapyrrolic macrocycle. The excess energy dissipates into the environment as the excited molecules undergo vibrational cascade in 5-25 ps to form a (d,d) state in Boltzmann equilibrium with the thermal bath (cool).\textsuperscript{24-26}

\textit{Tetrabenzozyoporphyins}

Tetrabenzozyoporphyins (TBPs) are promising class of derivatized porphyrins.\textsuperscript{32} TBPs are still porphyrins, but they are similar to phthalocyanines inasmuch as each of the pyrrole rings is benzoannulated.\textsuperscript{33,34} Figure 1.6.
Figure 1.6. Structural formula of tetrabenzoporphyrin.

Koehorst et al.\textsuperscript{35} reported the preparation and the UV-Vis spectral data for pure TBPs. Since then, spectrum of TBP has been measured in 5% pyridine-THF solvent media, where the TBP showed a split Soret band at 412 nm ($\varepsilon=7.4\times10^4$) and 427 nm ($\varepsilon=8.5\times10^4$), while Q band appeared at 662 nm ($\varepsilon=1.6\times10^4$).\textsuperscript{36}

TBP complexes exhibit significant red shifts in their absorption spectra and an increased extinction coefficients of the lowest energy $\pi\rightarrow\pi^*$ Q-band relative to the Soret band.\textsuperscript{37, 38} The extended conjugation gives rise to more complicated $\pi\rightarrow\pi^*$ spectra of TBP.

Rogers et al.\textsuperscript{39} investigated the effects of the extension of porphyrin macrocycles, as well as central metal effect, on their photophysical properties. It was observed that tetrabenzo- and tetranaphto- annulation of the porphyrin ring leads to dramatic red shift of Q and Soret bands in the ground state absorption spectrum, due to increased conjugation effects with the small contribution from distortion of the porphyrin ring.\textsuperscript{39} Also, the red shift of ground state was observed when changing the central metal from Pd(II) to Zn(II).\textsuperscript{39}

Metallo-TBPs (MTBPs) have attracted attention in different areas of technology and medicine due to their high photostability and their unique optical properties. As such, they
present a potential class of compounds to be used as agents in photodynamic therapy of
tumors.\textsuperscript{40}

Ara et al.\textsuperscript{41} have pointed out 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.\textsuperscript{42}

An ideal photothermal sensitizer has to possess features including a very short lifetime of its
electronically excited state and high photostability.\textsuperscript{43} The other important feature of a potential
photothermal sensitizer is the high extinction coefficients between 600 nm and 1000 nm, in the
so called “phototherapeutic window” (characterized by maximum light penetration into tissues).

Nickel meso-tetraphenyltetrabenzoporphyric (NiTPTBP) is a very suitable compound for
this application. The phenyl substituents on the MTBP macrocycle increase its solubility in most
non-polar solvents and shift the MTBP ground absorption spectrum more to the red region
compared to Ni(II)TBP\textsuperscript{38}, Figure 1.7.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{ground_spectra.png}
  \caption{Ground state spectra of Ni(II)TBP and Ni(II)TPTBP in dimethylformamide.\textsuperscript{44}}
\end{figure}
REFERENCES


44. This work, Chapter 4.
CHAPTER 2: MATERIALS AND METHODS

2.1 MATERIALS

The solvents dimethyl sulfoxide (SPECTRANAL, >99.7%, Aldrich), deionized water, toluene (99.5%, Aldrich, Spectrophotometric grade), butyronitrile (99.9%, Sigma, HPLC grade), dimethylformamide (99%, Aldrich), benzonitrile (99.9%, Sigma, HPLC grade) and 2,6-lutidine (99%, Sigma) were used without further purification.

Nickel(II) meso-tetra (4-sulfonatophenyl) porphine (NiTPPS), Ni(II) meso-tetraphenylporphyrine (NiTPP), nickel(II) meso-tetraphenyltetrabenzoporphyrin (NiTPTBP) 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 a Varian Cary 50 Bio (Varian Corporation) single beam spectrophotometer. All spectra were recorded at room temperature (295 K) using 2 mm path length quartz cuvettes. All spectrophotometric titrations were conducted in a 1 cm quartz cuvette. For all titration series the concentration of titrate was $1 \times 10^{-5}$ and the concentration of titrant was 1 mM.
Femtosecond Transient Absorption Spectroscopy

Transient absorption experiments were performed in the Ohio Laboratory for Kinetic Spectrometry at BGSU. A Spectra-Physics Hurricane system was used as the laser source. This system 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 stretcher, a Ti:sapphire regenerative amplifier, and a compressor. The output of the system consists of pulses of 800 nm, 1 mJ, 100 fs (FWHM) at a repetition rate of 1 kHz. For the transient absorption experiments 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 time window) and then focused close to 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. Sum-Frequency Mixing Option (SFM) in the OPA was used to generate the 550 nm pulse. The residual fundamental (800 nm) at the OPA output was used to generate the 400 nm pulse. The second-harmonic generator consisted of a x3 telescope and 1 mm length BBO crystal. Figure 2.1 shows layout of the ultrafast spectrometer. The angle between two pumps and probe beam was 5°.
Figure 2.1. A schematic representation of ultrafast absorption spectrometer. OPA: optical parametric amplifier; B.S.: beam splitter; WLC- white light continuum generator; R_{AL}- reflector for visible range; FO- fiber optics.

The linear polarization of the probe beam was set at an angle 54.7° with respect to that of the pump beams, 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 optics 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 was not modulated, while the light at 550 nm passed through the chopper. The 550 nm pulse was delayed by 40 ps with respect to the 400 nm pulse. 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. In the case of two-pump-one-probe transient absorption, a transient
spectrum is a difference between the absorption spectrum of the sample excited by two subsequent pulses (400 nm and 550 nm) and the absorption spectrum of the sample excited by one pulse (400 nm). Typically, 500 transient spectra were averaged at a particular delay time. The CCD spectrograph and 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.

Some aspects of multiple pulse excitation techniques

In a pump-probe experiment, a strong pump pulse excites a sample of the material under investigation, and one measures the transmittance of a weak probe as a function of time. In a double pump-probe experiment, two pump pulses excite the sample sequentially. The first pulse populates various molecular excited states, while the second induces transitions whose rates depend on the various populations and cross-sections. As in a single pump-probe experiment, one measures the sample transmittance of a weak probe beam or pulse as a function of time, from which one can infer the relevant excitation and decay rates.

Two-pump (two-color or stepwise excitation) pulsed laser techniques\textsuperscript{1} have revealed that photoionization, bond cleavage, isomerization, energy transfer, and electron transfer within organic chromophores often involve higher electronic states of singlet,\textsuperscript{2,3} triplet,\textsuperscript{3-7} and radical ion\textsuperscript{4-6} states. This technique has been used to control electron and energy transfer within linear
and branch arrays of organic chromophores for approaches to optically controlled molecular switches.1,8

There are several examples of multiple pulse excitations of organic molecules. One of them is multi-excitation with more than two lasers, in which short-lived species such as excited molecules and reactive intermediates are generated by the first excitation of starting molecules, and used as starting molecules for the second excitation.9 Majima et al. have applied nanosecond-picosecond two-color flash photolysis, where the absorption and fluorescence of a series of ketyl radicals of benzophenone derivatives were successfully detected.9

Another example is the double-pulse pump-probe technique that utilizes two pump pulses of high energy density and one weak test pulse to monitor the transmission changes created by the pump pulses, Figure 2.2. Double-pulse pump-probe technique has shown that photoionization, energy transfer and electron transfer within organic chromophores often involve higher electronic states.

Wasielewski1 et al have measured the rates of triplet energy transfer using this technique. In his experiments the first pump pulse excited a certain amount of molecules into the $S_n$ state. After a certain time, some of these excited molecules in the $S_1$ state can undergo intersystem crossing and can be found in the long-living triplet state $T_1$ or in the silent states (d,d) or/and undergo direct $S_1$-$S_0$ relaxation. Therefore, the second pulse would be absorbed by distribution of new molecules in different states, Figure 2.3.
**Figure 2.2.** The schematic representation of double-pulse pump-probe experiment.

**Figure 2.3** Energy diagram for detecting the triplet quantum yield.
Quantum Chemical Calculations

DFT makes use of the Schrödinger equation in different formulation and is based on Hohenberg-Kohn theorem\(^1\) according to which the ground state energy of an electronic system is uniquely determined by the electron density \(\rho(r)\). This makes it possible to use electron density as basic variable and one can replace the complicated N-electron wave function \(\Psi(x_1, x_2, \ldots, x_N)\) by the much simpler electron density \(\rho(r)\). Thus, the ground state geometries and electronic structures for such big and complex molecules as metalloporphyrins\(^1\) can be computed relatively easy.

The Q-state of a nickel (II) porphyrin undergoes radiationless deactivation and the assignment of the mechanisms and dynamics is quite complex. To do it properly, it is necessary to know the nature and energies of the optically silent states existing in the \(S_1 \rightarrow S_0\) gap.\(^1\) The Time-dependent DFT (TDDFT) is a useful tool to compute excitation energies and the results obtained are quite accurate. When combined with experimental methods it can provide a comprehensive analysis of the ground state electronic structure of studied system.\(^1\) TDDFT is a precise and convenient method for calculating the properties of many-atom systems in external fields that vary in time. It is an extension of DFT, which provides the description of the dynamic evolution of electronic systems.\(^1,13\) The excited state characteristics, such as excitation energies, and the oscillator strengths are computed by TDDFT.\(^11,13\) TDDFT is applied to chemical processes utilizing the Runge and Gross theorem.\(^10\) This theorem implies that evolution of the electron density of a many electron system can be expressed as an additive purely time-dependent function when the external potential is varied.\(^12,13\) To calculate the energy is simple and straightforward since the symmetry aspects are taken into account so that the excited states belong to a particular irreducible representation.\(^12,13\)
The TDDFT calculations deal with one electron vertical transitions between two potential surfaces: one is of the ground electronic state and the other is of the excited one. Schematically the process and computed parameters are presented in Figure 2.4. Upon absorption of a photon the molecule is promoted to the excited state potential surface and the energy need is presented by the vertical absorption energy ($E_{va}$). That process occurs at the ground state optimized geometry. The adiabatic energies (the energy difference between potential surfaces minima) have been obtained according to the expression\textsuperscript{14}

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

$E_{ve}$ is the vertical emission energy that has been calculated at the TDDFT level using the relaxed excited state geometry. The $\Delta E$ term accounts for the ground state energy change upon deformation to the relaxed excited state geometry (Figure 2.4)\textsuperscript{14}

\textbf{Figure 2.4.} Schematic definition of the computed excitation energies (from ref. 14).

The calculations have been performed by Alexandra Soldatova in a collaborative agreement.
2.3 REFERENCES


CHAPTER 3: TWO-PUMP ONE PROBE FEMTOSECOND STUDIES OF Ni(II)

PORPHYRINS EXCITED STATES

3.1 INTRODUCTION

Tetrapyrrole macrocyclic ligands (e.g. porphyrins) have a set of highly delocalized $\pi$-orbitals situated on the carbon-nitrogen framework. When such a ligand is coordinated to a centrally-located metal atom of the transition series, having incompletely filled d-orbitals (Ni, Co, Fe, Cu, etc.), the $\pi$- and d-manifolds can interact. As a result the excited state deactivation dynamics becomes very dependent on the electronic nature of the central metal.

In order to investigate the interesting properties of these transition metal porphyrins, extensive studies have been performed.$^{1-5}$ Among them, Ni$^{1-6}$ and Co$^{7-12}$ porphyrins are most thoroughly investigated systems.

Co(II) has a d$^7$ electronic configuration. The odd d$_z^2$ electron interacts with the porphyrin $\pi$-system to produce doublets and quartets.$^8$ The ground state is a doublet. The $S_0$ ($\pi,\pi^*$) excited states become singdoublet. The triplet state is split into $^2T_1(\pi,\pi^*)$ tripdoublet and $^4T_1(\pi,\pi^*)$ tripquartet, where the latter is lower in energy by a few hundred wavenumbers.$^{9,10}$ Calculations and near-IR absorption spectra suggest that the $^2T_1(\pi,\pi^*)$ state is 1.5-2 eV above the ground state. Iterative extended Huckel calculations predict a low-lying ($\pi,d$) charge transfer state, porphyrin $a_{2u}(\pi)\rightarrow Co(d_z^2)$. $^8$ The metal-centered (d,d) states are predicted to be higher in energy than the ($\pi,\pi^*$) states.$^8$ It has been reported that singdoublet ($\pi,\pi^*$) excited states of porphyrins and phthalocyanines undergo very rapid intersystem crossing to populate lower lying states with
different multiplicity.\textsuperscript{9,10} The rate of intersystem crossing has been estimated to be less than 250 fs.\textsuperscript{11} It has been suggested that the deactivation of the $^2T_1(\pi,\pi^*)$ state of Co(II)TPP and Co(II)OEP takes place via a low-lying ($\pi$, d) charge transfer state with the lifetime less than 35 ps.\textsuperscript{8} More recent results obtained by Zewail et al. suggested that the formation of a charge transfer state, which is a result of intramolecular electron transfer from porphyrin to cobalt: $a_{2u}(\pi)\rightarrow\text{Co}(d_z^2)$, occurs on the time scale of about 2 ps.\textsuperscript{12}

On the other hand, Ni(II) porphyrins are known to rapidly form a metal-centered (d,d) state after photoexcitation into Soret band or Q band. One of the most important properties of the nickel porphyrins is the $d^8$ electronic configuration of the central metal ion. Thus, the highest occupied orbital of the metal is $d_z^2$ and the lowest unoccupied orbital is $d_x^2-y^2$.\textsuperscript{3} These molecules have a very low quantum yield of fluorescence ($\Phi<10^{-5}$).\textsuperscript{13} The results of extended Huckel calculations and the lack of luminescence supported the suggestion that the normally emissive ($\pi,\pi^*$) excited state of the porphyrin macrocycle deactivates to produce the lower lying singlet or/and triplet metal centered ($d_z^2, d_x^2-y^2$) excited state.\textsuperscript{9,13} Rodriguez et al. showed that common nickel porphyrins such as NiTPP and NiOEP have a ($\pi,\pi^*$) excited states that form (d,d) states within 1 ps,\textsuperscript{4-6} and the (d,d) states repopulates the ground states in 200-500 ps.\textsuperscript{1,14} An interesting feature of nickel porphyrins is the formation of vibrationally hot transients upon excitation. Rodriguez et al. observed 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.\textsuperscript{4-6}

Due to symmetry restrictions the $(d_z^2 \rightarrow d_x^2-y^2)$ transition is forbidden making the (d,d) excited state non-emissive and optically silent. The deactivation time constant of this (d,d) state in NiTPP in toluene is $\sim$450 ps.\textsuperscript{1,14} The sub-picosecond energy transfer from the $\pi$-system to the
metal system generates a porphyrin molecule with a ground state $\pi$-system and an excited metal center. The electronically changed metal center causes perturbation which results in small spectral shifts in the ground state absorption spectrum of the porphyrin.$^{1,3,5}$ The intrinsically high porphyrin extinction coefficients are not significantly affected by excited metal center which is evidenced by a symmetric derivative shape of the absorption difference spectra.$^{3,5}$

Therefore, these high extinction coefficients of a molecule with an excited metal center present a major opportunity to rapidly regenerate the $S_1$ excited state of the $\pi$-system.$^6$ It is interesting to generate molecular states with electronic excitation in two distinct regions of the metalloporphyrin and elucidate the mechanism of deactivation of such a doubly excited state. In order to do this femtosecond two-pump-one-probe transient absorption experiments can be employed, where following the initial pumping photon pulse with a second one, delayed by a few picoseconds, will generate an $S_1$ ($\pi$-localized) state with d-electron configuration different from the $S_1$ ($\pi$ -localized) state formed by the first photon pulse. We believe that such a procedure is novel, and the deactivation of these doubly states will show major departures from well-studied one photon situations.
3.2 RESULTS

Ground State Absorption Spectrometry

Figure 3.1 shows the ground state spectra of two Ni(II) porphyrins. The absorption spectrum for Ni(II)TPPS was taken in DMSO and water, and Ni(II)TPP spectrum was taken in toluene alone. The spectra exhibited strong near-UV Soret bands around 415 nm for Ni(II)TPP in toluene and at 410 nm for Ni(II)TPPS in water; and weaker visible Q-bands: at 527 nm and 524 nm, respectively.

![Figure 3.1](image_url)

**Figure 3.1.** The ground-state absorption spectra. a) Nickel(II) meso-tetraphenylporphyrine (NiTPP) in toluene; b) Nickel(II) meso-tetra(4-sulfonatophenyl) porphine (NiTPPS)
In DMSO solvent, Ni(II)TPPS showed Soret and Q bands that were slightly red-shifted: the former appearing at 418 nm and the latter at 528 nm. Traditionally, the Soret and Q bands are assigned to the $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$ transitions\(^2\), respectively.

*One-Pump-One-Probe Transient Absorption Spectroscopy*

Excitation of a $1 \times 10^{-5}$ M solution of Ni(II)TPPS at room temperature at 400 nm produced the dynamic surface shown in Figure 3.2. The results of the transient absorption experiments, i.e. the kinetics data and the relative amplitudes of the decay components are summarized in Table 3.1 and Table 3.2.

![Figure 3.2](image-url)  
*Figure 3.2* Three-dimensional representation of the Ni(II)TPPS transients produced via excitation at 400 nm
Figure 3.3 displays transient spectra of Ni(II)TPPS in DMSO at two times after excitation into the Soret band at 400 nm.

Figure 3.3 Transient spectra of Ni(II)TPPS in DMSO at two times after excitation into the Soret band at 400 nm.

The spectrum at 1 ps showed a broad, featureless positive absorption band throughout the visible region with a shoulder at around 490 nm and bleaching of the ground state centered at 530 nm. The 40 ps spectrum (solid line) revealed a negative absorption band centered at 525 nm and a positive one at 550 nm forming an S-shaped spectrum, which is characteristic of the metal centered (d,d) state. The one-pump-one-probe transient absorption experiments for Ni(II)TPPS in water and for Ni(II)TPP in toluene revealed behavior similar to that of Ni(II)TPPS in DMSO.
Two-Pump-One-Probe Femtosecond Transient Absorption Spectroscopy

**Ni(II)TPPS**

Excitation of Ni(II)TPPS (1x10^{-5} M) in DMSO with a 400 nm pulse and a 550 nm pulse 40 ps later produced the dynamic surface shown in Figure 3.4.

**Figure 3.4.** Dynamic surface of Ni(II)TPPS in DMSO after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps.
Transient spectra of the Ni(II)TPPS in DMSO after two subsequent excitation pulses are shown in Figure 3.5. The spectrum taken at 1 ps probe delay after the second excitation event corresponds to the first observed transient. It showed a positive broad absorption band at around 480 nm, bleaching centered at 548 nm and a positive band peaking at 575 nm.

Figure 3.5. Transient spectra of the Ni(II)TPPS in DMSO after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps.

The spectrum taken at 50 ps strongly resembled the S-shaped transient observed for Ni(II)TPPS metal centered (d,d) state. The kinetic profile at 480 nm, Figure 3.6 showed an instrument limited rise and a bi-exponential decay with lifetimes of 0.6 ps and 4 ps. Similar behavior was observed for the kinetic trace at 575 nm (Figure 3.6), although the second component of 575 nm profile was longer (8 ps) with respect to the one at 480 nm (4 ps).
Figure 3.6. Kinetics profiles of the Ni(II)TPPS transient absorption at different probe wavelengths. Solvent: DMSO
The two pulse excitation of Ni(II)TPPS in water under identical conditions to those above revealed the transients and kinetic behavior analogous to those of Ni(II)TPPS in DMSO (Figure 3.7, Figure 3.8 and Table 3.1).

Figure 3.7. Transient spectra of the Ni(II)TPPS in water after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps.
Figure 3.8. Kinetics profiles of the Ni(II)TPPS transient absorption at different probe wavelengths. Solvent: water
Table 3.1. Lifetimes and relative amplitudes of the two-pump-one-probe transient absorption dynamics of Ni(II)TPPS in DMSO and water.

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>$\tau_1$ (ps)</th>
<th>A1</th>
<th>$\tau_2$ (ps)</th>
<th>A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>0.6±0.02</td>
<td>0.6</td>
<td>4.0±0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>575</td>
<td>0.8±0.1</td>
<td>0.55</td>
<td>8.2±0.5</td>
<td>0.45</td>
</tr>
</tbody>
</table>

Ni(II)TPPS in DMSO

Ni(II)TPPS in water

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>$\tau_1$ (ps)</th>
<th>A1</th>
<th>$\tau_2$ (ps)</th>
<th>A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>480</td>
<td>0.7±0.02</td>
<td>0.6</td>
<td>10.2±0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>575</td>
<td>0.8±0.04</td>
<td>0.6</td>
<td>3.7±0.3</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Ni(II)TPP

The transient spectrum evolution of Ni(II)TPP (1x10^{-5} M) in toluene after the second excitation pulse is presented in Figure 3.9. The spectrum taken at a 1 ps probe delay corresponds to the first observed transient. It showed a positive broad absorption band appearing at around 475 nm, the bleaching centered at 545 nm and another positive band peaking at 575 nm. The spectrum taken at 50 ps strongly resembled the S-shaped transient observed for NiTPP metal centered (d,d) state. Figure 3.10 and Figure 3.11 display the kinetic profiles at three representative wavelengths with the corresponding lifetimes summarized in Table 3.2.
**Figure 3.9.** Transient spectra of the Ni(II)TPP in toluene after two subsequent excitation pulses (400 nm and 500 nm). Time delay between two pulses was 40 ps.

**Figure 3.10.** Kinetics profiles of the Ni(II)TPP transient absorption at 475 probe wavelengths. Solvent: toluene.
Figure 3.11. Kinetic profile of the Ni(II)TPP transient absorption at 575 nm probe wavelength. Solvent: toluene.

All kinetic profiles showed instrument limited signal formation. A kinetic profile at 475 nm could be well fitted with two exponentials: 0.6 ps and 4.3 ps. The kinetic at 575 nm displayed a bi-exponential decay with lifetimes of 1.2 ps and 7.4 ps.

Table 3.2. Lifetimes and relative amplitudes of the two-pump-one-probe transient absorption dynamics of Ni(II)TPP in toluene
3.3 DISCUSSION

In the two excitation pulse experiment, for Ni(II)TPPS in DMSO, the first pulse (400 nm) converts the porphyrin π-system into the $S_2(\pi,\pi^*)$ state, which produces the $S_1(\pi,\pi^*)$ state within the instrument response time (ca 130) fs. The $S_1(\pi,\pi^*)$ state decays to form the metal-centered excited (d,d) state that vibrationally relaxes within 14 ps and repopulates the ground state with the time constant of 470 ps. The $(\pi,\pi^*)\rightarrow(d,d)\rightarrow S_0$ pathway was proposed previously for both planar and distorted porphyrins. The second (550 nm) pulse selectively excited the $S_0\rightarrow S_1$ transition of those molecules having an excited metal center. The selectivity was based on the (d,d) excited Ni(II) porphyrin molecules absorbing ~ 4 times stronger at 550 nm than their ground states. Transitions within the d-manifold are forbidden, therefore the absorption spectrum of the (d,d) state is dominated by the absorption of the ground state π-system. The formation of the (d,d) state produced by the first excitation pulse slightly shifts the ground state spectrum (in this case to the red) due to the changed central metal electron configuration, Figure 3.12. This new absorption spectrum (dotted blue line), Figure 3.12, becomes a reference spectrum (or pump-off spectrum) in the two-pump-one-probe experiment. The second pulse was delivered to the sample approximately 40 ps after the first excitation event. At this time the excitation was localized at the metal center and the π-system was in its ground state. As the $S_1$ state is repopulated by the second pulse the deactivation of $S_1$ has to occur through a channel different from the conventional $(\pi,\pi^*)\rightarrow(d,d)\rightarrow S_0$ because the (d,d) state is already populated.
Figure 3.12 The proposed scheme for doubly excited states generation. Left side: the black line is the ground state absorption spectra of Ni(II)TPPS in DMSO; Middle: the dotted line is a red-shifted spectrum after excitation event. Right side: transient spectra of Ni(II)TPPS in DMSO.

The first possible pathway for the $S_1$ state relaxation after second pulse (550 nm) would be deactivation directly into the ground state and into the triplet state with subsequent regeneration of the ground state.$^{2,17}$ Such mechanism is observed for Zn porphyrins$^2$ where the interaction between the tetrapyrrole ring and the central metal ion is minimal and the intrinsic $S_1 \rightarrow S_0$ lifetime in such porphyrins is on the order of a few nanoseconds. In this case the newly restored $S_1$ excited state would be unable to reach the (d,d) state since that state is already occupied and thereby an emissive decay route for the $S_1$ state of the $\pi$- system could be opened. However our data show that the decay of the doubly excited state of Ni(II)TPPS occurs on a much shorter time scale and has a bi-exponential character.
The second possible pathway for the $S_1$ state deactivation after second pulse could involve the formation of an intramolecular charge transfer state. In this case the fast decay component ($\sim 1$ ps) corresponds to electron transfer from the porphyrin ring to the central metal and the slower component ($\sim 4$-10 ps) reflects the charge recombination process, which yields the ground state of the $\pi$ system.

In order to test this hypothesis we investigated the deactivation dynamics of the Ni(II)TPPS doubly excited states in two different solvents. Changing the solvent from water to DMSO, Table 3.1, showed that in the more polar solvent (water), the second component becomes longer (ca. 10 ps) compared to the less polar solvent (DMSO) (ca. 4 ps). Such increase in the reverse process lifetime is often for charge transfer states, whose recombination usually lies in the inverted region of the Marcus curve.$^{19}$

The Marcus theory implies that barrierless electron transfer that can occur if the reorganization energy ($\lambda$) equals to the Gibbs free energy change for charge separation ($-\Delta G_{cs}$), it is called the optimal region.$^{20}$ If $\lambda > -\Delta G_{cs}$, the electron transfer rate increases with larger driving forces. However, in the so called Marcus inverted region, if $\lambda < -\Delta G_{cs}$, the rate decreases with larger driving forces.$^{20}$ An important part of the reorganization energy, $\lambda$, is dependent on the solvent. The higher the dielectric constant of the latter the larger the value obtained for $\lambda$. Water with a high dielectric constant slows down electron transfer reactions.$^{21}$

Moreover, the electronic configuration of the four lowest d orbitals in the excited Ni(II) (d,d) state is identical to that of the ground state of Co(II). This suggests that the deactivation of the $S_1$ in Ni porphyrin is similar to the deactivation of $S_1$ in Co(II) porphyrin. In fact, the NiTPPS doubly excited state lifetimes resemble the kinetics reported$^{12}$ for Co(II)TPP. Hua-Zhong et al.$^{12}$ showed that deactivation of the Co(II)TPP $S_1$ state occurs through the formation of a charge
transfer state, which is a result of intramolecular electron transfer from the porphyrin ring to the metal center: $a_{2u}(\pi) \rightarrow \text{Co}(d^2)$, Figure 3.13. The lifetime for the charge separation process was reported to be on the order of 2 ps.\textsuperscript{12} Additionally, Hua-Zhong et al. have stated that the lifetimes of the Co(II)TPP CT state increased with increasing solvent polarity. This observation agrees well with our data.

![Energy diagram for Cobalt(II) porphyrin (Charge transfer)](image)

**Figure 3.13.** Energy diagram for Cobalt(II) porphyrin (Charge transfer)

Photoexcitation of Ni(II)TPP in toluene produced the transient absorptions shown in Figures 3.10 and 3.11. The decay dynamics summarized in Table 3.2 were very similar to those observed for Ni(II)TPPS. One observes a small solvent effect on the charge separation rate. This phenomenon is not surprising and can explained by subpicosecond electron transfer that is too fast to be affected by the nuclear motions of the polar solvent molecules, which occur on the $10^{-11}$-$10^{-9}$ s scale. Additionally, the fast ($10^{-15}$ s) electronic motions in the solvent molecules cannot significantly affect the rate of the ultrafast charge separation since the latter takes place at the rates comparable to those of solvent dipole reorganization.\textsuperscript{22-25}
These findings suggest that the Ni(II)TPP and Ni(II)TPPS doubly excited states follow the same deactivation mechanism.

In order to better illustrate the mechanism for the Ni(II) porphyrin dual excited state deactivation schematic diagrams are presented in Figure 3.14 and Figure 3.15.

Figure 3.14 represents the electronic configuration of the Ni(II) porphyrin (d,d) state. Figure 3.15 shows the proposed mechanism for the Ni(II) porphyrin excited state deactivation, involving the formation of an LMCT state.

**Figure 3.14** Electronic configuration of Ni(II) porphyrin d,d state. After one pulse (400 nm), the excitation is localized at the Ni(II) center. The area enclosed by the dotted line indicates similarity to the Co(II) porphyrin ground state.
Figure 3.15. A mechanism of deactivation of Ni(II) porphyrin excited state. After second pulse (550nm).

The residual spectrum (50 ps), Figure 3.6, Figure 3.7 and Figure 3.9, may arise for only one reason. It is due to the absorption of the second excitation pulse by the ground state molecules. The Q-bands of Ni(II)TPPS and Ni(II)TPP centered at around 530 nm with a shoulder extending over 550 nm therefore a fraction of the ground state porphyrin molecules could still absorb the 550 nm second excitation pulse. In this case the long lived (~450 ps) d,d state will form simultaneously with the doubly excited state and will remain present in the transient spectrum after the doubly excited states have deactivated.
3.4 REFERENCES


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CHAPTER 4: PHOTOPHYSICAL INVESTIGATION OF Ni (II) MESO-
TETRAPHENYLBENZOPORPHYRIN

4.1 INTRODUCTION

Nickel(II) porphyrins have rich photophysical behavior that can be exploited to probe the relationships among conformational, electronic and vibrational properties.\(^1\) The mechanism of deactivation of the excited states of planar porphyrins, such as Ni(II)TPP proceeds via a sequence of electronic deactivation steps, \((\pi,\pi^*) \rightarrow (d,d) \rightarrow \text{ground state}\).\(^2,3\) The deactivation appears to proceed largely in the singlet manifold, although some deactivation through the triplet excited states cannot be ruled out. The porphyrins that have planar configuration, such as Ni(II)TPP exhibit two main transitions in the UV-visible region, a strong near-UV, Soret band and a weak visible Q-band.\(^4\) The presence of different substituents change the position of these bands, but the separation between the Soret band and Q-band remains roughly the same.

Therefore, Ni(II) porphyrins can be divided into two groups. The first group can be attributed to the highly conformationally distorted (ruffled, saddled, etc.), where the (d,d) excited state spectral maximum shifts to a blue region, and it demonstrates the excited state lifetime dependence on solvent properties.\(^2\) The second one is the nominally planar Ni(II) porphyrins that exhibit red shifts of (d,d) excited state and show no lifetime dependence on solvent properties.\(^4\) The shifted excited state Q bands for both classes can be explained by population of the \(d_{x^2-y^2}\) 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 \((\pi,\pi^*)\) transition energies. The
blue shift in the transient Q band of the nonplanar porphyrins relative to the ground state of these complexes is explained if a less-distorted geometry is assumed in the ligand-field excited state.\textsuperscript{2} This new geometry displaces nickel (II) ion out of the plane of the $\pi$-system, and with the increased dipole moment the porphyrin excited state relaxation dynamics become sensitive to the solvent.\textsuperscript{5-7} The ground state of the porphyrin is usually symmetric and the dipole and quadruple moments are cancelled.\textsuperscript{2,8} Furthermore, the core size is expected to be larger the more planar the macrocycle, relieving electronic repulsion between the metal $d_{x^2-y^2}$ and the ring $a_{2u}$ electrons.

Drain et al. have investigated the photophysical properties of conformationally distorted nickel dodecaphenylporphyrin (Ni(II)DPP). According to their study, Ni(II)DPP has a number of accessible conformers and that the energies of these conformers and the barriers between them differ with electronic state.

The majority of studies on the photophysical properties of metallated tetrapyrrolic macrocycles are mainly focused on porphyrins. No studies on the fundamental deactivation process of nickel (II) tetraphenyltetrabenzoporphyrin have been reported.

Tetraphenyltetrabenzoporphyrins are the new class of porphyrins with extended conjugation of the $\pi$-system.\textsuperscript{9-14} This extended conjugation together with additional \textit{meso}-substitution causes the substantial distortion of the macrocyclic core and red-shifts ground electronic state absorption spectra compared to regular porphyrins.\textsuperscript{10,15} Non-planar nickel porphyrins such as nickel (II) dodecaphenylporphine,\textsuperscript{16} and nickel (II) tetraphenyltetrabenzoporphyrin 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.\textsuperscript{16}
4.2 RESULTS

Ground State Absorption Spectroscopy

Figure 4.1 shows the ground electronic state absorption spectra of Ni(II)TPTBP in four different solvents. In toluene, 2,6-lutidine, butyronitrile and dimethylformamide (DMF), the spectra showed strong near-UV Soret bands centered at 447 and weaker visible Q-band at around 643 nm. It can be observed that the ground state absorption spectra of Ni(II)TPTBP are essentially unchanged in these solvents. Similar behavior has been observed for most common nickel porphyrins, such as Ni(II)TPP.

Figure 4.1. The ground absorption spectra of Ni(II) meso-tetraphenyltetrabenzoporphyrin in four solvents.
Ultrafast transient absorption spectroscopy

The femtosecond transient absorption experiments for Ni(II)TPTBP were conducted in a number of solvents using 400 nm laser light for excitation. In each case, the time evolution of the spectra revealed two or three kinetic components, with time constants ranging from the subpicoseconds to the hundreds of picoseconds before complete ground-state recovery was observed. The photophysical behavior of Ni(II)TPTBP showed notable differences in various solvents and for these reasons the results in different media are presented separately.

Ni(II)TPTBP in Toluene

Excitation of a 1x10^{-5} molar solution of Ni(II)TPTBP at 400 nm for the first 70 ps at room temperature produced the dynamic surface shown in Figure 4.2. Figure 4.3 displays the three transient spectra of Ni(II)TPTBP in Q-band region with excitation into the Soret band.

The spectrum at 1 ps, Figure 4.3, shows a positive broad transient absorption that tails from the Soret region to past 720 nm and broken by bleaching in the Q bands. The prominent bleaching of the ground state Q-band centered at 647 nm. The spectrum that was taken at 5 ps delay after excitation event revealed a negative absorption band centered at 647 nm and a positive one at 668 nm forming an S-shaped spectrum. In contrast to regular Ni(II) porphyrins, such as Ni(II)TPP,\textsuperscript{4} that have a symmetric derivative shape of the absorption difference spectra, Ni(II)TPTBP has more negative absorption than positive counterpart. The spectrum taken at 30 ps probe delay showed an S-shaped spectrum that then decays to the baseline, reflecting complete ground state recovery. One can notice that the S-shaped spectrum exhibits a blue shift.
Figure 4.2. Dynamic surface of the Ni(II)TPTBP recorded in toluene after excitation at 400 nm.

Figure 4.3. Transient spectra of Ni(II)TPTBP in toluene at three times after excitation into Soret band at 400 nm.
Figure 5.4 displays the kinetic profiles at three representative wavelengths with corresponding lifetimes summarized in Table 4.1.

**Green: Probe 475 nm**: \( \tau_{\text{rise}} = 0.84 \text{ ps} \), \( \tau_{\text{decay}} = 33 \text{ ps} \)

**Blue: Probe 497 nm**: \( \tau_{\text{rise}} = 1.4 \text{ ps} \), \( \tau_{\text{decay}} = 32 \text{ ps} \)

**Probe: 475 nm**

**Rise**

\( t_1 = 0.84 \text{ ps} \)

**Probe: 648 nm**

\( t_1 = 1.9 \pm 0.06 \text{ ps} \)

\( t_2 = 21.8 \pm 0.15 \text{ ps} \)
Figure 4.4 Kinetics profiles of the Ni(II)TPTBP transient absorption at different probe wavelengths. Solvent: toluene

All three kinetic profiles showed instrument limited signal formation. The fitted data of the temporal decay profiles indicate that, as the probe wavelength moves towards the blue, the first component ($\tau_1$) became larger, and its contribution to the overall decay process became smaller. A kinetic profile at 475 nm revealed mono exponential rise and decay with lifetimes of 0.84 ps and 33 ps, respectively. A kinetic profile at 497 nm could be well fitted with two exponentials: 1.4 ps and 32 ps. A bleaching at 648 nm recovered with lifetimes 1.9 ps and 21 ps. The kinetic profile at 665 nm displayed a mono exponential rise and decay: 1.9 ps and 21 ps, respectively. The value of the first time constant changed slightly, the second component was essentially wavelength independent.
Table 4.1. Lifetimes and relative amplitudes of Ni(II)TPTBP in toluene

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>$\tau_1$ (ps)</th>
<th>$A_1$</th>
<th>$\tau_2$ (ps)</th>
<th>$A_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>475 (rise)</td>
<td>0.84±0.1</td>
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<tr>
<td>475</td>
<td></td>
<td></td>
<td>34.8±0.4</td>
<td>1</td>
</tr>
<tr>
<td>648</td>
<td>1.9±0.06</td>
<td>-0.2</td>
<td>21.8±0.1</td>
<td>-0.8</td>
</tr>
<tr>
<td>665 (rise)</td>
<td>1.9±0.02</td>
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<tr>
<td>665</td>
<td></td>
<td></td>
<td>21.5±0.3</td>
<td>1</td>
</tr>
</tbody>
</table>

Ni(II)TPTBP in 2, 6-lutidine

The Q-region transient absorption and kinetic data for Ni(II)TPTBP in 2,6-lutidine (not shown) were similar to the data obtained in toluene. The only difference was that the longer time constant of the ground state recovery increased slightly from 22 ps to 30 ps.
**Ni(II)TPTBP in butyronitrile**

To probe the effect of polarity of the solvents on the excited state relaxation dynamics, the experimental data for Ni(II)TPTBP were acquired in butyronitrile. The conditions of the experiment were identical to those used for the toluene and 2,6-lutidine experiments. The dynamic surface of the transient absorption in butyronitrile for the duration of 170 ps is depicted in Figure 4.5.

![Dynamic surface of the Ni(II)TPTBP recorded in butyronitrile after excitation at 400 nm.](image)

**Figure 4.5.** Dynamic surface of the Ni(II)TPTBP recorded in butyronitrile after excitation at 400 nm.

The transient spectra of Ni(II)TPTBP in butyronitrile are shown in Figures 4.6, 4.7 and 4.8 display kinetic profiles with corresponding lifetimes summarized in Table 4.2.
Figure 4.6. Transient spectra of Ni(II)TPTBP in butyronitrile after excitation at 400 nm.

Figure 4.7. Kinetics profiles of the Ni(II)TPTBP transient absorption at 475 nm probe wavelengths. Solvent: butyronitrile
Figure 4.8. Kinetics profiles of the Ni(II)TPTBP transient absorption at different probe wavelengths. Solvent: butyronitrile
Table 4.2. Lifetimes and relative amplitudes of Ni(II)TPTBP in butyronitrile

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>$\tau_1$(ps)</th>
<th>$A_1$</th>
<th>$\tau_2$(ps)</th>
<th>$A_2$</th>
<th>$\tau_3$(ps)</th>
<th>$A_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>475 (rise)</td>
<td>1.6±0.06</td>
<td>-1</td>
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<tr>
<td>475</td>
<td></td>
<td></td>
<td>23.6±0.5</td>
<td>0.31</td>
<td>151±1.3</td>
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</tr>
<tr>
<td>648</td>
<td>4.31±0.1</td>
<td>-0.36</td>
<td>23.6±1.3</td>
<td>-0.29</td>
<td>147.8±2.9</td>
<td>-0.35</td>
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<tr>
<td>665 (rise)</td>
<td>1.3±0.01</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>665</td>
<td></td>
<td></td>
<td>18.9±0.2</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The earliest absorption features were similar to the toluene and 2,6- lutidine cases. Subsequently, there is an appearance of the 150 ps third time constant. A kinetic profile at 475 nm revealed the mono exponential rise 1.6 ps and bi-exponential decay with lifetimes 23.6 ps and 151.5 ps, respectively. A bleaching at 648 nm recovered with lifetimes 4.3 ps, 23.6 ps and 147.8 ps. The kinetic trace at 665 nm displayed a mono exponential rise and decay: 1.3 ps and 18.9 ps, respectively.

NiTPTBP in dimethylformamide

Figure 4.9 displays the transient spectra of Ni(II)TPTBP in Q region with excitation into the Soret band. The kinetic profiles at three representative wavelengths with corresponding lifetimes are summarized in Table 4.3.
Figure 4.9. Transient spectra of Ni(II)TPTBP in dimethylformamide after excitation at 400 nm.

Table 4.3. Lifetimes and relative amplitudes of Ni(II)TPTBP in dimethylformamide

<table>
<thead>
<tr>
<th>Wavelength / nm</th>
<th>$\tau_1$ (ps)</th>
<th>$A_1$</th>
<th>$\tau_2$ (ps)</th>
<th>$A_2$</th>
<th>$\tau_3$ (ps)</th>
<th>$A_3$</th>
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<td>475</td>
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<td></td>
<td>24.2±0.3</td>
<td>0.42</td>
<td>844.7±14.2</td>
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<tr>
<td>648</td>
<td>3.2±0.1</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>670</td>
<td></td>
<td></td>
<td>13.8±0.15</td>
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</tbody>
</table>

The transient data in the Q-band region revealed three stages for the time evolution. The first two time constants are essentially similar to that observed in butyronitrile. The third time constant turned out to be significantly longer. For dimethylformamide, it appeared to be around 800 ps, indicating that the slowest kinetic phase, reflecting ground state recovery, in dimethylformamide is significantly slower than in butyronitrile.
Since X-ray data of Ni(II)TPTBP is not available, the geometry optimization was performed imposing, first, $D_{4h}$ and then, $D_{2d}$ symmetry. It was found that $D_{2d}$ saddled structure has a lower energy indicating that molecule is more stable in this conformation. Moreover, it is known from X-ray crystallography data\textsuperscript{17} that MTPP ring of metallated chromophore is fairly planar with a small saddling formation with the phenyl groups twisted out of the plane of the porphyrin by as much as 70-80°.\textsuperscript{14}

Indeed, the computed a twisting 70° angle and a saddling 25.20° angle of the porphyrin core supported the assumption of the saddled ground state molecular structure for Ni(II)TPTBP, Table 4.4. Figure 4.10 represents the $D_{2d}$ saddled configuration.

![Figure 4.10](image.png)

**Figure 4.10.** The structure of Ni(II)TPTBP. Left: representation of $D_{2d}$ saddled configuration. Right: notation of carbon atoms.
Table 4.4. Selected bond lengths (Å) and bond angles (deg) for Ni(II)TPTBP in the $D_{2d}$ saddle conformation

<table>
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<th>Ground state</th>
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$^3$(LMCT)

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<td>C6NC8</td>
<td>24.5°</td>
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$^3$(d,d)

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<tr>
<td>C6NC8</td>
<td>23.7°</td>
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The atomic orbital population analysis is given in Table 5.5.
Table 4.5. Energies and percent composition of the highest occupied and lowest unoccupied molecular orbitals of Ni(II)TPTBP expressed in terms of individual atoms.

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<th>MO</th>
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<th>C</th>
<th>C</th>
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<th>C</th>
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<td>40</td>
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<td>11 (2pγ)</td>
<td>16 (2pγ)</td>
<td>20 (2pγ)</td>
<td>10 (2pγ)</td>
<td>6 (2pγ)</td>
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<td>-</td>
<td>-</td>
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<td>6 (2pγ)</td>
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<td>-</td>
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<td>5 (2pγ)</td>
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<td>9 (2pγ)</td>
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<td>-</td>
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<td>18 (2pγ)</td>
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<td>4 (2pγ)</td>
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<td>2 (2pγ)</td>
<td>6 (2pγ)</td>
<td>8 (2pγ)</td>
<td>3 (2pγ)</td>
<td>-</td>
<td>8 (2pγ)</td>
<td>-</td>
<td>10 (2pγ)</td>
</tr>
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</table>
Table 4.6. Vertical excitation energies and oscillator strengths \((f)\) computed for the optically allowed \(^1E\) and \(^1B_2\) excited states of Ni(II)TPTBP in the \(D_{2d}\) conformation and compared to the experimental data.

<table>
<thead>
<tr>
<th>State</th>
<th>composition (%)</th>
<th>(E_{uv}) (eV/(\text{nm}))</th>
<th>(f)</th>
<th>(E_{exp}(\text{eV/(\text{nm}}))^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(5^1B)</td>
<td>(38e\rightarrow40e) (67) (18b_1\rightarrow18a_2) (20) (22b_2\rightarrow24a_1) (8)</td>
<td>3.11 (399)</td>
<td>0.013</td>
<td></td>
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<tr>
<td>(7^1E)</td>
<td>(18b_1\rightarrow42e) (99)</td>
<td>2.975 (417)</td>
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<tr>
<td>(6^1E)</td>
<td>(18b_1\rightarrow41e) (97)</td>
<td>2.877 (431)</td>
<td>0.01</td>
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</tr>
<tr>
<td>(3^1E)</td>
<td>(18b_1\rightarrow17a_2) (86) (38e\rightarrow40e) (8)</td>
<td>2.748 (452)</td>
<td>0.013</td>
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</tr>
<tr>
<td>(5^1E)</td>
<td>(22b_2\rightarrow40e) (58) (38e\rightarrow23b_1) (21) (18b_1\rightarrow40e) (10)</td>
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<td>0.95</td>
<td>2.78 (447) (B)</td>
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<tr>
<td>(4^1E)</td>
<td>(38e\rightarrow23b_2) (76) (22b_2\rightarrow40e) (17)</td>
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<tr>
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<td>(2^1E)</td>
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<td>1.941 (640)</td>
<td>0.21</td>
<td>1.931 (643) (Q)</td>
</tr>
</tbody>
</table>

\(^a\)Spectrum of \(\text{NiTPTBP in toluene, this work}\)

Figure 4.11 presents the computed contour plots of molecular orbitals in the ground electronic state configuration of Ni(II)TPTBP. It can be observed that even the Gouterman porphyrin orbitals \(a_{1u}\) \((18b_1)\) and \(a_{2u}\) \((22b_2)\) have a small amount of electron density placed onto the central metal. Likewise, the lowest occupied metal orbital \(d_{z^2}\) \((23a_1)\) has a substantial amount of mixing with \(p\)-orbitals of pyrrolic nitrogens. G-LUMO orbitals have their electron density almost evenly distributed among metal and porphyrin orbitals (see \(40e_x\) and \(40e_y\) in Figure 4.11).
Figure 4.11. Contour plots of G-HOMO, G-LUMO and metal HOMO and LUMO orbitals of Ni(II)TPTBP.
4.3 DISCUSSION

The excited state dynamics of Ni(II)TPTBP arise from deactivation of the lowest $^1(\pi,\pi^*)$ excited state. The broad transient absorption and the absence of the peaks between 750 and 950 nm indicate that the early-time spectra resemble the lowest $^1(\pi,\pi^*)$ state not a triplet state.\textsuperscript{2,4} Subpicosecond intersystem crossing from $^1(\pi,\pi^*)$ to $^3(\pi,\pi^*)$ was not expected for a porphyrin containing a first-row diamagnetic metal ion,\textsuperscript{2} due to insufficient spin-orbit coupling and an absence of mixing involving unpaired metal and ring electrons. However, considering the fact that stimulated emission has not been detected even at the 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.\textsuperscript{4} Therefore, if the first observed transient (FOT) in our experiments was $^1(\pi,\pi)^*$, stimulated emission would have been observed during the FOT lifetime.

As shown for others nickel (II) porphyrins\textsuperscript{4} the early time kinetics exhibited wavelength dependence and the transient difference spectra shifted to the blue, Figure 4.12. The wavelength dependence of the fast time constants indicates that the FOT is likely to be a metal centered excited state or a (d,d) state having excess of vibrational energy. Eom\textsuperscript{4} has called this state a “hot” (d,d) state. This “hot” metal-centered excited state undergoes a rapid intramolecular cooling process in which the vibrational energy is redistributed among the porphyrin internal modes within 1-2 ps.\textsuperscript{4,18-20} This process is responsible for the fast time constant. Subsequently intermolecular vibrational relaxation takes place involving participation of solvent vibrational modes. This process accounts for the second time constant of 15-25 ps.\textsuperscript{4}
Figure 4.12. A series of spectral cuts from the optical dynamic surface of Ni(II)TPTBP in the time range 1 → 40 ps, normalized at 665 nm maximum to clearly show the time-dependent blue shift.

Then the vibrationally relaxed (d,d) state undergoes vibronic relaxation to the electronic ground state. For regular nominally planar porphyrins, such as Ni(II)TPP the ground state repopulates in 200-300 ps.\textsuperscript{4,21} However, this is not the case for Ni(II)TPTBP which exhibits different sets of lifetimes in different solvents. Additionally, the second lifetime was not resolved when toluene and 2,6-dimethylpyridine were used as solvents (Table 4.7).

Table 4.7 Summary of kinetic data for Ni(II)TPTBP acquired in different solvents; ε- the dielectric constant

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>$\tau_1$ (ps)</th>
<th>$\tau_2$ (ps)</th>
<th>$\tau_3$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.4</td>
<td>~1</td>
<td>-</td>
<td>~20</td>
</tr>
<tr>
<td>2,6-dimethylpyridine</td>
<td>7.3</td>
<td>~1</td>
<td>-</td>
<td>~30</td>
</tr>
<tr>
<td>Butyronitrile</td>
<td>20.7</td>
<td>~1</td>
<td>~20</td>
<td>~150</td>
</tr>
<tr>
<td>DMF</td>
<td>36.7</td>
<td>~1</td>
<td>~20</td>
<td>~800</td>
</tr>
</tbody>
</table>

The lifetime of the relaxed ligand-field excited state of Ni(II)TPTBP varies from several picoseconds in less polar media to hundred picoseconds in more polar solvents (Figure 4.13)
Figure 4.13. Kinetic profiles of the transient absorption signal at 475 nm for Ni(II)TPTBP in different solvents after photoexcitation at 400 nm.

An interesting feature of figure 4.13 is the kinetic traces of the Ni(II)TPTBP excited states in butyronitrile and DMF. In these solvents, the transient absorption signal has a long-lived contribution with a lifetime in the range from 150 to 800 ps. This phenomenon can be explained by the presence of an additional deactivation route that is in competition with the main process involving the (d,d) excited state manifold. The excited state deactivation lifetime dependence on solvent polarity suggests participation of charge transfer states in the overall dynamics. The ground electronic state of Ni(II)TPTBP does not have a dipole moment. The absorption spectra presented in Figure 4.1 did not show significant shifts with increasing solvent polarity. This suggests that nickel (II) ion stays in plane with the macrocyclic core thus canceling any dipole
moments. The DFT computations revealed the presence of two $^3A_1$ and $^3A_2$ ligand-to-metal charge transfer states located close in energy to the $^3(d,d)$ state (Table 4.8)

Table 4.8 Energies of optically silent states responsible for Ni(II)TPTBP excited state deactivation

<table>
<thead>
<tr>
<th>State</th>
<th>composition (%)</th>
<th>Character</th>
<th>$E_{va}$ (eV)</th>
<th>$E_{adia}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1E$</td>
<td>18b$_1$→40e (82)</td>
<td>$\pi\pi^*$</td>
<td>1.941 (Q)</td>
<td></td>
</tr>
<tr>
<td>$^1A_1$</td>
<td>22b$_2$→23b$_2$ (99)</td>
<td>$^1$LMCT</td>
<td>1.881</td>
<td></td>
</tr>
<tr>
<td>$^3A_1$</td>
<td>22b$_2$→23b$_2$ (100)</td>
<td>$^3$LMCT</td>
<td>1.768</td>
<td></td>
</tr>
<tr>
<td>$^3E$</td>
<td>18b$_1$→40e (100)</td>
<td>$^3(\pi\pi^*)$</td>
<td>1.5585</td>
<td></td>
</tr>
<tr>
<td>$^3B_2$</td>
<td>23a$_1$→23b$_2$ (100)</td>
<td>$^3(d_z^2,d_{x^2-y^2})$</td>
<td>1.431</td>
<td>1.076</td>
</tr>
<tr>
<td>$^1A_2$</td>
<td>18b$_1$→23b$_2$ (100)</td>
<td>$^1$LMCT</td>
<td>1.2646</td>
<td>1.116</td>
</tr>
<tr>
<td>$^3A_2$</td>
<td>18b$_1$→23b$_2$ (100)</td>
<td>$^3$LMCT</td>
<td>1.2502</td>
<td>1.100</td>
</tr>
</tbody>
</table>

These LMCT states could be responsible for the lifetime dependence on solvent polarity. Holten at el. have observed this dependence of the excited state deactivation rate on solvent dielectric properties for Ni(II)DPP and Ni(II)T(t-Bu)P.$^3,5$ Holten et al. proposed that since the Ni(II)T(t-Bu)P has dipole moments that are comparable to the dipole moments of solvents, the energies of the various conformers in the ground and excited electronic states will change with respect to the solvent polarity.$^3$ However, this is not the case for Ni(II)TPTBP which shows no dependence of ground electronic state absorption spectrum on solvent polarity. Summarizing all the above, two different excited state relaxation pathways can be proposed: one for the less polar solvents and another for the more polar media (Figure 4.14)
Figure 4.14. Proposed mechanisms of deactivation of Ni(II)TPTBP excited state: A. in nonpolar toluene and lutidine; B. in polar butyronitrile and DMF.
Upon photoexcitation two competing processes depopulate the porphyrin lowest singlet excited state $S_1$. One involves the charge transfer states manifold and another involves the metal excited state manifold. Due to a number of optically silent states between the $S_1$ Q-state and $^3\text{LMCT}$ or $^3(d,d)$ states the nonradiative thermal relaxation and intersystem processes are facilitated and take place in subpicosecond regime. Thus, the FOT might be a superposition of vibrationally hot LMCT and (d,d) states spectra. The early time spectra (blue lines in Figures 4.3, 4.6 and 4.9) showed broad and featureless absorption characteristic of charge transfer and “hot” (d,d) state spectra which superimposed ground state bleaching. This process is essentially independent of solvent polarity and is present in both polar and nonpolar media. Once the LMCT and (d,d) states relax to their excited state potential surface minima they provide two different routes for ground state repopulation (Figure 4.14).

Charge transfer states have much better Franck-Condon factors compared to (d,d) states, the reason being the similar geometries of the former and the ground state, while (d,d) state deactivation involves substantial nuclear rearrangement.\(^3\) Thus LMCT state decay is expected to be much faster than (d,d) state deactivation. Since both LMCT and (d,d) states are populated concomitantly at early times the overall excited state lifetime is determined by the relative contributions and mixing of those states. In nonpolar solvents (toluene and 2,6-dimethylpyridine) the almost degenerate charge transfer and metal centered excited states can effectively mix, thus speeding up the excited state deactivation process. This explains the 20 ps overall lifetime of ground state repopulation (Figure 4.14 A). The overall lifetime in this case is the cumulative rate constant that has contributions from both LMCT and (d,d) states decay. In polar solvents (butyronitrile and DMF) the $^3\text{LMCT}$ state is believed to be stabilized and lowered in energy compared to the $^3(d,d)$ state. In this case the mixing between these two manifolds is disrupted.
Despite the fact that LMCT state is located below the (d,d) state in energy there seems to be little or no $^3(d,d) \rightarrow ^3$LMCT interconversion involved and the resulting lifetimes are comparable to those of the regular porphyrins (150 ps and 800 ps). There could be a substantial energy barrier between (d,d) and LMCT potential state surfaces that prevents such a crossing. In the case of DMF the energy gap between the charge transfer and the (d,d) states increases and the excited state lifetime increases to 800 ps. Thus, two separate routes of ground state repopulation exist in the polar solvents (Figure 4.14 B). The fraction of molecules that deactivate through the LMCT manifold repopulates ground state within approximately 20 ps concomitant with (d,d) state vibrational relaxation process. Therefore, the second time constant reflects the $^3$LMCT state depopulation and the (d,d) state cooling processes. It can be assumed that the longest time constants are the ones of $^3(d,d)$ state directly depopulating to the ground state. The longer (d,d) state lifetime in the case of DMF as a solvent can be explained by either smaller charge transfer state involvement or greater energy barrier that exists between the (d,d) state and ground electronic state surfaces and prevents effective crossing.

The unusual excited state behavior exhibited by Ni(II)TPTBP presumably originates in cooperative contribution of structural distortions of tetrapyrrolic macrocycle induced by extended conjugation and electron rich and bulky meso-substituents. This species has demonstrated very interesting excited state properties that can be tuned by altering the solvent polarity. Thus this molecule becomes a very attractive candidate for studying conformational and electronic factors that govern the excited state behavior of many natural systems containing the porphyrin macrocycle.
4.4 REFERENCES


Appendix A. Glossary of Compounds

Nickel(II) meso-tetra(4-sulfonatophenyl) porphine (NiTPPS)

Nickel(II) meso-tetraphenylporphine (NiTPP)
Ni(II) meso-tetraphenyltetrabenzoporphyrin
(NiTPTBP)