



## Review

# New insight into metalloporphyrin excited state structures and axial ligand binding from X-ray transient absorption spectroscopic studies



Megan L. Shelby<sup>a</sup>, Michael W. Mara<sup>a,b</sup>, Lin X. Chen<sup>a,b,\*</sup>

<sup>a</sup> Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

<sup>b</sup> Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

## Contents

1. Introduction .....	291
2. Photoinduced and ground state ligation of metalloporphyrins: nickel porphyrin case .....	292
2.1. Broad metal centered molecular orbital energy distribution in the ground state and its implications .....	292
2.2. Photoinduced axial ligation dynamics .....	294
2.3. A unified axial ligation mechanism for the ground and excited state nickel porphyrin .....	295
3. Ligand recombination in hemoproteins and iron porphyrins .....	295
3.1. X-ray transient absorption of carbonmonoxy myoglobin photolysis .....	296
3.2. Iron protoporphyrin IX as a model for MbCO, similarities and differences .....	297
4. Summary .....	298
Acknowledgments .....	298
References .....	298

## ARTICLE INFO

### Article history:

Received 8 April 2014

Received in revised form 23 May 2014

Accepted 23 May 2014

Available online 1 July 2014

### Keywords:

Metalloporphyrins

Photodissociation of the ligand

Hemoproteins

Excited state molecular structures

X-ray transient absorption

Catalysis

## ABSTRACT

Metalloporphyrin axial ligation is an important process in catalysis and the enzymatic chemistry of proteins and is metal center dependent. Direct structural dynamics measurements on different metalloporphyrins using X-ray transient absorption spectroscopy (XTA) have brought new insight into this extensively studied process. This review uses two representative open shell metalloporphyrins, nickel tetramesitylporphyrin (NiTMP) and iron protoporphyrin (FePP), to demonstrate the capability of XTA in resolving both electronic and nuclear structures of these porphyrins in axial ligation processes. A surprisingly broad 3d orbital energy level distribution has been related to differences in the conformational distribution of NiTMP in the ground and excited state, which suggests a unified mechanism for axial ligation in open shell metalloporphyrins driven by transient vacancies in the 3d<sub>z<sup>2</sup></sub> orbital, which is aligned with the axial ligation coordinate. XTA studies also show that dynamic and structural differences in the CO dissociation process are influenced by the metal site environments, demonstrated by the comparison of FePP in solution and heme in myoglobin. These results imply a porphyrin conformational control of ligation and therefore insight into metalloporphyrin catalyst design involving control the axial ligation/deligation processes as well as deduction of enzymatic regulation of ligand binding.

© 2014 Published by Elsevier B.V.

## 1. Introduction

Free base and metal containing porphyrins have been studied extensively for decades and a massive well of knowledge of synthesis, structure, excited state and electrochemical properties as well

as a wide range of applications has been accumulated [1]. In particular, these molecules continue to play important roles in solar energy conversion processes, such as dye-sensitizing photovoltaics [2], and photocatalytic reactions [3]. Many of these photochemical processes are triggered by the generation of metalloporphyrins excited states as reactants to deliver energy, electrons, or provide binding sites. Therefore, detailed structural information is necessary for understanding and controlling reactions involving metalloporphyrins. Ultimately, we would like to find ways to control desired catalytic, enzymatic, and photochemical reactions mediated by

\* Corresponding author at: Department of Chemistry, Northwestern University, Evanston, IL 60208, USA. Tel.: +1 847 491 3479.

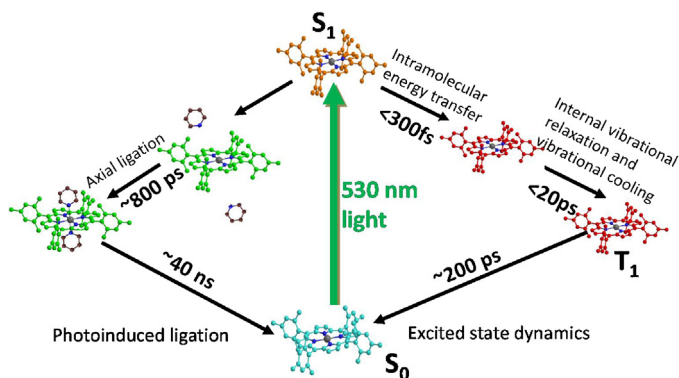
E-mail addresses: [lchen@anl.gov](mailto:lchen@anl.gov), [l-chen@northwestern.edu](mailto:l-chen@northwestern.edu) (L.X. Chen).

metalloporphyrins via variation of the electronic and nuclear structures of the macrocycle. Hence, we need to ascertain the interplay between the electronic properties of the ring and metal by selecting a suitable porphyrin structure or by selecting the environment with which the metalloporphyrin interacts. In catalysis-relevant reactions involving metalloporphyrins, one would like to find a way to drive the electron transfer direction and rates in excited state metalloporphyrins involved in redox reactions. The oxidation or reduction potential of the metalloporphyrin can be modulated by the selection of the metal center in the porphyrin core and by the peripheral functionalization of the porphyrin macrocycle. Moreover, metalloporphyrin functions in the context of their catalytic abilities often involve axial ligation with substrates at the metal site where chemical bond formation and breakage take place. Axial ligation dynamics are strongly metal center dependent based on the metal electronic configuration. Because porphyrin macrocycles can accommodate different metal centers, the ligand binding and dissociation dynamics can vary according to the electronic structure and radius of the metal center. Thus, it is desirable to know the correlation of the electronic and nuclear structures of metalloporphyrin transient states with the redox potentials, metal ligation states, and rates of redox reactions. However, knowing such a correlation is not always feasible due to the poor characterization of the electronic and nuclear structures of these various transient states, which may be photoexcited states. Although optical transient spectroscopic measurements have been used extensively to investigate properties of porphyrin excited states [4–7], they are insensitive to some optically “dark” states that are closely related to metalloporphyrin redox potentials, such as metal centered excited states. These states play important roles in catalytic reactions, but cannot be easily detected via standard optical transient spectroscopic measurements.

The emergence of intense pulsed X-ray sources at third generation synchrotron facilities over a decade ago enabled the capture of metalloporphyrin excited state structures in solution, where much of porphyrin chemistry takes place [8–19]. Many important processes, such as bond-breaking or formation and electron or proton transfer, initiated by light and occurring on the ultrafast time scale can thus be monitored. In the ongoing effort to harness the energy of the sun toward catalysis and energy generation, the goal has been to design synthetic systems with both good coverage of the solar spectrum, absorbing light throughout the visible to near-IR regimes, and the ability to convert light energy into chemical and electronic potential.

X-ray transient absorption (XTA) spectroscopy [10,16,20–22] is essentially the X-ray-probe analog to optical transient absorption spectroscopy or TA. XTA measurements are capable of describing both the electronic and structural properties of a single specific element in a system, which is complementary to what can be obtained from optical TA. XTA measures element-specific local structure around transition metal centers without the need for sample crystallization, which allows one to focus the measurement on a specific part of the system such as a transition metal active site in a protein matrix. Using both TA and XTA together allows for the full characterization of the photophysical properties of a chemical system.

One of the important chemical reactions involving metalloporphyrins is the axial ligation of the metal center which enables key functions in numerous catalytic and enzymatic systems [23–25]. This axial ligation in metalloporphyrins can directly affect the atomic orbital energy levels, and electronic configuration, and the spin state of the metal center, consequently impacting their chemical reactivity [26,27]. For example, photoinduced electron transfer can be realized in a supramolecular system containing an electron donor Zn(II) porphyrin and an electron acceptor Fe(III) porphyrin, but only when the porphyrins have axial ligands such as pyridine, which changes the energy levels in favor of the long distance



**Fig. 1.** Photochemical pathways of NiTMP at the lowest energy excited state,  $S_1$ . The left and right sides represent respectively the reaction pathways in the presence and absence of the axial ligating molecules, such as pyridine.

electron transfer [27]. The excited state relaxation pathways in such systems can also be modulated by the spin state of the iron center which can be altered by ligation of strong and weak field ligands at Fe(III) [28]. In spite of long history of metalloporphyrin research, there were still new aspects of their chemistry discovered in recent XTA studies regarding axial ligation structural dynamics.

In this review, we will focus on recent progress in XTA studies of photoinduced association/dissociation of axial ligands in excited state metalloporphyrins. Two metalloporphyrins are chosen as examples, nickel porphyrin and iron porphyrin, because (1) both have rich photochemistry involving axial ligation governed by both electronic and nuclear structures at the metal centers, which will serve as references for other metalloporphyrins, and (2) the iron porphyrin axial ligation has a direct connection with heme protein enzymatic function in small molecule transport, sensing, and catalytic oxidation. In particular, we will focus on (1) the nuclear structural dependence of 3d orbital energies and their influence in the ligation reactions, and (2) environmental effects in ligand dissociation reactions.

## 2. Photoinduced and ground state ligation of metalloporphyrins: nickel porphyrin case

Although many metalloporphyrins have interesting excited state properties and axial ligation structural dynamics, only two of them have been studied so far by XTA methods which will be reviewed here. One metalloporphyrin studied by XTA was Ni(II) tetramesitylporphyrin (NiTMP), whose analogs were previously investigated by ultrafast TA [29–36], resonance Raman spectroscopy [37–45], previous XTA measurements [18,46–49] and quantum mechanical calculations [49–53] due to their rich photochemical reaction pathways which can be used to understand similar processes in other metalloporphyrins (Fig. 1).

### 2.1. Broad metal centered molecular orbital energy distribution in the ground state and its implications

In the absence of ligating solvent molecules (Fig. 1, right side), the Ni(II) ( $3d^8$ ) in the ground state NiTMP has an approximately square planar geometry with a vacant  $3d_{x^2-y^2}$  orbital (Fig. 2). As for most metalloporphyrins, the initial excited state is created via a  $\pi-\pi^*$  transition of the macrocycle induced by the light from the laser pulse, adding one electron to the  $\pi^*$  orbital and leaving a hole in the  $\pi$  orbital [30]. The electron promoted to the  $\pi^*$  orbitals subsequently transfers to the vacant iron  $3d_{x^2-y^2}$  orbital, while one electron in the originally filled  $3d_{z^2}$  orbitals moves to fill the hole left in the  $\pi$  orbital [29]. The above processes take place in less than 20 ps, resulting in singly occupied  $3d_{x^2-y^2}$  and  $3d_{z^2}$

Download English Version:

<https://daneshyari.com/en/article/7748121>

Download Persian Version:

<https://daneshyari.com/article/7748121>

[Daneshyari.com](https://daneshyari.com)