CHAPTER 1

INTRODUCTION

1.1 Background

Since the first discovery of macrocyclic compounds in the 1960's, researchers have been working to develop and produce new macrocycles for a variety of applications. Macrocycles are highly demanding compounds in many areas, especially in catalysis, bioinorganic, coordination chemistry and the medical field due to their diverse chemical properties. Tetraaza macrocyclic ligand containing nitrogen atoms easily reacts with many types of organic and inorganic compounds. Besides, it has a high tendency to form coordination bond with transition metal ions. However, there is an inherence challenge in synthesis tetraaza macrocyclic ligand using the metal template method as not all metal ions can act as templates during cyclisation process. Besides, it is also very hard for the metal ion to be removed from the complex during demetallization process to obtain a free ligand.

Therefore, Bohari and his team devised a novel method that involves preparing free macrocyclic ligand before converting it into a metal complex in a simple step with a promising yield (Hassan et al., 2014). The discovery of the non-template method of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium salts ligand has widened the complexation reaction with various transition metal ions such as copper, nickel, and zinc complexes (Fairus et al., 2015). In addition, the ultraviolet (UV)-visible spectrometric analysis indicated the existence of the azomethine chromophore and the intense *d-d* transition indicates that the metal complex was successfully maintained in its original tetraaza ligand structure. Hence, this research utilizes the theoretical approach to understand the metal-ligand during complexation, the structural, electronic, and optical properties of the Pd(II) tetraaza macrocyclic ligand as a cationic compound. Pd(II) ion acts as central metal ion because it provides empty orbitals to be shared with tetraaza macrocyclic ligand, hence indirectly elevating the probability of electron transfer during the excitation process.

Based on recent research, metal complex is actively explored as promising material for optoelectronic potential application since it has non-linear optical properties (NLO) such as switchable, tuneable, and multi-dimensional structure. In addition, the polarity of the solvent also influences the NLO properties of metal complex. This happens when the polarity of solvent combined with a proper structural design can lead to extraordinary NLO properties. Compared to the organic species, the square-planar metal complexes have electron-donating ability which is expected to demonstrate non-linear optical behaviour (Fackler et al., 1999). Therefore, this work further examines the optical response of Pd(II) complex in different solvation media at excited state using TD-DFT approach.

1.2 Problem Statement

The conventional preparation of such complexes mentioned above contains drawbacks of multistep, expensive supply and lower yield. The demetallization for the template method was also found to be difficult (Edwards et al., 2011). Recent experimental studies have reported the successful template-free synthesis of protonated tetraaza macrocyclic ligand and metal complex as cationic compounds (Chandra et al., 2005b) (Tseberlidis et al., 2019). However, until today, there are limited theoretical studies that specifically reported on metal-ligand interaction during complexation, structure of protonated tetraaza macrocyclic ligand and cationic Pd(II) tetraaza macrocyclic complex. As a result, this research aims to provide better understand the role of protonated tetraaza macrocyclic ligand in the complexation process with Pd(II) ion, as well as to investigate their structural behaviour using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. Besides, it is also aims to explore the electronic and optical properties of Pd(II) tetraaza macrocyclic complex. This is because metal complex containing tetraaza macrocyclic ligand is a growing material for optoelectronic applications (Alsharari et al., 2020) (Al-Zubaidi et al., 2020). Hence, this research identifies the potential of Pd(II) tetraaza macrocyclic ligand as optoelectronic material by providing a breadth of view of how its electronic and optical properties at excited state response towards different solvation polarity.

1.3 Research Question

1. What is the factor influence Pd(II) metal to be fit at the centre of the tetraaza macrocyclic ligand?
2. What is the energy gap for electron transfer of Pd (II) tetraaza macrocyclic in the time-dependent system?
3. What is the implication of the optical properties of Pd (II) tetraaza macrocyclic by using different solvent polarity at excited states?

1.4 Hypothesis

1. The presence of lone pair at each N atom from the tetraaza macrocyclic ligand will guide the Pd(II) to occupy the centre of the macrocyclic ligand.

2. Small excitation energy will be released during intramolecular charge transfer in response to external perturbation at excited state.
3. The increase in solvation polarity may enhance the optical properties of Pd(II) tetraaza macrocyclic complex.

1.5 Objectives

This research has the following objectives:

1. To determine the structural and electronic behaviour of tetraaza macrocyclic ligand and Pd(II) tetraaza macrocyclic complex at ground state using DFT calculation.
2. To calculate the optical properties of Pd(II) tetraaza macrocyclic complex at excited state using TD-DFT calculation.
3. To measure the optical properties of Pd(II) tetraaza macrocyclic complex at excited state using various solvents conditions via polarizable continuum model.

1.6 Scope of Research

The purpose of this research is to determine the structural behaviour of tetraaza macrocyclic ligand and its complex using DFT. The initial structure of tetraaza macrocyclic ligand and its complex were optimized using a different level basis set to determine their lowest conformation energy and then the optimized structures will be analysed through geometrical parameters such as bond length and bond angle. Next, the metal-ligand interaction of Pd(II) tetraaza macrocyclic complex was examined from the electronic properties such as natural bond orbital (NBO), molecular electrostatic potential surface (MEPS), and surface contour. Besides, the aim of this research is to calculate the optical properties of Pd(II) tetraaza macrocyclic complex at excited state using TD-DFT calculation. The structure was optimized at gas phase and important output such as HOMO-LUMO, energy gap, hyperpolarizibility and dipole moment will be extracted. Finally, the optical responses on Pd(II) tetraaza macrocyclic complex were analysed via various solvent (hexane, chloroform, methanol, acetonitrile, water) by applying IEF-PCM.