# SYNTHESIS, CHARACTERIZATION AND EVALUATION OF PHOTOPHYSICAL AND ELECTROCHEMICAL PROPERTIES OF RUTHENIUM(II) COMPLEXES FOR DYE-SENSITIZED SOLAR CELLS

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University of Fort Hare Together in Excellence

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Being a thesis submitted to the Faculty of Science and Agriculture in fulfilment of the requirements for the degree of

**Doctor of Philosophy in Chemistry** 

Of the

**University of Fort Hare** 

Supervisor: Professor P. A. Ajibade

Co-supervisor: Professor O.O Oyedeji

January, 2018

## DECLARATION BY CANDIDATE ON PLAGIARISM

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This is to certify that this research is a record of original work carried out by Shadrack John ADJOGRI under our supervision in the Inorganic Material Research Laboratory of the Department of Chemistry, University of Fort Hare in fulfilment of requirements for the award of Doctor of Philosophy in Chemistry.

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## **DEDICATION**

TO GOD, THE FATHER AND JESUS CHRIST, THE SON AND GOD, THE HOLY SPIRIT. THE ALMIGHTY GOD, THE HOLY ONE OF ISRAEL, THE ANCIENT OF DAYS, THE JESUS CHRIST OF YESTERDAY TODAY AND FOREVER, THE SHEPHERD AND BISHOP OF MY SOUL WHO HAS MADE THIS RESEARCH WORK POSSIBLE TO HIM BE GLORY FOREVER AND EVER! AMEN!

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## List of Abbreviations

NMR	nuclear magnetic resonance
ATR-FTIR	attenuated total reflectance fourier transform infrared
UV-VIS	ultraviolet-visible
PL	photoluminescence
IR	infrared
MLCT	metal-to-ligand charge transfer
LC	ligand centre
MC	metal centre
DMSO	dimethylsulfoxide
NCS	thiocyanate
H <sub>2</sub> dcbpy	4,4'-dicarboxylic-2,2'-bipyridine
LUMO	lowest unoccupird molecular orbital
НОМО	highest occupied molecular orbital
DSSC	dye-sensitized solar cell
TiO <sub>2</sub>	titanium dioxide
CSP	concentrated solar powers
bdmpmaa	N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl)-anthranilic acid (L1)
bdmpmeta	N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl)-4-methoxy-2-nitro
	aniline (L2)
bdmpmal	N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl) aniline (L3)
bdmpmt	N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl) toluidine (L4)
bdmpmcy	N,N-bis(3,5-dimethylpyrazol-1-yl-methyl)cyclohexylamine (L5)
bdmpmas	N,N-bis(3,5-dimethylpyrazol-1-yl-methyl) anisidine (L6)
vpdiinp	11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (L7)
vpbpp	4-(4-Vinylphenyl)-2.6-bis(phenyl)pyridine (L8)
vptpy	4-(4-Vinylphenyl)-2,2':6'2''-terpyridine (L9)

#### ABSTRACT

Eight series of thirty (30) novel heteroleptic ruthenium(II) complexes were designed, synthesized and spectroscopically characterized, with the following general molecular formulae as [Ru(bdmpmar)(H<sub>2</sub>dcbpy)(NCS)]<sup>+</sup>, [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2,+</sup>, [Ru(bdmpmar)(vpbpp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)(NCS)]<sup>+</sup>,

 $[Ru(H_2dcbpy)_2(N^{*})_2]^{2+}$ ,  $[Ru(H_2dcbpy)(N^{)}_2(NCS)_2], [Ru(H_2dcbpy)(N^{)}(NCS)_3]^$ and  $[Ru(vptpy)(H_2dcbpy)(N^{^})]^{2+}$  where *bdmpmar* is a tridentate ligand of N,Nbis(3, 5-dimethylpyrazol-1-yl-methyl) aromatic organic compound (such aromatic organic compounds(Ar) are anthranilic acid, 4-methoxy-2-nitroaniline, aniline, toluidine, cyclohexylamine and anisidine), *vpdiinp* represents a monodentate ligand of 11-(4-vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine, vpbpp represents a monodentate ligand of 4-(4-vinylphenyl)-2.6-bis(phenyl)pyridine and *vptpy* represents a tridentate ligand of 4'-(4-vinyl)-2,2':6',2''-terpyridine. Meanwhile, N<sup>^</sup> represents any of the monodentate ligands of either *vpdiinp* or *vpbpp* and (N^^^) represents any of the monodentate ligands either of *vpdiinp* or *vpbpp* or NCS as disclosed in series VIII. The complexes were characterized by conductivity measurement, solubility, melting point, UV-Vis, PL, FTIR (ATR), NMR, Cyclic and square wave voltammetry. Nine chelating ligands, comprising of six (6) tripodal chelating ligands, two (2) vinyl monodentate ligands and one (1) vinyl tridentate ligand, were used for the synthesis of ruthenium(II) complexes.

ATR-FTIR spectra of all the ruthenium(II) complexes measured as solid samples, exhibited fine resolution IR bands in region between 3473-3438 cm<sup>-1</sup> of carboxylic group in H<sub>2</sub>dcbpy. The bands in the range 3040-2950 cm<sup>-1</sup> were ascribed to C-H bond

stretching for the CH<sub>3</sub> groups. The coordination of NCS group in the sphere of ruthenium(II) complexes related to series I, IV, VI VII and one compound of series VIII was investigated by ATR-FTIR spectroscopy. Bands in the range of 2116-2106 cm<sup>-1</sup> and 777-770 cm<sup>-1</sup> are ascribed to the respective N=C and the C=S bond stretching vibration which confirms the N-coordination of the SCN group. For all the complexes, the stretching vibration of Ru-N bonding was between 466 and 411 cm<sup>-1</sup> due to coordination of the nitrogen atoms of the ligands to ruthenium central metal atom.

The introduction of the two vinyl monodentate ligands (*vpdiinp* and *vpbpp*) in the coordination sphere of [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>, [Ru(bdmpmar) (vpbpp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)(NCS)]<sup>+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)<sub>2</sub>]<sup>2+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)<sub>2</sub>]<sup>2+</sup>, [Ru(H<sub>2</sub>dcbpy)(N^)<sub>2</sub>(NCS)<sub>2</sub>], [Ru(H<sub>2</sub>dcbpy)(N^)(NCS)<sub>3</sub>]<sup>-</sup> and

[Ru(vptpy)(H<sub>2</sub>dcbpy)(N<sup>^^</sup>)]<sup>2+</sup> respectively, all related to series II, III, IV, V, VI, VII and two compounds of series VIII ruthenium(II) complexes, has been studied using the <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy techniques. The <sup>1</sup>H NMR spectra of series II-VII and the two compounds of series VIII of the ruthenium(II) complexes show multiplets in the aromatic region above 6 ppm due to the presence of either *vpdiinp or vpbpp* ligand, situated in different magnetic environment. However, no splitting pattern was observed in series I and part of VIII complexes possibly due to the absence vinyl monodentate subunits (*vpdiinp* and *vpbpp*) in series I and one of compound in series VIII ruthenium(II) complexes show no signals of complex splitting patterns. Carbon-13 NMR spectra data of series I to VIII ruthenium(II) complexes show most resonance signals range in the aromatic region of ( $\delta$  116.54-199.63ppm) corresponding to the molecular formulation of ruthenium(II) complexes

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incorporating 4,4-dicarboxy-2,2'-bipyridine, bdmpmar, *vptpy*, *vpdiinp or vpbpp* and NCS ligands respectively, depending on the intrinsic ligand variations. Carbon-13 NMR spectra data of series I, IV, VI VII and one compound in VIII show resonance peaks within the range 130-135 ppm are ascribed to NCS ligand confirming the presence of N-coordinated thiocyanate.

Cyclic voltammograms of series I-IV and VI-VIII complexes display ruthenium-based oxidative peaks and the pyridines ligand-based reductive peaks. The redox behavior of complexes **4-12**, **14-16**, **18-20**, **24-26** and **30** is dominated by the Ru(II)/R(III) redox couple in region ( $E_{1/2}$  between 0.53 and 1.18) and the pyridines ligand-based redox couples in the region between ( $E_{1/2}$  between -0.25 and -1.45).

The photophysical property studies of the Ru(II) complexes are determined through the acquisitions of the absorption spectra, which tends to have profound effect on the short circuit current of DSSC. The absorption maxima were tuned by the introduction and variation of six (6) tripodal chelating ligands, two (2) vinyl monodentate ligands and one (1) vinyl tridentate ligand. From the studies, the results show that series IV, V, VI, VII and VIII complexes of molecular formula [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)(NCS)]<sup>2+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)<sub>2</sub>]<sup>2+</sup>, [Ru(H<sub>2</sub>dcbpy)(N^)<sub>2</sub>(NCS)<sub>2</sub>]<sup>2+</sup>, [Ru(H<sub>2</sub>dcbpy)(N^)(NCS)<sub>3</sub>]<sup>2+</sup> and [Ru(vptpy)(H<sub>2</sub>dcbpy)(N^^)]<sup>2+</sup> respectively, have higher and multiple local absorption maxima near-IR region than the complexes of series I, II and III of molecular [Ru(bdmpmar)(H<sub>2</sub>dcbpy)(NCS)]<sup>2,+</sup>, [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2,+</sup>, [Ru(bdmpmar)(vpbpp)(H<sub>2</sub>dcbpy)]<sup>2,+</sup> respectively.

#### **CHAPTER ONE**

### **1.0. INTRODUCTION AND LITERATURE REVIEW**

#### **1.0.1 Introduction**

For many people, a typical day starts by turning on the lights, cooking breakfast and taking our bath with warm water. Essentially, human activities depend on the huge supply of energy [1]. Global advancement in science and technology has placed a great demand on the use of electricity [2]. Therefore, energy is important to human development including other areas such as the ecosystem, technology, medicine etc [3].

Energy is defined as the driving force of either physical or chemical processes that directly convert matter to products or equally energizes global cycles serving as a determinant for environmental phenomena [4]. Generally, energy sources can be broadly classified into renewable and non-renewable energy types. Renewable energy is replenishable and sustainable in economic, social and environmental provisions. It is important because of its capacity to provide cost-effective energy to remote communities without fossil generation [5]. Examples of natural renewable energy include sunlight, wind, geothermal, ocean thermal, tidal and biomass [6]. They should be the renewable energy sources supply 14% of the total world energy demand [6, 7]. Non-renewable energy cannot be replenished and its persistent use will eventually lead

to physical or economic depletion [8]. The sources of non-renewable energy are oil, coal, natural gas and nuclear energy [9].

At present, fossil and mineral fuels alongside with nuclear and hydroelectric sources are our main energy sources for human activities. These main energy sources have adverse effects on the environment because they cause global warming, ozone layer depletion, ecological devastation and biosphere and geosphere destruction. Around the world, conventional fossil fuel consumption has recorded 80% weight of carbon dioxide emissions and thereby, considered to be a challenge to our global existence [10].

Nuclear energy is a useful source of energy in most developed countries. However, a series of nuclear disasters has occurred in several nuclear power stations especially those of Three Mile Island, USA (1979), Chernobyl, Ukraine (1986) [11]. Recently, a disaster triggered by the earthquake and tsunami in Japan in March 2011 has earned great concern and interest around the world of the risk involved in producing nuclear energy [2, 12]. The health hazards experienced by victims because of accidental discharge of radioactive material from nuclear reactor as well as the controversy over the problem of radioactive waste disposal have led to substantial world-wide opposition to the use of nuclear energy [13].

As a result, governments of most countries have granted financial support for alternate energy sources as a means to mitigate the adverse environmental effects. Hence, these initiatives will help promote safe and benign environment. Renewable sources of energy are promising candidates and serve as alternate sources of energy. Among the wide variety of renewable sources of energy, solar energy has attracted considerable attention. Previous research indicates that the world's current energy needs using solar cells with 13% power conversion efficiency at full sun illumination [2].

#### 1.0.2 The Sun

The sun is the primary source of energy for most life found on earth [14, 15]. It consists of hot gaseous matter enveloped spherically with a diameter of  $1.39 \times 10^9$  m and takes duration of 8 min and 20 s to strike our planet. Also, it is  $1.5 \times 10^{11}$  m away from the planet with an effective blackbody temperature of 5762 K. At the central region of the sun, the temperature is much higher and estimated at  $8 \times 10^6$  to  $40 \times 10^6$  K. The sun's surface is 63 MW/m<sup>2</sup> which is equivalent to the sun's total energy output of  $3.8 \times 10^{20}$  MW emitting along all courses. Usually, the Sun with a small portion of  $1.7 \times 10^{14}$  kW is intercepted by the earth. And it is estimated that 30 mins of striking the earth's surface is equivalent to the world energy demand per year [16].

The sun emits solar energy having the largest global renewable energy source [17]. Solar energy is of tremendous benefits to our society. These benefits are based on vast expansion of energy supply, provison of thermal energy to heat the houses of people and drastic reduction in the world's dependence on other sources of energy [14, 15]. Hence, the channels for exploring the applications of solar energy in different areas were investigated with the view to improving utilization efficiency:

- Natural Photosynthesis- Plants convert solar energy to chemical energy to provide human vitality.
- Photovoltaic devices (artificial photosynthesis) Solar cells convert sunlight to generate electrical current. A typical example is the dye sensitized solar cells
- Photoelectrochemical cells convert solar energy into chemical fuels. A typical example is the water splitting process to produce hydrogen fuel, a clean energy.
- Photocatalysis process (application is familiar in environmental pollution)- solar energy is trapped and converted to excite a series of redox reactions to photodegrade pollutant molecules [17].

#### 1.0.3. Solar energy conversion cycle

Solar energy conversion pathway can be identified through two different routes such as solar thermal and solar photovoltaic routes respectively. Solar-thermal devices such as solar collectors and receivers are used for the conversion of solar energy to thermal energy. The creation of Photovoltaic (PV) direct current (DC) electricity is converted to alternating current (AC) or stored for subsequent use [18]. Solar energy irradiation is transient that can be captured and converted into useful forms that carry the energy. These energy carriers are heat, electricity and fuels as shown in fig 1.1. Heat is the lowest form of energy because all other forms of energy are converted into it. Electricity is a carrier with property of high energy value. Fuels are carriers with property of high energy density [19].



Figure 1.1 The solar energy conversion cycle [19]

Fig 1.1 shows the conversion of solar energy into heat, electricity and fuels that can be used further as energy carriers whereby heat transforms into electricity by using technologies such as a steam turbine or a stirling engine known as concentrated solar powers (CSP) or fuels by high temepature (above 500 °C) thermochemical cycles.

Solar electricity can be used to produce a fuel in an electrolyzer and can generate electricity in fuel cells. However, in each step there are energy losses.

#### **1.0.4** What are Photovoltaics?

Photovoltaics, also called "Solar Electricity", is an alternative route to obtaining electrical energy without the consumption of fossil fuels (coal, oil or natural gas), or by means of nuclear energy [19]. The photovoltaic cell is a conventional solar cell, invented in the 1950s [20-23]. The word "Photovoltaic" coined from 'photo' means light and 'voltaic' having its state in chemical potential difference that occur in material following absorption of sunlight [24]. Photovoltaics is defined as the technology that generates electricity in watts (W) or kilowatts (kW) from semiconductors through the absorption of photons [25]. The semiconductor made of crystal silicon performs dual processes simultaneously such as absorption of light and the separation of electric charges. The absorption of light by the crystals results in the formation of charges, electrons and positively charge holes but the electrons and holes are excited to higher energy level. The use of highly pure and defect-free silicon is ensured to prevent the recombination of electrons and holes [26]. At present, Photovoltaic technology has technically and commercially grown to generate and supply electricity based on both short and long time measures [27].

#### 1.0.5 Classification of solar cells

Through the process of photovoltaics, solar cells are devices that directly convert light into electrical energy. These solar cells are broadly divided into three generations [28-31]. The first generation solar cells are the silicon-based phovoltaic, examples are the monocrystalline and polycrystalline solar cells. Due to its high efficiency, these solar cells have a wider market distribution despite the high manufacturing cost. The second generation solar cells, also known as thin-film solar cells, are significantly cheaper to manufacture than the first generation cell, but have lower efficiency; examples include Amorphous silicon (a-Si), cadmium telluride (Cd-Te), Gallium arsenide (Ga-As) and copper indium gallium selenide (CIGS). These inorganic materials used in both generations are not environmentally friendly and cost effective. Thus, Scientist developed the third generation solar cells to overcome the respective problems. The third generation solar cells are the excitonic solar cells, broadly divided into nanocrystalline, dye-sensitized solar cells (DSSCs) and organic/polymer solar cells. Of these, dye-sensitized solar cells are on the verge of commercialization [31, 32]. Figure 1.2 depicts the photovoltaic material chart showing simplified classification model.



**Figure 1.2:** A Photovoltaic material chart showing a simplified classification model [27].

#### 1.0.6. Dye sensitized solar cells

Dye-sensitized solar cells are devices that convert sunlight into electrical energy based on the sensitization of the broad band-gap of semiconductors [32-35]. It is a low cost alternative to conventional inorganic photovoltaic device [36-45]. And It is said to be a non-conventional solar electric device, also known as Gratzel cell, invented by Michael Gratzel in 1991 [36, 46, 47]. Photochemistry is the discipline underlying the non-conventional dye-sensitized solar cells rather than solid state physics for conventional solar cells [46]. The main attractive characteristics attributed to today's dye solar cell are as follows: low cost of fabrication, semi transparency, tunable properties, flexibility and light weight, application and integration to wide variety of devices [48]. The major idea behind this technology is to mimic the natural process of photosynthesis in a cost-effective and easily manufacturable pattern. The fabrication and operating principle of a DSSCs are entirely different from those of first and second generation solar cells [49]

#### **1.1. Historical Background of DSSCs**

The photoelectric effect was discovered by a French scientist named Edmund Becquerel in 1839 [50, 51]. The research reflected on the illumination of solutions containing a metal halide salt which produced a current between two platinum electrodes immersed in the electrolyte. In 1837, Daguerre [52] made the first photographic images. While Fox Talbot [52] made the silver halide process in 1839. Gurney and Mott [52] succeeded in formulating the art of silver halide to become a scientific procedure in 1938 [52].

Through his work on dye at Berlin, Hermann Wilhelm Vogel [53,54]. studied the first panchromatic film rendered on the image of a scene relating to different parts of the light by associating dyes with silver halide in 1873 [53, 54]. In the subsequent year, Sir William de Wiveleslie Abney [55] proceeded to achieve the sensitization of photographic emulsion with a benchmark of passing the whole optical solar spectrum from violet to infrared. After a century, the application of sensitization to
photoelectrochemical systems became the main subject of research recognition. However, in the sixties and seventies, there was a lingering debate on the issue of energy or electron transfer mechanism due to photosensitization. Thus, it was agreed the sensitization process involved electron (or hole) injection from the excited state of the dye rather than energy transfer [55]. The experiment of Gerischer and Tributshch [56] in 1968 gave the evidence of electron transfer mechanism instead of the competing energy transfer mechanism by using electrochemical methods to measure current under illumination while initial reports measured conductance [56].

During the early 20<sup>th</sup> century, the photography industry witnessed lot of activities on the sensitization of low band gap semiconductors to extend their visible absorption to the red absorption wavelengths. Putzeiko and Trenin [56], in 1949, gave the first experimental proof of sensitization of a wide band-gap semiconductor by excluding absorption of visible light. Their research was on photoconductivity of pressed ZnO powder based on a variety of organic dyes such as rhodamine B and eosin exposed to visible light. In 1968, Gerischer and workers [56] improved on the studies by reporting current voltage characteristics using electrochemical cell composed of a crystal ZnO and solution having organic constituents such as fluorescein, rose bengal or pseudoisocyanine chloride. Through the characteristics of electrochemical, the earliest versions of a DSSCs came into existence [56]. In 1991 Brian O'Regan and Michael Grätzel [51] had a breakthrough in making a new prototype solar cell using an idea based on biomimetics, particularly mimicking the photosynthesis process in plants. This prototype of solar cell is known as a dye-sensitized solar cell [51]. The breakthrough made in dye-sensitized solar cell was also accompanied with the establishment of TiO<sub>2</sub> nanoparticle on the basis of photoanode possessing a large surface area. The TiO<sub>2</sub> porous film, being coated with a thin layer of dyes, preferentially collects the photogenerated electrons from the dyes [57]. The first dye sensitized solar cell has a power conversion efficiency of 7.1% under the irradiation of AM 1.5. Meanwhile, researches are still on course to improve the efficiency [57-60].

### **1.2. DSSCs operating principles**

The DSSC has popularly become the most important alternative to conventional silicon solar cells and Gratzel as well as coworkers [61-65] reported 10% conversion efficiency of the Dye- sensitized solar cell [61-65]. The Dye solar cell consist of (i) photoelectrode with porous nanocrystalline TiO<sub>2</sub>, (ii) Dye phtosensitizer (iii) The electrolyte (iv) Counter electrode. The operation of the DSSC involves the utilization of the photoelectrode sintered with a thin film of porous nanocrystalline TiO<sub>2</sub> nanoparticles anchored with a ruthenium complex as the dye-sensitizer, which harvests the light energy. The excitation of the dye by photons leads to a fast injection of electrons into the conduction band of TiO<sub>2</sub> and then the photo generated electrons pass through the interconnecting network of TiO<sub>2</sub> particles and are collected by the

conducting glass substrate. At this stage, the dye is oxidized, thereby regenerated by electron donation from the electrolyte solution which is usually an organic solvent containing the iodide/triiodide redox couple. The triiodide ions formed in this regeneration process diffuse to the counter electrode, where they are rapidly reduced to iodide ions by capture of the electrons migrating from the external circuit. The DSSC optimally generates electric power from light without undergoing any permanent chemical transformation [65-68].



Figure 1.3: Schemetic Structure of Dye Sensitized solar Cells [70]

### **1.3.** Components of dye sensitized solar cells

The DSSCs consist of five major components: (1) transparent conducting substrate (2) nanocrystalline semiconductor film (3) dye photosensitizers (4) redox couple electrolyte and (5) counter-electrode [71-74].

### **1.3.1.** Transparent conducting substrate

Transparent conductive oxides (TCOs) are known to have wider applications in optoelectronics and solar cells because they give integrated physical features of visible light transmittance for light harvest and electrical conductivity for receiving current. Thus, TCO is an essential material for solar cells [75]. Up till now, the commonly used TCOs materials in DSSCs are indium tin-doped oxide (ITO), fluorine-doped tin oxide (FTO), aluminum-doped zinc oxide (AZO) [76-77] and indium zinc oxide [77]. For DSSCs, TCO coated on glass or transparent flexible polymer foils are mainly used as substrates. Basically, Using a layer of transparent conducting oxides (TCOs) such as fluorinedoped tin oxide (FTO, SnO<sub>2</sub>:F) is coated on glass to form a nanoporous layer with a dimension of 10µm thickness and containing 10-20 nm radii particles of titanium dioxide TiO<sub>2</sub>. Meanwhile a layer of an organic dye, usually ruthenium complex ion, is coated on the  $TiO_2$  forming the photoelectrode [78]. Similarly, the conducting glass substrate is used in coating with Pt in forming the counter [80]. So far the fluorinedoped tin oxide (FTO, SnO<sub>2</sub>:F) glass substrate has given the best power conversion efficiency of 11% [81].

The standard choice for TCO coated on glass is obtained due its excellent transmittance (about 90%) in visible wavelength and high electrical conductivity (~ $10^{-4} \Omega$ -cm) [82]. However, the glass substrates have some clear limitations such as inflexibility, fragility, heavy weight, and high price. Therefore, the need on alternative flexible, lightweight and cost-efficient substrates such as plastics has been advocated for in order to enhance DSSC technology. The conductive plastic substrates such as indium doped tin oxide-coated polyethyleneterephtalate (ITO-PET) or polyethylenenaphtalate (ITO-PEN) are most widely used as substitute for glass substrates in DSSCs [83].

The main setback noticed with plastics towards the development of DSSCs is the coating of TiO<sub>2</sub> film on the substrate. Using the traditional batch process of blade coating or screen-printing, a colloidal TiO<sub>2</sub> suspension is coated onto a glass substrate. Then, the films are annealed at high temperatures, 450 °C for 30 minutes. An electrically-connected network of TiO<sub>2</sub> network is formed with the aid of the sintering process of removing the organic binder and solvent. But in the fabrication of ITO–PET electrode, the thermal treatment is restricted to 150 °C, above this temperature polymer is seen to undergo thermal breakdown, loss of transparency and complete distortion. Thus, poor adhesion leading to reduced electrical contact becomes a problem due to coating of TiO<sub>2</sub> films on ITO–PET substrate at 150 °C. Due to the low annealing temperature, the organic residue is excluded because it increases the contact resistance at the interface and lowers the intake of dye on a large surface area [84, 85].

Since the traditional batch process requires elevated temperature for coating  $TiO_2$  on plastic substrates, several groups have suggested new methods. The press method was first introduced by Hagfeldt and coworkers [86] as an alternative means of fabrication whereby the semiconductor  $TiO_2$  films were continuously pressed onto the plastic substrate at low-temperature that enhanced the preparation of nanostructured  $TiO_2$ photoelectrodes; thereby achieving an efficiency of 5.5% under  $10 \text{mW/cm}^2$  (0.1 sun) irradiation. Subsequently, the lift-off process was developed by Durr and coworkers [86] as another possible way whereby the  $TiO_2$  layer was initially deposited onto a thin gold layer on a glass substrate to ensure that the gold layer dissolved completely. Then, the TiO<sub>2</sub> layer was transferred onto an ITO-coated PET film by application of high pressure thereby obtaining an efficiency of 5.8% under 100 mW cm<sup>-2</sup> (1 sun) [86, 87]. The press method was also developed by Yamaguchi and coworkers [87] as an endorsement to earlier development whereby an efficiency of 8% was obtained from such highly efficient 0.25cm<sup>2</sup> -sized plastic-substrate dye-sensitized solar cell under100 mW/cm<sup>2</sup> (AM 1.5,1 sun) while the fabrication of a 1.111cm<sup>2</sup>-sized plasticsubstrate DSSC had an efficiency of 7.6% [87]. Another report on the use of Ti-metal foil substrate and a Pt-electrodeposited counter electrode on ITO/polyethylene naphthalate (ITO/PEN) was given by Gratzel and coworkers [88] to show that metal foils are potential flexible substrates. Thus, an efficiency of 7.2% under back illumination was recorded accordingly [88].

#### 1.3.2. Nanostructured semiconductor titanium(IV) oxide

When a material has electrical conductivity between those of conductor (such as metals) and insulators (such as ceramic), it is simply called a semiconductor. The rise in temperature of a semiconductor leads to increase in conductivity. The basic electronic property of semiconductor is featured by its valence band (VB) and conduction band (CB). The formation of the valance band is based on the interactions of the highest occupied molecular orbital (HOMO), while the formation of the conduction band is based on the interaction of the lowest unoccupied molecular orbital (LUMO). Electron state is absent between the top of the VB and the bottom of CB. The forbidden bandgap (also called energy gap or bandgap) is the energy range between CB and VB. This is usually denoted as Eg. The light absorption property as well as the redox capability of a semiconductor is determined by its unique features of band structure, bandgap and the positions of VB and CB [89]. Fig 1.4 shows the photo absorption transition of VB and CB of a semiconductor. The major function of a semiconductor is to serve as an electrode due to its photoelectrochemical properties of the semiconductor electrolyte interface; that is, the generation of current following exposure to electromagnetic radiation (for example solar energy conversion) [91].

# Surface ?



**Figure 1.4:** Photoabsorption by transition of electrons in the valence band (VB) to the conduction band (CB) in a semiconductor [90].

Several nanostructured semiconductors metal oxides such as TiO<sub>2</sub> [92-106] ZnO [107-119] SnO<sub>2</sub> [120-129], In<sub>2</sub>O<sub>3</sub> [130], Nb<sub>2</sub>O<sub>5</sub> [131-133] WO<sub>3</sub> [134&135], Fe<sub>2</sub>O<sub>3</sub> [136], Zn<sub>2</sub>SnO<sub>4</sub> [140] and SrTiO<sub>3</sub> [141] have been investigated as martials for photoelectrode in DSSCs. TiO<sub>2</sub> is considered to be the best metal oxide so far in DSSCs owing to charge separation and transport including its potential attributes: (i) the ability getting mesoporous particles with ease (ii) the formation of band alignment with various organic and inorganic dyes and (iii) the ability to be stable [142]. TiO<sub>2</sub> is a member of the 3d family of transition metal oxides [143-146]. In the valence and conduction band, TiO<sub>2</sub> shows a divergent parity of electrons, that is, an electronic configuration owing to the hybridization of oxygen 2p states with titanium 3p states in the valence band, and pure 3d states in the conduction band. Hence, the electron configuration helps to favour efficient current collection as well as reducing the impact of electronhole recombination [145]. The physical properties of  $TiO_2$  include high dielectric constant (60 – 80), high refractive index approximate value 2.6, conductivity  $\sim 0.3$ micro S / M, low cost, non-toxicity, chemical and thermal stability, transparency to visible light, wide band gap ~ 3.0 - 3.5 eV, ensuring absorption UV light with no absorption in the visible region [144]. TiO<sub>2</sub> exists in three crystalline natures such as anatase, rutile and brookite [147-150]. Rutile phase is highly thermodynamically stable while anatase and brookite phases are metastable and the conversion of the respective phases to rutile phase can occur through heating. The attributes of higher refractive index, higher dielectric constant, higher electric resistance and higher chemical stability, makes rutile phase more preferable than anatase phase. The rutile TiO<sub>2</sub> is useful in the electronic industry due to high dielectric constant and high electrical resistance. Hence, it is used as capacitor, filter, power circuits and temperature compensating condenser [151]. However, DSSC investigation shows that anatase particles prepared by hydrothermal synthesis gave higher performance than rutile particles. In the laboratory, the brookite phase research is scarce due the rigorous preparation stages [152].

## 1.3.3. Dye sensitizers

Dye sensitizers are light absorbing materials attached to a wide band gap semiconductor of nanocrystalline morphology whereby they tend to be associated with

dye sensitized solar cells. As a result, the dye sensitized solar cells carry out optical absorption and the charge separation the processes [153, 154]. The major function of the dye sensitizer is to serve as efficient visible light absorber designed to create electrons and photoelectric conversion efficiency in a dye solar cell [155, 156]. These sensitizers play crucial role in determining the light harvesting efficiency as well as long-term stability of the solar device based on their electrochemical and spectroscopic properties [157]. They have promising value for future photovoltaic applications based on their high efficiency and low production cost [158, 159]. Recently, extensive efforts have been focused on the synthesis of new highly efficient sensitizers and the search for stable electrolytes and/or new photoanode material inorder to improve the photovoltaic and stability of DSSCs [160]. The standard requirements that a dye molecule must fulfill in order to be used as a photosensitizer in DSSCs include:

- It should absorb all photons close to a threshold wavelength of about 920 nm
- It must have attachment groups such as carboxylate or phosphonate to firmly hold unto the semiconductor oxide surface
- It should inject electrons into the conductor with a quantum yield of unity when excitation takes place.
- The energy level of the excited state should be lesser than the conduction band of the oxide to minimize energetic losses due to the electron transfer reaction.
- The redox potential should be highly positive that it can be regenerated via electron donation from the redox electrolyte.
- The dye should be stable enough to sustain about 10<sup>8</sup> turnover cycles corresponding to about 20 years of exposure to natural light [154, 161-164].

#### 1.3.3.1 Classification of sensitizers

Dye photosensitizers that are used in DSSCs are classified into two major types such as organic and inorganic dyes based on the chemical structure. The inorganic dye includes metal complexes, such as transition complexes of ruthenium and osmium, metalloporphyrins and phthalocyanines, and inorganic quantum dots, while the organic dye consist of natural organic dyes and synthetic organic dye. Typical examples of synthetic organic dye are coumarin dyes, indoline dyes, tetrahydroquinoline dyes, triarylamine dyes and heteroanthrancene dyes [165-167].

### **1.3.3.1.1 Inorganic Sensitizers**

### (A.) Metal Complex Sensitizers

Metal complex sensitizers are made up of the two ligands namely the anchoring and ancillary ligands. Anchoring ligands are used for the adhesion of the sensitizers onto the surface of the semiconductors while the ancillary ligands are used for tuning the overall properties of the complexes [168, 169]. The metals that have been successfully used as photosensitizers for DSSCs investigation include: ruthenium, osmium, Rhenium, platinum, Copper, Iron, Iridium and Nickel complexes [170-182]. However, ruthenium complexes are predominantly used in DSSCs due to its unique features of spectral, electrochemical, photophysical and tunable properties [183].







N Pt S CN COOEt

(**d**)







Chart 1.1: Chemical structures of metal based sensitizers (a) Ruthenium(II) complex(b) Osmium(II) complex (c) Rhenium(I) complex (d) Platinum(I) complex (e)Copper(I) complex (f) Iron(II) complex (i) Iridium(III) complex (j) Nickel(II) complex[170-179, 182].

### **(B.)** Metalloporphyrins sensitizers

Metalloporphyrin Sensitizers are viable sensitizers based on their photostable and photophysical properties as well as favorable light harvesting nature in the visible region [184-186]. They have the lowest unoccupied molecular orbital (LUMO) levels that stay above the conduction band of the TiO<sub>2</sub> and the highest occupied molecular orbital (HOMO) levels that lie below the redox couple in the electrolyte solution that is required for charge separation at the semiconductor/dye/electrolyte surface. These makes them good donor moieties [187]. The molecular structures of the porphyrins have good electron donating/accepting nature with many reaction sites for different substitutions and their strong, intense absorption at 400–450 nm (Soret or B band) with respect to moderately intense absorption band at 500–650 nm (Q-band) for the fabrication of DSSCs [188-190].

Lee *et al* [191] reported that zinc porphyrins as sensitizers fall into two main functional sites of meso and  $\beta$ - substituted porphyrins. The meso substituted site produced the highest efficiency for DSSCs of 11.9% under 1 sun condition as compared to 7.1% efficiency of  $\beta$ - substituted porphyrins. Analysis of the respective substituted porphyrins showed that meso-substituted porphyrins have higher molar extinction coefficient and red-shift on both Q and B bands. The HOMO and LUMO energy levels of about 0.4 eV compared to  $\beta$ - substituted porphyrins [191].



(a) meso-substituted porphyrin

(b)  $\beta$ - substituted porphyrin

**Chart 1.2:** Structure for functional sites of meso and  $\beta$ - substituted porphyrins.

Campbell *et al.* [192] found the  $\beta$ - substituted monoporphyrin carboxylic acid derivative 4-trans-2'-(2"-(5",10",15",20"tetraphenylporphyrinatozinc-(II)yl)ethen-1'-yl)-1-benzoic acid gives an overall photon-to-current conversion efficiency of 4.2% under AM1.5 conditions in DSSCs [192]. Gratzel and Coworkers [193] recently reported the 12% efficiency of zinc porphyrins in conjunction with a cobalt redox couple [193]. The chemical structure of zinc porphyrins dyes below include:





**Chart 1.3:** Structures of porphyrins sensitizers (I) porphyrins dye (n=7.1%) [194] (ii) YD0 dye (n=4.3%) 195] (iii) YD1dye (n=6.2%) [195] (iv) YD2 dye (n=6.6%) [195] (v) YD2-*o*-C8 dye (n=12.3%) [196] (vi) YD12 (n=6.7%)[197].

#### (C.) Metallophythalocyanine sensitizers

Phthalocyanine is a cyclic tetra pyrrolic cyclic organic molecule [31, 198]. It carries out a unique function of providing 18  $\pi$ -electron aromatic cloud delocalized evenly over a planar framework of alternating carbon and nitrogen atoms so as to make difficult to inject the excited state electron into the conduction of band of  $TiO_2$  [198]. Its application is seen in several fields such as in molding of some photophysical process of photosynthesis, as photocatalysts in chemical sensors, in photodynamic reactions against cancer, photo degradation of organic pollutants and as a photosensitizer in nanocrystalline dye-sensitized solar cells (DSSC's [199]. The major reason for its application in DSSC is the strong absorption of visible light in the near-IR/far-red region thereby possesses an intense Soret-band at 350 nm and Q-band in the 650–700 nm region [200, 201]. In spite of strong absorption bands in the near-IR region, metallophthalocyanines (MPcs) have drawbacks of low conversion efficiency in DSSCs. This is due to their strong tendency to aggregate on the TiO<sub>2</sub> surface and the lack of directionality of electron transfer in the excited state. Torres *et al* [202] recently reported a high conversion efficiency ( $\eta$ ) 3.5% for DSSCs using the unsymmetrical amphiphilic zinc phthalocyanine [202]. Similarly, Hagfeldt et al. [203] reported that the formation of molecular aggregates of zinc phthalocyanines largely prevented efficient electron injection into the semiconducting band when the sensitized film was irradiated [203].





Carboxyphthalocyanine TT1

**Chart 1.4**: Structures of pythalocyanins sensitizers (i) PCH001 dye ( $\eta$ =3.5%) [201] (ii) PCH003 dye ( $\eta$ =1.13%) [198] (iii) PCH008 dye ( $\eta$ = 2.35%) [204] (iv) TT1 dye ( $\eta$ =3.5%) [205]

### (D) Quantum dot as sensitizers

Quantum dots (QDs) are nanometer-sized crystals consisting of semiconductor materials, having sizes falling within a range of 2–10 nm [206]. Quantum dots dye sensitized solar cell defers from the DSSC by the use of a semiconductor quantum dot (QD) as the light absorber or sensitizers in replacement of a metal based dye [207]. The advantages of QDs are: tunable band gap [208-210] high extinction coefficients

[211-213] and large intrinsic dipole moment [214]. These inorganic semiconductor quantum dots (Q dots) have been duly investigated based on the following: cadmium selenide (CdSe) [215-218], cadmium sulfide (CdS) [219-223], Lead sulphide (PbS) [224], indium phosphide (InP) [225], indium arsenide (InAs) [226], bismuth sulfide (Bi<sub>2</sub>S) [227] but the largest percentage of reports emanates from CdSe QDs because of their easy preparation, stability, and futuristic results [228]. The respective inorganic semiconductor quantum dot can harvest visible light energy and transfer electrons to wide band gap semiconductors such as TiO<sub>2</sub>, SnO<sub>2</sub> and ZnO [229]. Their size quantization property determines how to tune the visible response and vary the band offset to modify the vectorial charge transfer across different sized particles [230-231]. Furthermore, they can generate multiple electron-hole pairs with a single photon [216].

Semiconductor quantum dots have low conversion efficiency around 4-5% [232]. The low conversion efficiency can be attributed to the issues of optical absorption, charge recombination, hole scavenging, electrolyte, recombination, series resistance and (counter electrode effect) [233]. Also unfavorable configuration of semiconductor quantum dots can contribute to low efficiency. Therefore, the modification of the configuration is an essential requirement to keep the favorable alignment for charge separation, charge transfer processes and stability [234]. The successful assembly and configuring of semiconductor QDs in a mesoscopic oxide film is a crucial yardstick for designing QDSSC [235]. This is because the semiconductor quantum dots serve as donors enable broadening of the spectral response and increased optical density of the

cell, thereby increasing the current while potentially decreasing the mesoscopic oxide film thickness [236].

### 1.3.3.1.2 Organic Sensitizers

Organic dyes are free from any traces of metal species and very attractive due to cost reduction [237]. Several advantages are linked with organic dyes as photosensitizers for DSSCs such as:

- They exhibit larger absorption coefficients usually attributed to an intermolecular ð-ð\* transition compared to the metal-complex photosensitizers, which are based on the MLCT absorption, thereby, leading to efficient light-harvesting properties.
- The introduction of substituents to their structures creates a platform for molecular designs, thereby, providing easy control of their absorption spectra.
- They are not confined to limited resources because organic dyes do not contain noble metals such as ruthenium.

However, they have certain setbacks used as photosensitizers for DSSCs:

- The emission lifetimes of their excited states are obviously shorter when compared with those of metal complexes.
- They exhibit relatively sharp absorption bands in the visible region, which constitutes a major setback for harvesting light [238].

Several organic molecular designs with very high conversion efficiency have been reported recently as the most viable organic photosensitizers used for DSSC. They include: MK2 dye with  $\eta$ =7.7% [239]. TA-St-CA dye with  $\eta$ =9.1 % [240], Indoline dye D205 with  $\eta$ = 9.52% [241] TA-DM-CA dye, [242], C217 dye with  $\eta$ = 9.8% [243] and C219 dye with  $\eta$ =10.3% [244].



Chart 1.5: Structures of Organic Sensitizers e.g Pythalocyanins sensitizers: MK2 [239], TA-St-CA [240], D205% [241], C217% [243], C219% [244] and TA-DM-CA [242]

## 1.3.3.1.3. Natural sensitizers

Natural parts of plants such as fruits, flowers, leaves and other parts of plants give different colours including the composition of pigments that can be extracted to be

utilized in dye sensitized solar cells [245]. The natural pigments such as chlorophyll, caratenoids and anthocyanins isolated from the plants have been widely reported as photosensitizers for DSSCs [246]. The extracted pigments as dyes normally perform poorly in the DSSC because of weak binding energy with the TiO<sub>2</sub> film and low charge transfer absorption in the whole visible range. However, the dyes are cheap, easily prepared and environmentally friendly compared to the inorganic dyes [247].

The anthocyanins belong to a group of family called the flavonoids. The flavonoids are sugar-bound polyphenols usually found in plants. The most common anthocyanin dyes are cyanin, colors poppies and cornflowers blue. A wide range of colours are attributed to the anthocyanins due to their complexation with other polyphenols, pectins and metal ions [248]. The Molecular structures of anthocyanin possess both the carbonyl and hydroxyl group. Due to the presence of the carbonyl and hydroxyl groups, the anthocyanin molecule is grafted to the TiO<sub>2</sub> porous film, which is directly responsible for the photoelectric conversion effect [249]. Based on the fact that anthocyanins are responsible for dispersion of colors in plants, it therefore, shows that the colors being dispersed are within the range of visible light from red to blue. Thus, it is expected that the anthocyanins are prospected to become high efficient sensitizers for wide band gap semiconductors [248, 249].

The widespread pigment in plants is chlorophyll with the ability to absorb light in the visible wavelength, primarily in the blue (420–460 nm) and red (650–700 nm) range, and reflection of green light (~550 nm). There are two kinds of chlorophyll in higher

plants: green-blue chlorophyll a, and green-yellow chlorophyll b. Their amounts depend on the species of plant, light conditions, and the availability of minerals such as magnesium (Mg) [250]. The chlorophyll derivatives as natural dyes have been utilized to sensitize  $TiO_2$  dye sensitized solar cell, thereby achieving efficiencies of 2.6% and 9.4 mA/cm<sup>2</sup>, however these dyes still require involved pigment purification and the co adsorption of other compounds on the  $TiO_2$  surface [248, 251].

Betalain pigments are present in caryophyllales plants, which have high molar extinction coefficients in the visible region and pH dependent redox properties. The pigments are present in the different parts of the plant including flowers petals, fruits, leaves, stems and roots [252]. The betalain pigments consist of the red-purple betacyanins, betanin and betanidin with maximum absorptivity at  $\lambda$ max about 535 nm, and the yellow betaxanthins with  $\lambda$ max near 480 nm. The structure of indicaxanthin, a common betaxanthin found in beet root, is shown below. Zhang *et al* [253] reported that the use of betalains for dye-sensitized solar energy conversion recorded a maximum photocurrents and power conversion efficiencies under full spectrum illumination of 100 mW/cm<sup>2</sup> [253].

Dye sensitized solar cell fabrication utilizing the use of Rose Bengal natural dye adsorbed into  $TIO_2$  and sandwiched with counter electrode gave electric energy conversion efficiency of 2.09% [254].



**Chart 1.6**: Structures of natural sensitizers: anthocyanin dye [248], chlorophyll dye [249], betalain dye [253], indixanthin dye [253] and rose bengal dye [254].

# **1.3.4. Electrolytes**

Electrolyte is one of the vital components of dye sensitized solar cells, which serves an effective medium: for charged regeneration, transport of the charged ions with respect to redox couple, and as gradient between the nanocrystalline semiconductor and the counter electrode surfaces. The basic requirements associated with electrolyte are: the ability to have a good charge transfer nature towards the dye even after electron ejection and low charge transfer resistances at the counter electrode. The Electrolyte consists of ingredients such as organic solvent, redox couple and additives. It is classed into three types: liquid electrolyte, quasi-solid state electrolyte and solid electrolyte.

According to the solvent used, liquid electrolyte can be divided into organic solvent electrolyte and ionic liquid electrolyte. The organic solvents used in organic liquid electrolytes have been considered to be widely used as potential electrolytes in dye sensitized solar cells. They include nitrile such as acetonitrile, valeronitirile, 3-methoxypropionitrile and esters such as ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolacetone [255]. Acetonitrile has emerged as the best electrolyte for basic electrochemical investigations based on its principal chemical stability, low viscosity and the ability to dissolve large number of components [256]. Ionic liquid electrolyte was first used to test the functionality of the dye sensitized solar in the Gratzel's lab [257] based on the sole objective of having new nonvolatile electrolyte solvents. The classification of the ionic liquid electrolytes linked to ionic liquids. The imidazolium family belongs to the ionic electrolyte which is basically used for electrochemical studies and in solar cells [257].

Since the redox couple or redox mediator is one of the main ingredients of the electrolyte, it plays a vital role in DSSCs. The redox couple is part of the parameters responsible for the determination of the open circuit voltage as well as charge transport

between the photoanode and the counter electrode. The open circuit voltage is a function of the difference between the Fermi energy of the illuminated working electrode and the electrochemical potential of the redox couple [256]. In DSSCs, iodide/triiodide has been investigated as the most efficient redox couple or redox mediator for regeneration of oxidized dye. However, other kinds of redox couples were investigated such as Br–/Br<sub>2</sub>, SCN–/SCN<sub>2</sub>, SeCN–/SeCN<sub>2</sub> bipyridine cobalt(III/II) complexes because iodide/triiodide redox couple has inert problems of severe corrosion [258]. Nevertheless, the iodide/triiodide couple has peculiar properties namely: unique solubility quality, low absorption of light, good redox potential, and rapid dye regeneration. However, the iodide/triiodide is very slow compared to other redox mediators [259, 260]. Up till now, iodide/triiodide has been the almost sole choice as the redox couple used in for DSSCs' operation [261-265].

Additives are another vital ingredient in liquid electrolyte with the sole aim to enhance the photovoltaic performance of DSSCs. Nitrogen-containing heterocyclic compounds such as ter-butylpyridine and pyridine are used as additives to enhance the open circuit voltage but decrease the short circuit current [255]. The additives also help to suppress dark current, improve the electric conversion efficiency and reduce the recombination of electron associated with the conduction band [259].

However, the electrolyte has its own setback that may limit the stability of DSSCs. Since the electrolyte is in its liquid state, it may evaporate when the cell is not perfectly sealed. Also, the penetration of water or oxygen into the electrolyte results in a reaction which impedes cell performance [34].

### 1.3.5 Counter electrode

Counter electrode is generally known to play a vital role in DSSCs. The main function of the counter electrode is to transfer electrons arriving from the external circuit to the electrolyte in order to regenerate the redox couple. As a result, a good counter electrode should mainly have an excellent catalytic activity for the reduction of triiodide ions as well as exhibiting high conductivity. The material widely used for the construction of cathode electrode is platinum, deposited on the conductive substrate by various methods like spin-coating, screen-printing, sputtering. In order to reduce the cost of the CE and prevent the corrosion of platinum by the iodide solution, other inexpensive, mainly carbonaceous, materials have been used also; these include carbon black (9.1%) and multi-walled carbon nanotubes (7.7%). Recently, graphene composites have been identified as potential catalysts for DSSC cathodes due to graphene's large surface area and conductivity [266-269].

For any material to be used as counter- electrode in a DSSC, the basic requirements include: (i) materials having a low charge-transfer resistance and high exchange current densities for the reduction of the oxidized form of the charge mediator (ii) materials having the potential test of chemical and electrochemical stability in the electrolyte medium used in the cell [270].

Since platinized transparent CEs, carbon CE and conductive polymer CE are found suitable for DSSCs' fabrication; Counter electrode selection is based on the particular application of the DSSCs. For the fabrication of power-producing windows or metal-foil-supported DSSCs, a transparent counter electrode is a suitable candidate. A typical example includes the deposition of small amount of platinum on F-doped tin oxide coated glass (FTO-glass) or plastic. Alternatively, the fabrication of low cost DSSCs requires the use of inexpensive materials like carbon catalyst for the CE [271].

## 1.4 Electron transfer mechanism in DSSCs

Two basic electron transfer processes of an operating dye sensitized solar cells are electron injection and dye regeneration. However, a process called recombination annihilates the flow of the moving electrons [272]. The overall mechanism of electron transfer processes and undesirable process are shown below [273-275].

Dye Injection and Regeneration (Desirable Reactions)

$S_{(adsorbed)} + hv \rightarrow S^{*}_{(adsorbed)}$	Photoexcitation	Eq. (1)
$S^*_{(adsorbed)} \rightarrow S^+_{(adsorbed)} + e^{(injected)}$	Electron injection	Eq. (2)
$I_3^- + 2. e^-(\text{cathode}) \rightarrow 3I^-(\text{cathode})$	Reduction	Eq. (3)
$S^+_{(adsorbed)} + 3/2 I^- \rightarrow S_{(adsorbed)} + 1/2 I^3$	Dye regeneration	Eq. (4)

Dye Recombination (Undesirable Reactions)

$$S^+_{(adsorbed)} + e^-_{(TiO2)} \rightarrow S_{(adsorbed)}$$
 Recombination Eq. (5)  
 $I^-_3 + 2. e^-_{(TiO2)} \rightarrow 3I^-_{(anode)}$  Recombination Eq. (6)

From the above reaction steps, equation 1 shows the photoexcitation of the dye which results in the intramolecular MLCT transition; equation 2 represents the injection of electron from the sensitizers into the conduction band of semiconductor such as Titanium(IV); equation 3 gives the reduction of the redox mediator by the injected electron at the counter electrode (3); equation 4 shows dye regeneration by the redox mediator is equation. However, equation (5) and (6) show the undesirable reactions due to recombination of electrons with oxidized sensitizers and with the redox couple at the Titanium(IV) oxide surface respectively [273-275].



**Figure 1.5:** Electron-transfer processes in a DSSC based on Ru(II) bpyridine complex dye photosensitizer [276]

### 1.5. Measurement and evaluation of dye-sensitized solar cell performance

The dye-sensitized solar cell performance can be measured and evaluated by majorly six parameters such as Incident Photon to Current Efficiency (IPCE), Photocurrent/Voltage Curves (J/V) curves, Open-circuit photovoltage (Voc), short-circuit photocurrent Jsc, fill factor (ff) and solar- to-electric conversion efficiency under a definite simulated intensity of light such as the AM 1.5 solar spectrum [13, 277]. A typical circuit setup is shown below for the evaluation of dye sensitized solar cell performance:

- The dye-sensitized solar cell is connected in series with the aid of a variable resistor while the voltmeter is connected across the variable resistor to estimate the voltage across the resistor.
- The generation of electricity is realized upon the irradiation of DSSC with with a halogen lamp. The corresponding current is estimated by the formula [167]

Current (I) =  $\frac{\text{Voltage (V)}}{\text{Resistance (I)}}$ 



**Figure 1.6**: A circuit set up for evaluation of dye sensitized solar cell performance [167].

# **1.5.1 Incident Photon to Current Efficiency (IPCE)**

The incident monochromatic photon-to-current conversion efficiency (IPCE), also known as the external quantum efficiency" (EQE), is described as the number of electrons produced by light divided by the number of incident photons that hits the cell and can be obtained from the mathematical expression below [66, 278].

$$IPCE = \frac{1240 \times Jsc \,(\mu Acm^{-2})}{\lambda(nm) \times P(Wm^{-2})}$$

The incident monochromatic photon-to-current conversion efficiency is estimated by three key parameters: (a) light harvesting efficiency  $(LHE)(\lambda)$  (determined by the spectral and photophysical characteristics of the dye), (b) the quantum yield of charge injection  $\phi$ inj(determined by the excited state potential and the life time and (c) the efficiency of collecting the charge at the back electrode  $\eta c$  (determined by the structure and morphology of the TiO<sub>2</sub> layer [279].

The maximum IPCEs for DSSCs lies in the 80–85% range; they do not reach 100 % experimentally because of reflection and absorption losses (10–15%) due to the FTO glass [13].

### 1.5.2 Photocurrent/Voltage (J/V) curves

The simple and useful method for the evaluation of the photovoltaic performance of DSSC is through the measurement of the J/V curves under AM 1.5 simulated sunlight (100mWcm<sup>-2</sup>). The performance of DSSC is widely determined by the following four key factors: Voc, Jsc, ff, and  $\eta$  [13].



**Figure 1.7:** Representative of Photocurrent/Voltage (J/V) curves of the dye sensitized solar cell [280].

# **1.5.3 Open-Circuit Photovoltage** (Voc)

Open-Circuit Photovoltage is defined as the difference in electrical potential between two terminals of a cell under illumination when the circuit is open (i.e., maximum voltage obtainable from DSSC occurring at zero current). The Voc value can be expressed as by the equation [13].

 $Voc = E_{cb}/e + KBT/e \ln(n/N_{cb})$  -  $E_{redox}$ 

Where e = elementary charge

n = number of the electron in TiO<sub>2</sub>

 $K_B = Boltzmann \ constant$ 

T = absolute temperature

 $N_{cb} = effective density of states$ 

 $E_{redox} = redox potential$ 

#### **1.5.4 Short-Circuit Photocurrent Density** (Jsc)

Short-Circuit Photocurrent Density is defined as the photocurrent per unit area (mA cm<sup>-2</sup>) when a DSSC under irradiation is short-circuited (i.e., when the voltage across the solar DSSC is zero). The  $J_{sc}$  value largely relies on the photophysical and electrochemical properties and molecular structures of the dye sensitizers. The  $J_{sc}$  value corresponds to the interaction between TiO<sub>2</sub> and the dye sensitizer, as well as the absorption coefficient of the dye sensitizer whereas  $V_{oc}$  value equates to the difference between  $E_f$  of the electron in TiO<sub>2</sub> and the redox potential of the electrolyte (I<sub>3</sub>/I). A high  $J_{sc}$  value greatly depends on the following factors: (i) intense light-absorption abilities of sensitizers over the wide wavelength range (ii) efficient electron-injection from photoexcited dyes to the CB of TiO<sub>2</sub> (iii) high re-reduction of the oxidized dye. The  $J_{sc}$  value can be derived by integrating the IPCE spectra [13].

$$\mathbf{J}_{\rm sc} = \mathbf{e} \int IPCE \left[\lambda\right] \, I_s(\lambda) d\lambda$$

Where  $I_s(\lambda)$  = the photon flux at wavelength in AM 1.5 (100Wcm<sup>-2</sup>)

#### **1.5.5 Fill Factor (ff)**

The fill factor can assume values between 0 and 1 and is defined by the ratio of the maximum power ( $P_{max}$ ) of the solar cell divided by the open-circuit voltage ( $V_{oc}$ ) and the short-circuit current ( $I_{sc}$ ):

$$ff = P_{max}/(I_{sc} \times V_{oc})$$

 $P_{max}$  is the product of photocurrent and photovoltage at the voltage where the cell's power output is maximal. The value of the fill factor reflects the extent of electrical (Ohmic) including the electrochemical (overvoltage) losses that occur during operation of the DSSC. Increasing the shunt resistance and decreasing the series resistance as well as reducing the overvoltage for diffusion and electron transfer will lead to higher fill factors, thus resulting in greater efficiency and pushing the cells output power closer toward its theoretical maximum [281].

### **1.5.6 Overall Conversion Efficiency (η)**

Overall Conversion Efficiency is defined as the ratio of the maximum output electrical power of the DSSC to the energy of incident sunlight and is therefore determined by Voc, Jsc, ff, and  $I_o$ . In conclusion, under full sunlight (air mass 1.5 global, intensity Is= 1,000W/cm<sup>2</sup>), short circuit photo-currents ranging from 16 to 22mA/cm<sup>2</sup> have been reached with state-of-the art ruthenium sensitizers, while Voc is 0.7–0.86 V and the fill factor values 0.65–0.8. An overall power conversion efficiency of 10.4% was obtained in 2001. New record power efficiency over 11.2 % was achieved recently [13, 282].

 $\frac{\eta(\%) = [J_{sc}(\text{mAcm}^{-2})V_{oc}(V)ff]}{I_o(\text{mAcm}^{-2})}$ 

Where I<sub>o</sub> is intensity of incident light.

### **1.5.7 Solar Radiation and Air Mass**

The solar radiation is an ideal and non-exhausting reservoir of energy [283]. The efficiency of a solar cell can be determined by the variation of the intensity and the energy distribution of the incident light derived from solar radiation. Therefore, solar radiation touching the surface of the earth introduces significant changes due to time of the day, atmospheric conditions, location, earth/sun distance and solar rotation. The solar spectrum depends on so many variables and therefore, it is necessary to define standard spectrum and power density for the exact comparison among different solar devices [284]. The Sun gives out light resembling the spectrum of a blackbody at temperature of 5670K as shown in figure 1.11.



**Figure 1.8:** Spectra of a black body at temperature of 5670 K, extraterrestial sunlight and terrestrial sunlight (AM1.5). Ultraviolet rays are filtered out by ozone. Water and CO<sub>2</sub> absorb mainly in the infrared [284].

The power density of the Sun is equated to 62 MW m<sup>-2</sup>, however, on reaching a point just above the earth's atmosphere, reduction is observed being equated to 1353 MW
m<sup>-2</sup>. This reduced value is referred to as solar constant, which quantitatively explains rate of incoming perpendicular solar radiation measured on the outer surface of earth's atmosphere, when the Sun and Earth are separated by a distance of 149,597,890 km (one astronomical unit, AU) [284]. Before reaching the ground, the solar radiation passes through the earth's atmosphere components such as ozone, oxygen, carbon dioxide, and water vapour, which give rise to selective absorption [283, 284]. This process modifies the solar spectrum including both intensity and energetic distribution. The final irradiation that reaches the ground is determined by the length of the path the radiation must pass. This optical path is clearly defined as *Air Mass* (AM), considering the attenuation radiation, suffers due to atmospheric absorption and depends on the position of the Sun. The Air Mass is defined

$$AM = \frac{1}{Cos(\theta)}$$

Taking  $\theta$  as the angle of elevation is shown in figure 1.9



**Figure 1.9:** Illustration of the zenith point and different air mass (AM) positions. The zenith point stands for the path length vertically upward at 90 and is defined as AM 1.0 [285].

The air mass 1.5 G<sup>2</sup> according to  $\theta = 48.2^{\circ}$  is the standard spectral distribution of the light used for efficiency measurements of solar cells. The magnitude of optical path is 1.5 times longer than in the case of A.M 1 light. Through the atmosphere thickness, the solar spectrum is attenuated to a mean irradiance reaching around a value of 900 Wm<sup>-2</sup>. But for convenient reasons the normalization of standard spectrum is done so that the integrated irradiance of this spectrum per unit area and unit time is 1000 Wm<sup>-2</sup> (considered as 1 sun illumination). As a result, this light intensity is used for solar

cells standard testing conditions. The "G" in AM 1.5 G denotes the word global which serves as a standard reference for differentiation between direct radiation and global radiation, also taking into account the diffuse light. DSSCs have added advantage due to their rough surfaces which are mostly preferred for diffuse light than flat surfaces. Hence, they are considered less sensitive to movements of the Sun [284].

# **1.6 Chelating ligands**

Chelating ligands are compounds known to form multidentate complexes by virtue of their bonding with metal ions forming a structural ring closure. Most of the chelating compounds contain three important heteroatoms with electron donating nature e.g. Nitrogen (N), Oxygen (O) and Sulphur (S) [286]. Over a century, the incorporation of NN-bidentate chelating ligands with binding domains have been used as ligands and shown to coordinate with most metals in periodic table [287]. Bidentate and tridentate ligands are two general classes of ligands widely used for designing, synthesizing, characterizing and evaluating novel ruthenium(II)-based photosensitizers [288].

# **1.6.1 Bidentate ligands**

Bidentate ligands containing six-membered rings forms the class of nitrogen heterocyclic compounds such as 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), etc. They create soft site for metal coordination and exhibit as unique  $\pi$ -acceptors because of their  $\pi$ -electron deficiency. As a result, they have been widely used in transition metal chemistry [289]. The class of bidentate ligands widely used for the design and synthesis of sensitizers for DSSCs are stated as follows: 4, 4'-

Dicarboxylic-2,2'-bipyridine [290, 291], 4,7-Dicarboxy-1,10-Phenanthroline [292],4, 4'- Dicarboxylic-2,2'-biquinoline [293], 4'- Carboxy-2-(2'-pyridyl)quinoline [294],



4, 4'-Dicarboxy-2,2'-bipyridine



4, 7'-Dicarboxy-1,10-phenanthrolin

HOOC



4, 4'-Dicarboxy-2,2'-biquinoline



4, 4'-Carboxy-2-(2'-(pyridyl)quinoline

## Chart 1.7: Molecular structures of major bidentate ligands used in DSSCs

## 1.6.2 Tridentate ligands

Tridentate ligands equally contain six-membered rings which forms the class of nitrogen heterocyclic compounds such as 2, 2':6', 2''-terpyridine (terpy) etc. They also create soft site for metal coordination and exhibit as unique  $\pi$ -acceptors because of their  $\pi$ -electron deficiency. As a result, they have been widely used in transition metal chemistry [289]. The class of tridentate ligands used for the design and synthesis of sensitizers for DSSCs are as follows: 2, 2': 6', 2''-terpyridine-4, 4', 4''-tricarboxylic

acid [295, 296]. 2, 6-bis (l-methylbenzimidazol-2-yl) pyridine [297], 2, 6-bis (3, 5-Dimethyl-N-pyrazoyl) pyridine [298, 299], tridentate bipyridine pyrazolate [300, 301].



4, 4', 4"-Tricarboxy-2, 2':6', 2"-terpyridine



2, 6-Bis(1-methylbenzimidazol-2-yl)-pyridine



2, 6-Bis(3,5-dimethylpyrazol-1-yl)-pyridine



Trident bipyridine pyrazolate

Chart 1.8: Molecular structures of major tridentate ligands used in DSSCs.

# 1.7 Ruthenium(II) polypyridyl sensitizers

Polypyridyl ruthenium sensitizers are the most widely used metal dye complexes due to their appropriate redox, spectroscopic and excited-state properties [302-309]. They are grouped into three categories such as carboxylate polypyridyl, phosphonate polypyridyl and polynuclear bipyridyl ruthenium. Based on their role and individual functions, metal sensitizers are known to have ligands classified as ancillary and anchoring ligands. The anchoring ligands perform the function of adsorption; determine the binding energy including the injection rate of electrons with respect to the dye on the semiconductor surface, whilst ancillary performs the function of tuning of the overall properties of the complex [168, 310, 311]. Though having lots of advantages, carboxylate polyridyl ruthenium sensitizers are easily desorbed from the surface of the semiconductor in an aqueous medium with a pH value below 5. But the phosphonate polypyridyl ruthenium sensitizers having phosphonate group hardly desorbed from the semiconductor even at high pH value, however, phosphonate group does not conjugate with the polypridyl plane due to their none-plane structures, which sets a major drawback for the injection of electron [61].

Polypyridyl ruthenium sensitizers have a general structure of  $ML_{2}(X)_{2}$ , where M can be Ru or Os and L is 2,2<sup>•</sup>-bipyridyl-4,4<sup>•</sup>-dicarboxylic acid and X presents a halide, cyanide, thiocyanate, acetyl acetonate, thiacarbamate or water substituent group [153, 312]. Three polypyridyl ruthenium sensitizers such as such as N3, N719 and N749 (black dye) have been considered as benchmark of sensitizers in DSSCs [36, 291, 295]. As a result, the overall photovoltaic performance of N3 dye-sensitized TiO<sub>2</sub> solar cell is linked with the photocurrent action spectrum. It measures the incident photon-tocurrent conversion efficiency to monochromatic radiation (IPCE) corresponding to exhibited values exceeding ca. 80% in the wavelength range between 480 and 600 nm, reaching 85-90% between 510 and 570 nm [270]. A solar-to-electric energy conversion efficiency of 10% was obtained with N3 dye [291, 313].



Chart 1.9: Molecular structures of N3, N719 and N749 sensitizers

N719 dye adsorbed on nanocrystalline TiO<sub>2</sub> films show the incident monochromatic photon-to-current conversion efficiency(IPCE) 90% and gives a short circuit current of of 17mA cm<sup>-2</sup>, open-circuit potential of 750mV, and fill factor of 0.72 yielding power conversion efficiencies over 9.18% under AM 1.5 Sun [314, 315]. However, the main drawback of this sensitizer is the relatively low molar extinction coefficient in the visible and near-IR [316]. While for N749 (black dye) due to its very efficient panchromatic sensitization of nanocrystalline TiO<sub>2</sub>, the effective IPCE value covers the entire visible spectrum and extends into the near IR region up to 920 nm [295, 317]. It is a promising dye because its LUMO is located just above the conduction

band (CB) of TiO<sub>2</sub> [318]. Also, it is produces an overall efficiency of 10.4% because its theoretical efficiency has been calculated to be 19.6% but the challenge to optimize still persists [319]. However, the overall efficiency was increased to 11% after resolving setbacks such as reduction of the internal resistance and the preparation of a high haze electrode [318].

# 1.7.1 Bidentate ruthenium(II) polypyridyl sensitizers

The design of bidentate ruthenium(II) polypyridyl sensitizers is based on the combination of ruthenium ion with two bidentate ligands of 2, 2'-bipyridyl-4,4'- dicarboxylic acids and the other ligand can be formed by changing the functional group of bipyridyl compound with different moieties based on their desired function or set objectives.

# 1.7.1.1 Bidentate protonated sensitizers

The design and development of tetrakis(tetrabutylammonium)[cis-di(thiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II)] denoted as N712 has been reported to show how efficient the immobilized sensitizer absorbs a photon to produce an excited state leading to the transfer of its electron onto the TiO<sub>2</sub> conduction band. The investigation showed that one proton dye is the optimum for high electric conversion efficiency of the cell. As a result, a photoelectric conversion efficiency of 8.2% was reached when compared to both N3 and N719 of 7.4% and 8.4% respectively [320]. The photovoltaic performance of cis-di(thiocyanato)-(2,2'-bipyridyl-4,4'- dicarboxylic acid)(4,4'-ditridecyl-2,2'-bipyridyl)-ruthenium(II) denoted as N621 showed incredible power conversion efficiency at 1 sun, 9.57% [321].



Chart 1.10: Molecular structures of N712 [320], N612 [321] and N945 [322] sensitizers

In a quest to increase the molar extinction of prototype sensitizer of N719, a high molar extinction sensitizers of [ruthenium(4,-carboxylic acid-4 -carboxylate-2,2 - bipyridine)(4,4 - di-(2-(3,6-dimethoxyphenyl) ethenyl)-2,2 -bipyridine)(NCS)<sub>2</sub>] denoted as N945 was developed and reported. The sensitizer adsorbed on TiO<sub>2</sub> harvested visible light over a large spectral range and gave an incredible electric conversion efficiency of 10.82% at 1 Sun standard air mass. The incorporation of the 4,4 -di-(2-(3,6-dimethoxyphenyl)ethenyl)-2,2 -bipyridine ligand containing extended

-conjugation plus substituted methoxy groups in the sensitizer is to enhance the molar extinction coefficient [322].

#### **1.7.1.2 Bidentate hydrophobic sensitizers**

The development of amphiphilic heteroleptic ruthenium sensitizer of [cis-[bis((2,2'bipyridyl-4,4'-dicarboxylic-acid)(4,4'-dinonyl-2,2'-bipyridyl)bis(isothiocyanato) ruthenium (II)] coded as Z907 was reported to have solar electric conversion efficiency of 6% with a solar cell [323]. It has hydrophobic alkyl chains attached to one of the bipyridine ligands and it puts away water molecules from the chemical bonds between the dye and titanium dioxide. While its phosphonate polypyridyl analogue reached a conversion efficiency of 8%, it has been used for solar cell fabrication. The major advantage of Z907 is based on its outstanding stability. A durability test showed stable performance of the DSSCs with Z907 for 1000 h at 80 °C in darkness and at 55 °C under light irradiation [167]. The structural modification of Z907 by extending the  $\pi$ conjugation of the hydrophobic ligand and incorporating it with electron donating alkoxy groups rise to ruthenium(4,4'-dicarboxylicacid-2,2'-bipyridine)(4,4'-Di(3methoxystyryl)-2,2'-bipyridine)(NCS)<sub>2</sub> denoted as Z910 dye. The dye yielded 10.2%power conversion efficiency with high molar coefficients of  $17.0 \times 10^3$  and  $16.85 \times 10^3$ significantly higher than the corresponding molar coefficients of Z907 analogous. The photovoltaic performance is due to the extension of the  $\pi$ - conjugation system [324].









Chart 1.11: Molecular structures of Z907 [323], Z910 [324] and Z955 [325] sensitizers

The successful replacement of the carboxylic acid anchoring groups in Z907 by two phosphonic acid anchoring groups serves the purpose of grafting or binding more TiO<sub>2</sub> leading to development of cis-ruthenium(4,4'strongly onto the diphosphonicacid-2,2'-bipyridine)(4,4'-dinonyl-2,2'-bipyridine)(NCS)<sub>2</sub> coded as Z955. The nanocrystalline dye-sensitized solar cells (DSSCs) with nanocrystalline dye-sensitized solar cells (DSSCs) with Z955 dye yielded 8.0% light conversion efficiencies under 1.5 AM sunlight conditions. Also, the devices exhibited excellent stability under light soaking at 55 to 60 °C. Based on rate of dye regeneration, this new sensitizer seems to be quite similar but the charge recombination is significantly slower in comparison to the analogues carboxylated sensitizer [325].

## 1.7.1.3 Bidentate electrolyte ion photostability sensitizers

The construction of ruthenium((4,4'-dicarboxylic acid-2,2'-bipyridine)(4,4'-bis(p-hexyloxystyryl)- 2,2'-bipyridine)(NCS)<sub>2</sub> coded K19 as a sensitizer has been reported in a bid to improve on the shortcomings of Z907 sensitizers in the area of molar extinction coefficients and thermal stability under stress and light soaking. K-19 sensitizer showed good photo stability under light intensity of 100 mW cm<sup>-2</sup>. A power conversion efficiency of 7% was reached and remained at this level after 1000h of light soaking [158]. Also, the development of ruthenium(4-carboxylic acid-4'-carboxylate)(4,4'-bis[(triethylene glycol methyl ether) methyl ether]-2,2'-bipyridine)-(NCS)<sub>2</sub> sodium salt (coded as K51) had been reported as a sensitizer to coordinate the effect of Li<sup>+</sup> in conjunction with its performance in mesoscopic titanium dioxide. The sensitizer has ion trapping application and hinders the ions from reaching the TiO<sub>2</sub> surface. A solar electric conversion efficiency of 7.8% in standard air mass 1.5 sunlight and a spectrum peak of incident photon-to-current quantum efficiency (IPCE) of approximately 80% at a 540 nm incident wavelength were reached [326].





Chart 1.12: Molecular structures of K19 [158], K51 [326], K60 [327] and K77 sensitizers [160]

K51 had disadvantages in terms of lower molar extinction coefficient and high solubility in organic solvents. Thus, the development of ruthenium(4,4-dicarboxylic acid-2,2'-bipyridine)(4,4'-bis(2-(4-(1,4,7,10-tetraoxyundecyl)phenyl)ethenyl)-2,2'-bipyridine)(NCS)<sub>2</sub>, coded K-60 was initiated to overcome the setbacks. The solar electric conversion efficiency of K-60 dye is 8.4% at 1.5 AM sunlight conditions, with remarkable thermal stability under thermal stress at 80°C [327]. Subsequently, a

newly designed high molar coefficient sensitizer of ruthenium(2,2'-bipyridine-4,4'-dicarboxylicacid)(4,4'-bis(2-(4-*tert*-butyloxyphenyl)ethenyl)-2,2'-bipyridine)(NCS)<sub>2</sub> coded as K-77 was synthesized. The K-77 dye in conjuction with a nonvolatile electrolyte showed 9.0% of photoelectric conversion efficiency at 1.5 AM sunlight conditions, with remarkable thermal stability under thermal stress at 80°C [160].

# **1.7.1.4 Bidentate high molar coefficient sensitizers**

A high molar extinction coefficient ruthenium sensitizer of ruthenium(4,4'(-bis(5hexylthiophen-2-yl)-2,2'(-bipyridine)(4-carboxylic acid-4'-(-caboxylate-2,2'bipyridyl)(NCS)<sub>2</sub>) sodium salt denoted as C101, containing a hexylthiopheneconjugated bipyridyl group as an ancillary ligand has been developed to enhance the light harvesting efficiency of DSSCs device. The fine tuning of both the lowestunoccupied-molecular-orbital (LUMO) and the highest-occupied-molecular-orbital (HOMO) levels of the complex was initiated through the thiophene moiety channeled between hydrophobic alkyl chain and the pyridine ring, pumped electrons more effectively into the conduction band of the titania as well as transported the holes to the redox species. A photoelectric conversion efficiency of 11.3% has been reached [328]. Likewise a heteroleptic polypyridyl ruthenium sensitizer of *cis*ruthenium(4,4'-bis(5-octylthieno[3,2-b]thiophen-2-yl)-2,2'-bipyridine)(4,4'dicarboxyl-2,2'-bipyridine)(NCS)<sub>2</sub> designated as C104 has been constructed and reported to have a high molar extinction coefficient of  $20.5 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> at 553 nm. The extension of the  $\pi$ -conjugated unit of the ancillary ligand in the ruthenium

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sensitizer improved the optical absorptivity of mesoporous nanocrystalline titania dioxide giving rise an overall electric conversion efficiency of 10.53% measured at the air mass of 1.5 global condition for dye sensitized solar cell [329]. Also, a high molar extinction ruthenium sensitizer of ruthemium(4,4'-bis(5-hexylselenophen-2yl)-2,2'-bipyridine)(4-carboxylic acid-4'-carboxylate-2,2'-bipyridine)(NCS)<sub>2</sub> sodium salt denoted as C105 has been developed and reported. The introduction of a conjugated electron-rich selenophene unit into the ancillary ligand of the sensitizer improved the optical absorptivity of mesoporous titania thereby exhibiting a chargetransfer band at 550 nm with a molar extinction coefficient of  $18.7 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> when anchored on a mesoporous titanium film. The sensitizer has an overall power conversion efficiency of 10.6% measured under the air mass 1.5 global conditions for a dye sensitized solar cell [330].





C101 dye





C107 dye

Chart 1.13: Molecular structures of C101 [328], C104 [329], C105 [330], C106 [331] and C107 sensitizers [332]

Subsequently, strategic designs of ruthenium(4,4'-bis(5-hexylthiophen-2-yl)-2,2'bipyridine)(4-carboxylic acid-4'-carboxylate-2,2'-bipyridine)(NCS)<sub>2</sub> sodium salt denoted as C106 were developed and reported to a charge-transfer band at 550 nm with a molar extinction coefficient of  $18.7 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup> by incorporating a hexylthiothiophene conjugated bipyridine ligand to improve the optical absorptivity of mesoporous titania films, giving rise to an overall power conversion efficiency of 11.4% measured at the air mass 1.5 global conditions for dye sensitized solar cell [332]. Another high molar extinction coefficient ruthenium sensitizer of [ruthenium(4,4'-bis(5-octyl-2,2'-bis(3,4-ethylenedioxythiophen)-5'-yl)-2,2'-

bipyridine)(4-carboxylic acid-4'-carboxylate-2,2'-bipyridine)(NCS)<sub>2</sub> sodium salt designated as (C107), featuring the electron-rich 5-octyl-2,2'-bis(3,4ethylenedioxythiophene) moiety conjugated with 2,2'-bipyridine with 5-hexyl-3,4ethylenedioxythiophene and nonyl attached respectively, has reached a overall photoelectric conversion efficiency of 10.7% measured at the AM1.5G conditions. This C107 sensitizer has an extremely high molar extinction coefficient of  $27.4 \times 10^3$  $M^{-1}$ cm<sup>-1</sup> at 559 nm in comparison Z907 (12.2 × 10<sup>3</sup>  $M^{-1}$  cm<sup>-1</sup> at 521 nm) with the corresponding 5-hexyl-3,4-ethylenedioxythiophene- or nonyl-substituted bipyridyl unit [332].

Again, a ruthenium (II) sensitizer with an alkyl bithiophene group, denoted as CYC-B1 was designed and developed. The solar light-to- electricity conversion efficiency of 10% was obtained and has the highest absorption molar extinction coefficient among ruthenium based sensitizers used in DSSCs [333]. Likewise, a novel, heteroleptic ruthenium(II) sensitizer of (cis-di(thiocyanato)(4,4' -di-octyl-bithienyl)-2,2'-bipyri-dine) (4,4'-di-carboxylvinyl-2,2'-bipyridine) ruthenium(II) designated as CYC-B5 whereby both the conjugation length of both ancillary and anchoring ligands

were extended with a conjugated moiety has been constructed and reported. The sensitizer exhibited a high molar coefficient of  $2.51 \times 10^4$  M<sup>1</sup> cm<sup>1</sup> at wavelength of 562 nm largely due to its metal-to-ligand charge transfer band. The solar light-to-electricity conversion efficiency of 9.12 % measured at Air Mass 1.5 (100 mW/cm<sup>2</sup>) irradiation was obtained [334].









Chart 1.14: Molecular structures of CYC-B1 [333], CYC-B5 [334] and CYC-B11 [335] sensitizers

Nevertheless, a new heteroleptic ruthenium sensitizer of TBA (ruthenium[(4carboxylic acid-4'-carboxylate-2,2'-bipyridine)(Ligand-11)(NCS)<sub>2</sub> designated as CYC-B11 exhibits a charge-transfer band at 554 nm with a molar extinction coefficient of  $2.42 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup> higher than all of those reported ruthenium sensitizers featuring thiophene derivatives for DSSCs. This significant growth rate of the charge-transfer absorption band cross section is attributed to the hexylthio-bithiophene antennas' action in increasing both the electron donating ability and extension of the  $\pi$ -conjugation to the bipyridyl ancillary ligand. The corresponding DSSC cell using a volatile liquid electrolyte shows an excellent power conversion efficiency of 11.5% obtained under an irradiation of full sunlight (air mass 1.5 global). The cell using a low-volatility electrolyte shows good performance and stability under visible light soaking at 60 °C during 1000 hours of accelerated tests [335].

Another high molar extinction coefficient ruthenium sensitizer of [*cis*-ruthenium(4,4'di(hexylthienylvinyl)-2,2'-bipyridine)(4,4'-dicarboxylic acid-2,2'-bipyridyl)(NCS)<sub>2</sub>] denoted as HRS-1 has been developed and reported. The strategy for this design is to introduce a  $\pi$ -conjugated group into the ruthenium complex sensitizers as a kind of hybrid of a ruthenium sensitizer with an organic sensitizer. The incorporation of organic sensitizer is partly due to the high molar extinction coefficient of the conjugated  $\pi$ -bonds coupled with the aromatic ring for the purpose of giving respectable incident photon to current efficiency (IPCE). The sensitizer was applied successfully to sensitization of nanocrystalline TiO<sub>2</sub>-based solar cells, giving a conversion efficiency of 9.5% under irradiation with AM 1.5 solar light. Thus, it exhibits a respectable light harvesting performance in the visible-light region, and a reversible, one electron oxidation process [336]. Similarly, a high molar extinction coefficient ruthenium sensitizer of cis-(ruthenium(II)(L1)(L2)(NCS)<sub>2</sub>, L1 = 4,4' dicarboxylic acid-2,2' -bipyridine (dcbpy), L2 = 4,4' -bis[p-diethylamino]-a-styryl]- 2,2' –bipyridine has been synthesized and reported. The sensitizer exhibited extremely high molar extinction coefficient of  $2.8 \times 10^4$  M<sup>-1</sup>cm<sup>-1</sup> at wavelength of 535 nm, which is higher in comparison to organic dyes. A photoelectric power conversion efficiency of 8.65% under light intensity of 1 Sun standard air mass was obtained [337].



HRS-1 dye

HRS-2 dye

Chart 1.15: Molecular structures of HRS-1 [336] and HRS-2 [337] sensitizers

# 1.8 Thiocyanate-free cyclometalated ruthenium(II) complexes

Cyclometallated ruthenium(II) complexes are new sets of sensitizers designed and synthesized for dye sensitized solar cell [338-340]. These complexes contain Ru–C bond of aromatic ring in addition to the Ru–N bonds all respectively related to a group of organometallic ruthenium complexes [341]. Due to the presence of the carbon anionic ligand, the metal center of cyclometalated ruthenium(II) complexes is electron rich compared to conventional trisbipyridine or bisterpyridine ruthenium complexes [342]. The essence of featuring cyclometallating moiety is towards the enhancement of HOMO–LUMO energy tuning by ligand functionalization and light conversion

efficiencies equal to or more than that of the standard ruthenium dye N719. The primary ligands that form the main families of cyclometallated ruthenium(II) complexes are ,2,2'-bipyridine (bpy), 2-phenylpyridine (Hppy), and 2,2': 6',2''-terpyridine (tpy) [339].



**Chart 1.16**: Molecular structures of thiocyanate-free cyclometalated ruthenium sensitizer (I)  $[Ru(dFppy)(dcbpy)_2]^+PF6 X=F, Y=CF_3[340]$  (II)  $[Ru(tpy)L1b-L5b]^+PF_6$  [342] (III) D-bisCF3,D-CF3, X=F, Y=CF\_3 (IV) D-OMe, and D-DPA dyes [343] (IV)  $[Ru(H_2dcbpy)(2-Ph-2CN)]^+PF_6$  [341], (V)  $[Ru(bpy)_2(H5)]PF_6$  [339], (VI)  $[Ru(CH_3CN)L4]PF_{6}[344]$ 

In chart 1.15, the complex  $[Ru(H_2dcbpy)(2-Ph-2CN)]^+PF_6$  entitled as bis(4,4'-dicarboxy-2,2'-bipyridine)(2-phenylpyridine-

2C,N)ruthenium(II)hexafluorophosphate(1) adsorbed on titanium dioxide which was applied onto conducting FTO shows a performance of power conversion efficiency of 7.1% [341]. D-CF<sub>3</sub> sensitizer gives a higher conversion efficiency of 8.74% when compared to other same kind of dye such as D-bisCF<sub>3</sub>, D-OMe, and D-TPA. The performance is due to its broad range of visible light absorption, appropriate localization of the frontier orbitals and high charge collection efficiency [334]. However cyclometalated complex of [Ru(tpy)L1b-L5b]<sup>+</sup>PF<sub>6</sub> prepared with *bis*(benzimidazolyl)benzene ligands shows inferior performance with respect to power conversion efficiency of 3.7% [342]. Other dyes have lower power conversion efficiency of 2.98% for [Ru(CH<sub>3</sub>CN)L4]PF<sub>6</sub>[344] and 0.104% for [Ru(bpy)<sub>2</sub>(H5)]PF<sub>6</sub> [339] respectively.

From chart 1.16, the featuring of two fluorine atoms in the phenylpyridine ligand of the cyclometaleted complex (complex 1) gives rise to a highly efficient charge transfer. The performance of the cell based on the adsorption of sensitizers onto nanocrystalline  $TiO_2$  films shows an excellent incident monochromatic photon-to-current conversion efficiency of 83% coupled with an overall solar light-electricity conversion efficiency of 10.1% at standard Air Mass 1.5 Sunlight [345]. Likewise, another thiocyanate-free cyclometaleted ruthenium sensitizer of Ru(II) *bis*(4,4-dicarboxy-2,2-bipyridine)-5-phenyl-3-(trifluoromethyl)-1H-pyrazole designated as HIS1 has been designed and developed. The sensitizer exhibits MLCT bands in the visible region at 546 nm with a

molar extinction coefficient of  $12 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$  as well as a photoelectric conversion efficiency of 4.76% under standard AM 1.5 Sunlight [346].



**Chart 1.17:** Molecular structures of thiocyanate-free cyclometalated ruthenium sensitizer [345] and HISI sensitizer [346]

# **1.9.** Tridentate ruthenium(II) polypyridyl sensitizers

Based on the first report of black dye as a tridentate sensitizer as wells as its ability to harvest photons near the infrared region, the design of tridentate ruthenium polypyridyl sensitizers has generated a lot of interest [347]. A good tridentate ruthenium polypyridyl sensitizer is neutral panchromatic ruthenium(II) terpyridine sensitizer denoted as PRT1. This sensitizer contains pyridine pyrazolate (pypz) chelates as an ancillary ligand. The development of PRT1 was carried out in order to enhance the light harvesting efficiency of DSSCs. The photosensitizer exhibited higher molar extinction coefficient at a wavelength of 400–550 nm due to the contribution of the  $\pi$ - extending conjugation from the pyrazolate (pypz) chelates

thereby achieving photoelectric conversion efficiency of 10% and having remarkable photostablity [348]. Also, a tridentate bipyridine pyrazolate coupled ruthenium(II) complex coded as HY2 has been designed based on the introduction of tridentate bipyridine pyrazolate (bpz) coupled with the modification of 2,2'-bypyridine motif as ancillary ligand which remarkably improved the absorptivity in the higher-lying electronic states ranging between 350 and 550 nm. Since the pyrazolate unit has a strong s-donor property, it aided tridentate binding characteristics given by the bpz ligand which provided a more stable complexation compared to a terpyridine moiety of similar ruthenium complex design. The sensitizer achieved electric conversion efficiency 8.07% illumination of under the 1.5 of Sunlight [300].





HY2 dye





Ru(II) 2,6-Bis(3,5-dim ethylpyrazol-1-yl) pyridi ne

# **Chart 1.18**: Molecular structure of PTR [348], HY2 [300], SPS-G3 [349] and Ru(II) 26-Bis(3,5-dimethylpyrazol-1-yl)pyridine sensitizers [299]

Furthermore, A novel ruthenium-based thiocyanate free photosensitizer incorporating 2,6-bis(1-methylbenzimidazol- 2-yl)pyridine denoted as SPS-G3 has been developed and reported to have an overall photoelectric conversion efficiency of 6.04%. The 2,6-bis(1-methylbenzimidazol-2'-yl)pyridine possessing both strong  $\sigma$ -donor (benzimidazole unit) and  $\pi$ -acceptor (pyridine ring) qualities acts a hybrid ligand, while the terpyridine ligand serves the purpose of grafting onto the surface of the nanocrystalline semiconductor of Titanium dioxide thereby promoting the ejection of electrons into the conduction band [349]. Likewise, the development of a new complex [Ru(II)(dcbpyH<sub>2</sub>)(bdmpp)Cl](PF<sub>6</sub>) (where bdmpp is 2,6-bis(3,5-dimethyl-N-pyrazoyl)pyridine, dcbpyH<sub>2</sub> is 2,2-bipyridine-4,4-dicarboxylic acid has been reported to have broad and very high intensity MLCT absorption band in the visible thereby making it a viable sensitizer for dye sensitized solar cell [299, 350].

#### **1.10 PHOTOPHYSICAL STUDIES**

#### 1.10.1 Introduction

Photophysical studies provide a framework in determining the ground and excited state including the photophysical properties of molecular sensitizers with a basic function of charge transfer dynamics at interfaces in dye sensitized solar cell [351]. A photophysical process is a state of transition whereby a molecule absorbs photons and gets promoted from the ground state to excited state. Upon absorption of photons, the transitions can be categorized as (i) metal-centred transition (MC) also known as d-d transition whereby electrons are promoted from a  $\pi$ M metal orbital to  $\sigma^*$ M orbital, (ii) ligand-centred (LC) or  $\pi$ - $\pi^*$  ligand-to-ligand transitions and (iii) Metal-to-ligand

charge transfer (MLCT), or ligand-to-metal charge transfer transitions (LMCT). At this high energy level, the molecule becomes unstable and undergoes the process of deactivation. The Excited state deactivation stages occur through the following: (i) the emission of light (luminescence), (ii) the release of excess heat (thermal deactivation), (iii) the interaction with other molecules within the neighbouring environment (quenching process) and (iv)the formation of a new species (photochemical reaction) [183].

Ruthenium(II) polypyridine complexes are most widely investigated amongst the transition metal complexes due to its peculiar qualities: chemical stability, redox properties, excited-state reactivity, emission, and excited-state lifetime [352]. The choice of ruthenium as a high value metal usually depends on its octahedral geometric configuration with the ease to combine with chosen ligands in an organized and controlled manner. Its ruthenium complex formation promotes the photophysical and electrochemical properties to be fine-tuned in predictable route and at the centre. Also, its oxidation states from I to III is stable and obtainable [351]. Among the group of ruthenium(II) polypyridine complexes, the prototype of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> have been selected to conveniently discuss the general properties of its compounds [352]. The Photophysical and electrochemical properties of the ruthenium complex appropriately define the optimal performance of dye sensitized solar cell. Therefore, absorption properties clearly give the short circuit current while the oxidation potential determination establishes the maximum open-circuit voltage of the device [273].

#### **1.10.2.** Absorption spectroscopy

Ruthenium(II) polypyridine complexes contain both d<sup>6</sup> electronic configuration of  $Ru^{2+}$  and polypyridine ligands incorporating  $\sigma$  donor orbitals localized on the nitrogen atoms and  $\pi$  donor and  $\pi*$  acceptor orbitals delocalized on aromatic rings [352]. To describe the electronic transition states and redox properties of ruthenium(II) polypyridine complexes, a representation of a localised molecular orbital configuration is usually adopted from figure 1.6.

Figure 1.10 shows a simplified representation of the molecular orbital of transition metal complex of d<sup>6</sup> geometry [353]. The molecular orbital field has the ground and the low lying excited states of both the  $t_{2g}$  (stabilized) and  $e_g$  (destabilized) of d orbital in the Ru metal ion and  $\pi_L$  bonding and  $\pi_*$  antibonding orbital of the polypyridine ligand aromatic configuration. Upon the absorption of light, four possible transitions can occur such as  $\pi *_L - \pi_L$ , d-d\*,  $\pi_L - d^*$  and d- $\pi *_L$  [354]. The transient movement of electrons from the  $t_{2g}$  to  $e_g$  orbital are situated within the ruthenium metal, usually called metal-centred (MC), ligand field or d-d transitions. Promotion of electrons from the Ru metal  $t_{2g}$  to  $\pi *_L$  antibonding orbital of the polypyridine ligand gives rise to d- $\pi *_L$  states. Usually, the displacement of electronic charge from the metal to ligand or vice versa is called charge transfer differentiated into metal-to- ligand charge transfer (MLCT) and ligand-to- metal charge transfer transition (LMCT). Electronic transition can take place within the ligand  $\pi_L$  bonding orbital to  $\pi_{*L}$  antibonding orbital, usually called ligand-centred (LC) or  $\pi^{*-\pi}$  transitions. Interactions take place for other less frequently occurring electronic transitions such as the promotion of electrons from the metal centred orbital to a solvent orbital labelled as Charge-transfer to solvent(CTTS)

or within two orbital localised on separate ligands on the same metal centre labelled as ligand-to-ligand charge-transfer, (LLCT) [353, 354].



**Figure 1.10:** Molecular orbital of electronic transitions for metal complex in octahedral configuration [353].

The excited states orbitals are obtained when light absorption processes are allowed for transitions between the ground and excited state having the same spin orientation. Such transitions are captured as intense bands in the absorption spectra of the molecules. Transitions between the ground and excited state with the different spin orientation are said to be forbidden and are not captured in absorption spectra [183].

Figure 1.11 shows the electronic absorption spectrum of the Ru(bpy)<sup>2+</sup> complex in aqueous solution at room temperature. Showed are the proposed assignments. The absorption bands at bands at 185 nm and 285 nm have been assigned to spin-allowed

ligand centred (LC)  $\pi \rightarrow \pi *$  transitions of bipyridine ligand. The intense band in the visible region at 450 nm have been assigned to spin allowed MLCT d  $\rightarrow \pi *$  transitions. Absorption band with a long wavelength is assigned at about 550 nm due to spin-forbidden MLCT transition(s). The electronic transitions of Ru(bpy)<sup>2+</sup> such MC, LC, and MLCT may have been assigned due to 'singlet or triplet' multiplicity arising from spin-orbit coupling in the complex [352]. The LC, MC and MLCT excited states of transition-metal complex are determined by the redox potential of the metal complex, the ligand field strength and intrinsic properties of the ligands [183]. For this reason, ruthenium(II) polypyridine undergoes ligand structural modification which tends to vary the relative energy positions of the excited states and change in its photophysical properties [183]. Figure 1.7 is a representation of the electronic absorption spectrum of Ru(bpy)<sup>2+</sup> in aqueous solution [352].



Figure 1.11: Electronic absorption spectrum of  $Ru(bpy)^{2+}$  in aqueous solution [352].

## 1.10.3. Emission spectroscopy

The photophysical scheme of Ru(bpy)<sup>2+</sup> can be explained by the Jablonski diagram in (Figure 1.12). Upon the absorption of energy within the visible region of the spectrum, it leads to the population of higher energy metal-to-ligand charge transfer (<sup>1</sup>MLCT) state that accounts for the promotion of an electron from the metal centred HOMO to the ligand centred LUMO. The lower energy metal-to-ligand charge transfer (<sup>3</sup>MLCT) state is quantitatively populated by means of intersystem crossing that corresponds to deactivation through the emission of photons [355].



Figure 1.12 A simplified Jablonski diagram for Ru(II) polypyridine complexes [355].

## 1.11. Electrochemical processes

The main thrust behind the electrochemical processes is to investigate the changes of inorganic compounds due to loss or gain of electrons [356]. The localised Molecular orbital approximation is usually used to describe the oxidation and reduction processes being viewed as metal or ligand centred. The metal centred possesses the highest energy occupied molecular orbital (HOMO) whereas the lowest empty molecular orbital (LUMO) is located on metal or ligand centred, depending on the relative energy ordering. The ligand field strength determines whether the ligands can be easily reduced or cannot be easily reduced. The ligands can be easily reduced when the ligand field indicates that the ligands cannot be easily reduced at the centre, thereby, the lowest empty orbital can be metal centred. The electrochemical properties are related to the orbital nature of the lowest excited state due to the involvement of HOMO and LUMO orbitals in oxidation and reduction processes. However, electrochemical potentials are related to the spectroscopic energies [353, 357].

Ruthenium (II) polypyridyl complexes show excellent performance in electrochemical processes which can be distinguished into three types such as reversible electrochemical processes, irreversible electrochemical oxidation or reduction, which leads to ligand decomposition and redox processes which leads to structural changes. These complexes actively control the three processes which leads to metal-cantered oxidation and ligand-based reduction reactions. As a result, the oxidation state (+2) of

the ruthenium centre has been has been widely investigated as well as versatile electrochemical and light-harvesting properties have been [358].

# 1.11.1. Reversible processes

The reversibility of the redox processes involves a situation whereby metal complex cannot undergo chemical reaction due to addition or extraction of electrons. Ruthenium (II) Polypyridine complexes belong to the category of metal complexes that undergo reversible electrochemical processes. In general, a proof that complexation occurred is based on the change in the potential values at which the metal is oxidized and the ligands are reduced [359]. However, investigation has revealed that oxidation and/or reduction can lead to the decomposition of the other metal complex whereas in other cases such as ruthenium(II) complexes the oxidized and/or reduced form are stable, which of course is a basic requirement for most device-type utilization [353].

## 1.11.2. Irreversible oxidation process

The oxidation of Ruthenium(II) complexes, with diamagnetic as well as  $t_2g^6$  configuration, involves removal of an electron from the HOMO, usually a  $\pi_M$  ( $t_2g$ ) metal-centred orbital leading to the formation of Ruthenium(III) complexes with a paramagnetic and  $\pi_M$  ( $t_2g$ ) <sup>5</sup>configuration, which are usually inert to ligand substitution [183].

$$[Ru^{II}(L)_3]^{2+}$$
  $=$   $[Ru^{III}(L)_3]^{3+}$  +  $e^{-1}$ 

The reduction potential of Ru(III)/Ru- (II) complexes incorporating only polypyridinetype ligands falls within the narrow range of +1.25 V (vs SCE, acetonitrile solution). The potential increases to +0.32 V on the substitution of one bpy ligand by two Cl<sup>-</sup> ions giving rise to [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>] whereas the involvement of a strong  $\pi$ -acceptor CO leads to an increase of the reduction potential above +1.9 [353, 357].

## 1.11.3. Irreversible reduction process

Reduction mainly occurs in the  $\pi^*$  orbital of the polypyridine ligands when coordinated to the ruthenium metal ion, with d<sup>6</sup> low-spin configuration. Thus, the reduced specie of Ruthenium is usually inert and the reduction process is reversible [183, 353].

$$[Ru^{II}(L)_3]^{2+} + e^- = [Ru^{II}(L)_2L]^+$$

However, when the localisation of the added electron is largely on the metal-centred orbital due to the possession of lowest-energy empty orbital, the reduction of these complexes give rise to unstable low-spin d<sup>7</sup> electronic configuration, thereby, leading to fast ligand dissociation and the reduction process is considered irreversible [183].

$$[\operatorname{Ru}^{II}(L)_3]^{2+} + e^- \longrightarrow [\operatorname{Ru}^{II}(L)_3]^+ \longrightarrow [\operatorname{Ru}^{II}(L)_2]^+ + L$$

\_

#### 1.12. Tunability of spectroscopic and electrochemical processes

The concept of tunability is described as the feasibility of synthesizing metal complexes with desired optical absorption, photophysical and redox properties [360]. The energy and conversion process of metal complexes has been greatly influenced by the nature of ligands around the metal [361]. In Ruthenium (II) complexes, the energy of the MLCT transition can be given by the demarcation between the lowest polypyridine ligand  $\pi^*$  and the Ru (t<sub>2g</sub>) orbitals. The reduction of the MLCT state energy can be attained by either decreasing the energy of polypyridine ligand  $\pi^*$  or increasing the energy of the Ru  $(t_{2g})$  orbitals [360]. Thus, the tuning of CT transition state in a bid to enhance the spectral and redox properties of Ru polypyridyl complexes can be achieved in two ways. Firstly, a ligand with a low-lying  $\pi$ \* molecular orbital should be introduced and secondly by introducing a strong donor ligand would strongly influence the destabilization of the metal  $t_{2g}$  orbital. Due to charge transfer transition from metal  $t_{2g}$  (HOMO) orbitals to  $\pi^*$  (LUMO) orbitals of the ligand, Ruthenium complexes show strong visible bands [362]. This lowest energy MLCT transition can be found between the region of 400 and 600 nm [360]. Pervious spectroscopic and electrochemical Studies carried on Ruthenium (II) polypyridine complexes has reached a conclusion, stating that the oxidation and reduction potentials are the best indicators of the energy levels of the HOMO and LUMO respectively [362].

# **1.13.** AIMS AND OBJECTIVES OF THE THESIS

The specific aims of this thesis is to synthesize, characterize and carry out photophysical studies of ruthenium(II) complexes for Dye sensitized solar cells.

## **Objectives:**

1. To synthesize N, N-bis(3, 5-dimethylpyrazol-1-ylmethyl) chelating ligands with other ligands such as 4-(4-vinylphenyl)-2.6-bis(phenyl)pyridine,11-(4-

vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine and 4'-(4-vinyl)-2,2':6',2''-terpyridine.

2. To synthesize ruthenium(II) complexes using the synthesized ligands as coordinating compounds.

3. To characterize the ruthenium(II) complexes using spectroscopic techniques

4. To investigate the photophysical and electrochemical properties of the synthesized ruthenium(II) complexes in relation to DSSCs applications.

## **CHAPTER TWO**

# 2.0. EXPERIMENTAL

# 2.1 Chemicals and solvents

All chemicals and solvents used for this study were reagent grade and obtained from commercial suppliers without further purification.

## Chemicals

3.5-Dimethylpyrazole, ammonium thiocyanate, 2.2'-bipyridine-4,4'-dicarboxylic acid, *tetrakis*(triphenylphosphine)palladium(0), ruthenium (III) chloride trihydrate, tributylvinyltin, potassium hydroxide, 4-bromobenzaldehyde, ammonium acetate, ammonium hexafluorophosphate, 1-indanone, 2-acetylpyridine, anthranilic acid, 4-methoxy-2-nitroaniline, aniline, toluidine, cyclohexylamine, anisidine, acetophenone.

## **Solvents**

Ethanol, methanol, chloroform, dichloromethane, acetone, ethyl acetate. tetrahydrofuran, dimethyl sulfoxide, diethyl ether, toluene, *N*,*N*'-dimethylformamide,

acetonitrile, glacial acetic acid, formaldehyde
#### **2.2 Physical Measurement and Instrumentation**

#### 2.2.1 Melting Point

The melting point determination of the ligands and complexes were carried out with Stuart Melting Point instrument (SMP II).

#### 2.2.2 Infrared Spectroscopy

The infrared spectra were measured as clean solids on a Perkin Elmer spectrum two spectrometer in the range 4000-370 cm<sup>-1</sup> by utilizing an attenuated total reflectance (ATR) assembly.

#### 2.2.3 UV-Visible Spectroscopy

The UV-Vis spectroscopy were recorded in 1 cm path length quartz cuvettes on Perkin Elmer Lambda-365 spectrophotometer in the region 190-1000 nm using dimethyl sulfoxide as solvent.

#### 2.2.4 <sup>1</sup>H and <sup>13</sup>C NMR Spectrometer

The <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker Avance (400MHz) spectrometer whereby deuterated DMSO was used as solvent. Recorded chemical shifts are referenced according to the residual solvent signals; and the respective splitting patterns are noted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Appendix I shows their presentation.

#### 2.2.5 Photoluminescence Spectroscopy

The photoluminescence measurement were recorded in 1 cm path length quartz cuvettes on Perkin Elmer LS 45 Fluorimeter using dimethyl sulfoxide as solvent.

#### 2.2.6 Conductivity

The molar conductance of complexes was verified in DMSO at room temperature by the use of Crison EC-Meter Basic 30+ Conductivity Cell.

#### 2.2.7 Electrochemistry

Cyclic voltammetry and square wave measurements were done using an Autolab potentiostat equipped with a glassy carbon working electrode, a pseudo Ag/AgCl reference electrode and an auxiliary Pt counter electrode. The complexes were freshly prepared at 2 x  $10^{-3}$  M concentration in DMSO containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Autolab Nova 1.7 software was used for the analysis with the following settings made; set potential (5 mV), scan rate 25 mVs<sup>-1</sup> frequency 25 Hz, amplitude 20 mV.

The glassy carbon working electrode surface was polished with alumina and ultrapure water slurry on Buechler felt polishing pad thereafter rinsed with excess ultrapure water between each experiment.

#### 2.3. Preparation of ligands

#### 2.3.1. Synthesis of 1-Hydroxomethyl-3, 5-Dimethylpyrazole

The precursor was synthesized according to reported method in literature [363]. To 20 mL of ethanol and 25 mL of formaldehyde solution 35% at room temperature was added (20 g, 208 mmol) of 3, 5-Dimethylpyrazole in a beaker. The mixture was agitated at room temperature for 12 hours. One half of the original volume of the solvent was removed and ice was added to the concentrate solvent. The deposited precipitate was collected by vacuum filtration, washed with water and dried under pressure yielding a white compound (8.3 g, 32 % yield) with following characteristics melting point 106-108°C. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta_{\rm H}$  (ppm) 2.13 (s, 3H, Pz-CH<sub>3</sub>), 2.24 (s, 3H, Pz-CH<sub>3</sub>), 5.23 (s, 1H, OH), 5.72 (s, 2H, HPz), 5.82 (s, 1H, HPZ). <sup>13</sup>C NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta_{\rm C}$  (ppm) 10.70 (CH<sub>3</sub>Pz), 13.69 (Pz-CH<sub>3</sub>), 105.93 (CPZH), 139.91(CPz CH<sub>3</sub>).



**Figure 2.1:** Chemical structure of 1-Hydroxomethyl-3,5-Dimethylpyrazole as precursor

# 2.3.2. Synthesis of [*N*,*N*-bis(3, 5-dimethylpyrazol-1-yl-methyl)-anthranilic acid (*bdmpmaa*)-(L1)

The ligand was synthesized as reported in literature with slight modification [364]. One equal amount of anthranilic acid (0.69 g, 5 mmol) and two equal amount (1.26 g, 10 mmol) of 1-Hydroxymethyl-3, 5-dimethylpyrazole were dissolved in acetonitrile (1 mL). The mixture was heated in a water bath at 65 °C for 4 hours. The recuperated residue was extracted with dichloromethane and washed with water. The concentration of the organic solution was done under reduced pressure and the solid recrystallized with ethyl acetate to obtain a white crystal. (0.25 g, 14 % yield) with the following characteristics melting point 156 °C. The yield was low due to unavoidable losses during workup.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: ): 3370 (s) (OH), 2921 (m), 2860 (m) 1607 (vs) (C=C), 1524 (vs), 1468 (m), (C=N), 1374 (s), 1291 (m), 1227 (vs), 1152 (s), 1119 (m), 1042 (m), 942 (m), 823 (s), 749 (vs), 640 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm δ<sub>H</sub> (ppm) 2.02 (s, 6H, Pz-CH<sub>3</sub>), 2.18 (s, 6H, Pz-CH<sub>3</sub>), 5.56 (s, 4H, N-CH<sub>2</sub>-N), 5.78 (s, 2H, HPz), 6.72 (t, 1H, Hph (m)), 7.30 (d, 1H, Hph (m)), 7.80 (d, 1H, Hph (o)).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm): δ<sub>C</sub> (ppm) 11.07 (CH<sub>3</sub>Pz), 12.57 (Pz- CH<sub>3</sub>), 56.69 (N- CH<sub>2</sub>-N), 106.01 (CPzH), 119.78 (CPh (m)), 130.45 (Cph (o)), 132.02 (N- CPh), 139.06 (CPz- CH<sub>3</sub>), 146.06 (N-CPz), 170.25 CPh-COOH).



**Figure 2.2:** Chemical structure of [*N*,*N*-bis(3, 5-dimethylpyrazol-1-ylmethyl)anthranilic acid (bdmpmaa) ligand 1

### 2.3.3. Synthesis of [*N*,*N*-bis(3, 5-dimethylpyrazol-1-yl-methyl)-4-methoxy-2nitroaniline (*bdmpmeta*)-(L2)

The ligand was synthesized as reported in literature with slight modification [364]. One equivalent amount of -4-Methoxyl-2-nitrophenylamine (0.84 g, 5 mmol) and two equivalent amount (1.26 g, 5 mmol) of 1-Hydroxymethyl-3,5-dimethylpyrazole were dissolved in acetonitrile (2 mL). The mixture was heated in a water bath at 65 °C for 4 hours. The residue was extracted with dichloromethane and washed with water. The concentration of the organic solution was done under reduced pressure and the solid was recrystallized with ethyl acetate to obtain a red crystal. (0.87 g, 45 % yield) with the following characteristic melting point 86 °C. FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3127 (m), 2933 (m), 2830 (m) 1607 (vs) (C=C), 1524 (s) (C=N), 1348 (s), 1291 (m), 1232 (vs), 1143 (m), 1054 (s), 971 (s), 831 (m), 754 (vs), 635 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 2.08 (s, 6H, Pz-CH<sub>3</sub>), 2.12 (s, 6H, Pz-CH<sub>3</sub>), 5.57 (s, 2H, N-CH<sub>2</sub>-N), 5.81 (s, 2H, HPz), 7.02 (d, 1H, Hph (m)), 7.36 (d, 1H, Hph (o)).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 11.05 (CH<sub>3</sub>Pz), 13.67 (Pz- CH<sub>3</sub>), 66.79 (N-CH<sub>2</sub>-N), 105.32 (CPzH), 117.71 (CPh (m)), 126.54 (Cph (o)), 129.96 (N-CPh), 139.15 (CPz- CH<sub>3</sub>), 146.40 (N-CPz).



**Figure 2.3:** Chemical structure of [*N*,*N*-bis(3, 5-dimethylpyrazol-1-ylmethyl)-4-Methoxy-2-nitroaniline (bdmpmeta) ligand 2

# **2.3.4.** Synthesis of [*N*,*N*-bis(3, 5-dimethylpyrazol-1-yl-methyl) aniline (*bdmpmal*) -(L3)

The ligand was synthesized as reported in literature with slight modification [364]. One equal amount of aniline (0.37 g, 4 mmol) and two equal amount (1.01 g, 8 mmol) of 1-Hydroxymethyl-3,5-dimethylpyrazole were dissolved in acetonitrile (1 mL). The mixture was heated in a water bath at 65°C for 4 hours. The residue was extracted with dichloromethane and washed with water. The concentration of the organic solution was done under reduced pressure and the solid product was further purified by column chromatogram silica gel Chloroform-Methanol 100:1 (v/v) which yielded a pale yellow compound. (0.49 g, 40 % yield) with the following characteristic melting point 83 °C.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3037 (m), 2933 (m), 2852 (m) 1675 (m) (C=C), 1503 (s) (C=N), 1380 (s), 1256 (s), 1222 (v), 1163 (s), 1123 (s), 1035 (s), 966 (s), 867 (s), 749 (vs), 633 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 2.03 (s, 6H, Pz-CH<sub>3</sub>), 2.17 (s, 6H, Pz-CH<sub>3</sub>), 5.45 (s, 2H, N-CH<sub>2</sub>-N), 5.75 (s, 2H, HPz), 6.88 (t, 1H, Hph (m)), 7.02 (d, 1H, Hph (o). <sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 11.18 (CH<sub>3</sub>Pz), 13.73 (Pz- CH<sub>3</sub>), 57.75 (N-CH<sub>2</sub>-N), 105.70 (CPzH), 117.47 (CPh (m)), 120.34 (Cph (o)), 129.27 (N-CPh), 138.58 (CPz- CH<sub>3</sub>), 145.63 (N-CPz).



**Figure 2.4:** Chemical structure of [N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl) aniline (bdmpmal) as ligand 3

# 2.3.5. Synthesis of [N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl) toluidine (*bdmpmt*) -(L4)

The ligand was synthesized as reported in literature with slight modification [364]. An equal amount of p-toluidine (0.43 g, 4 mmol) and two equivalent amount (1.01 g, 8 mmol) of 1-Hydroxymethyl-3,5-dimethylpyrazole were dissolved in acetonitrile (1 mL). The mixture was heated in a water bath at 65 °C for 4 hours. The residue was extracted with dichloromethane and washed with water. The concentration of the organic solution was done under reduced pressure and the solid was recrystallized with ethyl acetate to obtain a white crystal (0.59 g, 47 % yield) with the following characteristics melting point 91°C.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3048 (m), 2938 (w), 2849 (w) 1607 (w) (C=C), 1545 (s) (C=N), 1375 (s), 1256 (s), 1222 (s), 1158 (m), 1113 (s), 1028 (s), 966 (s), 867 (s), 774 (s), 631 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm 2.08 (s, 6H, Pz-CH<sub>3</sub>), 2.18 (s, 6H, Pz-CH<sub>3</sub>), 5.53 (s, 2H, N-CH<sub>2</sub>-N), 5.82 (s, 2H, HPz), 6.75 (d, 1H, Hph (o)), 6.91 (d, 1H, Hph (m). <sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) ) 11.13 (CH<sub>3</sub>Pz), 13.73 (Pz- CH<sub>3</sub>), 58.04 (N-CH<sub>2</sub>-N), 105.94 (CPzH), 116.05 (CPh (o)), 125.88 (Cph (m)), 129.70 (N-CPh), 139.16 (CPz- CH<sub>3</sub>), 145.62 (N-CPz).



**Figure 2.5:** Chemical structure of [N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl) toluidine (bdmpmt) ligand 4

# 2.3.6. Synthesis of [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)cyclohexylamine (*bdmpmcy*)-(L5)

The ligand was synthesized as reported in literature with slight modification [364]. An equal amount of cyclohexylamine (0.40 g, 4 mmol) and two equivalent amount (1.01 g, 8 mmol) of 1-Hydroxymethyl-3,5-dimethylpyrazole were dissolved in acetonitrile (1 mL). The mixture was heated in a water bath at 65 °C for 4 hours. The residue was extracted with dichloromethane and washed with water. The concentration of the

organic solution was done under reduced pressure and the solid product was further purified by column chromatogram silica gel Chloroform-Methanol 100:1 (v/v) which yielded a titled compound of cream colour. (0.55 g, 43 % yield) with the following characteristic melting point 87 °C.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3079 (w), 2926 (vs), 2837 (s) 1607 (w) (C=C), 1558 (vs) (C=N), 1365 (m), 1256 (m), 1232 (m), 1182 (w), 1123 (w), 1030 (m), 966 (s), 861 (s), 759 (s), 636 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 1.05 -1.80 (m, 11H, CH<sub>2</sub>- cyclohexyl), 2.11 (s, 6H, Pz-CH<sub>3</sub>), 2.2 3(s, 6H, Pz-CH<sub>3</sub>), 4.92 (s, 4H, N-CH<sub>2</sub>-N), 5.80 (s, 2H, HPz). <sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 10.90 (CH<sub>3</sub>Pz), 13.79 (Pz- CH<sub>3</sub>), 57.87 (N-

CH<sub>2</sub>-N), 105.70 (CPzH), 117.47 (CPh), 139.31 (CPz- CH<sub>3</sub>), 146.02 (N-CPz).



**Figure 2.6:** Chemical structure of [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)cyclohexylamine (bdmpmcy) ligand 5

# 2.3.7. Synthesis of [N,N-bis(3,5-dimethylpyrazol-1-yl-methyl) anisidine (bdmpmas)-(L6)

The ligand was synthesized as reported in literature with slight modification [364]. An equal amount of p-anisidine (0.51 g, 4 mmol) and two equivalent amount (1.01 g, 8 mmols) of 1-Hydroxymethyl-3,5-dimethylpyrazole were dissolved in acetonitrile (1 mL). The mixture was heated in a water bath at 65 °C for 4 hours. The recuperated residue was extracted with dichloromethane and washed with water. The concentration of the organic solution was done under reduced pressure. The solid product was further purified by column chromatogram silica gel Chloroform-Methanol 100:1 (v/v) which yielded a titled compound of cream colour (0.87 g, 64 % yield) with the following characteristics melting point 68 °C.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3127 (s), 2926 (s), 2837 (w) 1607 (w) (C=C), 1545 (vs) (C=N), 1360 (m), 1256 (m), 1232 (vs), 1183 (m), 1118 (w), 1025 (s), 966 (s), 882 (w), 774 (s), 635 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm2.03 (s, 6H, Pz-CH<sub>3</sub>), 2.22 (s, 6H, Pz-CH<sub>3</sub>), 5.48 (s, 4H, N-CH<sub>2</sub>-N), 5.82 (s, 2H, HPz), 6.87 (d, 1H, Hph (o)), 7.02 (d, 1H, Hph (m). <sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 11.01 (CH<sub>3</sub>Pz), 13.82 (Pz- CH<sub>3</sub>), 58.64 (N-CH<sub>2</sub>-N), 105.72 (CPzH), 118.22 (CPh (o)), 121.94 (Cph (m)), 139.56 (CPz- CH<sub>3</sub>), 145.62 (N-CPz).



**Figure 2.7:** Chemical structure of [N,N-bis(3,5-dimethylpyrazol-1-ylmethyl) anisidine (bdmpmas) ligand 6

#### 2.3.8. Synthesis of 11-(4-Bromophenyl)diindeno[1,2-b:2',1'-e]pyridine

The ligand was synthesized as reported in literature with slight modification [365]. In a 100 mL round bottom flask, 4-Bromobenzaldehyde (0.37 g, 2 mmol), ammonium acetate (0.31 g, 4 mmol), and 1-Indanone (0.53 g, 4 mmol) were dissolved in water (2 mL). The reaction mixture was refluxed for 3 hours and cooled to room temperature. The crude yellow product was separated by filtration. It was further purified by recrystallization from 95 % EtOH to obtain the pure yellow compound (0.79 g, 95 % yield) with a characteristic melting point of 179 °C.

FT-IR (ATR)  $v_{max}/cm^{-1}$ : 3031 (s), 2926 (s), 2852 (w) 1608 (w) (C=C), 1551 (vs) (C=N), 1365 (s), 1292 (s), 1188 (s), 1097 (s), 1029 (s), 955 (s), 822 (s), 735 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>,  $\delta$ , ppm) 7.81 (m, 8H, diindeno), 7.62 (dd, 4H, Phenyl).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 32.20, 123.79, 124.15, 127.17, 128.25, 131.98, 132.44, 133.05, 134.58, 135.55, 136.37, 137.54, 150.49.



**Figure 2.8:** Chemical structure of 11-(4-Bromophenyl)diindeno[1,2-b:2',1'-e]pyridine as precursor

#### **2.3.9.** Synthesis of 4-(4-Bromophenyl)-2,6-bis(phenyl)pyridine

The ligand was synthesized as reported in literature with slight modification [365]. In a 100 mL round bottom flask, 4-Bromobenzaldehyde (0.37 g, 2 mmol), ammonium acetate (0.31 g, 4 mmol), and acetophenone (0.48 g, 4 mmol) were added in water (2 mL). The reaction mixture was refluxed for 3 hours and cooled to room temperature. The crude product was separated by filtration. It was further purified by recrystallization from 95 % EtOH to obtain the pale green compound (0.66 g, 85 % yield) with a characteristic melting point of 121 °C.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3038 (s), 2934 (s), 2858 (w) 1621 (w) (C=C), 1558 (s) (C=N), 1365 (s), 1210 (s), 1119 (s), 1067 (m), 1011 (m), 987 (s), 839 (vs), 817 (vs), 734 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 7.55-7.60 (t, 4H, ArH), 7.65-7.75 (m, 5H, ArH), 7.86 (d, 2H, ArH), 7.95 (s 1H, ArH), 7.99 (s 1H, ArH), 8.15 (d, 2H ArH).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 121.32, 129.02, 129.20, 131.25, 134.42, 137.89, 143.08.



**Figure 2.9:** Chemical structure of 4-(4-Bromophenyl)-2,6-bis(phenyl)pyridine as precursor

#### 2.3.10. Synthesis of 4-(4-Bromophenyl)-2,2':6'2''-terpyridine

The ligand was synthesized as reported in literature with slight modification [366]. In a 100 mL round bottom flask, a solution of 2-Acetylpyridine (2.02 g, 1.67 mmol) in ethanol (25 mL) was combined with potassium hydroxide (10 M, 1.7 mL) and stirred at room temperature for 30 minutes. Afterwards, 4-Bromobenzaldehyde (1.55 g, 8.4 mmol) was added to the solution and stirred at room temperature for 15 minutes. And 25 % ammonium solution (12.5 mL) was added subsequently. The reaction mixture was stirred at 50 °C overnight. The precipitate was separated by filtration and washed first with water (3 x 5 mL) and then with cold methanol (2 x 5 mL). It was further purified by recrystallization using 95 % EtOH to obtain a white compound (1.2 g, 36 % yield) with following characteristic melting point 135 °C.

FT-IR (ATR)  $v_{max}/cm^{-1}$ : 3045 (s), 2948 (s), 2858 (w) 1627 (w) (C=C), 1538 (m) (C=N), 1358 (s), 1292 (s), 1192 (s), 1097 (s), 1029 (s), 899 (s), 813 (s), 791 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) ) 8.80-8.75 (m, 2H, H-2A, H-2), 8.72 (s, 2H, H-3B, H-5B), 8.70- 8.63 (m, 4H Ar-H), 8.05 (t, 2H, H3A, H-3), 7.91 (d, 2H, Ar-H), 7.77 (d, 2H, H-5A, H-5). 7.54 (t, 2H, H-4A, H-4).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 118.22 (C-3B, C-5B), 121.45 (C-4A, C-4) 123.55 (C-3A, C-3), 130.37 (C-3C, C-5C), 130.74 (C-2C, C-6C), 131.00 (C-1C, C-4C), 132.76 (C-4B), 137.95 (C-4A, C-4), 148.71 (C-6A, C-6), 149.80 (C-2A, C-2), 155.27(C-2B, C-6B).



**Figure 2.10:** Chemical structure of 4-(4-Bromophenyl)-2,2':6'2''-terpyridine as precursor.

# **2.3.11.** Synthesis of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (*vpdinp*)-(L7)

The ligand was synthesized as reported in literature with slight modification [367]. A 100 mL round bottom flask was charged with a mixture of 11-(4-

Bromophenyl)diindeno[1,2-b:2',1'-e]pyridine (0.41 g,1 mmol),

tributyl(vinyl)stannane (0.32 g, 1 mmol), Tetra(triphenylphosphine)palladium(0)

(0.02 g, 0.02 mmol) were dissolved in toluene (40 mL). The mixture was refluxed at

85°C under nitrogen atmosphere for 16 hours. The crude product was isolated by

evaporation. It was further purified on silica gel column by using chloroform and

methanol mixed solvent (100:1, v/v) as eluent to obtain the pure pale yellow title

compound (0.33 g, 92 % yield) with following characteristic melting point 136 °C.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3031 (s), 2920 (s), 2851 (w) 1608 (w) (C=C), 1551 (s) (C=N), 1362 (m), 1296 (m), 1114 (m), 1093 (s), 1024 (s), 839 (m), 731 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 5.36 (d, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 7.50-7.62 (dd, 4H, Phenyl), 7.75-7.78 (m, 8H, diindeno).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 123.76, 124.06, 124.14, 127.13, 127.17,
121.17, 128.17 128.23, 131.60, 131.96, 132.42, 132.87, 133.03, 134.57, 134.89,
135.36, 135.43, 135.52, 136.34, 136.46, 137.54, 137.70, 138.91, 150.46.



**Figure 2.11:** Chemical structure of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (vpdinp) ligand 7

#### 2.3.12. Synthesis of 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (*vpbpp*)-(L8)

The ligand was synthesized as reported in literature with slight modification [367]. A 100 mL round bottom flask was charged with a mixture of 4-(4-Bromolphenyl)-2,6-bis(phenyl)pyridine (0.39 g, 1 mmol), Tributyl(vinyl)stannane (0.32 g, 1 mmol), Tetra(triphenylphosphine)palladium(0) (0.02 g, 0.02 mmol) were dissolved in toluene (40 mL). The mixture was refluxed at 85 °C under nitrogen atmosphere for 16 hours. The crude product was isolated by evaporation. It was further purified on silica gel column by using chloroform and methanol mixed solvent (100:1, v/v) as eluent to obtain the pale green compound (0.23 g, 68 % yield) with following characteristic melting point 112 °C.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3031 (s), 2926 (s), 2851 (w) 1614 (w) (C=C), 1551 (s) (C=N), 1365 (s), 1336 (s), 1214 (s), 1175 (m), 1067 (s), 1007 (m), 847 (m), 826 (m), 779 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 5.36 (d, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 7.55-7.63 (t, 4H, Ar-H), 7.65-7.79 (m, 5H, Ar-H), 7.87 (d, 2H, Ar-H), 7.95 (s, 1H, Ar-H), 7.99 (s, 1H, Ar-H ) 8.15(d, 2H, Ar-H).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 116.39, 127.11, 128.27, 129.97, 129.74, 131.26, 134.67, 137.89, 136.27, 143.09, 144.02.



**Figure 2.12:** Chemical structure of 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (vpbpp) ligand 8

#### 2.3.13. Synthesis of 4-(4-Vinylphenyl)-2,2':6'2''-terpyridine (*vptpy*)-(L9)

The ligand was synthesized as reported in literature with slight modification [367]. A 100 mL round bottom flask was charged with a mixture of 4-(4-Bromophenyl)-2,2':6'2''-terpyridine (0.39 g, 1 mmol), Tributyl(vinyl)stannane (0.32 g, 1 mmol), Tetra(triphenylphosphine)palladium(0) (0.02 g, 0.02 mmol) were dissolved in toluene (40 mL). The mixture was refluxed at 85 °C under nitrogen atmosphere for 16 hours. The crude product was isolated by evaporation and further purified on silica gel column by using chloroform and methanol mixed solvent (100:1, v/v) as eluent to

obtain the pure colourless title compound (0.27 g, 80 % yield) with following characteristic melting point 129-131°C.

FT-IR (ATR)  $v_{max}/cm^{-1}$ : 3065 (s), 2933 (s), 2857 (w) 1614 (w) (C=C), 1524 (m) (C=N), 1351 (s), 1292 (s), 1214 (s), 1063 (s), 1067 (s), 8995 (s), 835 (s), 789 (s).

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 5.36 (d, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 7.54 (t, 2H, H-4A, H-4), 7.77 (d, 2H, H-5A, H-5). 7.91 (d, 2H, Ar-H), 8.05 (t, 2H, H3A, H-3), 8.70- 8.63 (m, 4H Ar-H), 8.72 (s, 2H, H-3B, H-5B), 8.75-8.80 (m, 2H, H-2A, H-2),

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 118.19 (C-3B, C-5B), 121.41 (C-4A, C-4) 123.53 (C-3A, C-3), 132.74 (C-3C, C-5C), 137.09 (C-2C, C-6C), 139.68 (C-1C, C-4C), 148.66 (C-4B), 155.25 (C-4A, C-4), 155.38 (C-6A, C-6), 156.13 (C-2A, C-2), 156.23(C-2B, C-6B).



**Figure 2.13:** Chemical structure of 4-(4-Vinylphenyl)-2,2':6'2''-terpyridine (vptpy) ligand 9

The hydrogen atoms of CH=CH<sub>2</sub> molecule bonded to the terpyridine ligands lead to different chemical shifts due to the fact that the vinyl hydrogens atoms are rarely equivalent. It well known that the chemical shifts for vinyl hydrogen atoms are between 4.5-6.5 ppm. But since the vinyl hydrogen atoms are deshielded due to anisotropic effect of the  $\pi$ -electrons of the C=C double bond and the vinyl molecule is a conjugated system, the chemical shift is further moved to the downfield region. Based on the fact that the neigbouring hydrogen atoms of the vinyl molecule are bonded to the double bond, they are hardly equivalent and thus they couple to each other forming a comlex coupling system as reported above.

#### 2.4. General synthetic procedure

The general synthesis of ruthenium(II) sensitizers for series I and VIII with general formula of  $[Ru(bdmpmar)(H_2dcbpy)(NCS)]^{2+}$  and  $[Ru(vptpy)(H_2dcbpy)(N^)]^{2+}$  were carried out according to literature reports [368, 369] with slight modification. For the general synthetic route of series I and VIII ruthenium(II) complexes, tridentate ligand of either N,N-bis(3, 5-Dimethylpyrazol-1-ylmethyl) aromatic organic compound (bdmpmar) or 4-(4-Vinylphenyl)-2,2':6'2''-terpyridine (vptpy) was used for the first step as shown below in scheme 2.1.



 $R_1 = COOH$  for L1 and NO<sub>2</sub> for L2  $R_2 = OCH_3$  for L2, L6 and CH<sub>3</sub> for L4

Scheme 2.1. The general synthetic route for series I and VIII ruthenium(II) complexes In terms of synthetic route, a slight modification was carried out for ruthenium(II) sensitizers of series II and III with general formula  $[Ru(bdmpmar)(vpdiinp)(H_2dcbpy)]^{2+}$  and  $[Ru(bdmpmar)(vpbpp)(H_2dcbpy)]^{2+}$ respectively as shown below in scheme 2.2



 $R_1 = COOH$  for L1 and NO<sub>2</sub> for L2  $R_2 = OCH_3$  for L2, L6 and CH<sub>3</sub> for L4

Scheme 2.2: The general synthetic route for series II and III ruthenium(II) complexes

A Similar synthetic procedure was carried out for synthetic route of set IV, V, VI and VII with general formulae of  $[Ru(H_2dcbpy)_2(N^{\circ})(NCS)]^{2+}$ ,  $[Ru(H_2dcbpy)_2(N^{\circ})_2]^{2+}$ ,  $[Ru(H_2dcbpy)(N^{\circ})_2(NCS)_2]^{2+}$ , and  $[Ru(H_2dcbpy)(N^{\circ})(NCS)_3]^{2+}$ , respectively, where N^ represents any of the monodentate ligands of either *vpdiinp* or *vpbpp*. The bidentate ligand of 4,4'-dicarboxy-2,2'-bipyridine (H\_2dcbpy) in the ratio of either one or two moles was used for the first step as shown below in scheme 2.2



Scheme 2.3. The general synthetic route for series IV, V, VI and VII ruthenium(II) complexes.

#### **2.5. Preparation of heteroleptic Ru(II) complexes**

#### 2.5.1. Synthesis of Ru(DMSO)<sub>4</sub>Cl<sub>2</sub>

The complex was synthesized as reported in literature but with slight modification [370]. In a 100 mL two neck round bottom flask, 10 mL of dimethyl sulfoxide was placed and nitrogen gas was bubbled through it for 10 minutes. 0.5 g of RuCl<sub>3</sub>.3H<sub>2</sub>O was weighed and dissolved into 10 mL of degassed DMSO. The solution was refluxed at a temperature of 140 °C with constant stirring. A colour change from dark brown to yellow was observed. Heat was then removed and the solution allowed to cool down to room temperature under nitrogen gas for 10 minutes. On addition of acetone, a yellow precipitate was formed. The yellow precipitate was then filtered under gravity and washed with 5 mL of acetone. It was then allowed to dry to obtain the pure yellow title compound (0.61 g, 66 % yield).

### 2.5.2. Synthesis of Ru(II) complexes of general molecular formula: [Ru(bdmpmar)( H2dcbpy)(NCS)]<sup>+</sup> Series I.

In series I, six novel heteroleptic ruthenium(II) complexes with the general molecular structure [Ru(bdmpmar)(dcbpyH<sub>2</sub>)(NCS)]<sup>+</sup>, were successfully synthesized as stated below:

# 2.5.2.1 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anthranilic acid)(4,4'-Dicarboxy-2,2'-bipyridine)thiocyanate)-ruthenium(II)

hexafluorophosphate [Ru(bdmpmaa)(H2dcbpy)(NCS)](PF6)-(Dye 1)

The complex was synthesized as reported in literature but with slight modification [368, 369]. In a typical one-pot synthesis, Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (119 mg, 0.25 mmol) and (bdmpmaa)-L1 of N,N-bis(3, 5-Dimethylpyrazol-1-ylmethyl)-anthranilic acid (88 mg, 0.25 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards,  $H_2$ dcbpy (61 mg, 0.25 mmol) was added and the solution further heated at reflux overnight. Subsequently, an excess amount of NH<sub>4</sub>NCS (190 mg, 2.5 mmol) added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting solid precipitated was separated by filtration. It was then washed with cold water (3 X 20 mL) and dried in vacuo over  $P_2O_5$  to obtain a dark brown compound (0.055 g, 25 % yield). The complex is soluble in acetone, tetrahydrofuran and moderably in ethanol.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3438, 3031, 2926, 2100, 1718, 1600, 1531, 1441, 1372, 1230, 1060, 1020, 916, 853, 771, 660, 542, 529 473, 446.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 7.85 (d, 1H, H-21), 7.70 (d, 1H, H-7), 7.60 (d, 1H, H-10), 7.00 (s, 1H, H-23), 6.90 (s 1H H-26), 6.75 (d, 1H, H-28), 6.55 (d, 1H, H-28), 2.20 (s, 6H Pz-CH<sub>3</sub>), 1.90 (s, 6H Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 166.49, 155.95, 151.04, 132.81, 123.93, 120.03.

2.5.2.2 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-4-Methoxy-2nitroaniline(4,4'-Dicarboxy-2,2'-bipyridine)thiocyanate)-ruthenium(II) (hexafluorophosphate) [Ru(bdmpmeta)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-(Dye 2)

The complex was synthesized as reported in literature but with slight modification [368, 369]. In a typical one-pot synthesis, Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol) and (bdmpmeta)-L2 of N,N-bis(3,5-Dimethylpyrazol-1-yl-methyl)-4-Methoxy-2-nitroaniline (58 mg, 0.15 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards, H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) was added and the solution was further heated at reflux overnight. Subsequently, an excess amount of NH<sub>4</sub>NCS (114 mg, 1.5 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting solid precipitated was separated by filtration.

Then, it was filtered, washed with cold water (3 X 20 mL) and dried in vacuo over  $P_2O_5$  to obtain a dark brown compound (0.053 g, 39 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3487, 3390, 3044, 2926, 2116, 1722, 1607, 1524, 1441, 1376, 1230, 1151, 1095, 1012, 846, 776, 667, 529, 501, 432.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.93 (d, 1H, H-20), 7.93 (s, 1H, H-23), 7.52 (s, 1H, H-7), 7.34 (d, 1H, H-9), 7.18 (d 1H, H-10), 2.30 (s, 6H, Pz-CH<sub>3</sub>), 2.10 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 166.49, 151.04, 149.68, 142.39, 132.81, 129.54, 127.03, 123.96, 121.25, 120.03.

2.5.2.3 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-aniline)(4,4'-Dicarboxy-2,2'-bipyridine)thiocyanate)-ruthenium(II)-hexafluorophosphate [Ru(bdmpmal)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-(Dye 3)

The complex was prepared in a similar procedure as described above for Dye 1 of Ru(N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-anthranilicacid)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>). In sequencial order as Dye 1, (bdmpmal)-L3 of N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-aniline (77 mg, 0.25 mmol),  $Ru(DMSO)_4Cl_2$  (119 mg, 0.25 mmol),  $H_2dcbpy$  (61 mg, 0.25 mmol) and excess amount of NH<sub>4</sub>NCS (190 mg, 2.5 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark grey complex (0.099 g, 47 % yield). The complex is soluble in acetone, chloroform and moderably in acetonitrile.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3445, 3031, 2933, 2118, 1734, 1610, 1524, 1441, 1378, 1234, 1075, 1012, 926, 812, 773, 688, 529, 473, 446.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.99 (d, 1H, H-19), 8.91 (s, 1H, H-22), 7.98 (s, 1H, H-25), 7.84 (m, 3H, Ar-H), 7.01 (d 1H, H-20), 6.98 (d, 1H, H-27), 2.19 (s, 6H, Pz-CH<sub>3</sub>), 2.12 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 166.49, 151.65, 140.02, 132.81, 123.95, 120.03.

## 2.5.2.4 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-toluidine)(4,4'-Dicarboxy-2,2'-bipyridine)thiocyanate)-ruthenium(II)-hexafluorophosphate [Ru(bdmpmt)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-(Dye 4)

The complex was prepared in a similar procedure as described above for Dye 1 of Ru(N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-anthranilicacid)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>). In sequencial order as Dye 1, (bdmpmt)-L4 of N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-toluidine (81 mg, 0.25 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (119 mg, 0.25 mmol), H<sub>2</sub>dcbpy (61 mg, 0.25 mmol) and excess amount of NH<sub>4</sub>NCS (190 mg, 2.5 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark grey complex (0.073 g, 34 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3466, 3031, 2933, 2117, 1731, 1608, 1531, 1441, 1372, 1230, 1136, 1067, 998, 922, 860, 770, 695, 542, 466, 446.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.99 (d, 1H, H-20), 8.97 (s, 1H, H-23), 8.77 (s, 1H, H-26), 7.99 (d, 2H H-7' 9), 7.97 (d 1H H-21), 7.59 (d, 2H, H-6'10), 7.15 (d 1H H-28), 7.13 (d, H, H-29), 5.29 (s, 2H, HPz), 4.27 (s, 2H, N-CH<sub>2</sub>-N), 4.24 (s, 3H H-11), 2.23 (s, 6H Pz-CH<sub>3</sub>), 2.10 (s, 6H Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 166.49, 151.15, 140.02, 132.81, 122.38, 120.03, 40.90.

### 2.5.2.5 Synthesis of *N,N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)cyclohexylamine)(4,4'-Dicarboxy-2,2'-bipyridine)thiocyanate)-ruthenium(II) hexafluorophosphate [Ru(bdmpmcy)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-(Dye 5)

The complex was prepared in a similar procedure as described above for Dye 1 of Ru(N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-anthranilicacid)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>). In sequencial order as Dye 1, (bdmpmcy)-**L5** of *N,N-bis*(3,5-Dimethylpyrazol-1-ylmethyl)-cyclohexylamine (79 mg, 0.25 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (119 mg, 0.25 mmol), H<sub>2</sub>dcbpy (61 mg, 0.25 mmol) and excess amount of NH<sub>4</sub>NCS (190 mg, 2.5 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark grey complex (0.091 g, 42 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3438, 3017, 2926, 2858, 2106, 1727, 1621, 1558, 1420, 1378, 1234, 1067, 1033, 916, 773, 660, 529, 459, 439.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.99 (d, 1H, H-19), 8.05 (s, 1H, H-22), 7.92 (s, 1H, H-20), 7.25 (d, 1H H-25), 2.21 (s, 6H Pz-CH<sub>3</sub>), 1.12 (s, 6H Pz-CH<sub>3</sub>), 1.00-1.59 (m, 10H, CH<sub>2</sub>-22 cyclohexyl).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 166.49, 140.02, 132.81, 123.95, 120.03, 106, 26.47, 25.02, 24.73.

## 2.5.2.6 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anisidine)(4,4'-Dicarboxy-2,2'-bipyridine)thiocyanate)-ruthenium(II)-hexafluorophosphate [Ru(bdmpmas)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-(Dye 6)

The complex was prepared in a similar procedure as described above for Dye 1 of Ru(N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)-anthranilicacid)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>). In sequencial order as Dye 1, (bdmpmas)-**L6** of N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anisidine (85 mg, 0.25 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (119 mg, 0.25 mmol), H<sub>2</sub>dcbpy (61 mg, 0.25 mmol) and excess amount of NH<sub>4</sub>NCS (190 mg, 2.5 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark grey complex (0.067 g, 31 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3452, 3031, 2920, 2116, 1718, 1614, 1516, 1448, 1378, 1234, 1082, 1013, 909, 846, 772, 522, 432.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.99 (d, 1H, H-20), 8.97 (s, 1H, H-23), 8.88 (s, 1H, H-26), 7.93 (d, 2H H-6' 10), 7.92 (d, 1H, H-21), 7.91 (d, 2H H-7' 9), 5.95 (s, 2H, HPz), 4.12 (s, 2H, N-CH<sub>2</sub>-N), 2.23 (s, 6H Pz-CH<sub>3</sub>), 2.10 (s, 6H Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 140.02, 132.81, 122.38, 120.03, 40.90.

### 2.5.3. Synthesis of Ru(II) complexes of general molecular formula: [Ru(bdmpmar)(vpdiinp)(dcbpyH<sub>2</sub>)]<sup>2+</sup>Series II.

In series II, six novel heteroleptic ruthenium (II) complexes with the general molecular structure  $[Ru(bdmpmar)(vpdiinp)(dcbpyH_2)]^{2+}$  were successfully synthesized as stated serially below.

2.5.3.1 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anthranilic acid)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)-ruthenium(II)-bis(hexafluorophosphate)

[Ru(bdmpmaa)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>,-(Dye 7)

The complex was synthesized as reported in literature but with slight modification [368, 369]. In a typical one-pot synthesis, Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol) and (bdmpmaa)-**L1** of *N*,*N*-bis(3,5-dimethylpyrazol-1-ylmethyl)-anthranilic acid (53 mg, 0.15 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards, 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (54 mg, 0.15 mmol) was added and the solution was further heated at reflux overnight. Subsequently, H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting solid precipitated was separated by filtration. Then, it was filtered,

washed with cold water (3 X 20 mL) and dried in vacuo over  $P_2O_5$  to obtain a black compound (0.074 g, 38 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3466, 3024, 2933, 1727, 1635, 1538, 1370, 1224, 1060, 1026, 922, 840, 784, 729, 680, 522, 487, 446.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.84 (d, 1H, H-20a), 7.84 (s, 1H, H-23a), 7.80-7.60 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.55 (d, 1H, H-21a), 7.52 (dd, 4H, C<sub>6</sub>H<sub>4</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 1.26 (s, 6H, Pz-CH<sub>3</sub>), 1.24 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.80, 150.40, 138.93, 137.55, 136.47, 136.37, 135.58, 135.46, 135.38, 134.59, 133.06, 132.44, 131.98, 131.62, 128.25, 128.19, 127.18, 124.16, 124.08, 123.79, 116.5, 26.85, 14.10

2.5.3.2 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-4-Methoxy-2nitroaniline)(11-(4-vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)-ruthenium(II)bis(hexafluorophosphate)

[Ru(bdmpmeta)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye 8)

The complex was prepared in a similar procedure as described above for Dye 7 of Ru(N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anthranilicacid)(11-(4-

Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>. In sequential order as Dye 7, (bdmpmeta)-**L2** of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-ylmethyl)-4-Methoxy-2-nitroaniline (58 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (54 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37

mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark red complex (0.087 g, 43 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3487, 3369, 3037, 2933, 2851, 1728, 1607, 1516, 1372, 1229, 1075, 1026, 951, 916, 840, 784, 729, 673, 542, 515, 480, 432.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.84 (d, 1H, H-20a), 7.81 (s, 1H, H-23a), 7.80-7.62 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.60 (d, 1H; H-21a), 7.52 (dd, 4H, C<sub>6</sub>H<sub>4</sub>), 7.48 (s, 1H, H-26a), 7.37 (s, 1H, H-7a), 7.25 (d, 1H, H-9a), 7.18 (d, 1H, H-10a), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 1.65 (s. 6H, Pz-CH<sub>3</sub>), 1.35 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 150.40, 149.46, 142.40, 138.93, 137.71,
137.55, 136.47, 136.37, 135.54, 135.45, 135.38, 134.90, 134.59, 133.05 132.88,
132.44, 131.98, 131.62, 129.54, 128.25, 127.18, 124.15, 124.07, 121.25, 116.54,
105.33, 55.96, 26.82, 14.10.

2.5.3.3 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-aniline)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(bdmpmal)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye 9)

The complex was prepared in a similar procedure as described above for Dye 7 of Ru(*N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anthranilicacid)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>. In sequential order as Dye 7, (bdmpmal)-**L3** of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-ylmethyl)- aniline (47 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 11-(4-Vinylphenyl)diindeno[1,2b:2',1'-e]pyridine (54 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark brown complex (0.087 g, 46 % yield). The complex is soluble in acetone, acetonitrile, chloroform and tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3459, 3044, 2933, 2864, 1727, 1621, 1516, 1378, 1227, 1068, 1020, 957, 936, 846, 777, 729, 680, 577, 502, 473, 432.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.84 (d, 1H, H-19a), 7.84 (s, 1H, H-22a), 7.80 (s, 1H, H-25a), 7.79-7.68 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.65 (d, 1H, H-21a), 7.52 (m, 4H, C<sub>6</sub>H<sub>4</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 4.90 (s, 2H, N-CH<sub>2</sub>-N), 1.26 (s. 6H, Pz-CH<sub>3</sub>), 1.24 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.78, 150.50, 138.93, 138.83, 137.71, 137.55, 136.47, 136.38, 135.46, 135.40, 134.90, 134.90, 134.59, 133.06, 132.89, 132.44, 131.62, 128.26, 127.18, 124.16, 124.08, 120.05, 116.54, 32.46, 32.29, 28.18, 26.82, 14.10.

2.5.3.4 Synthesis of N,N-bis(3,5-Dimethylpyrazol-1-yl-methyl)-toluidine)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(bdmpmt)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>(Dye 10)

The complex was prepared in a similar procedure as described above for Dye 7 of Ru(N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anthranilicacid)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>. In sequential order as Dye 7, (bdmpmt)-**L4** of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)- toluidine (49) mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (54 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark brown complex (0.086 g, 44 % yield). The complex is soluble in methanol, acetone, acetonitrile, chloroform ethyl acetate and tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3024, 2926, 2851, 1727, 1621, 1516, 1469, 1420, 1370, 1224, 1060, 1012, 951, 846, 736, 688, 549,501, 473, 439.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.84 (d, 1H, H-20a), 7.97 (s, 1H, H-23a), 7.84(d, 2H, H-7a' 9a), 7.82-7.65 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.60 (d, 2H, H-21a), 7.52 (dd, 4H, C<sub>6</sub>H<sub>4</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 4.15 (s, 2H, N-CH<sub>2</sub>-N), 4.12 (s, 3H, Ar-CH<sub>3</sub>), 1.64 (s, 6H, Pz-CH<sub>3</sub>), 1.34 (s, 6H, Pz-CH<sub>3</sub>)

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.80, 150.49, 139.83, 138.93, 137.71,
137.55, 136.37, 135.46, 135.38, 135.45, 133.06 132.88, 132.06, 131.98, 131.62,
128.25, 127.12, 124.18, 123.23, 116.54, 26.84. 14.11.

2.5.3.5 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)cyclohexylamine)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-4,4'-

Dicarboxy -2,2'-bipyridine) -ruthenium (II) -bis (hexafluorophosphate)

[Ru(bdmpmcy)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye 11)

The complex was prepared in a similar procedure as described above for Dye 7 of Ru(*N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anthranilicacid)(11-(4-

Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>. In sequential order as

Dye 7, (bdmpmcy)-L5 of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-

cyclohexylamine (47 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (54 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a black complex (0.042 g, 22 % yield). The complex is soluble in ethanol, methanol, acetone, acetonitrile, chloroform ethyl acetate and tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3024, 2920, 2851, 1722, 1634, 1558, 1462, 1420, 1378, 1234, 1144, 1054, 1012, 991, 916, 846, 764, 688, 556, 526, 453, 411.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.59 (d, 1H, H-19a), 7.62 (s, 1H, H-22a), 7.60-7.49 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.45 (d, 1H, H-20a), 7.35 (dd, 4H, C<sub>6</sub>H<sub>4</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 1.87 (s, 6H, Pz-CH<sub>3</sub>), 1.38 (s, 6H, Pz-CH<sub>3</sub>), 0.75-1.00 (m, CH2 cyclohexyl).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.79, 150.40, 138.93, 137.70, 137.54,
136.47, 136.37, 135.55, 135.45, 134.90, 134.58, 133.05 132.88, 132.44, 131.98,
131.62, 128.25, 128.18, 127.18, 124.16, 123.79, 116.5, 26.82, 14.10.

2.5.3.6 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)- anisidine)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)ruthenium(II)-bis(hexafluorophosphate)

[Ru(bdmpmas)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye 12)

The complex was prepared in a similar procedure as described above for Dye 7 of Ru(*N*,*N*-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anthranilic-acid)(11-(4-

Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>. In sequencial order as

Dye 7, (bdmpmas)-L6 of (N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anisidine (51
mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 11-(4vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (54 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a black complex (0.096 g, 49 % yield). The complex is soluble in methanol, acetone, acetonitrile, chloroform ethyl acetate and tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 2921, 2852, 1722, 1621, 1545, 1469, 1413, 1367, 1231, 1130, 1026, 906, 916, 846, 764, 673, 556, 508, 453, 418.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.84 (d, 1H, H-20a), 7.97 (s, 1H, H-23a), 7.80-7.72 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.70 (d, 1H, H-21a), 7.60 (dd, 4H, C<sub>6</sub>H<sub>4</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 4.15 (s, 4H, N-CH<sub>2</sub>-N), 4.13 (s, 3H, Ar-OCH<sub>3</sub>), 1.63 (s, 6H, Pz-CH<sub>3</sub>), 1.32 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 150.40, 138.93, 137.70, 137,54, 136.47, 136.37, 135.55, 135.45, 134.90, 134.58, 133.05 132.88, 132.44, 131.98, 131.62, 128.18, 128.26, 127.19, 124.16, 116.54, 26.85, 14.10.

## 2.5.4. Synthesis of Ru(II) complexes of general molecular formula: [Ru(bdmpmar)(vpbpp)(H2dcbpy)]<sup>2+</sup> Series III.

In series III, six novel heteroleptic ruthenium(II) complexes with the general molecular structure  $[Ru(bdmpmar)(vpbpp)(dcbpyH_2)]^{2+}$  were successfully synthesized as stated serially below,

2.5.4.1 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anthranilic acid)(4-Vinylphenyl)-2,6-bis(phenyl)pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(bdmpmaa)(vpbpp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>,-(Dye 13)

The complex was synthesized as reported in literature with slight modification [368, 369]. In a typical one-pot synthesis, Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71.3 mg, 0.15 mmol) and (bdmpmaa)-L1 of (N,N-bis(3,5-Dimethyl)pyrazol-1-yl-methyl)-anthranilic acid (53) mg, 0.15 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards, 4-(4-Vinylphenyl)-2,6bis(phenyl)pyridine (50 mg, 0.15 mmol) was added and the solution was further heated at reflux overnight. Subsequently,  $H_2$ dcbpy (37 mg, 0.15 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting solid precipitated was separated by filtration. Then, it was washed with cold water (3 X 20 mL) and dried in vacuo over  $P_2O_5$  to obtain a dark brown compound (0.073 g, 37 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3113, 2926, 2857, 1717, 1662, 1607, 1503, 1400, 1378, 1234, 1130, 1075, 1020, 957, 916, 846, 777, 673, 570, 529, 473, 424.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.93 (d, 1H, H-20a), 8.85 (s, 1H, H-23a), 8.15-7.96 (m, 4H, Ar-H), 7.87 (s, 2H, H-3, 5), 7.70-7.66 (m, 10H, Ar-H), 7.60 (m, 3H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 1.63 (s, 6H, Pz-CH<sub>3</sub>), 1.33 (s, 6H; Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 189.00, 151.06, 144.04, 143.10, 139.77,
138.85, 137.88, 136.37, 134.66, 134.42, 133.74, 133.61. 132.36, 131.26, 129.75,
129.29, 129.02, 128.97, 127.12, 124.47, 123.93. 120.03, 116.54, 26.83, 14.10

2.5.4.2 Synthesis of *N*,*N*-bis(3,5-dimethylpyrazol-1-yl-methyl)-4-methoxy-2nitroaniline)(4-vinylphenyl)-2,6-bis(phenyl)pyridine)-4,4'-dicarboxy-2,2'-

### bipyridine)-ruthenium(II)-bis(hexafluorophosphate)

[Ru(bdmpmeta)(vpbpp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>,-(Dye 14)

The complex was prepared in a similar procedure as described above for Dye 13 of Ru(N,N-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anthranilic acid)(4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine. In sequencial order as Dye 13, (bdmpmeta)-L2 of (*N,N-bis*(3,5-Dimethylpyrazol-1-ylmethyl)-4-Methoxy-2-nitroaniline (58 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark brown complex (0.085 g, 43 % yield). The complex is soluble in acetonitrile, chloroform, tetrahydrofuran, moderably soluble in acetonitrile.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3493, 3369, 3072, 2920, 2852, 1718, 1662, 1600, 1510, 1427, 1378, 1227, 1144, 1013, 929, 916, 846, 791, 695, 542, 480, 424.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.93 (d, 1H, H-20a), 8.83 (s, 1H, H-23a), 8.15-7.96 (m, 4H, Ar-H), 7.87 (s, 2H, H-3, 5), 7.70-7.66 (m, 10H, Ar-H), 7.37 (s, 1H, H-7a), 7.18 (d, 1H, H-9a), 7.02 (d, 1H, H-10a), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 2.51 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 149.46, 144.04, 143.10, 142.40, 137.88, 136.51, 134.74, 134.42, 133.74 133.63, 132.81, 132.36, 131.27, 131.62, 129.75, 129.54, 129.29, 129.27. 128.97, 127.61, 127.11, 124.47, 123.3, 122.29, 121.25, 116.4, 105.33, 55.96, 26.82, 14.10

2.5.4.3 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-aniline)(4-Vinylphenyl)-2,6-bis(phenyl)pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(bdmpmal)(vpbpp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>,-

(Dye 15)

The complex was prepared in a similar procedure as described above for Dye 13 of Ru(N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anthranilic acid)(4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine. In sequencial order as Dye 13, (bdmpmal)-L3 of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-ylmethyl)-aniline (46 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark brown complex (0.099 g, 53 % yield). The complex is soluble in acetone, chloroform and moderably soluble in acetonitrile.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3500, 3376, 3024, 2933, 2852, 1726, 1656, 1614, 1524, 1413, 1370, 1233, 1151, 1075, 1020, 929, 846, 764, 673, 660, 556, 522, 480, 411.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.84 (d, 1H, H-19a), 8.78 (s, 1H, H-22a) 8.15-7.96 (m, 4H, Ar-H), 7.87 (s, 2H, H-3, 5), 7.70-7.66 (m, 10H, Ar-H), 7.62 (m, 3H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 4.10 (s, 2H, N-CH<sub>2</sub>-N), 1.27 (s, 6H, Pz-CH<sub>3</sub>), 1.25 (s, 6H; Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 189.60, 144.04, 143.10, 139.77, 138.05, 137.66, 136.37, 134.42, 133.61, 132.36, 131.27. 129.75, 129.29, 122 134.90, 134.58, 133.05 132.88, 132.44, 131.98, 131.62, 128.97, 128.18, 127.12, 124.47, 123.94, 122.29, 116.54, 26.82, 14.10.

2.5.4.4 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-toluidine)(4-Vinylphenyl)-2,6-bis(phenyl)pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)-

**ruthenium(II) bis(hexafluorophosphate)** [Ru(bdmpmt)(vpbpp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>,-(Dye 16)

The complex was prepared in a similar procedure as described above for Dye 13 of Ru(N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anthranilic acid)(4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine. In sequencial order as Dye 13, (bdmpmt)-**L4** of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-ylmethyl)-toluidine (49 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark brown complex (0.074 g, 39 % yield). The complex is soluble in acetone, acetonitrile and chloroform.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3466, 3037, 2940, 2865, 1726, 1662, 1607, 1524, 1455, 1370, 1233, 1130, 1075, 1012, 916, 846, 764, 680, 564, 522, 480, 411.

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<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.91 (d, 1H, H-20a), 7.84 (s, 1H, H-23a), 8.15-7.96 (m, 4H, Ar-H), 7.87 (s, 2H, H-3, 5), 7.85 (d, 2H, H-7a, 9a) 7.70-7.66 (m, 10H, Ar-H), 7.68 (d, 2H, H-6a, 10a), 6.83 (s, 1H; H-26a) ), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 4.16 (s, 2H, N-CH<sub>2</sub>-N), 4.13 (s, 3H, Ar-CH<sub>3</sub>), 1.64 (s, 6H, Pz-CH<sub>3</sub>), 1.34 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 189.60, 144.04, 143.10, 137.88, 136.37, 134.
42, 133.74, 132.36, 131.27, 129.75, 129.29, 129.02, 128.97, 127.12, 124.47, 123.94, 122.29, 116.54, 26.85, 14.10

2.5.4.5 Synthesis of *N,N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)cyclohexylamine)(4-Vinylphenyl)-2,6-bis(phenyl)pyridine)-4,4'-dicarboxy-2,2'bipyridine)-ruthenium(II)bis(hexafluorophosphate)

[Ru(bdmpmcy)(vpbpp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye 17)

The complex was prepared in a similar procedure as described above for Dye 13 of Ru(N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anthranilic acid)(4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine. In sequencial order as Dye 13, (bdmpmcy)-L5 of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-ylmethyl)-cyclohexylamine (47 mg, 0.15 mmol),  $Ru(DMSO)_4Cl_2$  (71 mg, 0.15 mmol), 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark brown complex (0.080 g, 42 % yield). The complex is soluble in methanol, acetone, acetonitrile and chloroform.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3466, 3051, 2926, 2852, 1730, 1662, 1612, 1503, 1413, 1370, 1233, 1158, 1068, 1020, 916, 846, 764, 673, 563, 522, 473, 418.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.77 (d, 1H, H-19a), 7.79 (s, 1H, H-22a), 8.15-7.09 (m, 4H, Ar-H), 7.87 (s, 2H, H-3, 5), 7.70-7.66 (m, 10H, Ar-H), 7.32 (d, 2H, H-20a), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 1.58 (s, 6H, Pz-CH<sub>3</sub>), 1.25 (s, 6H, Pz-CH<sub>3</sub>). 1.12-1.00 (d, 2H, H-7a-H-9a).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 189.63, 144.04, 143.10, 143.00, 139.77, 138.15, 137.88, 136.37, 134.60, 132.36, 129.75, 129.29, 128.25, 127.11, 124.46, 123.30, 116.54, 26.83, 14.10.

2.5.4.6 Synthesis of *N*,*N*-bis(3,5-Dimethylpyrazol-1-yl-methyl)-anisidine)(4-Vinylphenyl)-2,6-bis(phenyl)pyridine)-4,4'-Dicarboxy-2,2'-bipyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(bdmpmas)(vpbpp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>(Dye 18)

The complex was prepared in a similar procedure as described above for Dye 13 of Ru(N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-anthranilic acid)(4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine. In sequencial order as Dye 13, (bdmpmas)-**L6** of (*N*,*N*-bis(3,5-Dimethylpyrazol-1-ylmethyl)- anisidine (51 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a black complex (0.100 g, 51 % yield). The complex is soluble in methanol, acetone, acetonitrile, chloroform and tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3031, 2948, 1730, 1648, 1607, 1510, 1372, 1228, 1151, 1075, 1026, 906, 846, 764, 688, 591, 563, 480, 424.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.98 (d, 1H, H-20a), 8.89 (d, 1H, H-23a), 8.15-7.06 (m, 4H, Ar-H), 7.87 (s, 2H, H-3, 5), 7.85 (d, 2H, H-7a, 9a) 7.70-7.66 (m, 10H, Ar-H), 6.90-6.50 (m, 3H; Ar-H) ), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>), 1.65 (s, 6H, Pz-CH<sub>3</sub>), 1.33 (s, 6H, Pz-CH<sub>3</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 189.63, 144.04, 143.10, 139.77, 138.05, 137.87, 136.51, 134.66, 134.42, 133.36, 133.61, 132.36, 129.75, 129.29, 128.97, 127.11, 124.47, 123.31, 122.29, 120.08, 116.54, 26.85, 14.10.

## 2.5.5 Synthesis of Ru(II) complexes of general molecular formula: [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N<sup>^</sup>)(NCS)]<sup>2+</sup> Series IV.

In series IV, two novel heteroleptic ruthenium(II) complexes with the general molecular structure  $[Ru(H_2dcbpy)_2(N^{\wedge})(NCS)]^{2,+}$ were successfully synthesized as stated serially below.

2.5.5.1 Synthesis of Bis(4,4'-Dicarboxy-2,2'-bipyridine)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-thiocyanate)-ruthenium(II) hexafluorophosphate) [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpdiinp)(NCS)](PF<sub>6</sub>)-(Dye 19)

The complex was synthesized as reported in literature with slight modification [368, 369]. In a typical one-pot synthesis,  $Ru(DMSO)_4Cl_2$  (71.3 mg, 0.15 mmol) and  $H_2dcbpy$  (73 mg, 0.3 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards, (*vpdiinp*)-**L7** of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine (54 mg, 0.15 mmol) was added and the

solution was further heated at reflux overnight. Subsequently, an excess amount of NH<sub>4</sub>NCS (114 mg, 1.5 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting dark brown solid precipitated was separated by filtration. It was then washed with cold water (3 X 20 mL) and dried in vacuo over P<sub>2</sub>O<sub>5</sub> (0.091 g, 54 % yield). The complex is soluble in acetone, ethyl acetate and tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3113, 3031, 2926, 2852, 2100, 1720, 1614, 1551, 1378, 1227, 1144, 1060, 1012, 957, 846, 777, 680, 556, 508, 459, 439.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.84 (d, 1H, H-6a'), 7.90 (s, 1H, H-3a'), 7.72-7.70 (m, 8H, 2C<sub>6</sub>H<sub>4</sub>), 7.65 (d, 1H, H-5a'), 7.50 (dd, 4H, C<sub>6</sub>H<sub>4</sub>), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.78, 150.51, 138.93, 137.69, 137.53,
136.46, 136.37, 135.44, 134.57, 133.05, 132.89, 132.44, 131.98, 131.6, 128.25,
127.17, 124.15, 123.79, 116.54

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# 2.5.5.2 Synthesis of Bis(4,4'-Dicarboxy-2,2'-bipyridine)(4-(4-Vinylphenyl)-2,6bis(phenyl)pyridine)-thiocyanate)-ruthenium(II)-hexafluorophosphate [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpbpp)(NCS)](PF<sub>6</sub>)-(Dye 20)

The complex was prepared in a similar procedure as described above for Dye 19 of Bis(4,4'-Dicarboxy-2,2'-bipyridine)(11-(4-Vinylphenyl)diindeno[1,2-

b:2',1'e]pyridine)-thiocyanate)-ruthenium(II)-hexafluorophosphate. In sequencial order as Dye 19, H<sub>2</sub>dcbpy (73 mg, 0.3 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71.3 mg, 0.15 mmol), (*vpbpp*)-**L8** of 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol), and excess amount of NH<sub>4</sub>NCS (114 mg, 1.5 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a black complex (0.073 g, 44 % yield). The complex is soluble in ethanol, methanol, acetone and moderably soluble in tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3487, 3031, 2926, 2110, 1720, 1607, 1558, 1469, 1378, 1234, 1151, 1075, 1026, 909, 867, 777, 680, 591, 535, 473, 432.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.89 (d, 1H, H-3a', 3), 8.15 (d, 1H, H-5a'), 7.90-7.75 (m, 5H, Ar-H), 7.62 (s, 2H, H-3, 5), 7.60-7.52 (dd, 4H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 144.03, 143.10, 139.76, 138.65, 137.87,
136.37, 133.61, 132.36, 129.75, 129.29, 128.96, 127.11, 124.46, 123.30, 116.54.

## 2.5.6 Synthesis of Ru(II) complexes of general molecular formula: [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N<sup>^</sup>)<sub>2</sub>]<sup>2+</sup> Series V.

In series V, three novel heteroleptic ruthenium (II) complexes with the general molecular structure  $[Ru(H_2dcbpy)_2(N^{\wedge})_2]^{2+}$  were successfully synthesized as stated serially below.

## 2.5.6.1 Synthesis of Bis(4,4'-Dicarboxy-2,2'-bipyridine)-di(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-ruthenium(II)

**bis(hexafluorophosphate)** [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpdiinp)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>-(Dye 21)

The complex was synthesized as reported in literature but with slight modification [368, 369]. In a typical one-pot synthesis, Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71.3 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (73 mg, 0.3 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards, (*vpdiinp*)-**L7** of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine (107 mg, 0.3 mmol) was added and the solution was further heated at reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting dark red solid precipitated was separated by filtration. It was then washed with cold water (3 X 20 mL) and dried in vacuo over P<sub>2</sub>O<sub>5</sub> (0.064 g, 27 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3072, 2940, 2865, 1703, 1626, 1500, 1448, 1413, 1370, 1227, 1130, 1060, 1020, 964, 909, 840, 722, 695, 549, 515, 473, 446.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 9.92-8.92 (m, 6H, Ar-H), 7.76-7.60 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 6.89-6.99 (m, 4H; Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 150.51, 136.37, 135.56, 133.07, 132.42, 131.63, 128.06, 127.19. 124.16, 116.54.

## 2.5.6.2 Synthesis of Bis(4,4'-Dicarboxy-2,2'-bipyridine)-di(4-(4-Vinylphenyl)-2,6bis(phenyl)pyridine)-ruthenium(II)-bis(hexafluorophosphate)

 $[Ru(H_2dcbpy)_2(vpbpp)_2](PF_6)_2-(Dye 22)$ 

The complex was prepared in a similar procedure as described above for Dye 21 of Bis(4,4'-Dicarboxy-2,2'-bipyridine)-di(11-(4-Vinylphenyl)diindeno[1,2-

b:2',1'e]pyridine)-ruthenium(II) bis(hexafluorophosphate). In sequencial order as Dye 21, H<sub>2</sub>dcbpy (73 mg, 0.3 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71.3 mg, 0.15 mmol) and (*vpbpp*)-**L8** of 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (100 mg, 0.3 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a dark red complex (0.090 g, 40 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3473, 3037, 2961, 2865, 1721, 1612, 1531, 1455, 1371, 1233, 1068, 1020, 922, 846, 771, 688, 522, 515, 473, 418.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.17 (m, 3H, Ar-H), 8.15-7.96 (m, 4H, Ar-H), 7.87 (m, 2H, H-3, 5), 7.70-7.60 (m, 10H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm 189.60, 144.03, 143.10, 136.37, 133.61, 132.61, 132.36, 129.75, 128.97, 127.12, 124.47, 123.31, 116.54

2.5.6.3 Synthesis of Bis(4,4'-Dicarboxy-2,2'-bipyridine)(4-(4-Vinylphenyl)-2,6bis(phenyl)pyridine)(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)ruthenium(II) bis(hexafluorophosphate) [Ru(H2dcbpy)<sub>2</sub>(vpbpp)(vpdiinp)](PF<sub>6</sub>)<sub>2</sub> -(Dye 23)

The complex was prepared in a similar procedure as described above for Dye 21 of Bis(4,4'-Dicarboxy-2,2'-bipyridine)-di(11-(4-Vinylphenyl)diindeno[1,2-

b:2',1'e]pyridine)-ruthenium(II) bis(hexafluorophosphate). In sequencial order as Dye 21, H<sub>2</sub>dcbpy (73 mg, 0.3 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71.3 mg, 0.15 mmol), (*vpdiinp*)-L7 of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine (54 mg, 0.15 mmol) and (*vpbpp*)-L8 of 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a dark brown complex (0.127 g, 55 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3431, 3072, 2926, 2858, 1717, 1662, 1614, 1500, 1469, 1400, 1370, 1220, 1116, 1075, 1026, 922, 846, 771, 722, 680, 556, 522, 473, 418.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.91 (d, 1H, H-6a'), 8.84 (s 1H, H-3a'), 8.16 (d, 1H, H-5a'), 8.05-7.05 (m, 18H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 150.51, 144.03, 139.10, 138.87, 137.53,
136.37, 135.56, 135.44, 134.57, 133.05, 132.44, 132.36, 131.99, 131.6, 129.75,
128.97, 128.25, 127.18, 127.18, 124.15, 123.79, 116.54.

2.5.7 Synthesis of Ru(II) complexes of general molecular formula: [Ru(H<sub>2</sub>dcbpy)(N^)<sub>2</sub>(NCS)<sub>2</sub>]<sup>2+</sup> Series VI.

In series VI, two novel heteroleptic ruthenium(II) complexes with the general molecular structure  $[Ru(H_2dcbpy)(N^{*})_2(NCS)_2]^{2+}$  were successfully synthesized as stated serially below.

2.5.7.1 Synthesis of 4,4'-Dicarboxy-2,2'-bipyridine-di(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-di(thiocyanate)-ruthenium(II) complexes [Ru(H<sub>2</sub>dcbpy)(vpdiinp)<sub>2</sub>(NCS)<sub>2</sub>]-(Dye 24)

The complex was synthesized as reported in literature with slight modification [368, 369]. In a typical one-pot synthesis, Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol. The solution was refluxed 11-(4overnight with constant stirring. Afterwards, (vpdiinp)-L7 of Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine (107 mg, 0.3 mmol) was added and the solution was further heated at reflux overnight. Subsequently, an excess amount of NH<sub>4</sub>NCS (228 mg, 0.3 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the

filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting black solid precipitated was separated by filtration. It was then washed with cold water (3 X 20 mL) and dried in vacuo over  $P_2O_5$  (0.051 g, 29 % yield). The complex is soluble in ethanol, methanol, acetone, chloroform, ethyl acetate and tetrahydrofuran moderably soluble in acetonitrile.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3051, 2933, 2851, 2077, 1709, 1621, 1500, 1469, 1420 1344, 1248, 1185, 1012, 957, 860, 846, 777, 715, 673, 604, 508, 459, 439.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 7.76-7.60 (m, 8H; 2(C<sub>6</sub>H<sub>4</sub>)), 6.89-6.75 (m, 4H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 150.51, 136.47, 136.37, 135.57, 135.40, 134.89, 134.58, 133.05 132.44, 131.99, 131.62, 128.26, 127.18, 124.15, 116.54.

## 2.5.7.2 Synthesis of 4,4'-Dicarboxy-2,2'-bipyridine-di(4-(4-Vinylphenyl)-2,6bis(phenyl)pyridine)-di(thiocyanate)-ruthenium(II)-complex

[Ru(H<sub>2</sub>dcbpy)(vpdbpp)<sub>2</sub>(NCS)<sub>2</sub>]-(Dye 25)

The complex was prepared in a similar procedure as described above for Dye 24 of  $Ru(H_2dcbpy)(11-(4-vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)_2(NCS)_2]$ . In sequencial order as Dye 24, H<sub>2</sub>dcbpy (37 mg, 0.15 mmol), Ru(DMSO)\_4Cl<sub>2</sub> (71.3 mg, 0.15 mmol), (*vpbpp*)-**L8** of 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (100 mg, 0.3 mmol), and excess amount of NH<sub>4</sub>NCS (228 mg, 0.3 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a black complex (0.046 g, 27 % yield). The

complex is soluble in ethanol, methanol, acetone, chloroform ethyl acetate, tetrahydrofuran and moderably soluble in acetonitrile.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3466, 3024, 2933, 2851, 2077, 1724, 1662, 1600, 1545, 1455, 1365, 1227, 1075, 1013, 978, 916, 909, 846, 771, 702, 667, 604, 542, 466.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.74 (s, 1H, H-3a'), 8.58 (s, 1H, H-3a), 8.15-7.96 (m, 4H, Ar-H), 7.87 (m, 2H, H-3,5), 7.70 -7.60 (m, 10H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 189.00, 144.03, 143.03, 137.87, 136.37, 134.42, 133.62, 132.36, 131.27, 129.22, 129.02, 128.97, 127.12. 124.46, 124.46, 123.31, 122.29, 116.54.

# 2.5.8 Synthesis of anionic Ru(II) complexes, ammonium salts of general molecular formula: [Ru(H2dcbpy)(N^)(NCS)3]<sup>-</sup> Series VII.

In series VII, two novel heteroleptic ruthenium(II) complexes ammonium salts with the general molecular structure  $[Ru(H_2dcbpy)(N^{\wedge})(NCS)_3]^-$  were successfully synthesized as stated serially below.

2.5.8.1 Synthesis of 4,4'-Dicarboxy-2,2'-bipyridine-di(11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)-tri(thiocyanate)-ruthenium(II) complex ammonium salt [Ru(H<sub>2</sub>dcbpy)(vpdiinp)<sub>2</sub>(NCS)<sub>3</sub>]<sup>-</sup>-(Dye 26)

The complex was synthesized as reported in literature with slight modification [368, 369]. In a typical one-pot synthesis,  $Ru(DMSO)_4Cl_2$  (71.3 mg, 0.15 mmol) and  $H_2dcbpy$  (37 mg, 0.15 mmol) were dissolved in 40 mL methanol. The solution was

refluxed overnight with constant stirring. Afterwards, (*vpdiinp*)-L7 of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'e]pyridine (54 mg, 0.15 mmol) was added and the solution was further heated at reflux overnight. Subsequently, an excess amount of NH<sub>4</sub>NCS (343 mg, 4.5 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting black solid precipitated was separated by filtration. It was then washed with cold water (3 X 20 mL) and dried in vacuo over P<sub>2</sub>O<sub>5</sub> (0.041 g, 30 % yield). The complex is soluble in ethanol, methanol, acetone, chloroform ethyl acetate, tetrahydrofuran, moderably soluble in acetonitrile.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3044, 2926, 2857, 2100, 1710, 1621, 1545, 1447, 1365, 1224, 1151, 1095, 1012, 957, 833, 777, 742, 680, 604, 563, 508, 473, 424.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.23 (d, 1H, H-5a'), 8.08 (s, 1H, H-6a'), 7.76-7.75 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.74-7.71 (m, 4H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.70, 150.03, 138.93, 137.69, 136.47, 136.37, 135.45, 135.40, 134.89, 134.69, 134.58, 133.06, 132.44, 131.99, 131.62, 128.20, 127.18. 124.16, 123.79, 116.54.

2.5.8.2 Synthesis of 4,4'-Dicarboxy-2,2'-bipyridine-(4-Vinylphenyl)-2,6bis(phenyl)pyridine)-tri(thiocyanate)-ruthenium(II) compex ammonium salt [Ru(H<sub>2</sub>dcbpy)(vpbpp)<sub>2</sub>(NCS)<sub>3</sub>]<sup>-</sup>-(Dye 27)

The complex was prepared in a similar procedure as described above for Dye 26 of  $[Ru(H_2dcbpy)(11-(4-vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)(NCS)_3](NH_4)$ . In sequencial order as Dye 26, H<sub>2</sub>dcbpy (37 mg, 0.15 mmol), Ru(DMSO)\_4Cl<sub>2</sub> (71.3 mg, 0.15 mmol), (*vpbpp*)-L8 of 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) and excess amount of NH<sub>4</sub>NCS (343 mg, 4.5 mmol) were dissolved in 40 mL methanol and refluxed overnight to afford a black complex (0.035 g, 27 % yield). The complex is soluble in ethanol, methanol, acetone and moderably soluble in tetrahydrofuran.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3473, 3044, 2961, 2851, 2100, 1720, 1662, 1607, 1558, 1448, 1365, 1227, 1068, 1041, 971, 816, 770, 702, 688, 618, 529, 466, 446.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 8.20 (d, 1H, H-6a'), 8.15 (s, 1H, H-3a'), 7.98 (s, 1H, H-3a), 7.90-7.80 (m, 4H, Ar-H), 7.60 -7.50 (m, 10H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 189.61, 144.03, 143.03, 139.87. 137.77, 136.37, 134.66, 134.22, 133.61, 132.29, 132.26, 131.27, 129.76, 129.30, 129.27
129.00, 128.97, 127.12, 124.47, 123.31, 116.54.

## 2.5.9 Synthesis of Ru(II) complexes of general molecular formula: [Ru(vptpy)(N^)(H<sub>2</sub>dcbpy)]<sup>2+</sup> Series VIII.

In series VIII, two novel heteroleptic ruthenium(II) complexes with the general molecular structure  $[Ru(vptpy)(N^{A})(H_{2}dcbpy)]^{2,+}$  were successfully synthesized as stated serially below.

2.5.9.1 Synthesis of 4-(4-Vinylphenyl)-2,2':6'2"-terpyridine-(4,4'-Dicarboxy-2,2'-bipyridine)-bis(11-(4-vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)ruthenium(II)-bis(hexafluorophosphate) [Ru(vptpy)(H<sub>2</sub>dcbpy)(vpdiinp)](PF<sub>6</sub>)<sub>2</sub>-

(Dye 28)

The complex was synthesized as reported in literature with slight modification [368, 369]. In a typical one-pot synthesis, Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71.3 mg, 0.15 mmol) and 4-(4-Vinylphenyl)-2,2':6'2''-terpyridine (50 mg, 0.15 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards, 11-(4-vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine (54 mg, 0.15 mmol) was added and the solution was further heated at reflux overnight. Subsequently, H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigeration for 2 days. The resulting black solid precipitated was separated by filtration. Excess  $NH_4PF_6$  was dissolved in 5 mL of water and added to the dark filtrate to form a solution. The solution was kept in the refrigerator for 2 days. The resulting dark red precipitate was separated by filtration. It was then washed with cold water (3 X 20 mL) and dried in vacuo over  $P_2O_5$  (0.095 g, 49 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3452, 3031, 2948, 2852, 1730, 1614, 1531, 1447, 1371, 1227, 1107, 1012, 943, 846, 777, 722, 667, 556, 508, 466.

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 9.48 (s, 2H, H-3B, 5B), 9.10 (d, 1H, H-2A), 8.88 (d, 2H, H-6a, 6a'), 8.42 (d, 2H, H-2C, 6C), 8.07 (t, 1H, H-4A), 7.98 (d, 1H, H-5A), 7.81 (d, 2H, H-3C, 5C), 7.76-7.60 (m, 8H, 2(C<sub>6</sub>H<sub>4</sub>)), 7.07 (t, 1H, H-3A), 7.00 -6.75 (m, 5H, Ar-H), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.78, 156.37, 155.59, 150.51. 138.93,
138.82, 137.69, 137.56, 136.46, 136.37, 135.44, 135.40, 134.88, 134.56, 133.05,
133.04, 132.89, 132.44, 131.99, 131.61, 130.15, 128.28, 128.16, 127.18, 124.47,
123.79, 116.54.

2.5.9.2 Synthesis of 4-(4-Vinylphenyl)-2,2':6'2''-terpyridine-(4,4'-Dicarboxy-2,2'-bipyridine)(11-(4-vinylphenyl)diindeno[1,2-b:2',1'e]pyridine)ruthenium(II)-bis(hexafluorophosphate) [Ru(vptpy)(H<sub>2</sub>dcbpy)<sub>2</sub>(vpbpp)](PF<sub>6</sub>)<sub>2</sub>-

(Dye 29)

The complex was prepared in a similar procedure as described above for Dye 28 of [Ru(4-(4-Vinylphenyl)-2,2':6'2''-terpyridine)(11-(4-Vinylphenyl)diindeno[1,2-

b:2',1'e]pyridine)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>. In sequencial order as Dye 28, (vptpy)-**L9** of 4-(4-Vinylphenyl)-2,2':6'2''-terpyridine (50 mg, 0.15 mmol), Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> (71 mg, 0.15 mmol), 4-(4-Vinylphenyl)-2,6-bis(phenyl)pyridine (50 mg, 0.15 mmol) and H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) were dissolved in 40 mL methanol and refluxed overnight to obtain a dark red complex (0.079 g, 41 % yield).

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3466, 3031, 2933, 2851, 1730, 1662, 1603, 1538, 1370, 1220, 1102, 1054, 998, 846, 777, 722, 667, 556, 515, 466

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 9.42 (s, 2H, H-3B, 5B), 9.04 (d, 1H, H-5A), 8.83 (d, 2H, H-6a, 6a'), 8.72 (d, 2H, H-5a, 5a'), 8.10 -7.99 (m, 4H, Ar-H), 8.08 (t, 1H, H-4A), 8.04 (d, 2H, H-2C, 6C), 7.93 (d, 1H, H-2A), 7.78 -7.49 (m, 10H, Ar-H), 7.48 (t, 1H, H-3A), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, δ, ppm) 193.28, 156.37, 155.59, 144.04, 138.93,
137.87, 137.74, 136.37, 133.74, 133.61, 133.05, 132.26, 131.26, 130.15, 129.92,
129.75, 129.29, 128.97, 128.28, 127.18, 124.47, 123.31, 116.54.

## 2.5.9.3 Synthesis of 4-(4-Vinylphenyl)-2,2':6'2"-terpyridine-(4,4'-Dicarboxy-2,2'-bipyridine)(thiocyanate)-ruthenium(II)-hexafluorophosphate

 $[Ru(vptpy)(H_2dcbpy)_2(NCS)](PF_6)_{-}(Dye 30)$ 

The complex was synthesized as reported in literature with slight modification [368, 369]. In a typical one-pot synthesis,  $Ru(DMSO)_4Cl_2$  (119 mg, 0.25 mmol) and 4-(4vinylphenyl)-2,2':6'2''-terpyridine (50 mg, 0.15 mmol) were dissolved in 40 mL methanol. The solution was refluxed overnight with constant stirring. Afterwards, H<sub>2</sub>dcbpy (37 mg, 0.15 mmol) was added and the solution was further heated at reflux

overnight. Subsequently, an excess amount of NH<sub>4</sub>NCS (114 mg, 1.5 mmol) was added to the reaction mixture which was heated to a gentle reflux overnight. After cooling down to room temperature, the solvent was removed under reduced pressure by a rotary evaporator and 2 mL of water was added to dissolve the residue. The dark solution was filtered under gravity to obtain the filtrate. Excess NH<sub>4</sub>PF<sub>6</sub> was dissolved in 5 mL of water and added to the dark filtrate to form a suspension. The suspension was kept in the refrigerator for 2 days. The resulting black solid precipitated was separated by filtration. It was then washed with cold water (3 X 20 mL) and dried in vacuo over P<sub>2</sub>O<sub>5</sub> (0.075 g, 58 % yield). The complex is soluble in acetone moderably soluble in ethanol, methanol and chloroform.

FT-IR (ATR) v<sub>max</sub>/cm<sup>-1</sup>: 3446, 3031, 2940, 2857, 2110 1725, 1621, 1538, 1372, 1232, 1075, 1013, 916, 846, 777, 722, 680, 556, 515, 432

<sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 9.07 (d, 1H, H-5A), 8.42 (d, 1H, H-2D), 8.41 (d, 2H, H-2C, 6C), 8.06 (t, 1H, H-4A), 7.93 (d, 1H, H-2A), 7.89 (d, 2H, H-3C, 5C), 7.28 (t, 1H, H-3A), 6.77 (q, 1H, CH=CH<sub>2</sub>), 5.94 (d, 1H, CH=CH<sub>2</sub>), 5.36 (d, 1H, CH=CH<sub>2</sub>).

<sup>13</sup>C-NMR (400 MHz, DMSO-d<sub>6</sub>, *δ*, ppm) 158.36, 156.01, 132.81, 128.20, 123.97, 116.54.

### **CHAPTER THREE**

### **3.0 RESULTS AND DISCUSSION**

#### **3.1.** Synthesis and Chemistry

In this chapter, thirty novel heteroleptic ruthenium(II) complexes with the general molecular structure  $[Ru(bdmpmar)(H_2dcbpy)(NCS)]^+$ , [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2,+</sup>,[Ru(bdmpmar)(vpbpp)(H<sub>2</sub>dcbpy)]<sup>2,+</sup>,  $[Ru(H_2dcbpy)_2(N^{*})(NCS)]^+$ ,  $[Ru(H_2dcbpy)_2(N^{*})_2]^{2,+}$ ,  $[Ru(H_2dcbpy)(N^{*})_2(NCS)_2]$ ,  $[Ru(H_2dcbpy)(N^{)}(NCS)_3]^-$  and  $[Ru(vptpy)(H_2dcbpy)(N^{^})]^{2,+}$  grouped under eight (8) were successfully designed and synthesized where *bdmpmar* is a tridentate ligand of N,N-bis(3, 5-dimethylpyrazol-1-yl-methyl) aromatic organic compound (such aromatic organic compounds(Ar) are anthranilic acid, 4-methoxy-2-nitroaniline, aniline, toluidine, cyclohexylamine and anisidine). The abbreviation *vpdiinp* represents a monodentate ligand of 11-(4-Vinylphenyl) diindeno[1,2-b:2',1'e]pyridine, vpbpp represents a monodentate ligand of 4-(4-Vinylphenyl)-2.6bis(phenyl)pyridine and *vptpy* represents a tridentate ligand of 4'-(4-Vinyl)-2,2':6',2''-terpyridine where NCS is a monodentate ligand of thiocyanate. Meanwhile, N<sup> $\wedge$ </sup> represents any of the monodentate ligands of either *vpdiinp* or *vpbpp* and (N<sup> $\wedge$ </sup>) represents any of the monodentate ligands either of *vpdiinp* or *vpbpp* or NCS as disclosed in series VIII. For all complexes, H<sub>2</sub>dcbpy is a bidentate ligand used primarily in synthesizing due to its interlocking abilities of the carboxylate group  $TiO_2$ surface. It is well established that  $H_2$  dcbpy serves an interlocking group between the complex and  $TiO_2$  surface through an ester-like linkage between carboxylate group and the surface hydroxyl groups of TiO2. This process is crucial for photosensitization based on intimate contact between the complex and the semiconductor [299].

Eight series of thirty (30) complexes formulation and their general molecular structures are shown below as follow:

Series I Complexes formulation with general molecular formula as [Ru(bdmpmar)( H<sub>2</sub>dcbpy)(NCS)]<sup>+</sup>

(1) [Ru(bdmpmaa)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)

- (2) [Ru(bdmpmeta)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)
- (3) [Ru(bdmpmal)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)
- (4) [Ru(bdmpmt)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)
- (5) [Ru(bdmpmcy)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)
- (6) [Ru(bdmpmas)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)



Figure 3.1: General structure of [Ru(bdmpmar)(H2dcbpy)(NCS)]+

Series II Complexes formulation with general molecular formula as [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

(7) [Ru(bdmpmaa)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>

(8) [Ru(bdmpmeta)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>

(9) [Ru(bdmpmal)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>

(10) [Ru(bdmpmt)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>

(11) Ru(bdmpmcy)(vpdiinp)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>

(12) Ru(bdmpmas)(vpdiinp)(H2dcbpy)](PF6)2



Figure 3.2: General structure of [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

Series III Complex formulation with general molecular formula as [Ru(bdmpmar)(vpbpp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

- (10)  $[Ru(bdmpmaa)(vpbpp)(H_2dcbpy)](PF_6)_2$
- (11)  $[Ru(bdmpmata)(vpbpp)(H_2dcbpy)](PF_6)_2$
- (12)  $[Ru(bdmpmal)(vpbpp)(H_2dcbpy)](PF_6)_2$
- (13)  $[Ru(bdmpmt)(vpbpp)(H_2dcbpy)](PF_6)_2$
- (14)  $[Ru(bdmpmcy)(vpbpp)(H_2dcbpy)](PF_6)_2$
- (15)  $[Ru(bdmpmas)(vpbpp)(H_2dcbpy)](PF_6)_2$



Figure 3.3: General structure of [Ru(bdmpmar)(vpbpp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

Series IV Complex formulation with general molecular formula as  $[Ru(H_2dcbpy)_2(N^{\wedge})(NCS)]^+$ 

- (16)  $[Ru(H_2dcbpy)_2(vdpdiinp)(NCS)](PF_6)$
- (17)  $[Ru(H_2dcbpy)_2(vpbpp)(NCS)](PF_6)$



Figure 3.4: Chemical structure of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vdpdiinp)(NCS)](PF<sub>6</sub>)



Figure 3.5: Chemical structure of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpbpp)(NCS)](PF<sub>6</sub>)

Series V Complex formulation with general molecular formula as  $[Ru(H_2dcbpy)_2(N^{\wedge})_2]^{2+}$ 

- (18)  $[Ru(H_2dcbpy)_2(vpdiinp)_2](PF_6)_2$
- (19)  $[Ru(H_2dcbpy)_2(vpbpp)_2](PF_6)_2$
- (20)  $[Ru(H_2dcbpy)_2(vpdiinp)(vpbpp)](PF_6)_2$



Figure 3.6: Chemical structure of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpdiinp)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>



Figure 3.7: Chemical structure of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpbpp)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>



Figure 3.8: Chemical structure of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpdiinp)(vpbpp)](PF<sub>6</sub>)<sub>2</sub>

Series VI Complex formulation with general molecular formula as [Ru(H2dcbpy)(N^)2(NCS)2]

- (21) [Ru(H<sub>2</sub>dcbpy)(vpdiinp)<sub>2</sub>(NCS)<sub>2</sub>]
- $(22) \qquad [Ru(H_2dcbpy)(vpbpp)_2(NCS)_2]$



Figure 3.9: Chemical structure of [Ru(H<sub>2</sub>dcbpy)(vpdiinp)<sub>2</sub>(NCS)<sub>2</sub>]



Figure 3.10: Chemical structure of [Ru(H<sub>2</sub>dcbpy)(vpbpp)<sub>2</sub>(NCS)<sub>2</sub>]

Series VII Complex molecular formulation with general molecular formula as [Ru(H2dcbpy) (N^)(NCS)3]<sup>-</sup>

- (23)  $[Ru(H_2dcbpy)(vpdiinp)(NCS)_3](NH_4)$
- (24)  $[Ru(H_2dcbpy)(vpbpp)(NCS)_3](NH_4)$



Figure 3.11: Chemical structure of [Ru(H<sub>2</sub>dcbpy) (vpdiinp)(NCS)<sub>3</sub>](NH<sub>4</sub>)



Figure 3.12: Chemical structure of [Ru(H<sub>2</sub>dcbpy) (vpbpp)(NCS)<sub>3</sub>](NH<sub>4</sub>)

Series VIII Complex molecular formulation with general molecular formula as  $[Ru(vptpy)(dcbpyH_2(N^{\wedge\wedge\wedge})]^{2+}$ 

- (25)  $[Ru(vptpy)(dcbpyH_2)(vpdiinp)](PF_6)_2$
- $(26) \qquad [Ru(vptpy)(dcbpyH_2)(vpbpp)(](PF_6)_2$
- (27)  $[Ru(vptpy)(dcbpyH_2)(NCS)](PF_6)_2$



Figure 3.13: Chemical structure of [Ru(vptpy)(H<sub>2</sub>dcbpy)(vpdiinp)](PF<sub>6</sub>)<sub>2</sub>



Figure 3.14: Chemical structure of [Ru(vptpy)(H<sub>2</sub>dcbpy)(vpbpp)](PF<sub>6</sub>)<sub>2</sub>



Figure 3.15: Chemical structure of [Ru(vptpy)(H<sub>2</sub>dcbpy)(vpbpp)](PF<sub>6</sub>).

### **3.2. SPECTROSCOPIC CHARACTERIZATION**

Spectroscopic characterization provides the framework for determing valuable information on the molecular structures and chemical properties as well as functional groups of the ruthenium(II) heteroleptic complexes for dye sensitized solar cells. This chapter contains the results and discussion of ATR-FTIR, UV-Vis, PL and <sup>1</sup>H and <sup>13</sup>C NMR with respect to eight series of thirty (30) novel heteroleptic ruthenium(II) complexes with the general molecular structure [Ru(bdmpmar)(H<sub>2</sub>dcbpy)(NCS)]<sup>+</sup>, [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2,+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)(NCS)]<sup>+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)(NCS)]<sup>+</sup>, [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N^)<sub>2</sub>]<sup>2,+</sup>, [Ru(H<sub>2</sub>dcbpy)(N^)<sub>2</sub>(NCS)<sub>2</sub>], [Ru(H<sub>2</sub>dcbpy)(N^)(NCS)<sub>3</sub>]<sup>-</sup> and [Ru(vptpy)(H<sub>2</sub>dcbpy)(N^^)]<sup>2,+</sup>respectively.

### **3.2.1 ATR-FTIR Spectroscopy**

The Infra red experimental measurement of the ligands and complexes were carried using attenuated total reflectance assembly mode. After the crystal area of the attenuated total reflectance assembly mode was cleaned and the background collected, the solid sample of ligand or complex was placed onto the small crystal area. For the purpose of achieving fine resolution IR bands, precautionary measures were taken into consideration such as ensuring that enough samples were placed to cover the crystal area with height not more than a few millimetres and also ensuring that there was good optical contact between the sample and the crystal.

The ATR-FTIR spectra of ligands and complexes were recorded in 4000-370 cm<sup>-1</sup> region (see supplementary information Table 3.1 for relevant FT-IR data and Appendix C for spectra.

	v(OH)	v(N=C)	v(C=O)	v(C=C)	v(C=N)	$v_{as}(CO_2)$	v(C-O)	v(C=S)	<i>v</i> (M-N)
	cm <sup>-1</sup>								
L1	3370	-	1683	1607	1524	1378	1227	-	-
L2	-	-	-	1607	1524	-	1227	-	-
L3	-	-	-	1610	1524	-	-	-	-
L4	-	-	-	1607	1545	-	-	-	-
L5	-	-	-	1607	1558	-	-	-	-
L6	-	-	-	1607	1545	-	-	-	-
L7	-	-	-	1608	1551	-	-	-	-
L8	_	-	-	1614	1558	-	-	-	-
L9	-	-	_	1614	1524	-	-	-	-
Dye 1	3452	2100	1718	1621	1558	1378	1230	771	446
Dye 2	3487	2116	1722	1600	1524	1376	1230	776	432
Dye 3	3445	2118	1734	1610	1524	1378	1234	773	446
Dye 4	3466	2117	1731	1608	1531	1372	1230	770	446
Dye 5	3438	2106	1727	1621	1558	1378	1234	773	439
Dye 6	3452	2116	1731	1614	1516	1378	1234	772	432
Dye 7	3466	-	1727	1638	1538	1370	1224	-	446
Dye 8	3487	-	1728	1607	1516	1372	1229	-	432
Dye 9	3459	-	1727	1621	1516	1378	1227	-	432
Dye 10	-	-	1727	1621	1516	1376	1234	-	439

 Table 3.1: AT-FTIR relevant data of ligands and complexes

Dye 11	-	-	1722	1634	1558	1378	1234	-	411
Dye 12	-	-	1722	1621	1545	1367	1231	-	418
Dye 13	-	-	1717	1607	1503	1378	1234	-	424
Dye 14	-	-	1718	1600	1510	1378	1227	-	424
Dye 15	-	-	1726	1614	1524	1370	1233	-	411
Dye 16	3466	-	1726	1607	1524	1370	1233	-	411
Dye 17	3466	-	1730	1612	1504	1370	1233	-	418
Dye 18	-	-	1730	1607	1510	1372	1228	-	424
Dye 19	3452	2100	1720	1614	1551	1378	1227	777	439
Dye 20	3487	2110	1720	1607	1565	1378	1234	777	432
Dye 21	-	-	1703	1626	1500	1370	1227	-	446
Dye 22	3473	-	1721	1612	1531	1371	1233	-	418
Dye 23	3431	-	1717	1614	1500	1370	1220	-	418
Dye 24	-	2077	1709	1621	1500	1344	1248	777	439
Dye 25	3466	2077	1724	1600	1545	1365	1227	771	411
Dye 26	-	2100	1710	1621	1545	1365	1224	777	424
Dye 27	3473	2100	1720	1607	1558	1365	1227	770	446
Dye 28	3452	-	1730	1614	1531	1371	1227	-	466
Dye 29	3466	-	1730	1603	1538	1370	1220	-	466
Dye 30	3446	2110	1725	1621	1538	1372	1232	777	432

The FT-IR spectra of the free nine (9) ligands and thirty (30) complexes showed unique characteristic absorption band that were compared and assigned in comparison to relevant literature. Since six (6) ligands (L1-L6) are similar in structure, L2 was found to have an exception of vibrational band at 3473 and 3370 cm<sup>-1</sup>. This shows the possibility of the N-H group due to the presence of aromatic nitroaniline moiety in the ligand. The absorption band at 3370 cm<sup>-1</sup> for L1 may be due to O-H stretching vibrations from the carboxylic acid moiety in the ligand. The spectra of ligands (L1-L9) show bands between  $3127-3031 \text{ cm}^{-1}$  may be due to the presence of aromatic C-H stretching vibrations and bands in the range 2933-2920 cm<sup>-1</sup> show the presence of C-H stretching of the methyl group. In the spectra of L2 and L6, the C-H stretching band appeared at 2837-2830 cm<sup>-1</sup> and these are ascribed to methoxy group of the ligands. The band at 1683 cm<sup>-1</sup> is due to the presence of C=O stretching vibrations of the carboxylic acid moiety in ligand L1. The strong bands in the range 1614-1607  $\text{cm}^{-1}$ <sup>1</sup> were ascribed to aromatic C=C stretching band in ligands (L1-L9). The C=N stretching bands were found in the region between 1558-1524 cm<sup>-1</sup> of the pyrazolic and pyridine groups in ligands (L1-L9). The vibrational bands at 1420 and 1323 cm<sup>-1</sup> ascribed to symmetric and asymmetric  $-NO_2$  stretching vibrations in ligand L2. The presence of C-O stretching vibration in ligand L1 was confirmed with the band at 1227 cm<sup>-1</sup>.

The FT-IR spectra of the complexes for O-H stretching vibration were found in region of 3487-3438 cm<sup>-1</sup> due to the presence of carboxylic acid moiety. However, the spectra of some complexes (**10-15**) were the absence of vibrational frequency band for O-H stretching vibration [299]. The spectra of complexes (**1-30**) show bands between 3127-
$3031 \text{ cm}^{-1}$  may be due to the presence of aromatic C-H stretching vibrations and bands in the range 2933-2920 cm<sup>-1</sup> show the presence of C-H stretching of the methyl group [299, 371]. Bands between 2116-2100 cm<sup>-1</sup> were ascribed to N=C stretching vibration of thiocyanate moiety in all complexes (**1-6, 19-20, 24-27 and 30**) having –NCS group coordination [283, 372, 373]. The vibrational bands between 1734-1718 cm<sup>-1</sup> ascribed to C=O stretching vibration of the carboxylic groups in complexes (**1-30**). The presence of aromatic C=C stretching vibration was found in region between 1638-1600 cm<sup>-1</sup> in complexes (**1-30**) [372-375].

However, bands between 1700 and 1638 cm<sup>-1</sup> ascribed to –COO- asymmetric stretching frequency were found for only complexes (**13-18, 22-24, 25-27** and **29**) while the –COO- asymmetric stretching frequency for other complexes (**1-12, 19-21, 24, 28** and **30**) were possibly found overlap with the C=C stretching vibration frequency [374. 376]. Hence, it was difficult to determine the vibrational frequency bands of –COO- asymmetric stretching in the complexes (**1-12, 19-21, 24, 28** and **30**). The absorption bands in the region 1558-1504 assigned to C=N stretching vibration of pyrazolic and pyridine groups in complexes (**1-30**). The bands between 1378-1368 cm<sup>-1</sup> and 1234- 1220 cm<sup>-1</sup> in the complexes (**1-30**) were ascribed to the symmetric –COO- and C-O stretching vibration of carboxylic acid group [374. 376]. The presence of C=S stretching vibration between 777-770 cm<sup>-1</sup> is ascribed to thiocyanate group in complexes (**1-6, 19-20, 24-27** and **30**) [374]. The vibrational band frequencies between 466 and 411 respectively ascribed to the coordination between the ligand and ruthenium metal [373].

#### **3.2.2 Electronic spectroscopy**

## 3.2.2.1 Series I complexes electronic absorption spectra of general formula [Ru(bdmpmar)(H2dcbpy)(NCS)]<sup>+</sup>

The electronic absorption spectra of series I complexes measured at ambient temperature in DMSO solvent are presented in Figure 3.16 and see supplementary information in Table 3.2. The absorption spectra of dyes (1-6) are predominated by metal-to-ligand charge transfer transition (MLCT). These broad and intense visible MLCT bands show between 370 and 650 nm. The MLCT bands of complexes were compared with relevant literature of reported ruthenium(II) polypyridyl complexes having broad and intense visible bands which exceeded values in 370-550 nm range, specifically standard N3 dye having values of 396 and 539 nm [374]. The structural features of dye **1-6** molecules have conjugated systems, the influence of functional groups thiocyante unit, and pyrazolic systems having one  $sp^3$  and two  $sp^2$  nitrogen atoms as donors. These are possibly the contributing factors responsible for their different absorptions as observed in the spectra. The absorption spectra show that Dye 1, 2, 3, 4, 5 and 6 have three major absorption wavelengths at 455, 573, 626 nm for 1; 454, 587 and 629 nm for **2**; 432, 590, 629 nm for **3**; 411, 585, 629 nm for **4**; 390, 553, 620 nm for **5** and 405, 580, 629 nm for **6**. These visible, intense and broad bands are assigned to the electronic transition from  $Ru^{II}$  based  $t_{2g}$  orbital to the ligand based  $\pi^*$ orbitals [374].

In particular, dye **2** exhibited an unusual photophysical behavior. The spectra displayed high absorption at a wavelength of 454 nm for dye **2**. The high absorption

can be related to the nature of the structure as well as the electronic activity taking in dye 2 molecule. We observed that dye 2 molecule has a structural features as functional groups. They are nitro and methoxy constituents as functional groups. These functional groups have great influence on its conjugated system. These factors were confirmed by comparing dye 2 and 6. In comparison, dye 2 and 6 molecules were seen to have structural similarity but the nitro group was conspicuously absent in dye  $\mathbf{6}$  molecule. Hence, we deduced that the nitro functional group in dye 2 molecule was largely responsible for the high absorption. Dye 2 molecule has both the methoxy group as electron releasing and the nitro group as electron withdrawing for promoting electronic activity. Dye 2 molecule experienced an increased electron drift from the electron donating of methoxy group to electron with drawing of nitro group through  $\pi$ -bond aromatic ring resulting to significant increase in absorptivity at a wavelength of 454 nm. However, dye 6 molecule which has only the methoxy group as electron donating, did not have significant increase in absorptivity at a wavelength of 508 nm due to the absence of the nitro group acting as the electron withdrawing group.

From the outcomes of dye 2 and 6 structural features comparison, it shows that their functional groups influence the conjugated systems thereby causing the absorption peaks to appear in longer wavelength with significant increase in absorptivity. Dye 2 showed that the functional groups of both the electron donating and electron withdrawing influenced the conjugated systems thereby causing high absorption at longer wavelength. The structural feature of dye 1 molecule has carboxylic group as an electron donating group while dye 4 has methyl group as an electron donating

group both to small extent do have influence on their conjugated systems. However, their influence cannot be compared to when both electron withdrawing and electron donating group are present in a compound as shown in dye 2 molecule. Dye 3 and 5 have no functional group but their advantage of fused rings has accounted for their different absorptions.

Complexes	ComplexesAbsorption $\lambda_{max} / nm$	
	$\pi$ - $\pi$ * band	MLCT band
[Ru(L1)( H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> ,-(Dye 1)	309, 355	455, 573, 626
$[Ru(L2)(H_2dcbpy)(NCS)](PF_6)_2-(Dye 2)$	292, 316	454, 587, 629
[Ru(L3)(H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 3)	300	432, 590, 629
$[Ru(L4)(H_2dcbpy)(NCS)](PF_6)_2-(Dye 4)$	297	411, 585, 629
[Ru(L5)( H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 5)	299	390, 553, 620
[Ru(L6)( H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 6)	301	405, 580, 629

 Table 3.2: Absorbance properties of series I complexes (1-6)

Measured in DMSO solution

At the UV and near-visible region, the bands at 309, 355 nm and 292, 316 nm are assigned to intraligand  $\pi$ - $\pi$ \* transitions of bidentate and tridendate ligands in dye **1** and **2**. Dye 3, 4, 5 and 6 show band in the UV region at 300, 297, 299 and 301 nm respectively, are due to H<sub>2</sub>dcbpy ligand  $\pi$ - $\pi$ \* charge-transfer transitions only. The choice of inequivalent and/or mixed-ligands combinations containing different electron-with drawing or electron donating groups on fused aromatic rings show

significant effect on the different absorption wavelengths of dyes **1-6**. For all series I complexes, visible absorption extended to higher wavelength near-IR region approximately 626 nm for dye **1**, 629 nm for dye **2**, 629 nm for dye **3**, 622 nm for dye **4**, 620 nm for dye **5** and 629 nm for dye **6** respectively which are very useful for harvesting and transforming less energetic photons thereby showing its importance for photosensitization process [299, 372, 377, 378].



**Figure 3.16:** Electronic absorption spectral of Series I with formula [Ru(bdmpmar)(H<sub>2</sub>dcbpy)(NCS)]<sup>+</sup>

#### 3.2.2.2 Series II complexes electronic absorption spectra of general formula [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

The absorption spectra of series II complexes in DMSO solvent are presented in Figure 3.17 and find supplementary information in Table 3.3. In general, dye **7-12** show broad visible bands which are in the range 370-550 nm and can be ascribed to MLCT transition as reported in literature for ruthenium(II) polypyridyl complexes [279]. The dyes display broad and intense absorption bands between 432 and 587 nm with some wavelength maxima at 571, 571, 587, 559 and 556 nm for dyes **7-12** respectively. These absorptions were assigned to the electronic transition from Ru<sup>II</sup> based t<sub>2g</sub> orbital to the ligand based  $\pi^*$  orbitals of the dyes. For the UV region, the dyes **7-12** display bands at 321 and 344 nm for dye **7**; 318 and 338 nm for dye **8**; 315 and 341 nm for dye **10**; 315 and341 nm for dye **11**; 317 and 341 nm for dye **12**. These bands are ascribed to intraligand  $\pi$ - $\pi^*$  transitions of bidentate and tridentate ligands respectively.

Complexes	Absorption $\lambda_{max}/nm$	
	$\pi$ - $\pi$ * band	MLCT band
[Ru(L1)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> ,-(Dye7)	321, 344	456, 571
[Ru(L2)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye8)	318, 338	456, 571
[Ru(L3)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye9)	315, 341	432, 587
[Ru(L4)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye10)	319, 341	460, 559
[Ru(L5)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye11)	315, 341	463, 556

Table 3.3: Absorbance properties of series II complexes (7-12)

#### Measured in DMSO solution

By replacing thiocyanate monodentate ligand in series I complexes 1-6 with 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine monodentate donor ligand (L7), it give rise to series II 7-12 complexes. Comparing the spectra of series I and II complexes, the alteration of the coordination chemistry of the complexes through variation of ligands did not improve the photophysical properties of series II 7-12 complexes over series I complexes 1-6. The unique absorption properties of series I complexes in the lower region may be possibly due to featuring a strong donor ligand such as thiocynate ligand having a low-lying molecular orbital or ability to destabilize the metal  $t_{2g}$  orbital [293]. It is also known that the energy level of  $t_{2g}$  is determined largely by the electron density at the metal centre which directly associated with the MLCT transition [379]. Thus, dye **7-12** compound featuring 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'elpyridine monodentate ligand could not give similiar results as observed in dye 1-6 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine molecule. This is because monodentate donor ligand (L7) could not destabilize the metal t<sub>2</sub>g orbital as seen by the same role played the thiocyanate monodentate ligand.

From the spectra, it was observed that dye **8** has higher absorption around the wavelength region of 456 nm when dye **7**, **9**, **10**, **11** and **12**. This is because dye **8** molecule experienced an increased electron drift from the electron donating of methoxy group to electron with drawing of nitro group through  $\pi$ -bond aromatic ring giving rise to significant increase in absorptivity at that particular wavelength.



Figure 3.17: Electronic absorption spectral of Series II with general formula [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

## 3.2.2.3 Series III dye sensitizers electronic absorption spectra of general formula [Ru(bdmpmar)(vpbpp)( H<sub>2</sub>dcbpy)]<sup>2+</sup>

The absorption spectral properties of Series III complexes with formulation, were recorded in DMSO solvent and summarized in Table 3.4 (see spectra in Figure 3.18).

Complexes	Absorpti	on $\lambda_{max}/nm$
	$\pi$ - $\pi$ * band	MLCT band
[Ru(L1)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye13)	319	471, 542
[Ru(L2)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye14)	319	460, 590
[Ru(L3)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye15)	315	466, 583
[Ru(L4)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye16)	315	416, 553
[Ru(L5)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye17)	316	451, 547
[Ru(L6)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye18)	313	460, 571

**Table 3.4**: Absorbance properties of series III complexes (13-18)

Measured in DMSO solution

Design strategies for the development of series III complexes (**13-18**) were carried out through structural variation of series 1 complexes (**1-6**) by replacing thiocyanate ligand with 4-(4-vinylphenyl)-2,6-bis(phenyl)pyridine monodentate ligand (**L8**). Comparing the spectra of series I and III complexes, it clearly reveals that the presence of thiocyanate ligand in series I complexes greatly influenced their photophysical properties. The absorption properties of series I complexes in the lower region may be possible due to featuring a strong donor ligand such as thiocynate ligand having a lowlying molecular orbital or ability to destabilize the metal  $t_{2g}$  orbital [293]. It is also known that the energy level of  $t_{2g}$  is determined largely by the electron density at the metal centre which directly associated with the MLCT transition [379]. Thus, dye **13**-**18** compound by featuring 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine monodentate ligand could not give the desired results as observed in dye **1-6** molecule. This is because 4-(4-vinylphenyl)-2,6-bis(phenyl)pyridine monodentate ligand (**L8**) could not destabilize the metal  $t_{2g}$  orbital as the role played the thiocyanate monodentate ligand.

From the spectra, it was observed that dye 14 has higher absorption around the wavelength region of 460 nm when compared to dye 13, 15, 16, 17 and 18. This is because dye 14 molecule experienced an increased electron drift from the electron donating of methoxy group to electron with drawing of nitro group through  $\pi$ -bond aromatic ring giving rise to significant increase in absorptivity at that particular wavelength.



Figure 3.18: Electronic absorption spectral of Series III with general formula  $[Ru(bdmpmar)(vpbpp)(H_2dcbpy)]^{2+}$ 

# 3.2.2.4 Series IV and V dye sensitizers electronic absorption spectra of general formula [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N<sup>^</sup>)(NCS)]<sup>+</sup>and [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N<sup>^</sup>)<sub>2</sub>]<sup>2,+</sup>respectively

The electronic absorption spectra of series IV and V complexes were recorded in DMSO and presented in in Figure 3.19 and corresponding data summarized in Table 3.5.

Complexes	Complexes Absorption $\lambda_{max}/nm$	
	$\pi$ - $\pi$ * band	MLCT band
[Ru(H <sub>2</sub> dcbpy) <sub>2</sub> (L7)(NCS)](PF <sub>6</sub> )-(Dye 19)	317, 344	400, 542
[Ru(H <sub>2</sub> dcbpy) <sub>2</sub> (L8)(NCS)](PF <sub>6</sub> )-(Dye 20)	316	400, 544
[Ru(H <sub>2</sub> dcbpy) <sub>2</sub> (L7) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> ,-(Dye 21)	322, 342	459, 590
$[Ru(H_2dcbpy)_2(L8)_2](PF_6)_2-(Dye 22)$	321	462, 593
[Ru(H <sub>2</sub> dcbpy) <sub>2</sub> (L7)(L8)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 23)	322	455, 590

 Table 3.5: Absorbance properties of series IV and V complexes (19-23)

Measured in DMSO solution

The UV-Vis absorption spectra of series IV and V reveals the shift in absorption wavelength to the red region at 544 nm for dye **19**, 544 nm for dye **20**, 590 nm for dye **21**, 593 nm for dye **22** and 590 nm for dye **23**. The red shift may be caused by the extension of the  $\pi$ -bond through the introduction of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine and 4-(4-vinylphenyl)-2,6-bis(phenyl)pyridine ligands in the complexes .



**Figure 3.19:** Electronic absorption spectral of Series IV and V with general formula  $[Ru(H_2dcbpy)_2(N^{*})(NCS)]$  and  $[Ru(H_2dcbpy)_2(N^{*})_2]$ 

## 3.2.2.5 Series VI, VII and VIII ruthenium(II) complexes electronic absorption spectra of general formula [Ru(H2dcbpy)(N^)2(NCS)2], [Ru(H2dcbpy)(N^)(NCS)3]<sup>-</sup> and [Ru(vptpy)(dcbpyH2(N^^^)]<sup>2+</sup> respectively

Figure 3.20 shows the absorption spectra of of series VI, VII and VIII complexes measured in DMSO and the corresponding data are presented in Table 3.6

Complexes	Absorption $\lambda_{max}/nm$	
	$\pi$ - $\pi$ * band	MLCT band
[Ru(H <sub>2</sub> dcbpy)( L7) <sub>2</sub> (NCS) <sub>2</sub> ]-(Dye 24)	337	540, 651
[Ru(H2dcbpy)( L8) <sub>2</sub> (NCS) <sub>2</sub> ]-(Dye 25)	324	537, 688
[Ru(H <sub>2</sub> dcbpy)( L7) <sub>2</sub> (NCS) <sub>3</sub> ](NH <sub>4</sub> )-(Dye 26)	322, 344	539, 765
[Ru(H <sub>2</sub> dcbpy)( L8) <sub>2</sub> (NCS) <sub>3</sub> ](NH <sub>4</sub> )-(Dye27)	322	538, 811
[Ru(L9)(H <sub>2</sub> dcbpy)( L7)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 28)	315, 339	499, 697, 825
[Ru(L9)(H <sub>2</sub> dcbpy) <sub>2</sub> (L8)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 29)	317	497, 753, 813, 873
[Ru(L9)(H <sub>2</sub> dcbpy) <sub>2</sub> (NCS)](PF <sub>6</sub> ) <sub>-</sub> (Dye 30)	302, 348	497, 877

 Table 3.6: Absorbance properties of series VI-VIII complexes (24-30)

Measured in DMSO solution

The striking absorption property of series VI, VII and VIII is their ability to exhibit visible absorption to higher wavelength near-IR region. This is deduced based on the justification that the MLCT can be extended to longer wavelengths by appropriate substituent changes on chromophoric ligands or by increasing the number of NCS

groups. It is well known that increasing the conjugation length of a ligand also serves as a practical technique boosting absorption to longer wevelength. The incorporation of ligands increasing the conjugation length into Series VI, VII and VIII ruthenium(II) complexes such as 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine. 4-(4vinylphenyl)-2,6-bis(phenyl)pyridine and 4-(4vinylphenyl)-2,2':6'2''-terpyridine are possibly responsible for different absorption exhibited at longer wavelength as displayed in the spectra. Series VI ruthenium(II) complexes of dye 24 and 25 displayed absorption wavelength at 651 and 688 nm respectively. While series VII ruthenium(II) complexes of dye 26 and 27 exhibit approximately around 765 and 811 nm respectively, Furthermore, series VIII dye sensitizers of dye 28, 29 and 30 showed absorption wavelength at 697, 753 and 877 nm respectively. These unique absorption capacities are very useful for harvesting and transforming less energetic photons thereby showing its importance for photosensitization process [290, 372, 377, 378, 380, 381].



**Figure 3.20:** Electronic absorption spectral of Series VI, VII and VIII with general formula  $Ru(H_2dcbpy)(N^{2}(NCS)_2]$ ,  $[Ru(H_2dcbpy)(N^{2}(NCS)_3]^{-1}$  and  $[Ru(vptpy)(dcbpyH_2(N^{^1})]^{2,+}$ 

#### **3.2.3** Photoluminescence spectroscopy

## 3.2.3.1 Series I dyes emission spectra of general formula [Ru(bdmpmar)(H2dcbpy)(NCS)]<sup>2+</sup>

The emission spectra of series I ruthenium(II) complexes are presented in Figure 3.21 (see Table 3.7 for supplementary information) and measured at ambient temperature in DMSO solvent. The emission spectra of following dye 1, dye 2, dye 3, dye 4, dye 5 and dye 6, exhibit luminescence at 698, 698, 699, 697,700 and 700 nm respectively, upon their excitation at respective wavelength such as 455, 454, 432, 411, 390 and 405 nm which are attributable to the fact that their primarily populated higher energy <sup>1</sup>MLCT are speedily converted to lower energy <sup>3</sup>MLCT. The emission wavelength of series I complexes are similar to the wavelength of 637 nm of tridentate ruthenium heteroleptic complex of type bis(pyrazol)pyridine formation as reported in literature [381]. Generally, the emission characteristics of ruthenium(II) polypyridyl complexes follow the energy gap law whereby the <sup>3</sup>MLCT state tends to be long-lived and deactivates into three processes such as radiative decay Kr, radiationless decay knr and thermal population of a higher lying excited state, koexp( $-\Delta E/RT$ ). The ligand excited state is attributed to the thermal population of a higher lying excited state. And the energy of the ligand field largely depends on the ligand field strength [382-386]. The metal centre (MC) excited state depends on the ligand field strength based on the  $\sigma$ donor and  $\pi$ -acceptor properties of the ligands, the steric hindrance around the metal and the bite angle of the ligand. Therefore, choosing of ligands is crucial. Moreover, ligand field strength controls the energy position of metal centre (MC) and ligand centre (LC), including the metal-to-ligand charge transfer (MLCT) of ruthenium(II)

polypyridine complexes. The basic properties of the ligands such as the HOMO-LUMO energy gap and the singlet-triplet splitting greatly influence the energy of the LC excited state. Studies have shown that involvement of ligand reduction potential in MLCT transition influences MLCT excited state [387, 388]. It further indicatess that metal oxidation potential controlled by electron gain and lose attributes of the ligand and by the charge separation caused by the transitions enhance the luminescent properties of ruthenium(II) complexes, depending on excited state reactant or product, energy ordering and orbital nature low energy excited state [387, 388].

Complexes	Emission maxima
	$\lambda_{max}(nm)$
[Ru(L1)(H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> ,-(Dye 1)	698
[Ru(L2)(H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 2)	698
$[Ru(L3)(H_2dcbpy)(NCS)](PF_6)_2-(Dye 3)$	699
[Ru(L4)(H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 4)	697
[Ru(L5)( H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 5)	700
[Ru(L6)( H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 6)	700

 Table 3.7: Photoluminescence properties of series I complexes (1-6)

Measured in DMSO solution



Figure 3.21: Emission spectral of Series I with formula [Ru(bdmpmar)(H<sub>2</sub>dcbpy)(NCS)]<sup>,+</sup>

## 3.2.3.2 Series II dyes emission spectra of general formula [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

The Series II complexes of dye 7, dye 8, dye 9, dye 10 dye 11 and dye 12 exhibit luminescence at 700, 699, 700,700, 699 and 699 nm when they were respectively excited at 479, 456, 463, 460 463 and 466 nm in DMSO. Figure 3.22 displays Emission Spectra of series II complexes (see Table 3.8 for supplementary information). Their emission features as well as maxima are attributable to the fact that their primarily populated higher energy <sup>1</sup>MLCT are speedily converted to lower energy <sup>3</sup>MLCT. The emission wavelength of series I complexes are similar to the wavelength of 637 nm of tridentate ruthenium heteroleptic complex of type bis(pyrazol)pyridine formation as reported in literature [381]. Generally, the emission characteristics of ruthenium(II) polypyridyl complexes follow the energy gap law whereby the <sup>3</sup>MLCT state tends to be long-lived and deactivates into three processes such as radiative decay Kr, radiationless decay knr and thermal population of a higher lying excited state,  $k_0 exp$  $(-\Delta E/RT)$ . The ligand excited state is attributed to the thermal population of a higher lying excited state. And the energy of the ligand field largely depends on the ligand field strength [382-386]. The metal centre (MC) excited state depends on the ligand field strength based on the  $\sigma$ -donor and  $\pi$ -acceptor properties of the ligands, the steric hindrance around the metal and the bite angles of the ligand. Therefore, choosing of ligands is crucial. Moreover, ligand field strength controls the energy position of metal centre (MC) and ligand centre (LC), including the metal-to-ligand transfer (MLCT) of ruthenium(II) polypyridine complexes. The basic properties of the ligands, such as the HOMO-LUMO energy gap and the singlet-triplet splitting greatly influence the energy

of the LC excited state. Studies have shown that involvement of ligand reduction potential in MLCT transition influences MLCT excited state [387, 388]. This suggest that the ruthenium(II) complexes luminescent properties are improved through the metal oxidation potential controlled by electron gain and lose attributes of the ligand and by the charge separation caused by the transitions and also, depending on excited state reactant or product, energy ordering and orbital nature low energy excited state [394, 395].

Complexes	Emission maxima
	$\lambda_{max}$ (nm)
$[Ru(L1)(L7)(H_2dcbpy)](PF_6)_2,-(Dye7)$	700
[Ru(L2)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye8)	699
[Ru(L3)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye9)	700
$[Ru(L4)(L7)(H_2dcbpy)](PF_6)_2-(Dye10)$	700
[Ru(L5)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye11)	699
$[Ru(L6)(L7)(H_2dcbpy)](PF_6)_2-(Dye12)$	699

**Table 3.8**: photoluminescence properties of series II complexes (7-12)

Measured in DMSO solution



Figure 3.22: Electronic absorption spectral of Series II with formula [Ru(bdmpmar)(vpdiinp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

## 3.2.3.3 Series III dyes emission spectra of general formula [Ru(bdmpmar)(vpbpp)(H<sub>2</sub>dcbpy)]<sup>2+</sup>

Figure 3.23 shows emission spectra of series III ruthenium(II) complexes measured in DMSO and corresponding data are presented in Table 3.9

Complexes	Emission maxima
	$\lambda_{max} (nm)$
[Ru(L1)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> ,-(Dye13)	700
[Ru(L2)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye14)	699
[Ru(L3)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye15)	699
[Ru(L4)( L8 )(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye16)	700
[Ru(L5)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye17)	702
[Ru(L6)( L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye18)	699

 Table 3.9: Photoluminescence properties of series III complexes (13-18)

Measured in DMSO solution

Ruthenium(II) complexes are emissive materials whose maximum are typical of a  ${}^{3}$ MLCT lowest lying excited state. These class of ruthenium(II) complexes are unique due to their emission properties which follow the energy gap law whereby the  ${}^{3}$ MLCT state tends to be long-lived and deactivates into three processes such as radiative decay Kr, radiationless decay knr and thermal population of a higher lying excited state,  $k_{o}exp$  ( $-\Delta E/RT$ ). The ligand excited state is attributed to the thermal population of a higher lying excited state. And the energy of the ligand field largely depends on the

ligand field strength [382-386]. The metal centre (MC) excited state depends on the ligand field strength based on the  $\sigma$ -donor and  $\pi$ -acceptor properties of the ligands, the steric hindrance around the metal and the bite angles of the ligand. Thus, the choice of a ligand takes priority because the ligand field strength controls the energy position of metal centre (MC) and ligand centre (LC), including the metal-to-ligand transfer (MLCT) of ruthenium(II) complexes. The cutting edge of ligands corresponds to HOMO-LUMO energy gap and the singlet-triplet splitting which greatly influence the energy of the LC excited state. Scientific reports have shown that involvement of ligand reduction potential in MLCT transition influences MLCT excited state [387, 388]. This suggest that the ruthenium(II) complexes luminescent properties are improved through the metal oxidation potential controlled by electron gain and lose attributes of the ligand and by the charge separation caused by the transitions and also, depending on excited state [387, 388].



Figure 3.23: Electronic absorption spectral of Series III dyes with formula  $[Ru(bdmpmar)(vpbpp)(H_2dcbpy)]^{2+}$ 

## 3.2.3.4 Series IV and V dyes emission spectra of general formula [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N<sup>^</sup>)(NCS)]<sup>2,+</sup>and [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(N<sup>^</sup>)<sub>2</sub>]<sup>2,+</sup>respectively

The emission spectral properties of series IV and V dye were measured in DMSO ashown in Figure 3.24 and corresponding data presented in Table 3.10

Complexes	Emission maxima
	$\lambda_{max}$ (nm)
$[Ru(H_2dcbpy)_2(L7)(NCS)](PF_6)-(Dye 19)$	703
[Ru(H <sub>2</sub> dcbpy) <sub>2</sub> (L8)(NCS)](PF <sub>6</sub> )-(Dye 20)	700
$[Ru(H_2dcbpy)_2(L7)_2](PF_6)_2-(Dye 21)$	700
[Ru(H <sub>2</sub> dcbpy) <sub>2</sub> (L8) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> -(Dye 22)	702
$[Ru(H_2dcbpy)_2(L7)(L8)](PF_6)_2$ -(Dye 23)	702

 Table 3.10: Photoluminescence properties of series IV and V complexes (19-23)

Measured in DMSO solution

The emission features and their maximum are typical of a <sup>3</sup>MLCT lowest lying excited state of ruthenium(II) complexes. Generally, the emission properties of ruthenium(II) complexes follow the energy gap law whereby the <sup>3</sup>MLCT state tends to be long-lived and deactivates into three processes such as radiative decay Kr, radiationless decay knr and thermal population of a higher lying excited state,  $k_0 exp$  ( $-\Delta E/RT$ ). The ligand excited state is attributed to the thermal population of a higher lying excited state. And the energy of the ligand field largely depends on the ligand field strength [382-386]. The metal centre (MC) excited state depends on the ligand field strength based on the

σ-donor and π-acceptor properties of the ligands, the steric hindrance around the metal and the bite angle of the ligand. Thus, the resulting choice of a ligand takes priority because the ligand field strength controls the energy position of metal centre (MC) and ligand centre (LC), including the metal-to-ligand transfer (MLCT) of ruthenium(II) complexes. The cutting edge of ligands centres on HOMO-LUMO energy gap and the singlet-triplet splitting which greatly influence the energy of the LC excited state. Studies have shown that involvement of ligand reduction potential in MLCT transition influences MLCT excited state [387, 388]. Therefore, the emissive ruthenium(II) complexes with improved photophysical properties derived upon the metal oxidation potential controlled by electron gain and lose attributes of the ligand and by the charge separation caused by the transitions could be linked to the relationship between the structure of a ligand and properties of the resulting complexes [387, 388].



**Figure 3.24:** Emission spectral of Series IV and V dyes with formula  $[Ru(H_2dcbpy)_2(N^{)}(NCS)]^{+}$  and  $[Ru(H_2dcbpy)_2(N^{)2}]^{2}$ ,

3.2.3.5 Series VI, VII and VIII dyes emission spectra of general formula [Ru(H2dcbpy)(N^)2(NCS)2]<sup>2,+</sup>, [Ru(H2dcbpy)(N^)(NCS)3]<sup>2,+</sup> and [Ru(vptpy)(dcbpyH2(N^^^)]<sup>2,+</sup> respectively

Figure 3.25 show emission spectra of series VI, VII and VIII ruthenium(II) complexes measured in DMSO and corresponding data are presented in Table 3.11

Complexes	Emission maxima
	$\lambda_{max}$ (nm)
[Ru(H <sub>2</sub> dcbpy)( L7) <sub>2</sub> (NCS) <sub>2</sub> ]-(Dye 24)	701
[Ru(H2dcbpy)( L8) <sub>2</sub> (NCS) <sub>2</sub> ]-(Dye 25)	701
[Ru(H <sub>2</sub> dcbpy)( L7) <sub>2</sub> (NCS) <sub>3</sub> ](NH <sub>4</sub> )-(Dye 26)	699
[Ru(H <sub>2</sub> dcbpy)( L8) <sub>2</sub> (NCS) <sub>3</sub> ](NH <sub>4</sub> )-(Dye27)	701
[Ru(L9)(H <sub>2</sub> dcbpy)(L7)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 28)	704
[Ru(L9)(H <sub>2</sub> dcbpy) <sub>2</sub> (L8)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 29)	699
[Ru(L9)(H <sub>2</sub> dcbpy) <sub>2</sub> (NCS)](PF <sub>6</sub> ) <sub>-</sub> (Dye 30)	699

Table 3.11: Photoluminescence properties of series VI-VIII complexes (24-30)

Measured in DMSO solution

Ruthenium(II) complexes are high value emissive materials whose maximum are typical of a <sup>3</sup>MLCT lowest lying excited state. These high value ruthenium(II) complexes are ascribed to their emission properties which follow the energy gap law whereby the <sup>3</sup>MLCT state tends to be long-lived and deactivates into three processes such as radiative decay Kr, radiationless decay knr and thermal population of a higher

lying excited state,  $k_0 exp$  ( $-\Delta E/RT$ ). The ligand excited state is attributed to the thermal population of a higher lying excited state. And the energy of the ligand field largely depends on the ligand field strength [382-386]. The metal centre (MC) excited state depends on the ligand field strength based on the  $\sigma$ -donor and  $\pi$ -acceptor properties of the ligands, the steric hindrance around the metal and the bite angle of the ligand. The choice of a ligands is important because the ligand field strength controls the energy position of metal centre (MC), ligand centre (LC) and the metalto-ligand transfer (MLCT) for the formation of high value ruthenium(II) complexes. A unique characteristics of ligands is the control derived by the energy of the LC excited state due to the HOMO-LUMO energy gap and the singlet-triplet splitting. Literature provides that participation of ligand reduction potential in MLCT transition controls MLCT excited state [387, 388]. Therefore, the emissive ruthenium(II) complexes with improved photophysical properties derived upon the metal oxidation potential controlled by electron gain and lose attributes of the ligand and by the charge separation caused by the transitions could be linked to the relationship between the structure of a ligand and the properties of the resulting complexes [387-389].



Figure 3.25: Emission spectral of Series VI, VII and VIII with formula $[Ru(H_2dcbpy)(N^{*})_2(NCS)_2],$  $[Ru(H_2dcbpy)(N^{*})(NCS)_3]^{-1}$  and $[Ru(vptpy)(dcbpyH_2(N^{**})]^{2,+}.$ 

#### **3.2.4 NMR Spectroscopy**

#### 3.2.4.1 <sup>1</sup>H and <sup>13</sup>C NMR of Series I

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all Series I ruthenium(II) complexes with general molecular formula of [Ru(L1-6)(H<sub>2</sub>dcbpy)(NCS)] were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra are presented in Figures 3.26 and 3.27 respectively for dye 1 as well as Figures 3.28 and 3.29 respectively for dye 2. Find supplementary information in Tables 3.12 for dye 3, 4, 5 and 6 respectively.

#### 3.2.4.1.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L1)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 1

The <sup>1</sup>H NMR spectrum of [Ru(**L1**)(H<sub>2</sub>dcpy)(NCS)](PF<sub>6</sub>)<sub>2</sub>,-dye 1 in DMSO-d<sub>6</sub> showed five doublet peaks and two singlet peaks in the aromatic region. The 4,4-Dicarboxy-2,2'-bipyridine hydrogen atoms were found as doublets at 7.85, 6.75 and 6.65 ppm for (H-21), (H-28), and (H-29) and two singlet peaks at 7.00 and 6.90 ppm for (H-23) and (H-26). Two doublet peaks at 7.70 and 7.60 ppm were assigned to (H-7) and (H-10) aromatic hydrogen atoms of **L1** ligand. At the aliphatic region, the singlet peaks at δ 2.20 and 1.97 ppm were assigned to (H-16, 19); (H-17, 18) of the methyl group due to the chemical equivalent pyrazolyl protons of **L1** ligand [299, 372, 377, 390].



Figure 3.26: <sup>1</sup>H NMR spectrum of [Ru(L1)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 1

In the <sup>13</sup>C NMR spectrum of [Ru(L1)(H<sub>2</sub>dcpy)(NCS)](PF<sub>6</sub>).dye (1), the spectrum of the complex shows 5 resonance signals in the aromatic region  $\delta$ = 120-167 ppm conforming to 4,4-Dicarboxy-2,2'-bipyridine and L1. The peak at downfield of 166.49 ppm is assigned to the C-30/C-31 carboxylate carbons of 4,4-Dicarboxy-2,2'bipyridine ligand. The peak at 155,95 ppm and 151.04 ppm respectively, are due to chemical equivalent pyrazolyl carbon C-1/C-15 and C-3/C-13 atoms in proximity to electron withdrawing nitrogen coordinated to L1. C-1 and C-15 are related because they quaternary carbons which are near to two electron withdrawing mitrogen coordinated to ligand. Same is applicable for C-3 and C-13 quaternary carbon atoms. The peaks at  $\delta = 120.03$  and 123.93 ppm respectively, are assigned to C-22 and C-26 pyridyl coordinated to 4,4-Dicarboxy-2,2'-bipyridine ligand [377]. The resonance peaks at 132.81 ppm are attributable to NCS ligand. Carbon-13 NMR spectra has become a useful tool for identifying NCS groups mode of coordination located in complexes. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals due to [Ru(L1)(H<sub>2</sub>dcpy)(NCS)](PF<sub>6</sub>)<sub>2</sub>, dye (1) within the region 130-135 ppm shows that NCS ligand is coordinated through the nitrogen atom.



Figure 3.27: <sup>13</sup>C NMR spectrum of [Ru(L1)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 1

#### 3.2.4.1.2 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L2)(H<sub>2</sub>dcpy)(NCS)](PF<sub>6</sub>)-Dye 2

For the <sup>1</sup>H NMR spectrum of [Ru(bdmpmeta)(H<sub>2</sub>dcpy)(NCS)](PF<sub>6</sub>).Dye 2, the NMR spectrum shows majority of its peaks around the aromatic region above 6 ppm. However, peaks were assigned upfield due to methyl group in **L2** ligand. The aromatic doublet and singlet at  $\delta = 8.93$  and 7.93 ppm were assigned to (H-20) and (H-23) of the 4, 4'-Dicarboxy-2, 2'-bipyridine ligand. Furthermore, one singlet peak at  $\delta = 7.52$  ppm (H-7) and two doublet peaks at  $\delta = 7.37$  (H-9), 7.18 (H-10) respectively, were assigned to the pyridinyl protons of **L2** ligand. The methyl signals at 2.10 and 2.23 ppm were assigned to (H-17'18) and (H-16'19) for the chemical equivalent pyrazolylic hydrogen atoms of **L2** ligand [299, 372, 377, 390].



Figure 3.28: <sup>1</sup>H NMR spectrum of [Ru(L2)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 2

In the <sup>13</sup>C NMR spectrum of  $[Ru(L2)(H_2dcpy)(NCS)](PF_6)_2$ -Dye 2, the spectrum of the complex shows 10 resonance signals in the aromatic region  $\delta = 120$ -167 ppm conforming to 4, 4'-Dicarboxy-2, 2'-bipyridine and L2 ligand. The peak at downfield of 166.49 ppm is assigned to the C-30/C-31 carboxylate carbons of 4, 4'-Dicarboxy-2, 2'-bipyridine ligand. Four sets of signals at  $\delta$ = 151.04, 149.64, 142.39 and 105.33 ppm respectively, are due to chemical equivalent pyrazolyl carbon atoms of C-1/C-15, C-3/C-13, C-4/C-12 and C-2/C-14 in proximity to electron withdrawing nitrogen coordinated to L2 ligand. Two sets of peaks at  $\delta = 129.54$  and 121.25 ppm respectively, are assigned to. C-7 and C-9 pyridyl carbon atoms located within the region of electron withdrawing oxygen and electron withdrawing nitro group of the pyridyl ring incorporated by the L2 ligand. The peak at  $\delta = 55.96$  ppm is due C-11 methyl carbon of pyridyl ring incorporated by the L2 ligand. The peaks at  $\delta = 127.61, 123.96$  and 120.03 ppm respectively, are assigned to C-21, C-26 and C-22 pyridyl carbon atoms coordinated to 4,4-Dicarboxy-2,2'-bipyridine ligand [377]. The resonance peaks at 132.81 ppm are attributable to NCS ligand. It is widely known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals due to  $[Ru(L2)(H_2dcpy)(NCS)](PF_6)_2$ -(dye 2) within region 130-135 ppm shows that NCS ligand is coordinated through the nitrogen atom.



Figure 3.29 <sup>13</sup>C NMR spectrum of [Ru(L2)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 2

Table 3.12: <sup>1</sup> H NMR and <sup>13</sup> C NMR data for series I complexes-(3, 4, 5 and 6)			
Formulation	Multiplicity &Chemical shift δ	Chemical shift $\delta^{13}$ C (ppm)	
	$^{1}\mathbf{H}$ (ppm)		
[Ru(L3)(H <sub>2</sub> dcbpy)(NC	L3	L3	
S)](PF <sub>6</sub> )-(Dye3),			
	7.84 (m, 3H, Ar-H, H7-H9)	151.65 (N-CPz-CH <sub>3</sub> , C1/C14)	
	2.19 (s, 6H, Pz-CH <sub>3</sub> H15/H18)	140.02 (CPzCH <sub>3</sub> , C4/C11)	
	2.12 (s, 6H, Pz-CH <sub>3</sub> H16/H17)		
	H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy	
	8.99 (d, 1H, H19)	166.49 (C29/C30)	
	7.01 (d, 1H, H20)	120.03 (C22)	
	8.91 (s,1H, H22)	123.95 (C25)	
	7.98 (s. 1H H25)		
	6.98 (d, 1H, H27)	132.81 (NCS)	
[Ru(L4)(H <sub>2</sub> dcbpy)(NC	L4	L4	
S)](PF <sub>6</sub> )-(Dye4),			
5.29 (s,1H, HPz, H2/H14)			
--			
4.27 (s, 2H, N-CH <sub>2</sub> -N, H4/H12)			
7.59 (d, 2H, Ar-H, H6/H10)			
7.99 (d, 2H, Ar-H, H7/H9)			
4.24 (s, 3H, H11)			
2.23 (s, 6H, Pz-CH <sub>3</sub> , H16/H19)			
2.10 (s, 6H, Pz-CH <sub>3</sub> , H17/H18)			

H<sub>2</sub>dcbpy 8.99 (d, 1H, H20) 7.97 (d,1H, H21) 8.97, (s, 1H, H23) 8.77 (s, 1H, H26) 7.15 (d, 1H, H28) 7.13 (d, 1H, H29)

# 151.15 (N-CPz-CH<sub>3</sub>, C1/C15) 140.02 (CPzCH<sub>3</sub>, C4/C12) 40.90 (C11)

H<sub>2</sub>dcbpy 166.49 (C30/C31) 122.38 (C26) 120.03 (C22)

132.81 (NCS)

Ru(L5)(H2dcbpy)(NCS))(	15	1.5
PF <sub>6</sub> )-(Dye5)		
	1.00- 1.59 (m, 10H, CH <sub>2</sub> cyclohexyl	106.00 (CPzH, C2/C13)
	H6-H10)	140.02 (CPzCH <sub>3,</sub> , C3/C12)
	2.21(s, 6H, Pz-CH <sub>3</sub> , H15/H18)	64.57 (N-CH <sub>2</sub> -N, C4/C12)
	1.12 (s, 6H, Pz-CH <sub>3</sub> , H16/H19)	26.47 (Cy C6/C10)
		25.02 (Cy, C7/C9)
		24.73 (Cy, C8)
	H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy
	8.99 (d, 1H H19)	166.49 (C29/C30)
	7.92 (d, 1H, H20)	123.95 (C25)
	8.05 (s, 1H H22)	120.03 (C22)
	7.25 (s, 1H, H25)	
		132.81 (NCS)
[Ru(L6)(H <sub>2</sub> dcby)(NCS	L6	L6
)](PF <sub>6</sub> )-(Dye6)		
	5.95 (s, 2H, HPz, H2/H14)	140.02 (CPzCH <sub>3</sub> , C3/C14)
	4.12 (s, 4H, N-CH <sub>2</sub> -N, H4/H12)	40.90 (C11)
	7.93 (d, 1H, Ar-H H6/H10)	
	7.91 (d, 1H, Ar-H, H7/H9)	
	H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy

8.99 (d, 1H, H20) 7.92 (d, 1H, H21) 8.97 (s, 1H, H23) 8.88 (s, 1H, H26) 120.03 (C22)

132.81 (NCS)

Abbreviations; s = singlet d = doublet, t = triplet q = quintet, dd = doublet doublet, m = multiplet

#### 3.2.4.2 <sup>1</sup>H and <sup>13</sup>C NMR of Series II

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of all Series II ruthenium(II) complexes with general molecular formula of [Ru(L1-6)( L7)(H<sub>2</sub>dcbpy)]<sup>2+</sup> were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra are presented in Figures 3.30 and 3.31 respectively for dye 9 as well as Figures 3.32 and 3.33 respectively for dye 10. Find supplementary information in Tables 3.13 for dye 7, 8, 11 and 12 respectively.

#### 3.2.4.2.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L3)(L7)(H2dcbpy)](PF6)2-Dye 9

Proton NMR spectra data of  $[Ru(L3)(L7)(H_2dcbpy)](PF_6)_2$ -(Dye 9) show complex splitting patterns in the aromatic region due to the presence of L7 monodentate ligand. The resonance peaks in the aliphatic region are due to the pyrazolyl protons of the tridentate ligands. The spectrum shows two doublets and two singlets peaks at  $\delta = 8.84$ (H19a) ppm, 7.72 (H-27a) ppm and 7.84 (H-22a) ppm, 7.80 (H-25a) ppm respectively, are assigned to the pyridyl protons of the 4, 4-Dicarboxy-2,2'-bipyridine ligand [299, 372, 377]. A multiplet signal at  $\delta = 7.68-7.79$  (H-4, H-5, H-6, H-7 and H-4', H-5', H-6', H-7') ppm is assigned to the eight hydrogen diindeno atoms (2(C<sub>4</sub>H<sub>4</sub>) moieties H- 4 to H-7 and H-4'to H-7') coordinated to **L7** monodentate ligand. A doublet of doublet signal  $\delta = 7.52$  (H-2'', H-3'', H-5'', H-6'') ppm is assigned to phenyl hydrogen atoms (C<sub>6</sub>H<sub>4</sub> moiety H-2''to H-6'') coordinated to **L7** monodentate ligand [393]. The peaks at  $\delta = 5.38$ , 5.97 and 6.77 are assigned to vinyl hydrogen atoms of the styryl group coordinated to **L7** monodentate ligand [394]. The spectrum shows that one singlet signal at  $\delta = 5.93$  (H-2a/H-14a) ppm of two hydrogen atoms, a singlet signal  $\delta = 4.90$  (H-4a/ H-12a) ppm of four hydrogen atoms, a singlet signal  $\delta = 1.26$  (H-16a/H-19a) ppm of six hydrogen atoms and another singlet signal  $\delta = 1.24$  (H-17a/H-18a) ppm of six hydrogen atoms respectively, are due to the chemical equivalent pyrazolyl hydrogen atoms [299, 372, 377, 390, 395].



Figure 3.30: <sup>1</sup>H NMR spectrum of [Ru(L3)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 9

Carbon-13 NMR spectra data of [Ru(L3)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye9) shows 21 resonance signals at aromatic region ( $\delta = 116.54$ -193.78ppm) corresponding to 4,4dicarboxy-2,2'-bipyridine, L3 and L7 ligands. Two major resonance peaks in the aliphatic region, at  $\delta = 26.84$  (C15a/C18a) ppm and 14.11 (C-16a/C-17a) ppm respectively, are due to the methyl group of the coordinated L3 ligands. The downfield signal at 193.78 ppm is assigned to the carbon atom of the carboxylate unit coordinated 4,4-dicarboxy-2,2'-bipyridine ligand. The signal at 150.50 ppm is assigned to quaternary C-2 and C-2" carbons in proximity to an electron withdrawing central nitrogen coordinated to L7 monodentate ligand. The signals at  $\delta = 138.93, 138, 83,$ 137.71, 137.55, 135.46 and 135.38 are assigned to the chemical equivalent diindeno (C-, C-3', C-4, C-4' C-5, and C-5') carbons atoms coordinated to the L7 monodentate ligand. The peaks at 136.37 and 116.54 ppm are assigned to C-7" and C-8" vinyl carbon atoms coordinated to the L7 monodentate ligand [394]. The C-2", C-3', C-4" C-5" and C-6" carbons are observed at  $\delta = 131.98, 132.06, 133.06$  and 132.88, 131.62 ppm respectively, due to phenyl carbon atoms coordinated to the L7 monodentate ligand. The  $H_2$ dcbpy carbons of C-28a, C-22a and C-24a were assigned to the peaks at  $\delta = 128.25$ , 127.18 and 124.18 ppm. [377].



Figure 3.31: <sup>13</sup>C NMR spectrum of [Ru(L3)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(dye 9)

## 3.2.4.2.2 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L4)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye10)

In the case of  $[Ru(L4)(L7)(H_2dcbpy)](PF_6)_2$ -(Dye 10), the proton NMR spectra data show complex splitting patterns in the aromatic region. From the spectrum, a set of two doublets and a set of two singlets peaks at  $\delta = 8.84$  ppm (H-20a), 7.60 ppm (H-21a) and 7.97 ppm (H-23a), 6.82 ppm (H-26a) respectively, are assigned to the pyridyl protons of the 4, 4-dicarboxy-2,2'-bipyridine ligand. The methyl protons of **L4** pyridyl ring signal was observed as doublet peak at 4.12 ppm [299, 372, 377, 390]. A multiplet peak at  $\delta = 7.65$ -7.82 ppm was assigned to (H-4, H-5, H-6, H-7 and H-4', H-5', H-6', H-7') eight hydrogen diindeno atoms while doublet of doublet peak at  $\delta = 7.52$  ppm was assigned to (H-2'', H-3'', H-5'', H-6'') four hydrogen phenyl atoms of **L7** monodentate ligand [393]. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 are assigned to vinyl hydrogen atoms of the styryl group coordinated to **L7** monodentate ligand [394]. At the aliphatic region, two singlet peaks at  $\delta = 1.64$  and 1.34 ppm were assigned to (H-16a/H-19a) and (H-17a/H-18a) of six chemical equivalent pyrazolyl hydrogen atoms [299, 372, 377, 390].



Figure 3.32: <sup>1</sup>H NMR spectrum of  $[Ru(L4)(L7)(H_2dcbpy)](PF_6)_2$ -Dye 10

Carbon-13 NMR spectrum of  $[Ru(L4)(L7)(H_2dcbpy)](PF_6)_2$ -(Dye 10) shows 26 resonance signals at aromatic region ( $\delta = 116.54-193.78$  ppm) corresponding to 4,4dicarboxy-2,2'-bipyridine, L4 and L7 ligand. Two major resonance peaks in the aliphatic region, at  $\delta = 26.84$  (C-15a/C-18a) ppm and 14.11 (C-16a/C-17a) ppm respectively, are due to the methyl group of the coordinated L4 ligand. The downfield signal at 193, 80 ppm is assigned to the carbon atom of the carboxylate unit coordinated to 4,4-Dicarboxy-2,2'-bipyridine ligand. The signal at 150.49 ppm is assigned to quaternary C-2 and C-2" carbons in proximity to an electron withdrawing central nitrogen coordinated to L7 monodentate ligand. The signals at  $\delta = 138.93, 138$ , 83, 137.71, 137.55, 135.46 and 135.38 respectively, are attributable to the chemical equivalent diindeno (C-3, C-3', C-4, C-4' C-5, and C-5') carbons atoms coordinated to the L7 monodentate ligand. The peaks at 136.37 and 116.54 ppm are assigned to C-7" and C-8" vinyl carbon atoms coordinated to L7 monodentate ligand [394]. The C-2'', C-3', C-4'' C-5'' and C-6'' carbons are observed at  $\delta = 131.98, 132.06, 133.06$ and 132.88, 131.62 ppm respectively, due to phenyl carbon atoms coordinated to the L7 monodentate ligand. The signals at  $\delta = 128.25, 127.12, 124.18$  and 123.25 ppm are assigned to C-28a, C-21a, C-23a and C-26a respectively, are due to their proximities to electrons withdrawing nitrogen coordinated to the H<sub>2</sub>dcbpy ligand [377].



Figure 3.33: <sup>13</sup>C NMR spectrum of [Ru(L4)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 10

Multiplicity & Chemical shift $\delta$	Chemical shift $\delta^{13}$ C (ppm)
${}^{1}\mathbf{H}$ (ppm)	
L1	L1
7.68 (m, 3H, Ar-H, H7a-H9a)	26.85 (PzCH <sub>3</sub> , C16a/C19a)
1.26 (s, 6H, Pz-CH <sub>3</sub> ,	14.10 (PzCH <sub>3</sub> , C17a/C18a)
H16a/H19a)	
1.24 (s, 6H, Pz-CH <sub>3</sub> ,	
H17a/H18a)	
H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy
8.84 (d, 1H, H20a)	193.80 (C29a/C30a)
7.55 (d, 1H, H21a)	128.25 (C28a)
7.84 (s, 1H, H23a)	127.18 (C21a)
	124.16 (C23a)
	123.79 (C26)
	Multiplicity & Chemical shift $\delta$ <sup>1</sup> H (ppm) L1 7.68 (m, 3H, Ar-H, H7a-H9a) 1.26 (s, 6H, Pz-CH <sub>3</sub> , H16a/H19a) 1.24 (s, 6H, Pz-CH <sub>3</sub> , H17a/H18a) H2dcbpy 8.84 (d, 1H, H20a) 7.55 (d, 1H, H21a) 7.84 (s, 1H, H23a)

**Table 3.13:** <sup>1</sup>H NMR and <sup>13</sup>C NMR data for series II complexes-(7, 8, 11 and 12)

L7
7.60-7.80 (m, 8H; diindeno)
7.55 (dd, 4H; Phenyl)
5.36 (d, 1H, CH=CH <sub>2</sub> )
5.94 (d, 1H, CH=CH <sub>2</sub> )
6.77 (q, 1H, CH=CH <sub>2</sub> )

**L7** 150.40 (C2/C2'')

116.5 (CH=CH<sub>2</sub>) 136.37 (CH=CH<sub>2</sub>)

138.93, 137.55, 136.47, 135.58, 135.46, 135.38, 134.59, 133.06, 132.44, 131.98, 131.62, 128.19, 124.08

[Ru(L2)(L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -(Dye 8),	L2	L2
		149.46 (CPh-CH=CH <sub>2</sub> )
	7.37 (s, 1H, Ar-H H7a)	142.40 (N-CPz, C4a/C12a)
	7.25 (d,1H, Ar-H H9a)	105.33 (CPz-H, C2a/C14a)
	7.18 (d, 1H, Ar-H. H10a)	55.96 (N-CH2-N, C11a)
	1.65 (s. 6H, Pz-CH <sub>3</sub> ,	26.82 (PzCH <sub>3</sub> , C16a/C19a)
	H16a/H19a)	14.10 (PzCH <sub>3</sub> , C17a/C18a)
	1.35 (s, 6H, Pz-CH <sub>3</sub> ,	
	H17a/H18a)	
	H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy
	8.84 (d, 1H, H20a)	128.25 (C28a)
	7.60 (d, 1H; H21a)	127.18 (C21a)
	7.81 (s, 1H, H23a)	124.15 (C23a)
	7.48 (s, 1H, H26a)	121.25 (C26a)
	L7	L7
	7.62-7.80 (m, 8H; diindeno) 7.52 (dd, 4H; Phenyl)	150.40 (C2/C2'')
	5.36 (d, 1H, CH=CH <sub>2</sub> )	116.5 (CH=CH <sub>2</sub> )
	5.94 (d, 1H, CH=CH <sub>2</sub> )	136.37 (CH=CH <sub>2</sub> )
	6.77 (q, 1H, CH=CH <sub>2</sub> )	
		138.93, 137.71, 137, 55, ,136, 47,
		135.54, 135.45, 135.38, 134.90,
		134.59,133.05 132.88, 132.44,
		131.98, 131.62, 129.54, 124.07
[Ru(L5)(L7)(H <sub>2</sub> dcbpy)](PF	L5	L5
$_{6}$ ) <sub>2</sub> -(Dye 11)		

## 26.82 (PzCH<sub>3</sub>, C16a/C19a) 14.10 (PzCH<sub>3</sub>, C17a/C18a)

5.80 (s, 4H, N-CH<sub>2</sub>-N, H4a/H11a) 5.12 (s, 2H, HPz, H2a/H13a) 0.75-1.00 (m 3H, Cy, H7a-H9a) 1.87 (s, 6H, Pz-CH<sub>3</sub> H15a/H18a) 1.38 (s, 6H, Pz-CH<sub>3</sub>, H16a/H17a)

> H2dcbpy 8.59 (d, 1H; H19a) 7.45 (d, 1H, H20a) 7.56 (s, 1H; H22a) 7.48 (s,1H; H25a)

#### L7

7.49-7.60 (m, 8H; diindeno) 7.35 (dd, 4H; Phenyl) 5.36 (d, 1H, CH=CH<sub>2</sub>) 5.94 (d, 1H, CH=CH<sub>2</sub>) 6.77 (q, 1H, CH=CH<sub>2</sub>) H<sub>2</sub>dcbpy 193.79 (C29a/C30a) 128.25 (C28a) 127.18 (C21a) 124.16 (C23a) 123.79 (C26a) **L7** 150.40 (C2/C2'')

116.5 (CH=CH<sub>2</sub>) 136.37 (CH=CH<sub>2</sub>)

138.93, 137.70,137,54, ,136,47, 135.55, 135.45, 134.90, 134.58,133.05 132.88, 132.44, 131.98, 131.62, 128.18

$[Ru(L6)(L7)(H_2dcbpy)](PF$	L6	L6
<sub>6</sub> ) <sub>2</sub> -(Dye 12)		
	4.15 (s, 4H, N-CH <sub>2</sub> -N,	26.85 (PzCH <sub>3</sub> , C16a/C19a)
	H4a/H12a)	14.10 (PzCH <sub>3</sub> , C17a/C18a)
	7.72 (m, 2H, Ar-H, H6a/H10a)	
	4.13 (s, 3H, Ar-OCH <sub>3</sub> , H11a)	
	1.63 (s, 6H, Pz-CH <sub>3</sub> ,	
	H16a/H19a)	
	1.32 (s, 6H, Pz-CH <sub>3</sub> ,	
	H17a/H18a)	
	H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy
	8.84 (d, 1H, H20a)	128.26 (C28a)
	7.97 (s, 1H; H23a)	127.19 (C21)
	7.80 (s,1H; H26a)	124.16 (C23a)
	7.70 (d, 1H, H21a)	
	L7	L7
	7.72-7.80 (m, 8H; diindeno)	150.40 (C2/C2'')

7.60 (dd, 4H; Phenyl) 5.36 (d, 1H, CH=CH<sub>2</sub>) 5.94 (d, 1H, CH=CH<sub>2</sub>) 6.77 (q, 1H, CH=CH<sub>2</sub>)

116.5 (CH=CH<sub>2</sub>) 136.37 (CH=CH<sub>2</sub>)

138.93, 137.70,137,54, ,136,47, 135.55, 135.45, 134.90, 134.58,133.05 132.88, 132.44, 131.98, 131.62, 128.18

Abbreviations; s = singlet d = doublet, t = triplet q = quintet, dd = doublet doublet, m = multiplet

#### 3.2.4.3 <sup>1</sup>H and <sup>13</sup>C NMR of Series III

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all Series III ruthenium(II) complexes with general molecular formula of [Ru(L1-7)(L8)(H<sub>2</sub>dcbpy)]<sup>2+</sup> were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra are presented in Figures 3.34 and 3.35 respectively for dye 17 as well as Figures 3.36 and 3.37 respectively for dye 18. Find supplementary information in Tables 3.14 for dye 13, 14, 15 and 16.

#### 3.2.4.3.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L5)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-(Dye 17)

Proton NMR spectra data of  $[Ru(L5)(L8)(H_2dcbpy)](PF_6)_2$ -(Dye17) show complex splitting patterns in the aromatic region due to the presence of **L7** monodentate ligand. The resonance peaks in the aliphatic region are due to the pyrazolyl protons of the tripod ligands. The spectrum shows two doublets and two singlet signals at  $\delta = 8.77$ (H19a) ppm, 7.32 (H-20a) ppm and 7.79 (H-22a) ppm, 7.61 (H-25a) ppm respectively, are assigned to the pyridyl protons of the 4, 4-Dicarboxy-2,2'-bipyridine ligand [377]. The spectrum displays a multiplet signal at  $\delta = 7.09$ -8.15 (H-2''', H-3''', H-5''', H- 6''') ppm attributable to the four phenyl hydrogen atoms (C<sub>4</sub>H<sub>4</sub> moiety H-2'''- 6''') coordinated to **L8** monodentate ligand. A singlet peak at  $\delta = 7.87$  (H-3, 5) ppm is attributable to the chemically equivalent one pyridyl hydrogen atom (C<sub>5</sub>H<sub>2</sub>N moiety H3-5) coordinated to **L8** monodentate ligand. The multiplet resonance peak at  $\delta = 7.66-7.70$  (H-2', H-3', H-4', H-5', H-6' and H2'', H-3'', H-4'', H-5'', H-6'') ppm is due to the ten phenyl hydrogen atoms (2(C<sub>6</sub>H<sub>5</sub>) moieties H2'- 6'and H2''- 6'') coordinated to **L8** monodentate ligand [396]. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 are assigned to vinyl hydrogen atoms of the styryl group coordinated to **L8** monodentate ligand [394], A multiplet peak at  $\delta = 1.00-1.12$  (H-7a-9a) ppm is due to the three cyclohexyl hydrogen atoms (C<sub>6</sub>H<sub>6</sub> moiety H7a-9a) coordinated to **L5** ligand. Two sets of singlet signal  $\delta = 1.58$  (H-15a/H-18a) ppm and 1.25 (H-16a/H-17a) ppm of six hydrogen atoms respectively, are due to the chemical equivalent pyrazolyl hydrogen atoms [363].



**Figure 3.34**: <sup>1</sup>H NMR spectrum of [Ru(L5)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 17

Carbon-13 NMR spectra data of  $[Ru(L5)(L8)(H_2dcbpy)](PF_6)_2$ -(Dye17) show 20 resonance signals in the aromatic region ( $\delta$  116.54-189.63ppm) corresponding to 4,4-dicarboxy-2,2'-bipyridine, **L1** and **L8** ligands. Two major resonance peaks in the aliphatic region, at  $\delta$ = 26.83 (C-15a/C-18a) ppm and 14.10 (C-16a/C-17a) ppm respectively, are due to the methyl group of the **L1** ligand. The downfield signal at 189.63 ppm is assigned to the carbon atom of the carboxylate unit coordinated to the 4,4-dicarboxy-2,2'-bipyridine ligand [377]. The signal at 144.04 ppm is assigned to quaternary C-2 and C-6 carbons in **L8** monodentate ligand. The peaks at  $\delta$  = 122.28 and 143.10 ppm are assigned to C-3/C-5 chemical equivalent hydrogen atoms and quaternary C4 carbons of **L8** monodentate ligand. The peaks at  $\delta$  = 138.15, 139.77 and

143.0 ppm are assigned to chemical equivalent phenyl (C-2'''/C-6''', C-3'''/C-5''') and C4'''carbons atoms in **L8** monodentate ligand [396]. The peaks at  $\delta$  = 129.02. 132.36, 134.60 and 137.88 ppm are assigned to pyridyl (C-4', C-3', C-2'/C-6'and C-1') carbons atoms in **L8** monodentate ligand. The signals at  $\delta$  = 128.25, 127.11, 124.46 and 123.30 ppm are assigned to C-27a, C-20a, C-22a and C-24a of H<sub>2</sub>dcbpy ligand. The peaks at 116.54 and 136.37 ppm are assigned to C-7'' and C-8'' vinyl carbon atoms coordinated to **L8** monodentate ligand [394].



Figure 3.35: <sup>13</sup>C NMR spectrum of [Ru(L5)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 17

#### 3.2.4.3.2 <sup>1</sup>H and <sup>13</sup>CNMR of [Ru(L6)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye18

Proton NMR spectra data of  $[Ru(L6)(L8)(H_2dcbpy)](PF_6)_2$ -(Dye 18) shows complex splitting patterns in the aromatic region due to the presence of monodentate ligand L8. The spectrum shows a set of two doublets signals at  $\delta = 8.98$  (H-20a) ppm, and 8.89 (H23a) ppm are assigned to the pyridyl protons of the 4, 4-Dicarboxy-2,2'-bipyridine ligand [377]. The spectrum displays a multiplet signal at  $\delta = 7.09-8.15$  (H-2<sup>'''</sup>, H-3<sup>'''</sup>, H-5" H-6") ppm attributable to the four phenyl hydrogen atoms (C<sub>4</sub>H<sub>4</sub> moiety H2<sup>\*\*\*</sup>- 6<sup>\*\*\*</sup>) coordinated to monodentate ligand L8. A singlet peak at  $\delta$  = 7.87 (H-3, 5) ppm is assigned to the chemically equivalent one pyridyl hydrogen atom (C<sub>5</sub>H<sub>2</sub>N moiety H-3'5) coordinated to monodentate ligand L8. The multiplet resonance peak at  $\delta$  = 7.66-7.70 (H-2', H-3', H-4', H-5', H-6' and H-2'', H-3'', H-4'', H-5'', H-6'') ppm is due to the ten phenyl hydrogen atoms ( $2(C_6H_5)$  moieties H-2' to H-6' and H2'' to H-6'') coordinated to L8 monodentate ligand [396]. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 are assigned to vinyl hydrogen atoms of the styryl group coordinated to monodentate ligand L8 [394], A multiplet peak at  $\delta = 6.50-6.90$  (H-6a, H-7a, H-9a and H-10a) ppm is due to the non-chemical equivalent four pyridyl hydrogen atoms  $(C_6H_4 \text{ moiety H-6a, H-7a, H-9a and H-10a})$  coordinated to **L6** ligand. At the aliphatic region, two sets of singlet signal  $\delta = 1.65$  (H-16a/H-19a) ppm and 1.33 (H-17a/H-18a) ppm of six hydrogen atoms respectively, are due to the chemical equivalent pyrazolyl hydrogen atoms of monodentate ligand L8 [377].



Figure 3.36: <sup>1</sup>H NMR spectrum of [Ru(L6)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 18

Carbon-13 NMR spectrum of  $[Ru(L6)(L8)(H_2dcbpy)](PF_6)_2$ -(Dye18) shows 23 resonance signals in the aromatic region ( $\delta$  116.54-189.63ppm) corresponding to 4,4-Dicarboxy-2,2'-bipyridine, **L6** and **L8** ligands. The downfield signal at 189.63 ppm is assigned to the carbon atom of the carboxylate unit coordinated to the 4,4-Dicarboxy-2,2'-bipyridine ligand [377]. The signal at 144.04 ppm is assigned to quaternary C-2 and C-6 carbons which are in proximity to an electron withdrawing central nitrogen coordinated to C-3/C-5 chemical equivalent hydrogen atoms and quaternary C-4 carbons respectively, in proximity to an electron withdrawing central nitrogen coordinated to C-3/C-5 chemical equivalent hydrogen atoms and quaternary C-4 carbons

**L8**. The peaks at  $\delta = 138.15, 139.77$  and 143.0 ppm are assigned to chemical equivalent phenyl (C-2<sup>'''</sup>/ C-6<sup>'''</sup>, C-3<sup>'''</sup>/ C-5<sup>'''</sup> and C-4<sup>'''</sup>) carbons atoms coordinated to **L8** monodentate ligand. The peaks at  $\delta = 129.02$ . 132.36, 134.60 and 137.88 ppm are assigned to pyridyl (C-4', C-3'/C-5', C-2'/C-6' and C-1') carbons atoms respectively, coordinated to **L8** monodentate ligand [396]. The signals at  $\delta = 128.25, 127.11, 124.46$  and 123.30 ppm are assigned to C-28a, C-21a, C-23a and C-26a respectively, are due to their proximities to electrons withdrawing nitrogen coordinated to the H<sub>2</sub>dcbpy ligand [372]. The peaks at 136.37 and 116.54 ppm are assigned to C-7<sup>''</sup> and C-8<sup>''</sup> vinyl carbon atoms coordinated to the **L8** monodentate ligand [394]. Two major resonance peaks in the aliphatic region, at  $\delta = 26.83$  (C-16a/C-19a) ppm and 14.10 (C-17a/C-18a) ppm are assigned to the methyl group of the **L6** ligand.



Figure 3.37: <sup>13</sup>C NMR spectrum of [Ru(L6)( L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 18

Formulation	Multiplicity & Chemical shift $\delta$	Chemical shift $\delta$ <sup>13</sup> C (ppm)
	<sup>1</sup> <b>H</b> (ppm)	
$[Ru(L1)(L8)(H_2dcbpy)]($	L1	L1
PF <sub>6</sub> ) <sub>2</sub> ,-(Dye13)	7(0) (as 211 A s H H7- H0-)	2(92)(D-CH, C1(-)(C10))
	1.60  (m, 3H, Ar-H, H/a-H9a)	$20.83 (PZCH_3, C10a/C19a)$
	$1.03 (8, 0H, PZ-CH_3, H10a/H19a)$	$14.10 (P2CH_3, C1/a/C18a)$
	1.55 (S, OH, FZ-CH <sub>3</sub> , H1/a/H18a)	
	H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy
	8.93 (d, 1H, H20a)	189.00 (C29a/C30a)
	8.85 (s, 1H, H23a)	128.97 (C28a)
		127.12 (C21a)
		124.47 (C23a)
		123.93 (C26a)
		120.03 (C22a)
	L1	L1
	7.96-8.15 (m, 4H, Ar-H)	151.06 (C2/C6)
	7.87 (s, 2H, H')	
	7.66-7.70 (m, 10H, Ar-H)	
	5 26 (d 111 CU_CU_)	$1165(CH-CH_{c})$
	$5.30 (d, 1H, CH=CH_2)$	$110.3 (CH=CH_2)$ 126.27 (CH=CH_2)
	$5.94 (u, 1H, CH-CH_2)$	130.37 (CH–CH <sub>2</sub> )
	0.77 (q, 111, CH–CH <sub>2</sub>	144 04 143 10 139 77 138 85
		137 88 134 66 134 42 133 74
		137.60, 137.60, 137.42, 135.74,
		129 29 129 02 (Cyphon)
		129.29, 129.02 (01000)
[Ru(L2)(L8)(H <sub>2</sub> dcbpy)](	L2	L2
PF <sub>6</sub> ) <sub>2</sub> -(Dye14),		
	5.95 (s, 2H; HPz, H2a/H14a)	149.46 (CPh-CH=CH <sub>2</sub> )
	7.37 (s, 1H, Ar-H, H7a)	142.40 (N-CPz, C4a/C12a)
	7.18 (d, 1H, Ar-H, H9a)	105.33 (CPz-H, C2a/C14a)
	7.02 (d, 1H Ar-H, H10a)	55.96 (N-CH2-N, C11a)
	2.51 (s, 6H, Pz-CH <sub>3</sub> , H16a/H19a)	$26.82 (PzCH_3, C16a/C19a)$
		14.10 ( $PzCH_{3}, C1/a/C18a$ )
	Hadabay	Hadahay
	8 03 (d 14 H20a)	128 07 (C28a)
	8 83 (c 1H H23a)	120.77 (C20a) 127 11 (C21a)
	7.25 (s, 11, 1123a)	127.11 (C21a) 124 A7 (C23a)
	7.23, (3, 111, 1120a)	123.3 (C26a)

# **Table 3.14:** <sup>1</sup>H NMR and <sup>13</sup>C NMR data for series III complexes- (13, 14, 15 and 16)

	<b>L8</b> 7.96-8.15 (m, 4H, Ar-H) 7.87 (s, 2H, H') 7.67 (s, 2H, H')	<b>L8</b> 144.04 (C2/C6) 143.10 (C4)
	5.36 (d, 1H, CH=CH <sub>2</sub> ) 5.94 (d, 1H, CH=CH <sub>2</sub> ) 6.77 (q, 1H, CH=CH <sub>2</sub> )	116.5 ( CH=CH <sub>2</sub> ) 136.37 (CH=CH <sub>2</sub> )
		C(vpbpp)—137.88, 134.74, 134.42,133.74 133.63, 132.36, 131.27, 131.62, 129.75, 129.54, 129.29, 129.27.127.61,122.29, 121.25
[Ru(L3)(L8)(H <sub>2</sub> dcbpy)]( PF <sub>6</sub> ) <sub>2</sub> -(Dye15)	L3	L3
	5.92 (s, 2H, HPz, H2a/H13a) 4.10 (s, 2H, N-CH <sub>2</sub> -N, H4a/H11a) 7.62 (m, 3H Ar-H, H7a-H9a) 1.27 (s, 6H, Pz-CH <sub>3</sub> , H15a/H18a) 1.25 (s, 6H; Pz-CH <sub>3</sub> , H16a/H17a)	26.82 (PzCH <sub>3</sub> , C15a/C18a) 14.10 (PzCH <sub>3</sub> , C16a/C17a)
	H2dcbpy 8.84 (d, 1H, H19a) 8.78 (s, 1H; H22a)	H2dcbpy 189.60 (C29a/C30a) 128.97 (C27a) 127.12 (C20a) 124.47 (C22a) 123.94 (C25a)
	<b>L8</b> 7.96-8.15 (m, 4H, Ar-H) 7.87 (s, 2H, H') 7.66-7.70 (m, 10H, Ar-H)	<b>L8</b> 144.04 (C2/C6) 143.10 (C4) 122.29 (C3/C5)
	5.36 (d, 1H, CH=CH <sub>2</sub> ) 5.94 (d, 1H, CH=CH <sub>2</sub> ) 6.77 (q, 1H, CH=CH <sub>2</sub>	116.5 (CH=CH <sub>2</sub> ) 136.37 (CH=CH <sub>2</sub> )
		139.77, 138.05, 137.66, 134.42, 133,61, 132.36, 131.27. 129.75, 129.29, 122 134.90, 134.58,133.05 132.88, 132.44, 131.98, 131.62, 128.18
$[Ru(L4)(L8)(H_2dcbpy)](PF_6)_2-(Dye16)$	L4	L4

5.95 (s, 2H, HPz, H2a/H	H14a) 26.85 (PzCH <sub>3</sub> , C16a/C19a)
4.16 (s, 2H, N-CH <sub>2</sub> -N H44	a/H12a) 14.10 (PzCH <sub>3</sub> , C17a/C18a)
7.85 (d, 2H, Ar-H, H7a	/H9a)
7.68 (d, 2H, Ar-H, H6a/	H10a)
4.13 (s, 3H, Ar-CH <sub>3</sub> H	11a)
1.64 (s, 6H, Pz-CH <sub>3</sub> , H16a	a/H19a)
1.34 (s, 6H, Pz-CH <sub>3</sub> , H17a	a/H18a)
H <sub>2</sub> dcbpy	H <sub>2</sub> dcbpy
8.91 (d, 1H, H20a)	189.60 (C30a/C31a)
7.84 (s, 1H, H23a)	128.97 (C28a)
6.83 (s, 1H; H26a)	127.12 (C21a)
	124.47 (C23a)
	123.94 (C26a)
L8	L8
7.96-8.15 (m, 4H, Ar	-H) 144.04 (C2/C6)
7.87 (s, 2H, H')	143.10 (C4)
7.66-7.70 (m, 10H, Ai	с-H) 122.29 (C3/C5)
5.36 (d, 1H, CH=CH	H <sub>2</sub> ) 116.5 (CH=CH <sub>2</sub> )
5.94 (d, 1H, CH=CH	136.37 (CH=CH <sub>2</sub> )
6.77 (q, 1H, CH=CH	$H_2$

137.88,134,42, ,133,74, 132.36, 131.27, 129.75, 129.29,129.02

Abbreviations; s = singlet d = doublet, t = triplet q = quintet, dd = doublet doublet, m = multiplet

## 3.2.4.4 <sup>1</sup>H and <sup>13</sup>C NMR spectra of Series IV

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all Series IV ruthenium(II) complexes with general molecular formula of  $[Ru(H_2dcbpy)_2(N^{*})(NCS)]^{+}$  were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $[Ru(H_2dcbpy)_2(L7)(NCS)](PF_6)$ -(Dye 19) and

[Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)(NCS)](PF<sub>6</sub>)-(Dye 20) are presented in Figures 3.38, 3.39 and 3.40,3.41 respectively.

## 3.2.4.4.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(vpdiinp)(NCS)](PF<sub>6</sub>)-(Dye 19)

From the <sup>1</sup>H NMR spectrum shown in Figure 3.38, the corresponding resonance peaks of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)(NCS)](PF<sub>6</sub>)-(Dye 19) in the aromatic region show shows complex splitting patterns in the aromatic region due to the presence of L7. The doublet peak at  $\delta = 9.94$  (H-6a') ppm is due to a pyridyl ring hydrogen atom of 4,4dicarboxy-2,2'-bipyridine in proximity to electron withdrawing nitrogen and NCS unit. Two sets of singlet peaks at 8.84 and 8,39 (H-3a' and H-3) ppm respectively, are attributable to pyridyl ring hydrogen atoms centrally located towards the electron withdrawing oxygen of carboxylic unit and nitrogen coordinated to 4,4-dicarboxy-2,2'-bipyridine ligand. Three sets of doublet peaks at 8.16, 7.79 and 7.74 (H-5a', H-5a and H-6a) ppm respectively, are attributable to pyridyl ring hydrogen atoms coordinated to 4,4-dicarboxy-2,2'-bipyridine ligand [377]. The multiplet peak at 7.60-7.76 ppm (H-4, H-5, H-6, H-7 and H-4', H-5', H-6', H-7') are due to eight diindeno ring hydrogen atoms of L7. Also, multiplet resonance peaks are observed at 6.75-6.89 ppm (H-2", H-3", H-4", H-5", H-6") are due to the four pyridyl hydrogen atoms of **L7** [374]. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to L7 [394].



Figure 3.38: <sup>1</sup>H NMR spectrum of  $[Ru(H_2dcbpy)_2(L7)(NCS)](PF_6)-(Dye 19)$ 

In the <sup>13</sup>C NMR spectrum of  $[Ru(H_2dcbpy)_2(L7)(NCS)](PF_6)-(Dye 19)$  shows 23 resonance signals in the aromatic region  $\delta$  120-170 ppm, The downfield signal at 193, 78 ppm is assigned to the carbon atom of the carboxylate unit coordinated to 4,4dicarboxy-2,2'-bipyridine ligand. The peak at downfield of 150.51 ppm is assigned to the chemically equivalent carbons (C-2, C-2') of **L7**. The peaks at  $\delta$  = 138.93, 137.69, 137.53, 136.46 and 135.44, ppm are assigned to pyridyl (C-3', C-4', C-5', C-6' and C-7') carbons atoms, while the peaks at  $\delta$  = 134.57, 132.89, 132, 44, 131.98 and 131.61 ppm are assigned to the other pyridyl (C-3, C-4, C-5, C-6 and C-7) carbons atoms and *trans* to 4,4-dicarboxy-2,2'-bipyridine ring. The peaks at 128.25 (C-5a'), 127.17 (C-5a), 123.79 (C-3a') and 124.15 (C-3a) are assigned to pyridyl carbons in proximity to electron withdrawing nitrogen coordinated to 4,4-dicarboxy-2,2'-bipyridine. The peaks at 136.37 and 116.54 ppm are assigned to C-7'' and C-8'' vinyl carbon atoms coordinated to the **L7** [394]. The resonance peaks at 133.05 ppm is assigned to the NCS ligands. Carbon-13 NMR spectra has become a useful tool for identifying NCS group mode of coordination located in complexes. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals due to  $[Ru(H_2dcbpy)_2(L7)(NCS)](PF_6)-(Dye 19)$  within the region 130-135 ppm shows that NCS ligand is coordinated through the nitrogen atom.



**Figure 3.39** <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)(NCS)](PF<sub>6</sub>)-(Dye 19)

## 3.2.4.4.2 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H2dcbpy)2(L8)(NCS)](PF6)-(Dye 20)

The <sup>1</sup>H NMR spectrum of  $[Ru(H_2dcbpy)_2(L8)(NCS)](PF_6)_2-(Dye 20)$  show corresponding resonance peaks in the aromatic region that the protons of the pyridyl rings.. The singlet peaks at 8.89 ppm was assigned to (H-3a' 3) chemical equivalent hydrogen protons of 4,4-dicarboxy-2,2'-bipyridine ligand [377]. A doublet peak at 8.15 ppm was assigned to (H-5a') hydrogen protons of 4,4-Dicarboxy-2,2'-bipyridine ligand. The doublet of doublet peak at 7.52-7.60 ppm was assigned to (H-2'''. H-3''', H-5''', H-6''') four phenyl hydrogen atoms of **L8**. The multiplet resonance peak at 7.75-7.90 ppm was assigned (H-2', H-3', H-4', H-5', H-6') five pyridyl hydrogen atoms of **L8**. A singlet at 7.62 was assigned to (H-3, 5) chemical equivalent hydrogen atoms of **L8**. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to **L8** [394].



Figure 3.40: <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)(NCS)](PF<sub>6</sub>)-(Dye 20)

<sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)(NCS)](PF<sub>6</sub>),-(Dye 20) shows 27 resonance signals in the aromatic region  $\delta$ = 120-170 ppm, The downfield peak at 189.60 ppm was assigned to carboxylate carbon atom of 4,4'-dicarboxylic-2,2'-bipyridine ligand. The peaks at downfield of 144.03 and 143.10 ppm are assigned to chemically equivalent carbons (C-2, C-6) and quaternary C-4 of monodentate ligand L8. The peaks at  $\delta = 137.87$ , 138.65 and 139.76 ppm were assigned to (C-1, C-1' and C-1'') quaternary carbons, while the peaks at  $\delta = 124.46$ , 127.11, 128.96, 129.29 and 129.75 ppm are assigned to (C-2', C-3', C-4', C-5' and C-6') aromatic carbons atoms of L8 monodentate ligand. The peaks at 120.05 ppm was assigned to chemically equivalent pyridyl carbons (C-3, C-5) of monodentate ligand **L8**. The signals at  $\delta = 123.30$  ppm are assigned to chemically equivalent carbons (C-3a, C-3a') of H<sub>2</sub>dcbpy ligand [377]. The peaks at 136.37 and 116.54 ppm are assigned to C7" and C8" vinyl carbon atoms coordinated to L8 [394]. The resonance peaks at 133.61 ppm was assigned to the carbon atom of NCS ligand. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals due to  $[Ru(H_2dcbpy)_2(L8)(NCS)](PF_6)$ -(Dye 20) within region 130-135 ppm shows that NCS ligand is coordinated through the nitrogen atom.



Figure 3.41: <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)(NCS)](PF<sub>6</sub>)-(Dye 20)

# 3.2.4.5 <sup>1</sup>H and <sup>13</sup>C NMR of Series V

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all Series V ruthenium(II) complexes with general molecular formula of  $[Ru(H_2dcbpy)_2 (N^{\circ})_2]^{2+}$  were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $[Ru(H_2dcbpy)_2(L7)_2](PF_6)_2$ -(Dye 21),  $[Ru(H_2dcbpy)_2(L8)_2](PF_6)_2$ -(Dye 22) and  $[Ru(H_2dcbpy)_2(L7)(L8)](PF_6)_2$ -(Dye 23) are presented in Figures 3.42, 3.43, 3.44, 3.45 and 3.46, 3.47 respectively

## 3.2.4.5.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>-(Dye 21)

The <sup>1</sup>H NMR spectra of  $[Ru(H_2dcbpy)_2(L7)_2](PF_6)_2$ -(Dye 21) due to chemical equivalency of the molecule show complex splitting in the aromatic region for multiplet peaks at 7.60-7.76 and 6.75-6.89 ppm. These were assigned to (H-4. H-5. H-6. H-7 and H-4'. H-5' H-6', H-7') and (H-2'', H-3'', H-4''. H-5''. H-6'') of eight aromatic hydrogen atoms and four pyridyl hydrogen atoms in **L7**. Also, the spectra showed a multiplet resonance peak at 8.89-8.92 ppm. This was accounted for (H-3a, H-5a, H-6a and H-3a', H-5a', H-6a') pyridyl hydrogen atoms of two 4,4-Dicarboxy-2,2'-bipyridine ligand. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm were assigned to vinyl hydrogen atoms of the styryl group coordinated to monodentate ligand [394].



**Figure 3.42:** <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>-Dye 21

<sup>13</sup>C NMR spectrum of  $[Ru(H_2dcbpy)_2(L7)_2](PF_6)_2$ -(Dye 21) shows 11 resonance signals in the aromatic region  $\delta = 120$ -170 ppm. The peak at downfield of 150.51 ppm is assigned to the chemically equivalent carbons (C-2 and C-2') in the monodentate ligand. The peaks at  $\delta = 135.56$ , 133.07, 132.46, and 131.63 ppm are assigned to (C-3', C-4', C-5'/C-7' and C-6') carbons aromatic atoms in one of **L7** electronically equivalent to the opposite **L7** ligand. The peaks at 128.06, 127.19 and 124.16 ppm are assigned to C-5a', C-5a and C-3a pyridyl carbon atoms in 4,4-dicarboxy-2,2'bipyridine. The peaks at 136.37 and 116.54 ppm are assigned to C7'' and C-8'' vinyl carbon atoms coordinated to monodentate ligand [394].



**Figure 3.43:** <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>-(Dye 21)

## 3.2.4.5.2 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H2dcbpy)2(L8)2](PF6)2,-(Dye 22)

The <sup>1</sup>HNMR spectra of  $[Ru(H_2dcbpy)_2(L8)_2](PF_6)_2$ ,-(Dye 22) show complex splitting due chemical equivalency of the molecule in the aromatic region. Three set of multiplet peaks at 7.96-8.15, 7.87 and 7.60-7.70 ppm respectively were assigned to (H-2'''. H-3'''. H-5'''. H-6'''), (H-3, H-5), (H-2', H-3', H-4', H-5', H-6' and H-2'', H-3'', H-4'', H-5'', H-6'') aromatic hydrogen atoms in one of **L8** and electronically equivalent to the opposite monodentate ligand. The presence of two 4,4-dicarboxy-2,2'-bipyridine, in which all the four pyridyl rings are electronically equivalent show a multiplet resonance peak at 8.17 ppm due to (H-3a H-3a' and H-5a') hydrogen atoms.



Figure 3.44: <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)<sub>2</sub>](PF<sub>6</sub>)<sub>2 2</sub>-Dye 22

<sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> dye 22 shows 23 resonance signals in the aromatic region  $\delta = 120-170$  ppm. Since the two **L8** are trans to four pyridyl rings of 4,4-dicarboxy-2,2'-bipyridine; the electron density of the two L8 are equivalent, The downfield signal at 189,00 ppm is assigned to the carbon atom of the carboxylate unit coordinated to 4,4-Dicarboxy-2,2'-bipyridine ligand. The peaks at downfield of 144.03 and 143.10 ppm are assigned to the chemically equivalent carbons (C-2/C-6) and quaternary C4 respectively, in proximity to the electron withdrawing central nitrogen coordinated to the monodentate ligand. The two L8 are in the same magnetic environment and *trans* to the four rings of 4,4'-Dicarboxy-2,2'-bipyridine, resulting to chemically equivalent resonance peaks. Therefore, the peaks at  $\delta = 133.74$ , 134.66, 137.87, 138.05 and 139.77 ppm are assigned to to pyridyl (C-2'), (C-3'), (C-4'), (C-5') and (C-6') carbons atoms of L8 and *trans* to 4,4-Dicarboxy-2,2'-bipyridine ring and electronically equivalent to the opposite monodentate ligand. The peaks at  $\delta$ = 129.75, 131.27, 132.36 and 133.61 ppm are assigned to the other pyridyl (C-3"/C-5", (C-2"/C-6"), (C-4"), and (C-1") carbons atoms and directly *trans* to L8 ring and indirectly *trans* to 4,4-dicarboxy-2,2'-bipyridine, also, electronically equivalent to the opposite monodentate ligand. The peaks at 128.97 (C-5a'), 127.12 (C-5a), 124.47 (C-3a) and 123.31 (C-3a') are assigned to pyridyl carbons close to electron withdrawing nitrogen as well as carboxylic unit coordinated to 4,4-Dicarboxy-2,2'bipyridine and *trans* to both monodentate ligands. The peaks at 136.37 and 116.54 ppm are assigned to C-7" and C-8" vinyl carbon atoms coordinated to the monodentate ligands [394].



Figure 3.45: <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>-(Dye 22)

#### 3.2.4.5.3 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)(L8)](PF<sub>6</sub>)<sub>2</sub>-(Dye 23)

From the <sup>1</sup>H NMR spectra of  $[Ru(H_2dcbpy)_2(L7)(L8)](PF_6)_2$ -(Dye 23), the corresponding complicated peaks in the aromatic region within  $\delta = 7.50$ -8.05 ppm is due to the presence of two 4,4'-Dicarboxy-2,2'-bipyridine *trans* to each other and *trans* to the protons of the **L8** and *trans* to protons of the **L7** respectively, whereby the pyridyl rings of **L8** and the diindeno rings of **L7** are electronically in different environment. The downfield shifted protons resonance signals due to two set of doublets and singlet at  $\delta = 8.91$  (H-6a') ppm, 8.16 (H-5a') ppm and 8.84 (H-3a') respectively, are assigned to 4,4-Dicarboxy-2,2'-bipyridine *trans* to The multiplet

peaks at  $\delta$  = 5.36, 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to **L8** and trans to **L7** respectively [394].



Figure 3.46: <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)(L8)](PF<sub>6</sub>)<sub>2</sub>-Dye 23

<sup>13</sup>C NMR spectrum of  $[Ru(H_2dcbpy)_2(L7)(L8)](PF_6)_2$ -(Dye 23) shows 32 resonance peaks in the aromatic region  $\delta$  120-170 ppm. Since the presence of the two 4,4'-Dicarboxy-2,2'-bipyridine are *trans* to each other and *trans* to one **L8** and trans to one **L7**; the electron density of the all the pyridyl rings of two,4-dicarboxy-2,2'-bipyridine all well as the respective **L8** and **L7** ligands are non-equivalent. The peak at downfield of 150.51 ppm is assigned to the chemically equivalent carbons (C-2 and C-2') close to the electron withdrawing central nitrogen coordinated to monodentate ligand **L7**. The peaks at downfield of 144.03 ppm are assigned to the chemically equivalent carbons (C-2/C-6) in proximity to the electron withdrawing central nitrogen coordinated to the monodentate ligand L8. The peaks at  $\delta = 135.56, 133.05, 132.44,$ and 131.99 ppm are assigned to diindeno (C-3i), (C-4i), (C-5i/C-7i) and (C-6i) carbons atoms of one L7 and *trans* pyridyl ring of 4,4-Dicarboxy-2,2'-bipyridine. The peaks at  $\delta = 133.75, 134.57, 137.53, 138.87$  and 139.10 ppm are assigned to to pyridyl (C-3'), (C-2'), (C-4'), (C-6') and (C-5') carbons atoms of **L8** ligand and *trans* to pyridyl ring of 4,4-Dicarboxy-2,2'-bipyridine. The peaks at  $\delta = 128.97$ , 129.75, 132.36 and 135.44 ppm are assigned to pyridyl (C3''/ C-5''), (C-2''/ C-6''), (C-4''), and (C-1'') carbons atoms of L8 ring and *trans* to aromatic ring of monodentate ligand L7. The peaks at 128.25 (C-5b'), 127.11 (C-5b), 124.47 (C-3a), 123.30 (C-3b') and 128.97 (C-5b'), 127.18 (C-5b), 124.15 (C-3b), 123.79 (C-3b') respectively, are assigned to pyridyl carbons close to electron withdrawing nitrogen as well as carboxylic unit coordinated to the two 4,4-Dicarboxy-2,2'-bipyridine ligands. The peaks at 136.37 and 116.54 ppm are assigned to C-7" and C-8" vinyl carbon atoms coordinated to the monodentate ligand L7 [394].



**Figure 3.47:** <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)(L8)](PF<sub>6</sub>)<sub>2</sub>- (Dye 23)

## 3.2.4.6 1H and <sup>13</sup>C NMR of Series VI

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all Series VI ruthenium(II) complexes with general molecular formula of  $[Ru(H_2dcbpy)(N^{2}(NCS)_{2}]$  were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $[Ru(H_2dcbpy)(L7)_{2}(NCS)_{2}]$ -(Dye 24), and  $[Ru(H_2dcbpy)(L8)_{2}(NCS)_{2}]$ -(Dye 25) are presented in Figures 3.48, 3.49, and 3.50, 3.51 respectively.

# 3.2.4.6.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H<sub>2</sub>dcbpy)(L7)<sub>2</sub>(NCS)<sub>2</sub>]-(Dye 24)

The <sup>1</sup>H NMR spectrum of  $[Ru(H_2dcbpy)(L7)_2(NCS)_2]$ -(dye 24) shows multiplet peaks at 7.60-7.76 and 6.75-6.89 ppm were observed in the aromatic region for (H-4, H-5, H-6, H-7 and H-4', H-5', H-6', H-7') and (H-2'', H-3'', H-4'', H-5'', H-6'') hydrogens atoms of vinyl monodentate ligands. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to monodentate ligand [394].



Figure 3.48: <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)<sub>2</sub>(NCS)<sub>2</sub>]-Dye 24

<sup>13</sup>C NMR spectrum of  $[Ru(H_2dcbpy)(L7)_2(NCS)_2]$ -(Dye 24) shows 17 resonance signals in the aromatic region  $\delta$  120-170 ppm which are complicated due to the presence of two **L7** and two 4,4-Dicarboxy-2,2'-bipyridine ligands in which all the diindeno and pyridyl rings of **L8** as well as all pyridyl rings of 4,4-Dicarboxy-2,2'bipyridine ligands are electronically in different environment. The peak at downfield of 150.50 ppm is assigned to the chemically equivalent carbons (C-2 and C-2') in proximity to the electron withdrawing central nitrogen coordinated to the monodentate ligand L7. The peaks at 136.47, 135.57, 135.40, 134.89, 132, 44, 131.99 and 131.62 are assigned to the diindeno and phenyl carbons of monodentate ligand L7. The peaks at 128.26 (C-5a'), 127.18 (C-5a) and 124.15 (C-3a) are assigned to pyridyl carbons in proximity to electron withdrawing nitrogen coordinated to 4,4-dicarboxy-2,2'-bipyridine. The peaks at 136.37 and 116.54 ppm are assigned to C-7'' and C-8'' vinyl carbon atoms coordinated to L7 monodentate ligand [394]. The resonance peaks at 133.06 ppm and 134.58 ppm respectively. Carbon-13 NMR spectra has become a useful tool for identifying NCS group mode of coordination located in complexes. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals in [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)(NCS)](PF<sub>6</sub>)<sub>2</sub>,-(dye 19) in 130-135 ppm shows that NCS ligands are coordinated through the nitrogen atom.



Figure 3.49: <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)<sub>2</sub>(NCS)<sub>2</sub>]-Dye 24
## 3.2.4.6.2 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H2dcbpy)(L8)2(NCS)2]-(Dye 25)

The <sup>1</sup>H NMR spectrum of  $[Ru(H_2dcbpy)(L8)_2(NCS)_2]$ -(Dye 25) shows two set of multiplet peaks at 7.96-8.15 7.60-7.70 ppm at the aromatic region. The resonances were assigned to (H-2''', H-3'''. H-5''', H-6''') ppm and (H-2', H-3', H-4', H-5', H-6'/H-2'', H-3'', H-4'', H-5'', H-6'') ppm aromatic hydrogen of **L8** monodentate. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to **L8** monodentate ligand [394]. Two sets of singlet peaks at 8.74 and 8.58 ppm are assigned to (H-3a' and H-3a) pyridyl ring hydrogen atoms coordinated to 4,4-Dicarboxy-2,2'-bipyridine ligand.



Figure 3.50: <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L8)<sub>2</sub>(NCS)<sub>2</sub>]–(Dye 25)

The <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L8)<sub>2</sub>(NCS)<sub>2</sub>]-(Dye 25) shows 19 resonance signals in the aromatic region  $\delta$ = 120-170 ppm. The downfield signal at 189. 00 ppm is assigned to the carbon atom of the carboxylate unit coordinated to 4.4-Dicarboxy-2,2'-bipyridine ligand. The peaks at downfield of 144.03 and 143.10 ppm are assigned to the chemically equivalent carbons (C-2/C-6) and quaternary C-4 respectively, in proximity to the electron withdrawing central nitrogen coordinated to monodentate ligand **L8**. The peaks at  $\delta = 122,29, 129.02, 129.22, 131.27, 132,36$  and 137.87 ppm were assigned to pyridyl carbons atoms of monodentate ligand L8. The peaks at 128.97, 127.12, 123.31 and 124.46 ppm were assigned to (C-5a'), (C-5a), (C-3a') and (C-3a) pyridyl carbons of 4,4-Dicarboxy-2,2'-bipyridine ligands. The peaks at 136.37 and 116.54 ppm are assigned to C-7" and C-8" vinyl carbon atoms coordinated to monodentate ligand L8 [394]. The resonance peaks at 133.62 ppm and 134.42 ppm respectively, are due to the presence of two NCS ligands. Carbon-13 NMR spectra has become a useful tool for identifying NCS group mode of coordination located in complexes. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals in [Ru(H<sub>2</sub>dcbpy)(L8)<sub>2</sub>(NCS)<sub>2</sub>]-(Dye 25) in 130-135 ppm shows that NCS ligands are coordinated through the nitrogen atom.



Figure 3.51: <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(vpbpp)<sub>2</sub>(NCS)<sub>2</sub>]-(Dye 25)

## 3.2.4.7 <sup>1</sup>H and <sup>13</sup>C NMR of Series VII dyes-[Ru(H<sub>2</sub>dcbpy)(N<sup>^</sup>)(NCS)<sub>3</sub>]<sup>-1</sup>

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all Series VII dye sensitizers with general molecular formula of  $[Ru(H_2dcbpy)(N^{)}(NCS)_3]^{-}$  were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $[Ru(H_2dcbpy)(L7)(NCS)_3](NH_4)$ -dye 26 and  $[Ru(H_2dcbpy)(L8)(NCS)_3](NH_4)$ -dye (27) are presented in Figures 3.52, 3.53, and 3.54, 3.55 respectively<sup>.</sup>

### 3.2.4.7.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H<sub>2</sub>dcbpy)(L8)(NCS)<sub>3</sub>](NH<sub>4</sub>)-Dye 26

The <sup>1</sup>H NMR spectrum of anionic ruthenium(II) complex as regards  $[Ru(H_2dcbpy)(L7)(NCS)_3](NH_4)$ .Dye 26 shows two multiplets at aromatic region at 7.75-7.76 and 7.71-7.74 ppm. The assignment of these peaks were due to (H-4, H-5, H-6, H-7 / H-4', H-5', H-6', H-7') and (H-2'', H-3'', H-4'', H-5'', H-6'') pyridyl hydrogen rings atoms coordinated to monodentate ligand **L7**. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to monodentate ligand **L7** [375]. Two sets of doublet peaks at 8.23 and 8.08 ppm were assigned to (H-5a' and H-6a') pyridyl ring hydrogen atoms of 4,4-Dicarboxy-2,2'-bipyridine ligand.



Figure 3.52: <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)(NCS)<sub>3</sub>](NH<sub>4</sub>)-(Dye 26)

<sup>13</sup>Carbon NMR spectra data of [Ru(H<sub>2</sub>dcbpy)(L7)(NCS)<sub>3</sub>](NH<sub>4</sub>)-Dye 26 show 23 resonance signals in the aromatic region between ( $\delta$ = 116.54-193.78 ppm) corresponding to three NCS groups and *trans* to monodentate ligand L7 and *trans* to 4,4-Dicarboxy-2,2'-bipyridine ligand, therefore, the electron density of the three NCS groups is non equivalent and different resonance peaks are observed. The downfield signal at 193.7 ppm is assigned to the carbon atom of the carboxylate coordinated 4,4-Dicarboxy-2,2'-bipyridine ligand. The peak at downfield of 150.04 ppm is assigned to the central carbons (C-2 and C-2') close to the electron withdrawing central nitrogen coordinated to the monodentate ligand L7. The two end pyridyl rings of the *vpdiinp* ligand are in different magnetic environment, in which one is *trans* to 4,4-Dicarboxy-2,2'-bipyridine ring and the other is *trans* to NCS ligand resulting to different resonance peaks. Therefore, the peaks at  $\delta = 134.69, 135.45, 136.47, 137.69$  and 138.93 ppm were assigned to pyridyl (C-3', C-2', C-4', C-6' and C-5') carbons atoms, while the peaks at  $\delta = 131.62, 131.99, 132.44, 132.90$  and 135.40 ppm are assigned to the other pyridyl (C-3"/C-5", C-2"/C-6", C-4", and C-1") carbons atoms. The peaks at 128.20, 127.18, 124.16 and 123.79 ppm were assigned to (C-5a'), (C-5a), (C-3a) and (C-3a') pyridyl carbons of 4,4-Dicarboxy-2,2'-bipyridine. The resonance peaks at 133.06, 134.58 and 134.89 ppm are attributable to three NCS ligands. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals due to [Ru(H<sub>2</sub>dcbpy)(L7)(NCS)<sub>3</sub>](NH<sub>4</sub>)-Dye 26 within the region 130-135 ppm shows that NCS ligands are coordinated through the nitrogen atom.



Figure 3.53: <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)(NCS)<sub>3</sub>](NH<sub>4</sub>)-(dye 26)

# 3.2.4.7.2 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(H<sub>2</sub>dcbpy)(L8)(NCS)<sub>3</sub>](NH<sub>4</sub>)]-Dye 27

The <sup>1</sup>H NMR spectrum of anionic anionic ruthenium(II) complex as regards  $[Ru(H_2dcbpy)(L8)(NCS)_3](NH_4)$ -Dye 27 shows coupling hydrogen above 6 ppm in the aromatic region. A triplet peak at  $\delta = 7.55$ -7.760 ppm was assigned to (H-2", H-

3''', H-5'''and H-6''') four phenyl hydrogen atoms of **L8** monodentate ligand. Two multiplet peaks at  $\delta$  = 7.65-7.75 and 7.05-8.05 ppm were assigned to the presence of five pyridinyl hydrogen atoms (C<sub>6</sub>H<sub>5</sub> moiety H-2', H-3', H-4', H-5' and H-6') and five phenyl hydrogen atoms (C<sub>6</sub>H<sub>4</sub> moiety H-2'', H-3'', H-4'' H-5'' and H-6'') coordinated to monodentate ligand **L8**. The peaks at  $\delta$  = 5.36, 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to monodentate ligand **L8** [394]. A doublet peak is observed at  $\delta$  = 8.75 ppm due to the presence of hydrogen atom of 4,4-Dicarboxy-2,2'-bipyridine.



Figure 3.54: <sup>1</sup>H NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L8)(NCS)<sub>3</sub>](NH<sub>4</sub>)-(dye 27)

Carbon-13 NMR spectra data of [Ru(H<sub>2</sub>dcbpy)(L8)(NCS)<sub>3</sub>](NH<sub>4</sub>)-dye 27 show 22 resonance signals in the aromatic region ( $\delta$ =116.54-193.78 ppm) corresponding to three NCS groups and *trans* to monodentate ligand L8 and *trans* to 2,2-bipyridine-4,4-Dicarboxylic acid, therefore, the electron density of the three NCS groups is non equivalent and different resonance peaks are observed. The downfield signal at 189.61 ppm is assigned to the carbon atom of the carboxylate coordinated 4,4-Dicarboxy-2,2'bipyridine ligand. The peak at downfield of 144.04 ppm is assigned to the central carbons (C-2 and C-6) close to the electron withdrawing central nitrogen coordinated to the monodentate ligand L8. The peaks at 143.50, 139.87. 137.77, 134.66, 132.29, 131.27, 129.76, 129.30, 129.27 and 129.00 ppm are assigned to the triarylpyridine and phenyl carbons of monodentate ligand L8. The pearks at 128.97 (C-5a'), 127.12 (C-5a), 124.47 (C-3a) and 124.47 (C-3a') ppm are assigned to pyridyl carbons 4,4-Dicarboxy-2,2'-bipyridine ligand. The resonace peaks at 132.26, 133.61 and 134.22 ppm are attributable to three NCS ligands. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. of The presence signals due to [Ru(H<sub>2</sub>dcbpy)(vpbpp)(NCS)<sub>3</sub>](NH<sub>4</sub>) dye (27) within the region 130-135 ppm shows that NCS ligands are coordinated through the nitrogen atom.



Figure 3.55: <sup>13</sup>C NMR spectrum of [Ru(H<sub>2</sub>dcbpy)(L8)(NCS)<sub>3</sub>](NH<sub>4</sub> (Dye 27)

## 3.2.4.8. <sup>1</sup>H and <sup>13</sup>C NMR of Series VIII

The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of all Series VIII ruthenium(II) complexes with general molecular formula of  $[Ru(H_2dcbpy)(N^{A})(NCS)_3]^{2+}$  were recorded in deuterated DMSO at ambient temperature and the sensitizers support their formulation and geometry. <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $[Ru(L9)(H_2dcbpy)(L7)](PF_6)_2$ -(Dye 28),  $[Ru(L9)(H_2dcbpy)(L8)](PF_6)_2$ -(Dye29) and  $[Ru(L9)(H_2dcbpy)(NCS)](PF_6)$ -(Dye 30) are presented in Figures 3.56, 3.57, 3.58, 3.59 and 3.60, 3.61 respectively

### 3.2.4.8.1 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L9)(H<sub>2</sub>dcbpy)(L7)](PF<sub>6</sub>)<sub>2</sub>-(dye 28)

The <sup>1</sup>HNMR spectra of  $[Ru(L9)(H_2dcbpy)(L7)](PF_6)_2$ -(dye 28) show corresponding resonance peaks in the aromatic region whereby pyridyl as well as phenyl hydrogen atoms of **L9** ligand is *trans* to pyridyl ring hydrogen atoms of the 4,4-Dicarboxy-2,2'bipyridine and trans pyridyl ring hydrogen atoms of monodentate ligand L7 respectively, therefore, all pyridyl ring of hydrogen atoms L9 ligand, pyridyl ring protons of 4,4-Dicarboxy-2,2'-bipyridine and pyridyl ring protons of monodentate ligand L7 are electronically in different environment. The spectrum shows a singlet signals at  $\delta = 9.48$  (H-3B/ H-5B) ppm assigned due the chemically equivalent pyridyl hydrogen atoms in proximity to the central nitrogen electron withdrawing atom coordinated to the L9 ligand. Four doublet resonance peaks at  $\delta = 9.10, 8.42, 7.98$  and 7.81 ppm were assigned to (H-2A), (H-2C/H-6C) (H-5A) and (H-3C/H-5C) pyridyl hydrogen atoms of L9 ligand. Two triplet resonance peaks are observed at  $\delta =$ 8.07 (H-4A) ppm and 7.07 (H-3A) ppm respectively due to pyridyl hydrogen atoms coordinated to L9 ligand and *trans* to 4,4-Dicarboxy-2,2'-bipyridine [397]. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to both L7 and L9 ligand respectively [394]. The aromatic region of spectrum also shows two doublets at  $\delta = 8.83$  and 8.72 ppm are assigned to (H6a and H6a') and (H5a and H5a') chemically equivalent pyridyl hydrogen atoms in proximity to the central nitrogen electron withdrawing atom coordinated to the 4,4-Dicarboxy-2,2'-bipyridine. The multiplet peak at 7.60-7.76 ppm (H-4, H-5, H-6, H-7 and H-4', H-5', H-6', H-7') are due to the two of the eight aromatic hydrogen atoms of L7 monodentate ligand. Also, multiplet resonance peaks are observed at 6.75-7.00 ppm

(H-2<sup>\*\*</sup>, H-3<sup>\*\*</sup>, H-4<sup>\*\*</sup>, H-5<sup>\*\*</sup> and H-6<sup>\*\*\*</sup>) due pyridyl hydrogen atoms of **L7** monodentate ligand. The peaks at 136.37 and 116.54 ppm are assigned to C-7<sup>\*\*</sup> and C-8<sup>\*\*</sup> vinyl carbon atoms coordinated to both **L7** and **L9** ligand [394].



**Figure 3.56:** <sup>1</sup>H NMR spectrum of [Ru(L9)(H<sub>2</sub>dcbpy)(L7)](PF<sub>6</sub>)<sub>2</sub>-(Dye 28)

Carbon-13 NMR spectra data of  $[Ru(L9)(H_2dcbpy)(L7)](PF_6)_2$ -(Dye 28) show 29 resonance signals in the aromatic region ( $\delta$ = 116.54-193.78 ppm) corresponding to 4,4-Dicarboxy-2,2'-bipyridine, **L9** and **L7** ligands. The downfield signal at 193, 78

ppm is assigned to the carbon atom of the carboxylate coordinated to 4,4-Dicarboxy-2,2'-bipyridine ligand. Two peaks at 156.37 and 155, 59 ppm are assigned to two chemically equivalent central carbons (C-2B/C-6B) and quaternary carbon of (C-6A) respectively, all in proximity to two electron withdrawing nitrogen coordinated to the **L9** ligand [397]. The peaks at 138.93, 133.05, 133.04, 130.15 and 128.28 ppm are assigned to the pyridyl ring carbons atoms of **L9** ligand. The peak at downfield of 150.51 ppm is assigned to the chemically equivalent carbons (C-2/C-2') close to the electron withdrawing central nitrogen coordinated to the monodentate **L7**. The peaks at 137.69, 137.53, 136.46, 136.36, 135, 44, 135.40, 134.88, 134.54, 132.89, 132.82, 132, 44, 131.99 and 131.61 ppm are assigned to pyridyl carbon atoms of **L7** ligand. The signals at 128.16, 127.18, 124.47 and 124.47 ppm are assigned to (C-5a'), (C-5a), (C-3a) and (C-3a') pyridyl carbons of 4,4-Dicarboxy-2,2'-bipyridine ligand [377].



Figure 3.57: <sup>13</sup>C NMR spectrum of [Ru(L9)(H<sub>2</sub>dcbpy)(L7)](PF<sub>6</sub>)<sub>2</sub>-(Dye 28)

## 3.2.4.8.2 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L9)(H<sub>2</sub>dcbpy)(L7)](PF<sub>6</sub>)<sub>2</sub>-(Dye 29)

The <sup>1</sup>H NMR spectra of  $[Ru(L9)(H_2dcbpy)(L7)](PF_6)_2$ -(Dye 29) show corresponding resonance peaks in the aromatic region whereby pyridyl as well as phenyl hydrogen atoms of **L9** ligand is *trans* to pyridyl ring hydrogen atoms of the 4,4-Dicarboxy-2,2'bipyridine and *trans* to pyridyl as well as phenyl ring hydrogen atoms of **L8** ligand respectively, therefore, all pyridyl ring of hydrogen atoms L9, pyridyl ring protons of 4,4-Dicarboxy-2,2'-bipyridine and pyridyl as well as phenyl ring hydrogen atoms of monodentate ligand L8 are electronically in different environment. The spectrum shows a singlet signals at  $\delta = 9.42$  ppm is assigned to (H-3B/H-5B) chemically equivalent pyridyl hydrogen atoms of L9 ligand. Three doublet resonance peaks at  $\delta$ = 9.04, 8.42 and 7.93 ppm respectively were assigned to (H-5A), (H-2C/H-6C) and (H-2A) pyridyl hydrogen atoms of L9 ligand [397]. Two triplet resonance peaks at  $\delta$ = 8.08 and 7.48 ppm were assigned (H-4A) and (H-3A) pyridyl hydrogen atoms coordinated to **L9** ligand. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to both L8 and L9 ligand respectively [394]. The aromatic region of spectrum also shows two doublets at  $\delta =$ 8.83 (H-6a and H-6a') ppm and 8.72 (H-5a and H-5a') due to chemically equivalent pyridyl hydrogen atoms of 4,4-Dicarboxy-2,2'-bipyridine. The multiplet peak at 7.99-8.10 ppm are assigned to (H-2"'H-3"' H-5"' and H-6"') four phenyl hydrogen atoms of L8 ligand, Another two sets of multiplet resonance peaks are observed at 7.61-7.78 and 7.49-7.60 ppm are assigned to (H-2', H-3', H-4', H-5' and H-6') and (H-2", H-3", H-4", H-5", H-6") due to inequality in the electron density on the two of five pyridyl hydrogen atoms of L8 ligand, in which one is in proximity to 4,4-Dicarboxy-2,2'-bipyridine ring and the other in proximity to the L9 ligand.



Figure 3.58: <sup>1</sup>H NMR spectrum of [Ru(L9)(H<sub>2</sub>dcbpy)(L8)](PF<sub>6</sub>)<sub>2</sub>-(Dye 29)

Carbon-13 NMR spectra data of  $[Ru(L9)(H_2dcbpy)(L8)](PF_6)_2$ -(Dye 29) show 22 resonance signals in the aromatic region ( $\delta$  116.54-193.78 ppm) corresponding to, 4,4-Dicarboxy-2,2'-bipyridine, **L7** and **L9** ligands. The downfield signal at 193. 78 ppm is assigned to the carbon atom of the carboxylate coordinated 4,4-Dicarboxy-2,2'-bipyridine ligand. Two peaks at 156.37 and 155.59 ppm are assigned to two chemically equivalent central carbons (C-2B /C-6B) and quaternary carbon of A6, all in proximity to two electron withdrawing nitrogen coordinated to the **L9** ligand [397]. The peaks at 138.93, 133.05, 133.04, 130.15 and 128.28 are assigned to the pyridyl ring carbons atoms of **L9** ligand and *trans* to 2,2-bipyridine-4,4-dicarboxylic acid. The

peak at downfield of 144.04 ppm is assigned to the chemically equivalent carbons (C-2/C-6) close to the electron withdrawing central nitrogen coordinated to the **L9** ligand. The peaks at 137.87, 137.74, 133.74, 133.61, 132.26, 131.26, 130.15, 129.75, 129.29 and 129.92 are assigned to both pyridyl and phenyl carbon atoms of monodentate ligand **L8**. The signals at 128.97, 127.18, 124.47 and 123.31 ppm are assigned to (C-5a'), (C-5a), (C3a) and (C3a') pyridyl carbons in proximity to electron withdrawing nitrogen coordinated to 4,4-Dicarboxy-2,2'-bipyridine ligand [377].



**Figure 3.59:** <sup>13</sup>C NMR spectrum of [Ru(L9)(H<sub>2</sub>dcbpy)(L7)]-(Dye 29)

### 3.2.4.8.3 <sup>1</sup>H and <sup>13</sup>C NMR of [Ru(L9)(H<sub>2</sub>dcbpy)(NCS)]-(Dye 30)

The <sup>1</sup>H NMR spectra of  $[Ru(L9)(H_2dcbpy)(NCS)](PF_6)$ -(Dye 30) show corresponding resonance peaks in the aromatic region whereby pyridyl as well as phenyl hydrogen atoms of L9 ligand is *trans* to pyridyl ring hydrogen atoms of the 4,4-Dicarboxy-2,2'bipyridine and *trans* to NCS ligand respectively, therefore, all pyridyl ring of hydrogen atoms of L9 and pyridyl ring protons of 4,4-Dicarboxy-2,2'-bipyridine ligands are electronically in different environment. Five doublet resonance peaks of which the first two sets are observed at  $\delta = 9.07$  and 7.93 ppm are assigned to (H-A5) and (H-2A) pyridyl hydrogen atoms of L9 ligand in proximity with its nitrogen electron withdrawing atom and *trans* to 4,4-Dicarboxy-2,2'-bipyridine acid, while the second set observed at 8.42 ppm is assigned to (H-2D) pyridyl hydrogen atoms of L9 tridentate ligand in proximity electron withdrawing oxygen the carboxylic as well as with its nitrogen electron withdrawing atom and *trans* to NCS unit, whereas, the third set observed at  $\delta = 8.41$  and 7.89 ppm are assigned to (H-2C/H-6C) and 7.89 (H-3C /H-5C) chemically equivalent phenyl hydrogen atoms of L9 ligand [397]. Two triplet resonance peaks are observed at  $\delta = 8.06$  and 7.28 ppm are ascribed to (H-4A) and (H-3A) pyridyl hydrogen atoms in L9 ligand. The peaks at  $\delta = 5.36$ , 5.94 and 6.77 ppm are assigned to vinyl hydrogen atoms of the styryl group coordinated to L9 ligand [394]



Figure 3.60: <sup>1</sup>H NMR spectrum of [Ru(L9)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-(dye 30)

Carbon-13 NMR spectra data of  $[Ru(L9)(H_2dcbpy)(NCS)](PF_6)$ -(dye 30) show 14 resonance signals in the aromatic region ( $\delta$ = 120.08-160.00ppm) corresponding to **L9** ligand, 4,4-Dicarboxy-2,2'-bipyridine and NCS ligands. Two peaks at 158.36 and 156.01 ppm are assigned carbon atom of (C-2A) in proximity to electron withdrawing nitrogen and two chemically equivalent central carbons of (C-2B/C-6B) repectively, all coordinated to the **L9** ligand and trans to NCS unit and trans to 4,4-Dicarboxy-2,2'- bipyridine ligand [397]. The signals at 128.20 and 123.97 ppm are assigned to (C-5a') and (C-3a') pyridyl carbons in proximity to electron withdrawing nitrogen coordinated to 4,4-Dicarboxy-2,2'-bipyridine [377]. The resonance peaks at 132.81 ppm are attributable to NCS ligand. It is well known that N-coordinated thiocyanate carbon resonance signals are observed at 130-135 ppm as reported in literature [391, 392]. The presence of signals due to [Ru(L9)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)<sub>2</sub>-(dye 30) within the region 130-135 ppm shows that NCS ligand is coordinated through the nitrogen atom.



Figure 3.61: <sup>13</sup>C NMR spectrum of [Ru(L9)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-(Dye 30)

### **CHAPTER FOUR**

### 4.0. RESULTS AND DISCUSSION

### 4.1. Conductivity measurement and Electrochemistry

This chapter contains the results and discussion of conductivity measurement and electrochemistry with respect to eight series of thirty (30) novel heteroleptic ruthenium(II) complexes with the general molecular structure  $[Ru(bdmpmar)(H_2dcbpy)(NCS)]^+$ ,  $[Ru(bdmpmar)(vpdiinp)(H_2dcbpy)]^{2,+}$ ,  $[Ru(bdmpmar)(vpbpp)(H_2dcbpy)]^{2,+}$ ,  $[Ru(H_2dcbpy)_2(N^{\Lambda})(NCS)]^+$ ,  $[Ru(H_2dcbpy)_2(N^{\Lambda})_2]^{2,+}$ ,  $[Ru(H_2dcbpy)_2(N^{\Lambda})(NCS)]^+$ , and  $[Ru(vptpy)(H_2dcbpy)(N^{\Lambda \Lambda})]^{2,+}$  respectively.

### **4.1.1 Conductivity Measurement**

The molar conductivity values for ligands and complexes in DMSO solvent were in the range of 0.12-0.70  $\mu$ Scm<sup>2</sup>/mol (see supplementary information in Table 4.1). This suggests that they are non-electrolytes in solution, and hence support the formulation of the complexes.

**Table 4.1**. Molar conductance of ligands and complexes

Compound	Conductivity (µScm <sup>2</sup> /mol)
L1	0.28
L2	0.14
L3	0.12

L4	0.21
L5	0.39
L6	0.24
L7	0.70
L8	0.38
L9	0.22
Dye 1	0.35
Dye 2	0.29
Dye 3	0.31
Dye 4	0.54
Dye 5	0.43
Dye 6	0.30
Dye 7	0.28
Dye 8	0.23
Dye 9	0.21
Dye 10	0.34
Dye 11	0.34
Dye 12	0.49
Dye 13	0.30
Dye 14	0.43
Dye 15	0.32
Dye 16	0.31
Dye 17	0.42
Dye 18	0.42

Dye 19	0.45
Dye 20	0.56
Dye 21	0.42
Dye 22	0.32
Dye 23	0.30
Dye 24	0.35
Dye 25	0.29
Dye 26	0.30
Dye 27	0.40
Dye 28	0.18
Dye 29	0.27
Dye 30	0.37

#### **4.1.2 Electrochemical Study**

#### **4.1.2.1** Electrochemistry of series I complexes (4, 5 and 6)

The electron transfers properties of series I complexes have been studied by cyclic and square voltammetry in DMSO containing tetrabutylammonium hexafluorophosphate as supporting electrolyte with a glassy carbon working electrode. All the potential is referenced to the Ag/AgCl electrodes. The cyclic and square Voltammograms are displayed in Figure 4.1-4.3. The relevant electrochemical data are summarised in Table 4.2. Due to the poor solubility of complex 1-3, it has not been possible to study their electrochemical behaviour. The complex 4-6 are electro active with respect to metal and ligand centre. It is well established that redox processes in ruthenium(II) polypyridine complexes are basically localized either or on the metal centre, (oxidation) or on the ligands centred (reduction) [398]. At positive potential of 0.53 V, Cyclic voltammogram of dye 4 display electrochemically reversible metal based Ru(II)/Ru(III) oxidations. While the oxidation potentials of dye 5 and 6 display quasireversible behaviour at 0.79 V and 0.53 V respectively. The ligand centred oxidation potential for dye 4-6 display at 0.10, 0.50 and 0.10 V respectively. This is ascribed to the ring oxidation of  $H_2$ dcbpy and the carboxylate ions present in the complexes [399]. For the negative potential, the complexes show reduction potentials at -0.76 V for dye 4, -0.97 V for dye 5 and -1.10 and -0.75 V for dye 6. These reduction potential shows the electron donating ability of the tripod pyrazolic ligand in the complexes.



**Figure 4.1:** Cyclic voltammetry and square wave voltammetry of Dye 4 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.2: Cyclic voltammetry and square wave voltammetry of Dye 5 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.3: Cyclic voltammetry and square wave voltammetry of Dye 6 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.

#### **4.1.2.2** Electrochemistry of series II complexes (7, 8, 10, 11 and 12)

The redox behaviour of series II complexes 7-12 were investigated in DMSO containing tetrabutylammonium hexafluorophosphate as supporting electrolyte by cyclic and square voltammetry at room temperature using glassy carbon as working electrode. The cyclic and square voltammograms are displayed in Figure 4.4-4.8. The relevant electrochemical data are summarised in Table 4.2. The oxidation potential of dye 7 displayed irreversible behaviour at 1.02 V, while a quasi-reversible peak was found for dye 8, 10 and 12 at 0.92, 0.83 and 1.10 V and reversible peaks at 0.85 for dye 11. These potentials were assigned to Ru(II/III) couple [400]. The ligand oxidation peak process for dyes 10, 11 and 12 show at 0.64, 0.61, and 0.51 mV respectively, which were ascribed to the bipyridine, and/or 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'elpyridine and, as well as the carboxylate ions present in the complex [399]. For the cathodic process, the complexes show reduction potential at -0.16 V for dye 7, -0.25, -1.29 V for dye 8, 0.24 V for dye 10 and -0.23 V for dye 11. No reduction potential was recorded for dye 12. The reduction potential in dye 8 is more negative, thereby indicating the increased electron drift from the electron donating of methoxy group to electron with drawing of nitro group through  $\pi$ -bond aromatic ring in the structure of the complex and giving rise to an increase in its electron donating ability.



Figure 4.4: Cyclic voltammetry and square wave voltammetry of Dye 7 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.5: Cyclic voltammetry and square wave voltammetry of Dye 8 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.6: Cyclic voltammetry and square wave voltammetry of Dye 10 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.7: Cyclic voltammetry and square wave voltammetry of Dye 11 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl



**Figure 4.8:** Cyclic voltammetry and square wave voltammetry of Dye **12** in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.

#### **4.1.2.3 Electrochemistry of series III complexes (14, 15 and 18)**

Cyclic and square wave voltammograms of series II complexes 14, 15 and 18 are displayed in (Figure 4.9-4.11) with relevant electrochemical data summarised in Table 4.2. Irreversible oxidation peaks were observed at 0.92 and 1.14 V for dye 14; 0.82 V for dye 15; and 0.46 and 0.80 V for dye 18. The oxidation potential of 1.14, 0.82 and 0.80 V vs Ag/AgCl for dye 14, 15 and 18 respectively, were derived from oxidation of Ru(II) to Ru(III) [399, 400]. While the ligand centred oxidation peaks at 0.92 V for dye 14 and 0.46 V for dye 18, were ascribed to the bipyridine, and/or 4-(4vinylphenyl)-2,6-bis(phenyl)pyridine ligand and, as well as the carboxylate ions present in the complex [399]. No oxidation peak for ligand centred was found in dye 15. The reduction peaks were observed at -1.25 and -1.43 V for dye 14, -0.20 and -1.41 V for dye 15 and -0.22 and -1.45 V for dye 18. Comparison of the reduction potential shows that dye 14 is more negative, thereby indicating the increased electron drift from the electron donating of methoxy group to electron with drawing of nitro group through  $\pi$ -bond aromatic ring in the structure of the complex and giving rise to an increase in its electron donating ability.



Figure 4.9: Cyclic voltammetry and square wave voltammetry of Dye 14 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.10: Cyclic voltammetry and square wave voltammetry of Dye 15 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.11: Cyclic voltammetry and square wave voltammetry of Dye 18 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.
# 4.1.2.4 Electrochemistry of series IV and VI-VIII complexes (19, 20, 25, 26 and 30)

The electrochemical investigation of series IV, VI, VII and VIII ruthenium(II) complexes as observed for **19**, **20**, **25**, **26** and **30** were studied. Cyclic and square voltammograms are displayed in (Figure 4.12-4.15) with relevant electrochemical data summarised in Table 4.2. The voltammograms of dye **19** display quasi-reversible peak at 1.09 V, while irreversible peaks were found for dye **20**, **25**, **26** and **30** at 1.17, 0.73, 0.74 and 1.18 V vs Ag/AgCl. These potentials were assigned to Ru(II/III) couple [400]. For dye **19**, **20**, **26** and **30**, irreversible oxidation peaks at 0.14, 0.74 V; 0.50, 0.89 V; 0.31 V and 0.48, 0.98 V respectively, were assigned to ring oxidation of H<sub>2</sub>dcby, pyridines and/or terpyridine ligands as well as the carboxylate ions present in the complex [399, 401]. The reduction peaks were observed at -0.25 and -1.33 V for dye **19**, -1.21 and -1.43 V for dye **20**, -1.42 V for dye **26** and -1.20 V for dye **30**.



Figure 4.12: Cyclic voltammetry and square wave voltammetry of Dye 19 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.13: Cyclic voltammetry and square wave voltammetry of Dye 20 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



**Figure 4.14:** Cyclic voltammetry and square wave voltammetry of Dye **26** in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.



Figure 4.15: Cyclic voltammetry and square wave voltammetry of Dye 30 in DMSO using glassy carbon working electrode, 0.1 M TBAPF<sub>6</sub> supporting electrolyte. Set potential = 5 mV, amplitude = 20 mV vs. Ag/AgCl, frequency = 25 Hz, scan rate 25 mVs<sup>-1</sup> vs. Ag/AgCl.

Compound	Ru(II/III)	Eanodic/V	E <sub>cathodic</sub> /V	$E_{1/2}/V$
Dye 4	0.53	0.10	-0.76	-
Dye 5	0.75	0.50	-0.97	0.13
Dye 6	0.53	0.10	-1.10	-0.75
Dye 7	1.02	0.83	-	-0.16
Dye 8	0.92	-	-1.29	-0.25
Dye 10	0.83	0.64	-	-0.24
Dye 11	0.85	0.61	-	-0.23
Dye 12	1.10	0.51	-	-
Dye 13	ND	-	-	ND
Dye 14	1.14	0.92	-1.42	-1.25
Dye 15	0.82	-	-1.41	-0.20
Dye 16	-0.85	0;63	-1.43	-0.23
Dye 17	ND	-	-	ND
Dye 18	0.80	0.46	-1.45	-0.22
Dye 19	1.09	-	-0.25, -1.33	0.14, 0.77
Dye 20	1.17	-	-1.21, -1.43	0.58, 0.89
Dye 21	ND	-	-	ND
Dye 22	ND	-	-	ND
Dye 23	ND	-	-	ND
Dye 24	0.74	-	-1.41	-
Dye 25	0.73	-	-1.41	-0.18

**Table 4.2**: Cyclic voltammetric data of series I-VIII complexes

Dye 26	0.74	-	-1.42	-0.31
Dye 27	ND	-	-	ND
Dye 28	ND	-	-	ND
Dye 29	ND	-	-	ND
Dye 30	1.18	0.83	-1.20	0.48, 0.90

Key: ND = Not well-Defined

#### **CHAPTER FIVE**

# 5.0. SUMMARY AND CONCLUSIONS

## **5.1 Summary of Results**

The essential ingredient or component of the dye sensitized solar cell is the sensitizer or dye. This research, therefore, deals with the synthesis, characterization and photophysical studies of ruthenium(II) complexes as sensitizers for dye sensitized solar cells. This thesis' presentation comprises of introduction and literature review as chapter one, experimental methods as chapter two, Results and discussion for ATR-FTIR, Ultraviolet visible (UV-vis), Photoluminescence (PL) spectroscopy and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic characterization as chapter three, Results and discussion for Conductivity measurement and Electrochemistry as chapter four and summary of results and conclusion as chapter five future work and recommendation as chapter six.

Chapter one basically deals with the review of previous studies to assess their impacts made so far thereby creating the foundation for this research to make its worthwhile contributions to knowledge. A structured literature review was carried out and divided into segments such as review on ruthenium(II) complexes of NN chelating ligands and the review of inorganic, organic and, natural sensitizers.

Chapter two centres on the experimental methods used for the preparation of ligands and complexes. Nine chealing ligands comprising of six (6) tripodal chelating ligands, two (2) vinyl monodentate ligands and one (1) vinyl tridentate ligand, were successfully synthesised, characterized and used for the coordination of ruthenium(II) complexes. The six (6) tripodal chelating ligands were synthesized through the condensation of two equivalent amount of 1-Hydroxymethyl-3,5-dimethylpyrazole and an equivalent amount of aromatic amine in acetonitrile to form a C-N-C junction compound possessing major characteristics of two sp2 and sp3 hybridized amine nitrogen atoms as donors. Their three sites of complexation formed ruthenium(II) complexes incorporating other ligands such as  $H_2$ dcby and any of NCS, L7 or L8 monodentate ligand. The respective L7 and L8 monodentate ligands were prepared by starting a first step one pot synthesis through a three constituents condensation of 4bromobenzaldehyde, either 1-indanone or acetophenone, and ammonium acetate. The Stille coupling reaction, as the second step, was used to prepare both vinyl subunits of vpdinp and vpbpp respectively. Similarly, this first and second step approach was also used for the preparation of L9 tridentate ligand. Three synthetic procedures were employed for the preparation of complexes depending on their respective compound formulations, The first step involves the coordination of 2,2'bipyridine-4,4dicarboxylic acid or L9 or (L1-L6) to the metal centre precursor of Ru(DMSO)<sub>4</sub>Cl<sub>2</sub> and then subsequent steps with the coordination of L7 or L8 or NCS ligands respectively, afforded intermediary complexes. Finally, the intermediary complexes were isolated by saturated solution of ammonium hexafluorophosphate salt (NH<sub>4</sub>PF<sub>6</sub>).

Chapter three provides the results and discussion of ATR-FTIR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic characterization for the determination of molecular structures and

chemical properties as well as functional groups of the ruthenium(II) heteroleptic complexes. Having synthesised eight series of thirty ruthenium(II) complexes, the results and discussion were carried out based on the order of series arrangements. Series I contained mixed ligands of ruthenium(II) complexes having 4.4'-dicarboxy-2,2'-bipyridine, thiocynato, tridentate ligand of N,N-bis(3, 5-dimethylpyrazol-1ylmethyl) and thiocynate ligand. Series II consist of heteroleptic mixed ligands of ruthenium(II) complexes bearing 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine. tripodal ligand of N,N-bis(3, 5-dimethylpyrazol-1-ylmethyl) and 4,4'-Dicarboxy-2,2'bipyridine. Series III comprises of mixed ligands of ruthenium(II) complexes bearing 4-(4-Vinylphenyl)-2.6-bis(phenyl)pyridine, tripodal ligand of N,N-bis(3, 5dimethylpyrazol-1-ylmethyl) aromatic organic compounds and 4,4'-Dicarboxy-2,2'bipyridine ligand. Series IV contained mixed ligands of ruthenium(II) complexes featuring 4,4'-Dicarboxy-2,2'-bipyridine, thiocynate groups and respective 11-(4vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine and 4-(4-Vinylphenyl)-2.6bis(phenyl)pyridine monodentate ligand. Series V ruthenium(II) complexes formed from mixed ligands of two equivalent 4,4'-Dicarboxy-2,2'-bipyridine and two equivalent of 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine or 4-(4-Vinylphenyl)-2.6-bis(phenyl)pyridine ligands. Series VI. ruthenium(II) complexes are formed from mixed ligands of two equivalent thiocynate units, 4,4'-dicarboxy-2,2'bipyridine, and two equivalent of 11-(4-vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine and 4-(4-Vinylphenyl)-2.6-bis(phenyl)pyridine ligands. Series VII ruthenium(II) complexes are made up of mixed ligands of three equivalent thiocynate ligand, 4,4'-Dicarboxy-2,2'-bipyridine, and one equivalent of 11-(4-Vinylphenyl)diindeno[1,2b:2',1'-e]pyridine and 4-(4-Vinylphenyl)-2.6-bis(phenyl)pyridine ligands. Lastly, series VIII presents heteroleptic mixed ligands of ruthenium(II) complexes having 4-(4-Vinylphenyl)-2,2':6'2''-terpyridine, 4,4'-Dicarboxy-2,2'-bipyridine and any of thiocynate unit, 11-(4-Vinylphenyl)diindeno[1,2-b:2',1'-e]pyridine or 4-(4-Vinylphenyl)-2.6-bis(phenyl)pyridine ligands.

Chapter four provides photophysical and electrochemical studies of ruthenium(II) complexes. With the aid of energy diagram, the photophysical properties of the complexes were discussed based on three possible excited states: (a) metal centered (MC), which are due to promotion of an electron from t2g to eg orbitals; (b) ligand centered (LC) that are  $\pi$ - $\pi$ \* transitions; and (c) charge transfer (CT) excited states, which are either metal-to-ligand (MLCT) or ligand-to-metal (LMCT), including the structural activity relationship of the complexes to the UV-Vis absorption features. The electrochemical properties were discussed based on the observation of the well defined redox processes in the voltammogram of the complexes to assert the metal centre oxidation or on the ligands centred reduction.

Chapter five provides summary of results and conclusion

Lastly, chapter six provides future work and recommendations.

# **5.2** Conclusion

The primary aim of this research studies as contained in this thesis is to design, synthesize characterize and investigate the photophysical as well as electrochemical properties of heteroleptic ligands of ruthenium(II) complexes as sensitizers for dye sensitized solar cells. The six (6) tripodal chelating ligands, two (2) vinyl monodentate ligands and one (1) vinyl tridentate ligand including their precursors and their ruthenium(II) complexes were characterized by UV-Vis, PL, FTIR (ATR) and NMR spectroscopy. The ATR-FTIR studies of all the ruthenium(II) complexes (1-30) show bands between 3127-3031 cm<sup>-1</sup> may be due to the presence of aromatic C-H stretchting vibrations and bands in the range 2933-2920 cm<sup>-1</sup> show the presence of C-H stretching of the methyl group. Bands between 2116-2100 cm<sup>-1</sup> and 777-770 were ascribed to N=C and C=S stretching vibration of thiocyanate moiety in all complexes (1-6, 19-20, 24-27 and 30) having –NCS group coordination. The vibrational bands between 1734-1718 cm<sup>-1</sup>, 1378-1368 cm<sup>-1</sup> and 1234- 1220 cm<sup>-1</sup> in the complexes (1-30) were ascribed to C=O, symmetric –COO- and C-O strectching vibration of carboxylic acid group. The exhibition of bands between 466 and 411 respectively ascribed to the coordination between the ligand and ruthenium metal atom. With the aid of ATR-FTIR spectroscopy, the chemical functional group determination and structure elucidation of the ruthenium(II) complexes were successfully characterized.

The <sup>1</sup>H and <sup>13</sup>C NMR studies confirmed the proposed structures of the six (6) tripodal chelating ligands, two (2) vinyl monodentate ligands and one (1) vinyl tridentate ligand

including their precursors and their ruthenium(II) complexes. The relevant <sup>1</sup>H and <sup>13</sup>C NMR spectra and data are presented in Figures 3.25 to 3.60 including appendix and Tables 3.6, 3.7 and 3.8 respectively. The results of both ATR-FTIR and NMR studies revealed that ruthenium(II) complexes of series I, IV, VI VII and one of VIII bearing thiocyanate groups confirms the presence of N-coordination of the SCN group and Carbon-13 NMR showed resonance peaks around 130-135 ppm which is attributable to NCS ligands, thereby, confirming that that NCS ligands are coordinated through the nitrogen atom. The proton NMR revealed the presence of vinyl protons around peaks at 5.30, 5.90 ad 6.70 ppm, hence, confirmed that the vinyl hydrogen atoms of the stryl group coordinated to the vinyl subunits.

Electronic spectroscopy of the eight series ruthenium(II) complexes showed broad band in the visible region in the electronic transition from  $Ru^{II}$  based  $t_{2g}$  orbital to ligand  $\pi^*$  orbitals. The relevant electronic spectra and data are presented in Figures 4.1 to 4.5 and Table 4.1-4.5. Series I, II and III ruthenium(II) complexes exhibited broad band metal to ligand charge transfer (MLCT) absorption in the visible region with maxima around 432-583 nm. Their positions of the low energy maxima are ascribed to the nature of monodentate, bidentate and tridentate ligands shifting to longer wavelength as degree of  $\pi$ -delocalization in the acceptor ligand increases. These complexes also showed strong UV band around 315 and 341 nm are ascribed to intraligand  $\pi$ - $\pi^*$  transitions of bidentate and tridentate ligands. It is interesting to note that series IV, V VI, VII and VII exhibit visible absorption to higher wavelength near-IR region which was prominent when compared to series I, II and III ruthenium(II) complexes. These outstanding absorption properties are very useful for harvesting and transforming less energetic photons which is crucial for photosensitization processes The superiority of series IV, V, VI, VII and VIII complexes against series I, II and III complexes can be ascribed to factors such as the presence of more phenyl group in the chromophoric ligands as well as increase in the conjugation length of the chromophoric ligands and by virtue of increasing the numbers of thiocyanate groups which are known to determine the increase in the absorption to longer wavelength of metal-to-ligand charge transfer (MLCT) transitions.

Emission spectroscopy of the eight series ruthenium(II) complexes exhibited luminescence around 700 nm can be ascribed to <sup>3</sup>MLCT lowest lying excited state of series I to VIII ruthenium(II) complexes, The relevant emission spectra and data are presented in Figures 4.6 to 4.10 and Table 4.6 to 4.10. Therefore, it can be deduced that the emissive ruthenium(II) complexes with improved photophysical properties.

Electrochemical measurements of the eight series ruthenium(II) complexes reveal Ru(II)/R(III) oxidations at positive potentials and ligand-based reduction at negative potentials. The relevant voltammograms and data are presented in Figures 4.11 to 4.25 and Table 4.11. The redox behavior of dye **4-12**, **14-16**, **18-20**, **24-26** and **30** respectively is dominated by the Ru(II)/R(III) redox couple in region ( $E_{1/2}$  between 0.53 and 1.18) and the pyridines-based redox couples in the region between ( $E_{1/2}$  between -0.25 and -1.45). The electrochemical properties showed that six (6) tripodal

chelating ligands, two (2) vinyl monodentate pyridines and one (1) vinyl terpyridine ligand featuring complexes have good electro-redox characteristics which can be applied as potential sensitizers for dye sensitized solar cells.

#### CHAPTER SIX

#### 6.0. FUTURE WORK AND RECOMMENDATIONS

# 6.1 Future Work

The objective of this research was to design and synthesize novel ruthenium(II) complexes as sensitizers for potential application in Dye sensitized solar cells. The results obtained in this research showed that structural features of series I to III due their functional groups influence the conjugated systems thereby causing the absorption peaks to appear in longer wavelength with significant increase in absorptivity. In series IV to VIII, it was deduced that the MLCT can be extended to longer wavelengths by appropriate substituent changes on chromophoric ligands or by increasing the number of NCS groups. It is well known that increasing the conjugation length of a ligand also serves as a practical technique of improving the photophysical and electrochemical properties of the Ru(II) complexes. An appreciable progress has been attained so far. However, future work is imperative and shall include the following:

- (i) Fabricate dye sensitized solar cell
- (ii) Evaluate the photovoltaic performance of the synthesized ruthenium(II) complexes as sensitizers for dye sensitized solar cells DSSCs using the following parameters: Incident-photon-to-current conversion efficiency (IPCE), Open-circuit photovoltage (Voc), Short-circuit photocurrent density (Jsc), Fill factor (ff) and solar energy-to-electricity eonversion efficiency (n)

(iii) To investigate the overall internal resistance of the cell by using the technique of electrochemical impedance spectroscopic analysis (EIS).

## **6.2. Recommendations**

The synthesized thirty novel ruthenium(II) complexes under eight series have shown through their photophysical and electrochemical properties that they have the potential of being light absorbing components which can be utilized for DSSCs applications. The results obtained in this research showed that structural features of series I to III due their functional groups influence the conjugated systems thereby causing the absorption peaks to appear in longer wavelength with significant increase in absorptivity. Hence, the recommendation will be that futher modifications should be carried out on the chemical structures of these compounds so to probe their various photophysical and electrochemical properties and how they can affect the performance of dye solar cells. By appropriate substituent changes on chromophoric ligands or by increasing the number of NCS groups, the series IV –VIII complexes exhibited good photophysical properties. Moreover, the use of other potential ligands with fused ring would help boost their performance. Thus, recommendation on further research on these compound would create ample opportunites for more dyes to be introduced into the industries.

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Formulation	Molar	Colour	M. Pt	% Yield
	mass		(° C)	
	(g/mol)			
$[Ru(L1)(H_2dcbpy)(NCS)](PF_6)_2-Dye 1$	901.73	Dark Brown	> 250	25
$[Ru(L2)(H_2dcbpy)(NCS)](PF_6)_2-Dye 2$	932.75	Dark Brown	> 250	39
[Ru(L3)(H <sub>2</sub> dcbpy)(NCS)](PF <sub>6</sub> ) <sub>2</sub> -Dye 3	857.72	Dark Gray	> 250	47
$[Ru(L4)(H_2dcbpy)(NCS)](PF_6)_2-Dye 4$	871.75	Dark Gray	> 250	34
$[Ru(L5)(H_2dcbpy)(NCS)](PF_6)_2-Dye 5$	863.77	Dark Gray	> 250	42
$[Ru(L6)(H_2dcbpy)(NCS)](PF_6)_2$ -Dye 6	887.72	Dark Gray	> 250	31
[Ru(L1)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -Dye 7	1314.08	Black	> 250	38
[Ru(L2)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -Dye 8	1377.08	Dark red	119	43
[Ru(L3)( L7)( H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -Dye 9	1302.06	Dark red	125	46
$[Ru(L4)(L7)(H_2dcbpy)](PF_6)_2$ -Dye 10	1316.08	Dark Brown	185	44
Ru(L5)( L7)( H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -Dye 11	1308.10	Black	175	22
[Ru(L6)( L7)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -Dye 12	1332.08	Black	165	49
[Ru(L1)(L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -Dye 13	1322.01	Dark Brown	> 250	37
$[Ru(L2)(L8)(H_2dcbpy)](PF_6)_2$ -Dye 14	1353.03	Dark Brown	83	43
[Ru(L3)(L8)(H <sub>2</sub> dcbpy)](PF <sub>6</sub> ) <sub>2</sub> -Dye 15	1278.04	Dark Brown	195	53
$[Ru(L4)(L8)(H_2dcbpy)](PF_6)_2$ -Dye 16	1292.03	Dark Brown	> 250	39
$[Ru(L5)(L8)(H_2dcbpy)](PF_6)_2$ -Dye 17	1284.08	Dark Brown	185	42
$[Ru(L6)(L8)(H_2dcbpy)](PF_6)_2$ -Dye 18	1308.03	Black	185	51
$[Ru(H_2dcbpy)_2(L7)(NCS)](PF_6)_2-Dye 19$	1149.97	Dark Brown	> 250	54
$[Ru(H_2dcbpy)_2(L8)(NCS)](PF_6)_2-Dye\ 20$	1125.95	Black	> 250	44

## Appendix A: Some physical properties of thirty novel ruthenium(II) complexes

$[Ru(H_2dcbpy)_2(L7)_2](PF_6)_2$ -Dye 21	1594.30	Dark red	> 250	27
$[Ru(H_2dcbpy)_2(L8)_2](PF_6)_2$ -Dye 22	1546.25	Dark red	175	40
[Ru(H <sub>2</sub> dcbpy) <sub>2</sub> (L7)( L8)](PF <sub>6</sub> ) <sub>2</sub> -Dye 23	1570.27	Dark Brown	> 250	55
[Ru(H <sub>2</sub> dcbpy)( L7) <sub>2</sub> (NCS) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub> -Dye 24	1176.33	Black	155	29
$[Ru(H_2dcbpy)(vL8)_2(NCS)_2](PF_6)_2-Dye 25$	1128.29	Black	170	27
[Ru(H <sub>2</sub> dcbpy)(L7)(NCS) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub> -Dye 26	943.05	Black	170	30
[Ru(H <sub>2</sub> dcbpy)(L8)(NCS) <sub>3</sub> ](PF <sub>6</sub> ) <sub>2</sub> -Dye 27	870.98	Black	170	27
[Ru(L9)(H <sub>2</sub> dcbpy)(L7)](PF <sub>6</sub> ) <sub>2</sub> -Dye 28	1328.05	Dark red	> 250	49
[Ru(L9)(H <sub>2</sub> dcbpy)(L8)](PF <sub>6</sub> ) <sub>2</sub> -Dye 29	1304.03	Dark red	> 250	41
$[Ru(L9)(H_2dcbpy)(NCS)](PF_6)_2Dye 30$	883.72	Black	> 250	58



Appendix B: <sup>1</sup>H and <sup>13</sup>C NMR spectra of Ligands and Series I-VI ruthenium(II) complexes

Figure 1: <sup>1</sup>H NMR Spectrum of bdmpmaa Ligand 1 (L1)



Figure 2: <sup>13</sup>C NMR spectrum of of bdmpmaa-Ligand 1 (L1)



Figure 3: <sup>1</sup>H NMR Spectrum of bdmpmeta-Ligand 2 (L2)



Figure 4: <sup>13</sup>C NMR spectrum of of bdmpmeta-Ligand 2 (L2)



Figure 5: <sup>1</sup>H NMR Spectrum of bdmpmal-Ligand 3 (L3)



Figure 6: <sup>13</sup>C NMR spectrum of of bdmpmal-Ligand 3 (L3)



Figure 7: <sup>1</sup>H NMR Spectrum of bdmpmt-Ligand 4 (L4)



Figure 8: <sup>13</sup>C NMR spectrum of of bdmpmt-Ligand 4 (L4)



Figure 9: <sup>1</sup>H NMR Spectrum of bdmpmcy-Ligand 5 (L5)



Figure 10: <sup>13</sup>C NMR spectrum of of bdmpmcy-Ligand 5 (L5)



Figure 11: <sup>1</sup>H NMR Spectrum of bdmpmas-Ligand 6 (L6)



Figure 12: <sup>13</sup>C NMR spectrum of of bdmpmas-Ligand 6 (L6)



Figure 13: <sup>1</sup>H NMR Spectrum of vpdiinp-Ligand 7 (L7)



Figure 14: <sup>13</sup>C NMR spectrum of of vpdiinp-Ligand 7 (L7)



Figure 15: <sup>1</sup>H NMR Spectrum of vpdpp-Ligand 8 (L8)



Figure 16<sup>13</sup>C NMR Spectrum of vpbpp Ligand (8),



Figure 17: <sup>1</sup>H NMR Spectrum of vtpy-Ligand 9 (L9)



Figure 18: <sup>13</sup>C NMR Spectrum of vtpy-Ligand 9 (L9)



Figure 19: <sup>1</sup>H NMR spectrum of [Ru(L3)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 3



Figure 20: <sup>13</sup>C NMR spectrum of [Ru(L3)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>) Dye 3



Figure 21: <sup>1</sup>H NMR spectrum of [Ru(L4)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 4



Figure 22: <sup>13</sup>C NMR spectrum of [Ru(L4)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>).Dye 4


Figure 23: <sup>1</sup>H NMR spectrum of [Ru(L5)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)<sub>2</sub>-Dye 5



Figure 24: <sup>13</sup>C NMR spectrum of [Ru(L5)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 5



Figure 25: <sup>1</sup>H NMR spectrum of [Ru(L6)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 6



Figure 26: <sup>13</sup>C NMR spectrum of [Ru(L6)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 6



Figure 27: <sup>1</sup>H NMR spectrum of [Ru(L1)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 7



Figure 28: <sup>13</sup>C NMR spectrum of [Ru(L1)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 7



Figure 29: <sup>1</sup>H NMR spectrum of [Ru(L2)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 8



Figure 30: <sup>13</sup>C NMR spectrum of [Ru(L2)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 8



Figure 31: <sup>1</sup>H NMR spectrum of [Ru(L5)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 11



Figure 32: <sup>13</sup>C NMR spectrum of [Ru(L5)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 11



Figure 33: <sup>1</sup>H NMR spectrum of [Ru(L6)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 12



Figure 34: <sup>13</sup>C NMR spectrum of [Ru(L6)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 12



Figure 35: <sup>1</sup>H NMR spectrum of [Ru(L1)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 13



Figure 36: <sup>13</sup>C NMR spectrum of [Ru(L1)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 13



Figure 37: <sup>1</sup>H NMR spectrum of [Ru(L2)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 14



Figure 38: <sup>13</sup>CNMR spectrum of [Ru(L2)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 14



Figure 39: <sup>1</sup>H NMR spectrum of [Ru(L3)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 15



Figure 40: <sup>13</sup>C NMR spectrum of [Ru(L3)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 15



Figure 41: <sup>1</sup>H NMR spectrum of [Ru(L4)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 16



Figure 42: <sup>13</sup>C NMR spectrum of [Ru(L4)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>- Dye 16





Figure 1: FTIR-(ATR) Spectrum of [Ru(L1)(H2dcbpy)(NCS)](PF6)-Dye 1



Figure 2: FTIR-(ATR) Spectrum of [Ru(L2)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 2



Figure 3: FTIR-(ATR) Spectrum of [Ru(L3)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 3



Figure 4: FTIR-(ATR) spectrum of [Ru(L4)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)-Dye 4



Figure 5: FTIR-(ATR) spectrum of [Ru(L5)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>).Dye 5



Figure 6: FTIR-(ATR) spectrum of [Ru(L6)(H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>).Dye 6



Figure 7: FTIR-(ATR) spectrum of [Ru(L1)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 7



Figure 8: FTIR-(ATR) spectrum of [Ru(L2)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 8



Figure 9: FTIR-(ATR) spectrum of [Ru(L3)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 9



Figure 10: FTIR-(ATR) spectrum of [Ru(L4)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 10



Figure 11: FTIR-(ATR) spectrum of [Ru(L5)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 11



Figure 12: FTIR-(ATR) spectrum of [Ru(L6)(L7)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 12



Figure 13: FTIR-(ATR) spectrum of [Ru(L1)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 13



Figure 14: FTIR-(ATR) spectrum of [Ru(L2)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 14



Figure 15: FTIR-(ATR) spectrum of [Ru(L3)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 15



Figure 16: FTIR-(ATR) spectrum of [Ru(L4)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 16



Figure 17: FTIR-(ATR) spectrum of [Ru(L5)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 17



Figure 18: FTIR-(ATR) spectrum of [Ru(L6)(L8)(H<sub>2</sub>dcbpy)](PF<sub>6</sub>)<sub>2</sub>-Dye 18



Figure 19: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L7)(NCS)](PF<sub>6</sub>)<sub>2 2</sub>-Dye 19



Figure 20: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)<sub>2</sub>(L8)(NCS)](PF<sub>6</sub>)<sub>2</sub>-Dye 20



Figure 21: FTIR-(ATR) Spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)<sub>2</sub>(NCS)<sub>2</sub>]-Dye 21



Figure 22: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)(L8)<sub>2</sub>(NCS)<sub>2</sub>]-Dye 22



Figure 23: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)(L8)](PF<sub>6</sub>)<sub>2</sub>-Dye 23



Figure 24: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)<sub>2</sub>(NCS)<sub>2</sub>]-Dye 24



Figure 25: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)(L8)<sub>2</sub>(NCS)<sub>2</sub>]-Dye 25



Figure 26: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)(L7)(NCS)<sub>3</sub>](NH<sub>4</sub>)-Dye 26



Figure 27: FTIR-(ATR) spectrum of [Ru(H<sub>2</sub>dcbpy)(L8)(NCS)<sub>3</sub>](NH<sub>4</sub>)-Dye 27



Figure 28: FTIR-(ATR) spectrum of [Ru(vptpy)(H<sub>2</sub>dcbpy)(L7)](PF<sub>6</sub>)<sub>2</sub>-Dye 28



Figure 29: FTIR-(ATR) spectrum of [Ru(vptpy) (H<sub>2</sub>dcbpy)(L8)](PF<sub>6</sub>)<sub>2</sub>-Dye 29



Figure 30: FTIR-(ATR) spectrum of [Ru(vptpy) (H<sub>2</sub>dcbpy)(NCS)](PF<sub>6</sub>)<sub>2</sub>-Dye 30