
# *SYNTHESIS AND CHARACTERIZATION OF BIPYRIDINE AND DIPYRIDOPHENAZINE BASED RUTHENIUM (II) COMPLEXES AS POTENTIAL DYE-SENSITIZED SOLAR CELLS SENSITIZERS*

**CHAN KENG FUONG**

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**By**

**CHAN KENG FUONG**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science**

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**Chair: Janet Lim Hong Ngee, PhD**
**Faculty: Science**

Dye sensitizers are one of the key factors that affects the performance of dye-sensitized solar cells (DSSCs). One of the limitation of ruthenium bipyridyl sensitizer is the limited light absorption in infrared region. Hence, extended cyclic π-conjugated bipyridyl derivative was studied to overcome this limitation. Potential DSSC sensitizers such as 2,2'-bipyridine (bpy), dipyrido[3,2-*a*:2′,3′-*c*]-phenazine (dppz) and 11,12-dimethyldipyrido[3,2-*a*:2′,3′-*c*]-phenazine (dppx)-based ruthenium complexes were synthesized and characterized in this study. Three heteroleptic ruthenium complexes, namely cis-[Ru(dcbpy)(bpy)$(NCS)_2$] (Rubpy), cis-[Ru(dcbpy)(dppz)$(NCS)_2$] (Rudppz), and cis-[Ru(dcbpy)(dppx)$(NCS)_2$] (Rudppx), where dcbpy = 2,2'-bipyridyl-4,4'-dicarboxylic acid, $NCS^-$ = isothiocyanate, were synthesized using a one-pot synthesis method and evaluated for their potential as dye-sensitized solar cells (DSSCs) sensitizers. Spectroscopic, electrochemical and electron impedance spectroscopic analysis were performed on the as-synthesized ruthenium complexes. The commercial dye sensitizer, cis-[Ru$(dcbpy)_2(NCS)_2$] (N719) was used as a benchmark. The introduction of the dimethyl groups in the Rudppx complex resulted in a bathochromic shift (10 nm) in the intraligand absorption maximum at 384 nm, an enhancement in the molar absorption coefficient of the metal-to-ligand charge transfer band (λ = 500 nm), and the destabilization of both the ground and excited state molecular orbitals of the complex, compared to Rudppz. In terms of photovoltaic performance, Rubpy exhibited higher short circuit current density (2.07 $mAcm^{-2}$) and power conversion efficiency (η = 0.57%) as compared to Rudppz which had a short circuit current density of 1.52 $mAcm^{-2}$ and a power conversion efficiency of 0.40%, demonstrating that the lower cyclic π-conjugation of the bipyridine ligand contributed to the lowest unoccupied molecular orbital in Rubpy that favoured electron injection. Rudppx exhibited improved power conversion efficiency (η = 0.61%) as compared to Rudppz upon the introduction of the dipyrido [3,2-*a*: 2′,3′-*c*] -phenazine ligand which had dimethyl groups. The dimethyl groups behaved as electron-donating substituents that increased the electron density of the 11,12-dimethyldipyrido [3,2-*a*: 2′,3′-*c*] -

phenazine ligand which helped in alternating the lowest occupied molecular orbital of Rudppx to enhance electron injection, resulting in an improved short circuit current density of 1.93 $mAcm^{-2}$ from 1.52 $mAcm^{-2}$ (Rudppz). The criteria for an efficient DSSC ruthenium-based sensitizer were drawn based on structure-property relationship studies of the ruthenium sensitizers in this study.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia, sebagai memenuhi keperluan untuk ijazah Master Sains

**SINTESIS DAN PENCIRIAN KOMPLEKS BERASASKAN RUTHENIUM (II) BIPRIDIN DAN BIPIRIDOPHENAZINE SEBAGAI PEMINAT BERPOTENSI SEL SURIA TERPEKA PEWARNA**

Oleh
**CHAN KENG FUONG**

**Ogos 2018**

**Pengerusi: Janet Lim Hong Ngee, PhD**
**Fakulti: Sains**

Salah satu faktor utama yang menentukan prestasi sel solar pewarna peka (DSSC) ialah pewarna. Salah satu had kemampuan pewarna bipiridil ruthenium ialah penyerapan cahaya terhad di kawasan infra merah. Oleh itu, derivatif bipiridil yang dilanjutkan dengan kitaran π-konjugasi telah dikaji untuk mengatasi had kemampuan tersebut. Pewarna DSSC seperti kompleks ruthenium berasaskan 2,2-bipiridina (bpy), dipyrido[3,2-*a*:2′,3′-*c*]-phenazine (dppz) atau 11,12-dimetildipirido[3,2-*a*:2′,3′-*c*]-phenazine (dppx) telah dibuat dan dikaji. Tiga kompleks ruthenium heteroleptik iaitu cis-[Ru(dcbpy)(bpy)$(NCS)_2$] (Rubpy), cis-[Ru(dcbpy)(dppz)$(NCS)_2$] (Rudppz), dan cis-[Ru(dcbpy)(dppx)$(NCS)_2$] (Rudppx), di mana dcbpy = 4,4'-dikarbosilik-2,2'-bipiridina, NCS = isothiocyanate, telah dibuat melalui sintesis satu langkah dan diguna sebagai pewarna berpotensi untuk sel solar pewarna peka (DSSC). Analisis spektroskopik, elektrokimia dan impedans elektron telah dilakukan pada kompleks ruthenium tersebut. Pewarna komersial, cis-[Ru(dcbpy)$_2$$(NCS)_2$] (N719) telah digunakan sebagai penanda aras untuk kompleks tersebut. Pernambahan kumpulan dimetil dalam struktur Rudppx menjadikan peralihan batrokromik (10 nm) maksima penyerapan intraligan di 384 nm, pernambahan penyerapan molar pemindahan caj dari logam ke ligan (λ = 500 nm), dan perubahan orbit molekular ruthenium kompleks, berbanding dengan Rudppz. Berdasarkan prestasi fotovoltaik, Rubpy mempunyai $J_{SC}$ (2.07 $mAcm^{-2}$) dan kecekapan penukaran kuasa (η = 0.57%) yang lebih tinggi daripada ketumpatan arus litar pintas (1.52 $mAcm^{-2}$) dan kecekapan penukaran kuasa (η = 0.40%) Rudppz, ini menunjukkan konjugasi π kitaran ligan bipyridin menyumbang kepada suntikan elektron ke HOMO Rubpy. Rudppx mempunyai kecekapan penukaran kuasa (η = 0.61%) daripada Rudppz selepas pernambahan dimetil atas ligan dipyrido[3,2-*a*:2′,3′-*c*]-phenazine. Dimetil yang berfungsi sebagai penderma elektron meningkatkan ketumpatan elektron ligan 11,12-dimethyldipyrido[3,2-*a*:2′,3′-*c*]-phenazine yang membantu mengubahsuaikan orbital molekul terendah kosong Rudppx untuk menambahbaikan suntikan elektron, menjadikan peningkatan ketumpatan arus litar

pintas dari 1.52 $mAcm^{-2}$ ke 1.93 $mAcm^{-2}$. Kriteria pewarna ruthenium untuk DSSC yang berkesan telah ditentukan melalui hubungan struktur dan ciri pewarna tersebut.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

**Janet Lim Hong Ngee, PhD**
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

**Haslina binti Ahmad, PhD**
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

**ROBIAH BINTI YUNUS, PhD**
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Signature: _____
Name of Chairman of Supervisory Committee: Janet Lim Hong Ngee, PhD

Signature: _____
Name of Member of Supervisory Committee: Haslina binti Ahmad, PhD

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| | |
|---|---|
| Bpy | Bipyridine |
| CV | Cyclo Voltammetry |
| Dcbpy | 4,4'-dicarboxylic-2,2'-bipyridine |
| Dppx | 11,12-dimethyldipyrido[3,2-*a*:2′,3′-*c*]-phenaz |
| Dppz | Dipyrido[3,2-*a*:2′,3′-*c*]-phenazine |
| Dpq | 1,10-phenanthroline-5,6-dione |
| DSSC | Dye-sensitized solar cells |
| $E_{0\text{-}0}$ | Band Gap Energy |
| $E^0_{S+/S}$ | Ground State Oxidation Potential |
| $E^0_{S+/S*}$ | Excited State Oxidation Potential |
| $E_{HOMO}$ | HOMO Energy Level |
| EIS | Electron Impedance Spectroscopy |
| $E_{LUMO}$ | LUMO Energy Level |
| $E_{ox}$ ($L/L^-$) | Ligand-Centered Oxidation Peak |
| $E_{ox}$ ($Ru^{II}/Ru^{III}$) | Ru-Centred Oxidation Peak |
| FF | Fill Factor |
| FTO | Fluorine-doped Tin Oxide |
| HOMO | Highest Unoccupied Molecular Orbital |
| $I_3^-/I^-$ | Iodide/triiodide Redox Mediator |
| IPCE | Incident Photon to Current Efficiency |
| ITO | Indium Tin Oxide |
| $J_{SC}$ | Short Circuit Current Density |
| J-V | Current Density vs Potential |
| LSV | Linear Scan Voltammetry |
| LUMO | Lowest Unoccupied Molecular Orbital |
| MLCT | Metal-to-ligand Charge Transfer |
| $\eta$ | Power Conversion Efficiency |
| NCS | Isothiocyanate |
| NH4NCS | Ammonium Isothiocyanate |
| NP | Nanoparticle |
| NW | Nanowire |
| $R_{ct}$ | Charge Transfer Resistance Between the $TiO_2$/dye/electrolyte Interface |
| $R_{Pt}$ | Charge Transfer Resistance Between the Pt Counter Electrode and the Electrolyte Interface |
| Rubpy | Cis-(bis-isothiocyanato)-(2,2'-bipyridyine)-(4,4'-dicarboxylato-2,2'-bipyridine) ruthenium (II), cis-[Ru(dcbpy)(bpy)$(NCS)_2$] |
| Rudppx | Cis-(bis-isothiocyanato)-(4,4'-dicarboxylato-2,2'-bipyridine)-(11,12-dimethyldipyrido[3,2'-a;3,2'-c]phenazine) ruthenium (II), cis-[Ru(dcbpy)(dppx)$(NCS)_2$] |
| Rudppz | Cis-(bis-isothiocyanato)-(4,4'-dicarboxylato-2,2'-bipyridine)-(dipyrido[3,2'-a;3,2'-c]phenazine) ruthenium (II), cis-[Ru(dcbpy)(dppz)$(NCS)_2$] |
| $TBAPF_6$ | Tetrabutylammonium Hexafluorophophate |
| $TiO_2$ | Titanium Dioxide |
| TMS | Tetramethylsilane |

| | |
|---|---|
| TPA | Triphenylamine |
| $V_{OC}$ | Open Circuit Potential |
| $\tau$ | Electron Lifetime |

# CHAPTER 1

# INTRODUCTION

## 1.1 Dye-sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells (DSSCs) have been recognized as a promising third generation solar cells employing facile fabrication methods and low cost materials while harnessing light energy at comparable efficiencies to first generation solar cells (efficiency around 15% to 20%) and second generation solar cells (efficiency around 10% to 15%) (Roy-Mayhew *et al.*, 2010; Xue *et al.*, 2012). A basic DSSC contains a nanocrystalline titanium dioxide ($TiO_2$) layer on an indium tin oxide (ITO) glass substrate, a monolayer of light absorber (dye sensitizer) on the $TiO_2$ surface, an electrolyte containing an iodide/triiodide redox mediator ($I_3^-/I^-$) which acts as a hole transmitting medium, and a Pt counter electrode. When sunlight is irradiated onto the dye-absorbed $TiO_2$ photoanode, electrons in the dye molecules are excited by the photons and are injected into the conduction band (CB) of $TiO_2$ creating a current called photocurrent. The oxidized dye molecules are reduced by a redox couple in the electrolyte which are then regenerated at the Pt counter electrode (Roy *et al.*, 2010). The common types of dye sensitizers that have gained vast research attention include metal complex-based sensitizers (ruthenium (II) and cobalt (II)), metal-free organic dyes, and zinc-based porphyrin sensitizers (L. L. Li & Diau, 2013; Mishra *et al.*, 2009; Qin & Peng, 2012).

### 1.1.1 Factors Affecting the Efficiency of DSSCs

Each component in the DSSCs have different factors that affect their efficiency. For the photoanode, the morphology, surface area and thickness of the $TiO_2$ semiconductor layer are some factors that could affect the overall efficiency (Mohamed & Selim, 2017). The electrolyte that has optimum redox properties and high stability helps to improve the efficiency (Lenzmann & Kroon, 2007). Particularly, the fact that the photovoltaic performance of the DSSCs are strongly dependent on the nature of the dye sensitizer used has prompted much research on the relationship between molecular structure of a dye and its performance (Hara *et al.*, 2002). Basically, the molecular design of efficient dye sensitizers is associated with high absorption coefficients, high anchoring properties, favourable electron transfer and injection kinetics.

### 1.1.2 DSSCs With Ruthenium (II)-Based Sensitizers

The presence of metal-to-ligand charge transfer (MLCT) bands in the visible light spectra of polypyridyl ruthenium (II) complexes has attracted attention to the use of such complexes as photosensitizers in DSSCs (Fan *et al.*, 2010). Ruthenium (II) polypyridyl complexes developed by Gratzel and co-workers (1991) such as *cis*-

di(thiocyanato) bis(2,2′ -bipyridyl-4,4′ -dicarboxylate) ruthenium (II) N719, have been the paradigm dye sensitizers for DSSCs due to their outstanding power conversion efficiencies (η) of about 10% (M. Nazeeruddin *et al.*, 1993). However, the absorption of N719 only covered the visible region up to *ca*. 650nm, rendering improvement of light absorption near the infra-red region necessary. Since then, various functionalized ruthenium (II) polypyridyl complexes have been synthesized and investigated as efficient and stable sensitizers, ranging from functionalization of the bipyridyl ligand with extended hydrocarbons (η = 3.28%) (Sygkridou *et al.*, 2015), thiophene (η = 3.86%) (Lobello *et al.*, 2014) and ion-coordinating groups (η = 1.34%) (Cisneros *et al.*, 2016), modification on the terpyridyl (η = 5.40%) (Giribabu *et al.*, 2011) and quarterpyridyl ligands (η = 5.7%) (Abbotto *et al.*, 2011), to the development of cyclometalated (η = 5.7%) (Kisserwan & Ghaddar, 2011) and thiocyanate-free ruthenium (II) complexes (η = 10.2% (S. W. Wang *et al.*, 2013), η = 3.4%, (Colombo *et al.*, 2015), η = 3.4% (G. Li *et al.*, 2015b)).

### 1.1.3 Dipyrido[3,2,-A;2',3-C]Phenazine-Based Ruthenium Complexes

Research on dye sensitizers has also been extended to rigid and electron-rich heteroaromatic bipyridyl ligands such as dipyrido[3,2,-f;2',3-h]quinoxaline and dipyrido[3,2,-a;2',3-c]phenazine (dppz) due to their ability to prevent bending or rotation along σ orbitals of the molecule and π-electron conjugation system which enabled strong and long distance electronic interactions within the aromatic system (Gholamkhass *et al.*, 2001). Dppz complexes of ruthenium have been extensively studied as luminescent probes due to their intense photoluminescence in non-aqueous media attributed to their long-lived MLCT abilities (Brennaman *et al.*, 2004; Nair *et al.*, 1998; Olson *et al.*, 1997). There has also been much focus on the photophysical properties (Kitao & Sugihara, 2008; Nickita *et al.*, 2007), excited state dynamics (Peña *et al.*, 2012) and electron transfer reactions (Dupont *et al.*, 2011) of functionalized dppz complexes of ruthenium as well as their applications including as DSSC photosensitizers. A previous study has shown that heteroleptic ruthenium (II) complex sensitizer containing the dppz ligand exhibited a broad MLCT transition band in the visible light spectrum, rendering η=5.3% (Onozawa-Komatsuzaki *et al.*, 2006). It was also revealed that the electron injection into the $TiO_2$ CB remained as one of the shortcomings of the dppz-based ruthenium(II) complexes, therefore the introduction of electron-donating moieties was recommended to enhance the electron injection process of the dye upon photoexcitation. Therefore, in their work, the dppz ligands were modified with electron-donating dimethyl groups to yield the 11,12-dimethyl-dipyrido[3,2,-a;2',3-c]phenazine (dppx) ligand.

Four ruthenium (II) complexes, Ru(II)(bpy)(dcbpy)$(NCS)_2$ (Rubpy), Ru(II)(dppz)(dcbpy)$(NCS)_2$ (Rudppz), Ru(II)(dppx)(dcbpy)$(NCS)_2$ (Rudppx) [bpy = bipyridine, dcbpy = 4,4'-dicarboxyl-2,2'-bipyridine and NCS = isothiocyanate], were and synthesized and characterized together with cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II); N719. The ruthenium complexes are illustrated in Figure 1. dcbpy functioned as the anchoring ligand for $TiO_2$ grafting, and isothiocyanate (NCS) was employed as the electron mediator. Based on Rudppz and Rudppx, the effect of the dimethyl groups in enhancing the light harvesting properties

and electron transfer kinetics of the metal complexes as DSSC sensitizers was studied *via* various spectroscopic, electrochemical and photovoltaic characterization techniques. The bipyridyl-containing ruthenium (II) complex, Rubpy was also studied in order to compare the effectiveness of extended heteroaromatic dppz-containing ruthenium (II) complexes as DSSC sensitizers. N719, as the commercial dye, was studied as the benchmark for the as-synthesized sensitizers and as the analogue with double carboxylic anchoring groups.

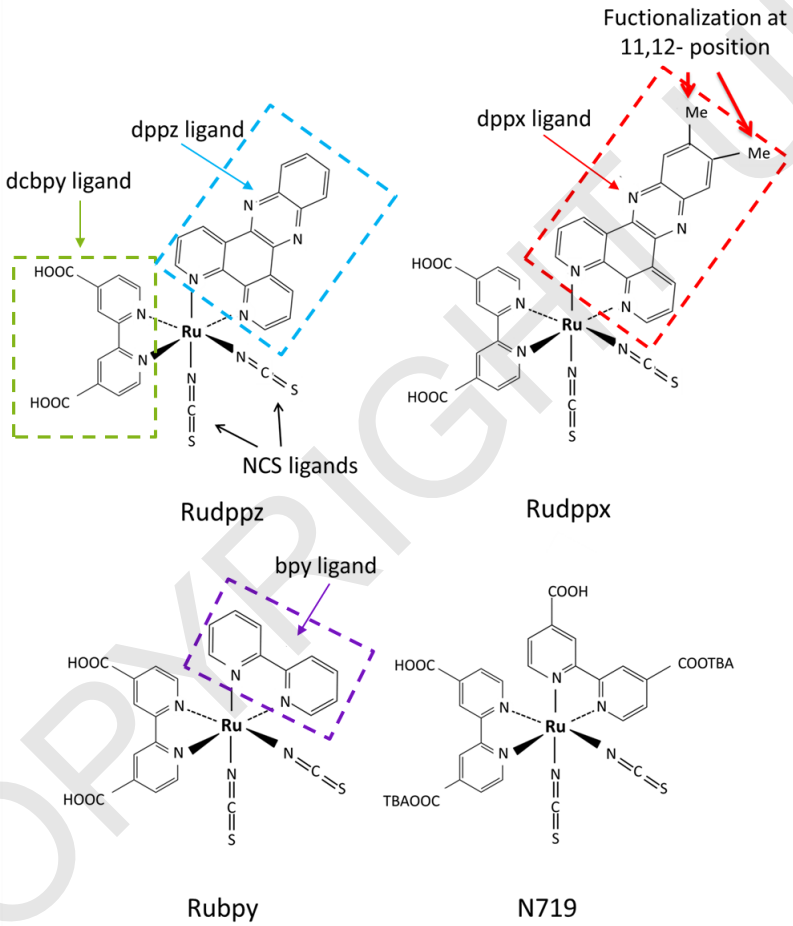


**Figure 1: Molecular Structure of *cis*-[Ru(Dcbpy)(Bpy)(Ncs)$_2$] (Rubpy), *cis*-[Ru(Dcbpy)(Dppz)(Ncs)$_2$] (Rudppz), *cis*-[Ru(Dcbpy)(Dppx)(Ncs)$_2$] (Rudppx), and *cis*-[Ru(Dcbpy)$_2$(Ncs)$_2$] (N719).**

Rudppx was derived from Rudppz with the functionalisation of two dimethyl groups at positions 11,12 of the dppz ligand. Rubpy was used to compare with Rudppz and Rudppx in terms of the light harvesting ability of different cyclic π-conjugation moieties of the bpy and dppz/dppx ligands.

## 1.2 Problem Statement

The key factors that affect the photovoltaic performance of DSSCs are the electron injection rate into the conduction band of $TiO_2$ and the rate of electron-hole recombination at the $TiO_2$/dye/electrolyte interface. The current limitation of bpy based ruthenium complex sensitizer is the absorption of light in near infrared region and the limited electron density of the bpy ligand. In this research, the dppz ligand was studied as a potential ligand for ruthenium(II)-based DSSC sensitizers due to its heterocyclic aromatic system which possessed a higher degree of cyclic π-conjugation as compared to that of the bpy ligand. Previous study has showed that dppz ligand possess strong light absorbing ability through strong metal-to-ligand charge transfer. Hence, the aim of this study is to study the performance of DSSC based on dpy and dppz based ruthenium complexes though few spectroscopic, electrochemical, electron impedance and photovoltaic analysis. The criteria in designing effective ruthenium (II)-based DSSC sensitizers are also drawn from the result.

## 1.3 Objectives and Scope of Research

In this research, three ruthenium (II) complexes with bipyridine, dppz and dppx based-ligands were synthesized using a one-pot synthesis method. The as-synthesized ruthenium (II) complexes were characterized in terms of their spectroscopic performance including electron impedance spectroscopy and electrochemical performance to evaluate their potential as DSSC sensitizers. The dppx ligand with dimethyl moieties was bonded to ruthenium (II) to investigate its performance as a potential sensitizer. Lastly, the criteria in designing the molecular structure of ruthenium (II) complexes as effective DSSC sensitizers were determined.

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