Dipyrrin Complexes as Dyes for Dye-Sensitised Solar Cells

A thesis submitted in partial fulfilment of the requirements for the degree of

Masters in Science
in Chemistry

at
Massey University, Palmerston North,
New Zealand.

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2009
ABSTRACT

DIPYRRIN COMPLEXES AS DYES FOR DYE-SENSITISED SOLAR CELLS

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With increasing concerns of global warming and the impending exhaustion of fossil fuels attention is being turned to renewable sources of energy. The sun supplies $3 \times 10^{24}$ J per year to the earth which is around $10^4$ times more energy than what the human race consumes. The world's energy needs would be satisfied if a mere 0.1% of the planet's surface was covered with solar cells($\eta = 10\%$)$^1$, causing the conversion of solar energy (sunlight) into electricity to represent a very practical renewable source.

Past research into solar energy has produced a photovoltaic device, which when coupled with highly coloured coordination compounds, enables this conversion. This device is known as a dye-sensitised solar cell (DSSC). Further research has been conducted into the properties of the dyes, and has shown that highly coloured coordination compounds are able to convert solar energy into electrical energy with the highest efficiencies. The dominant compounds in this area to date have been Grätzel's ruthenium complexes and porphyrins.

However, there exists a class of smaller compounds called dipyrins, described most simply as “half a porphyrin”, which possess many of the attractive qualities for DSSC dyes. Although there are no examples of ruthenium-dipyrin complexes in the literature, the combination of advantageous properties from both components represent very attractive synthetic targets with huge potential as dyes for DSSCs.

The objectives of this thesis were firstly to develop a series of dipyrin complexes which would be suitable as dyes for DSSCs; then to fully characterise the complexes and investigate the spectroscopic properties of each complex; and finally to determine the suitability of the complexes as dyes for DSSCs. These objectives were fully met, resulting
in a set of generic target compounds characterised via $^1$H NMR, $^{13}$C NMR, mass spectrometry (ESI-MS), elemental analysis, and x-ray crystallography. From analyses of the UV-visible, fluorescence, emission, and Raman spectra; and electrochemistry results; the complexes were concluded to be suitable as dyes for DSSC’s. An additional bonus is that the syntheses for these complexes are applicable to any dipyrrin, thus aiding future studies into the use of dipyrrins as dyes for DSSC’s. This thesis summarises the findings of the above outlined research project.

I wish to acknowledge my supervisors Dr Shane Telfer and Dr Mark Waterland for their assistance, advice and patience throughout the duration of my research project.

I also wish to extend my gratitude to my parents (Steve and Joy Smalley), sisters (Sian and Michaela Smalley), and partner (Alex Cade); particularly during times of frustration and waning motivation. Without the endless supply of loving support and encouragement they gave me this thesis and the laboratory work that went into it would never have come to fruition.

Thanks to the Manawatu branch of the New Zealand Federation for Graduate Women for the financial assistance that allowed me to complete the research component of my Masters in Science. Finally, thanks also to Dr Paul Plieger and his wife Isabel who provided paid work which allowed me to complete the final stages of writing this thesis.

**Acknowledgements for technical assistance:**

*Laboratory Assistance:* Dr Carl Otter for answering my many questions and providing practical assistance in the laboratory.

*Nuclear Magnetic Resonance Spectroscopy:* Dr Pat Edwards for help running NMR experiments, and also assistance in construction of the NMR diagrams in Chapter 2.

*X-Ray Crystallography:* Dr Shane Telfer for collecting data, solving and refining structures, and preparing ORTEP plots. Dr Geoff Jameson who assisted with the interpretation of the x-ray crystal structures.

*Raman Spectroscopy:* Tracey McLean who assisted with collection of spectroscopic data.

*Electrochemistry:* Dr Sivakumar Balakrishnan who assisted with the collection of the electrochemistry data. Dr Simon Hall who assisted with the interpretation of the electrochemistry data.

*Solar Cell Testing:* Dr Wayne Campbell for assistance in the preliminary solar cell testing of my complexes and also for the use of the DSSC animated power point slide which was used as the basis for the DSSC schematic in Chapter 1.
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ABBREVIATIONS AND SYMBOLS

acac. acetylacetone

bipy. Bipyridine (2,2’-bipyridine, unless otherwise stated)

BODIPY. Borondifluoride dipyrrin

CH$_3$OH. Methanol. Also abbreviated to MeOH. Deuterated methanol is represented as MeOD or CD$_3$OD.

CHCl$_3$. Chloroform. Deuterated chloroform is represented as CDCl$_3$

dcbipy. Dicarboxybipyridine (4,4’-dicarboxy-2,2’-bipyridine, unless otherwise stated)

DMF. Dimethylformamide

DMSO. Dimethylsulfoxide

dp. Dipyrrin

dpm. Dipyrrromethane

DSSC. Dye-sensitised solar cell. Sometimes abbreviated further to DSC

ESI-MS. Electrospray ionisation mass spectrometry

HOMO. Highest occupied molecular orbital

HTM. Hole transport material

LHE. Light harvesting efficiency

LUMO. Lowest unoccupied molecular orbital

MC. Metal centered

MLCT. Metal-to-ligand charge transfer

molL$^{-1}$. moles per litre, measure of concentration. May be abbreviated further to M, inverse is Lmol$^{-1}$. Also appears in the text as mmolL$^{-1}$ which denotes milimoles per litre.

NEt$_3$. Triethylamine

NMR. Nuclear magnetic resonance
phen. Phenanthroline (1,10-phenanthroline, unless otherwise stated)

ppm. Parts per million

Ru(II). Ruthenium(II), Ru$^{2+}$

SCN. Thiocyanate

SEM. Scanning electron micrograph

TCO. Transparent conducting oxide

TFA. Trifluoroacetic acid

THF. Tetrahydrofuran

TiO$_2$. Titanium dioxide

TLC. Thin layer chromatography

TnBA. Tetra-n-butyl ammonium

UV. Ultraviolet

1-T. Transmittance

A. Absorbance

Bu. Butyl group i.e C$_4$H$_9$

$^{13}$C. Carbon. In reference to NMR spectroscopy utilising the $^{13}$C isotope of carbon.

e$^-$. Electron

$^1$H. Proton (hydrogen). In reference to NMR spectroscopy utilising the $^1$H isotope of hydrogen.

In. Light, photons

I$^-$/I$_3^-$. Iodide/Triiodide

Jsc. Short-circuit current (Amps)

kT. Boltzman constant (JK$^{-1}$) multiplied by temperature (K)

M. generic metal
Me. Methyl group i.e CH₃

nm. Nanometres = 10⁻⁹ m

Pmax. The maximum quantity of power supplied (watts)

Psoure. Quantity of power supplied from the power source (watts)

R. generic functional group

s⁻¹. per second, unit.

V. volts – the unit for voltage

Voc. Open-circuit voltage (V)

ΔE. Change in energy (Joules). Also appears in the text as ΔEₙ, where n denotes a number to differentiate the changes in energy of different processes.

ε. Molar absorptivity or absorbance coefficient (L mol⁻¹ cm⁻¹)

η. Solar cell efficiency (%)

λex. Excitation wavelength (nm)

λmax. Wavelength maximum or energy maximum (nm)

µm. Micrometres = 10⁻⁶ m
GLOSSARY

**Complex solution.** The volumetric solution containing the quantitative sample of the complex under investigation.

**Dipyrrin.** A compound containing two pyrrole rings joined via a methine (–C=) group.

**Free-base.** Refers to the deprotonated dipyrrin, where the proton on the tautomeric pyrrole rings of the body of the dipyrrin has been removed.

**Heteroleptic.** A metal centre bearing two or more different ligands.

**Homoleptic.** A metal centre bearing two or more identical ligands.

**Redox Potential.** A measure, in volts (V), of the affinity of a chemical species for electrons. Indicative of the species ability to gain electrons and thereby be reduced.

**Trituration.** The purification of a solid by using a solid in which the impurity is soluble, but the desired compound is not (or vice versa).