# The synthesis and spectroscopy of dipyrrins and their metal complexes

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

**Doctor of Philosophy**
**in Chemistry**

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**For Mum and Dad**

# Abstract

Dipyrrin ligands can be considered as 'half-porphyrins'. They absorb light in the visible region due to a strongly allowed $\pi-\pi^*$ transition. With the energy crisis being one of the most important issues of our time, the strong absorption in the visible region endows dipyrrinato complexes with promise in solar energy conversion applications. The focus of this project was to undertake some fundamental synthesis and spectroscopy of dipyrrin ligands and dipyrrinato complexes for their applications in photochemical devices.

The well-known characteristics of Ru(II)-bipyridine chemistry were combined with the light absorbing properties and synthetic versatility of dipyrrin ligands to prepare and test a range of Ru(II)-dipyrrinato-bipyridine complexes as dyes for applications in dye-sensitised solar cells. The preliminary results of the solar cell measurements show evidence that the Ru(II)-dipyrrinato-bipyridine complexes show promise as light harvesters in solar energy conversion applications. A series of Re(I)-dipyrrinato complexes has also been designed and prepared for potential applications as catalysts in carbon dioxide reduction.

Metallodipyrrin complexes also exhibit strong exciton coupling. A library of transition metal dipyrrinato complexes has been prepared to investigate the exciton interactions in dipyrrin systems. Understanding the exciton interactions in dipyrrin systems and the ability to control the exciton interactions are desirable for improving the solar energy conversion efficiency of dye-sensitised solar cells containing Ru(II)-dipyrrinato-bipyridine complexes as the dye.

Raman spectroscopy and more specifically resonance Raman, as a technique for probing the excited state of dipyrrinato complexes, has largely been overlooked in the literature. Therefore the spectroscopy aspect of this thesis has a central focus on the Raman spectroscopy of dipyrrins, including the first full characterisation of dipyrrin ligands by Raman spectroscopy at a variety of wavelengths (visible and near infrared). Strong resonance enhancement was observed for the dipyrrin ligands, which lays the foundation for fundamental single-molecule SERS studies but also for a broad range of bioanalytical applications.

# Acknowledgements

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I must also acknowledge Dr Matthias Lein (Victoria University of Wellington) for always being available for assisting with the DFT calculations and Professor Keith Gordon (University of Otago) for allowing laboratory visits for data collection, Dr Attila Mozer and his students (Intelligent Polymer Research Unit, University of Wollongong) and Professor Yong Soo Kang and his students (Energy Materials Lab, Hanyang University) for solar cell measurements.

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*Fear is temporary, achievement is permanent*

# Table of Contents

# Abbreviations

| | |
|---|---|
| acac | acetylacetonato |
| aq | aqueous |
| Ar | aromatic |
| ATR | attenuated total reflection |
| bipy | 2,2'-bipyridine |
| BODIPY | boron difluoride complex of dipyrrin |
| Calcd | calculated |
| CD | circular dichroism spectroscopy |
| $CDCl_3$ | deuterated chloroform |
| conc. | concentrated |
| COSY | correlation spectroscopy |
| dcb | 4,4'-dicarboxy-2,2'-bipyridine |
| DDQ | 2,3-dichloro-5,6-dicyanobenzoquinone |
| DFT | density functional theory |
| DIPEA | *N*,*N*-diisopropylethylamine |
| dmcb | 4,4'-dimethoxycarbonyl-2,2'-bipyridine |
| DMF | *N*,*N*-dimethylformamide |
| DMSO | dimethyl sulfoxide |
| DSSC | dye-sensitised solar cell |
| EDD | electron density difference |
| EF | enhancement factor |
| en | 1,2-diaminoethane |
| equiv. | equivalent |
| ESI | electrospray ionisation |
| EtOH | ethanol |
| FF | fill factor |
| FT | fourier transform |
| FWHM | full-width half maximum |
| hfacac | hexafluoroacetylacetonato |
| HOMO | highest occupied molecular orbital |

| | |
|---|---|
| HPLC | high performance liquid chromatography |
| IC | internal conversion |
| IR | infra-red spectroscopy |
| ISC | intersystem crossing |
| ITO | indium tin oxide |
| $J_{sc}$ | short circuit current |
| LUMO | lowest unoccupied molecular orbital |
| MAD | mean average deviation |
| MALDI | matrix assisted laser desorption ionisation |
| MeCN | acetonitrile |
| MeOH | methanol |
| MLCT | metal-to-ligand charge transfer |
| $NEt_3$ | triethylamine |
| NMR | nuclear magnetic resonance |
| PDT | photodynamic therapy |
| Ph | phenyl |
| ppm | parts per million |
| RR | resonance Raman spectroscopy |
| RRIA | resonance Raman intensity analysis |
| RT | room temperature |
| S | singlet state |
| SERS | surface-enhanced Raman spectroscopy |
| SE(R)RS | surface-enhanced (resonance) Raman spectroscopy |
| SM-SERS | single molecule surface-enhanced Raman spectroscopy |
| T | triplet state |
| TD-DFT | time-dependent density functional theory |
| TFA | trifluoroacetic acid |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| TPP | tetraphenyl porphyrin |
| UV-Vis | ultraviolet-visible spectroscopy |
| $V_{oc}$ | open circuit voltage |
| $\mu$ | transition dipole moment |
| $\pi-\pi^*$ | pi-to-pi star |

All the work in this thesis was completed by Tracey M. McLean

except

**Chapter 2**

- Solid and solution state non-resonance Raman data of **34** were collected by Dr Cushla McGoverin at the University of Otago.
- Time-dependent DFT calculations of **34** were undertaken with the assistance of Dr Mark Waterland.
- TEM images of silver nanoparticles were collected at the Manawatu Microscopy and Imaging Centre with the assistance of Mr Doug Hopcroft.

**Chapter 3**

- After initial attempts of optimising the geometry of **43**, Dr Matthias Lein (Victoria University of Wellington) was contacted for assistance. He subsequently undertook all DFT and time-dependent DFT calculations of **43**.
- Mr Graham Freeman synthesised the azadipyrrin ligand **44**.
- With the exception of **38** and **44** all the crystal structures presented were determined by Associate Professor Shane Telfer.

**Chapter 4**

- Serena Smalley established the general synthetic protocol for Ru(II)-dipyrrinato complexes including the synthesis of **46** and **47**.
- Associate Professor Shane Telfer synthesised Ru(II)-dipyrrinato complex **46b**.
- All DFT calculations of **46**-**H** including the Mulliken analysis were undertaken by Dr Mark Waterland.
- All DFT calculations of **46** were undertaken by Sam Lind (University of Otago).
- Resonance Raman data at excitation wavelengths 413 nm, 444 nm and 532 nm were collected by Sam Lind and Deirdre Cleland (University of Otago).
- Solid state absorption spectroscopy on $TiO_2$ or NiO, device fabrication and solar cell testing were undertaken by members of Dr Attila Mozer's research group (Intelligent Polymer Research Institute, University of Wollongong) and

Professor Yong Soo Kang's research group (Energy Materials Lab, Hanyang University).

**Chapter 5**

- Janice Moody established the general synthetic protocol for Re(I)-dipyrrinato complexes including the synthesis and characterisation of **59**, **60**, **64**, and **70**.
- Serena Smalley developed the synthesis of dipyrrin ligand **61**.

Publications by Tracey M. McLean related to this PhD thesis:

- McLean, T. M., Waterland, M. R., Telfer, S. G., Gordon, K. C., McGoverin, C. M., Raman spectroscopy of dipyrrins: non-resonant, resonant, and surface-enhanced cross-sections and enhancement factors. *J. Raman Spec.* **2011**, 42, 2154-2164.
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- McLean, T. M., Moody, J. L., Waterland, M. R., Telfer, S. G., Luminescent Re(I)-dipyrrinato complexes. *Inorg. Chem.* **2012**, 51, 446-455.