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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 dipyrinato complexes with promise in solar energy conversion applications. The focus of this project was to undertake some fundamental synthesis and spectroscopy of dipyrin ligands and dipyrinato 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 dipyrin ligands to prepare and test a range of Ru(II)-dipyrinato-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)-dipyrinato-bipyridine complexes show promise as light harvesters in solar energy conversion applications. A series of Re(I)-dipyrinato complexes has also been designed and prepared for potential applications as catalysts in carbon dioxide reduction.

Metallo-dipyrin complexes also exhibit strong exciton coupling. A library of transition metal dipyrinato complexes has been prepared to investigate the exciton interactions in dipyrin systems. Understanding the exciton interactions in dipyrin 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)-dipyrinato-bipyridine complexes as the dye.

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

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Fear is temporary, achievement is permanent

Table of Contents

	<i>Page</i>
Abstract.....	i
Acknowledgements	ii
Table of Contents.....	iv
Abbreviations.....	x
Disclaimer.....	xii
Publications by Tracey McLean	xiv
Chapter 1: Introduction	1
1.1 Perspective.....	1
1.2 Dipyrins and their complexes.....	3
1.2.1 General background and structure of dipyrins	3
1.2.2 Synthesis of dipyrins	4
1.2.3 Dipyrinato complexes	6
1.2.4 Complexation geometries of dipyrinato complexes.....	6
1.2.5 BF ₂ -dipyrinato complexes.....	8
1.2.6 Azadipyrins and azadipyrinato complexes	9
1.2.7 Chemical manipulations of dipyrinato complexes	10
1.2.8 Electronic properties of dipyrins	12
1.2.9 Electronic properties of dipyrinato complexes.....	13
1.2.10 Recent advances in dipyrin chemistry.....	15
1.3 Raman spectroscopy	18
1.3.1 Historical background and theory of Raman spectroscopy	18
1.3.2 Basic theory and principles of Raman spectroscopy	19
1.3.3 Magnitude of Raman scattering.....	21
1.3.4 Resonance Raman spectroscopy and surface-enhanced Raman spectroscopy	22
1.3.4.1 Introduction to resonance Raman spectroscopy (RR)	23
1.3.4.2 Introduction to surface-enhanced Raman spectroscopy (SERS).....	24
1.4 Electronic absorption spectroscopy	26
1.5 Fluorescence spectroscopy	27

1.6 Thesis structure.....	29
Chapter 2: Raman spectroscopy of dipyrrens: non-resonant, resonant, and surface-enhanced cross-sections and enhancement factors	31
2.1 Introduction	31
2.2 Objectives of this work	32
2.3 Background to Raman cross-sections.....	32
2.4 Experimental details	34
2.4.1 Computational procedures	34
2.4.2 Experimental procedures	35
2.4.2.1 Synthesis of dipyrren ligands 34 and 35	35
2.4.3 General procedures	35
2.4.3.1 Preparation of samples for non-resonance Raman and resonance Raman spectroscopy	35
2.4.3.2 Preparation of silver nanoparticles	35
2.4.3.3 Preparation of samples for SERS	35
2.4.3.4 Raman cross-sections	36
2.5 Results and discussion	36
2.5.1 Synthesis of dipyrren ligands	36
2.5.2 Absorption spectrum and TD-DFT calculations	37
2.5.3 Non-resonance Raman spectroscopy	41
2.5.4 Resonance Raman spectroscopy, resonance cross-sections and enhancement factors	45
2.5.5 Surface-enhanced Raman spectroscopy, surface-enhanced cross-sections and enhancement factors	49
2.6 Summary.....	55
2.7 Future work.....	56
Acknowledgements	56
Chapter 3: Exciton interactions in metallodipyrrens	57
3.1 Introduction	57
3.2 Background to exciton coupling.....	59
3.3 Exciton coupling in dipyrrenato complexes.....	63
3.4 Objectives of this work and target complexes.....	65

3.5 Experimental procedures	66
3.5.1 Computational procedures	66
3.5.2 Experimental procedures	67
3.5.2.1 Synthesis of dipyrinato complexes 36-42 and 12	67
3.5.2.2 Synthesis of azadipyrinato complex 43	71
3.6 Results and Discussion	71
3.6.1 Synthesis	71
3.6.2 Complexation geometries and the orientation of the transition dipole moments.....	74
3.6.3 Exciton effects in the absorption spectra of dipyrinato complexes.	80
3.6.4 Exciton effects in azadipyrinato complexes	84
3.6.5 DFT investigations of the exciton effects of 43	85
3.7 Summary.....	91
3.8 Future work.....	92
3.8.1 Exciton coupling in Ru(II)-dipyrinato complexes.....	92
3.8.2 Further investigations into the exciton effects of 43 and other azadipyrinato complexes.....	92
Acknowledgements	93
Chapter 4: Ru(II)-dipyrinato complexes and their applications.....	94
4.1 Introduction	94
4.2 Ru(II) complexes as dyes in DSSCs and as water splitting photocatalysts.....	95
4.2.1 Dye-sensitised solar cells (DSSCs)	95
4.2.2 Ruthenium based DSSCs.....	96
4.2.3 Water splitting devices	98
4.2.4 Essential dye characteristics and previous Ru(II)-dipyrinato complexes	100
4.3 Objectives of this work and target complexes.....	104
4.3.1 Target DSSC complexes.....	104
4.3.2 Other targets	107
4.4 Experimental details	108
4.4.1 Computational procedures.....	108
4.4.2 Experimental procedures	108
4.4.2.1 Synthesis of dipyrin ligands 52 and 56	108

4.4.2.2 Synthesis of complexes 49-51 and 53-55	109
4.4.3 General procedures	114
4.4.3.1 Resonance Raman solutions	114
4.4.3.2 Electrochemistry	114
4.4.3.3 Solid state UV-Vis, device fabrication and solar cell testing.....	115
4.5 Results and Discussion	115
4.5.1 Synthesis	115
4.5.2 Characterisation	120
4.5.3 Analysis of the electronic structure of 46	122
4.5.4 Time-Dependent DFT (TD-DFT) calculations of 46 and 46-H	123
4.5.5 Absorption spectroscopy and TD-DFT calculations	124
4.5.6 Resonance Raman spectroscopy.....	133
4.5.7 Resonance Raman intensity analysis (RRIA).....	136
4.5.8 Excited state dynamics in other dipyrinato complexes	140
4.5.9 Application of Ru(II)-dipyrinato complexes in solar energy conversion.....	142
4.5.10 Solid state absorption spectroscopy.....	143
4.5.11 Electrochemistry	145
4.5.12 Solar cell testing	150
4.6 Summary.....	153
4.7 Future work.....	154
Acknowledgements	156

Chapter 5: Luminescent Re(I)-dipyrinato complexes and their applications..... 157

5.1 Background to Re(I)-polypyridine complexes	157
5.1.1 Applications of Re(I)-polypyridyl complexes.....	157
5.1.1.1 Catalytic reduction of CO ₂	157
5.1.1.2 Photochemical ligand substitution (PLS) reactions.....	158
5.1.1.3 Solar cells	159
5.2 Objectives of this work and target complexes.....	159
5.3 Experimental details	161
5.3.1 Computational procedures.....	161
5.3.2 Experimental procedures	162

5.3.2.1 Synthesis of dipyrin ligands	162
5.3.2.2 Synthesis of <i>fac</i> -[ReL(CO) ₃ Cl][NEt ₃ H], 59 and <i>fac</i> -[ReL(CO) ₃ PR ₃] 60 and 62-66	162
5.3.2.3 Synthesis of [ReL(CO) ₂ (PR ₃) (PR' ₃)], 67-73	167
5.3.2.4 Photochemical synthesis of [ReL(CO) ₂ (PPh ₃)(CD ₃ CN)], 74	171
5.3.3 General procedures	172
5.3.3.1 Resonance Raman solutions	172
5.3.3.2 Fluorescence protocol.....	172
5.3.3.3 Relative quantum yield measurements	172
5.3.3.4 Quenching studies.....	173
5.3.3.5 Photochemical ligand substitution (PLS) reactions.....	174
5.4 Results and Discussion	174
5.4.1 Synthesis	174
5.4.2 NMR spectroscopy	176
5.4.3 Electronic and vibrational spectroscopy and TD-DFT calculations	178
5.4.4 Photochemical ligand substitution (PLS) reactions.....	192
5.5 Summary.....	196
5.6 Future work.....	197
Acknowledgements	197
References.....	198
Appendix A.....	218
A1 Resonance Raman theory	218
A1.1 Albrecht theory of resonance Raman	218
A1.2 Resonance Raman Intensity Analysis (RRIA)	220
A2 Albrecht theory applied to SERS.....	221
Appendix B.....	223
B1 Basis sets and frequency calculations	223
B2 Conversion of molar absorptivity (ϵ) to oscillator strength(f)	225
B3 TD-DFT studies of 34	226

Appendix C	234
C1 Resonance Raman of 43	234
Appendix D	235
D1 Electrochemistry methods	235
D2 Cyclic voltammetry	236
D2.1 Cyclic voltammograms of Ru(II)-dipyrrinato and Rh(III)-dipyrrinato complexes.....	236
D2.2 Cyclic voltammograms of dipyrin ligands	239
D3 Solid state absorption spectroscopy.....	240
D4 Solar cell device fabrication	240
D5 Current-voltage curves.....	243
D5.1 Current-voltage curves on TiO ₂	243
D5.2 Current-voltage curves on NiO.....	246
D6 Structure of the reference dyes	249
Appendix E	250
E1 ¹ H NMR spectra	250
E2 Absorption spectra	251
E3 Resonance Raman spectroscopy	253
E4 Time-dependent DFT studies	259
E5 Excitation and emission spectra	262
E6 Photochemical ligand substitution of 60	269
Appendix F (General Experimental Details)	274
F1 NMR spectroscopy	274
F2 Mass spectrometry.....	274
F3 Microanalysis	274
F4 UV-Vis absorption spectroscopy.....	274
F5 Fluorescence spectroscopy	275
F6 Infrared spectroscopy (IR).....	275
F7 Electrochemistry.....	275
F8 Raman spectroscopy.....	275
F9 Solvents and reagents	276

Abbreviations

acac	acetylacetonato
aq	aqueous
Ar	aromatic
ATR	attenuated total reflection
bipy	2,2'-bipyridine
BODIPY	boron difluoride complex of dipyrin
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	<i>N,N</i> -diisopropylethylamine
dmcb	4,4'-dimethoxycarbonyl-2,2'-bipyridine
DMF	<i>N,N</i> -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
μ	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 TiO₂ 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)-dipyrinato complexes including the synthesis and characterisation of **59**, **60**, **64**, and **70**.
- Serena Smalley developed the synthesis of dipyrin 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 dipyrrens: non-resonant, resonant, and surface-enhanced cross-sections and enhancement factors. *J. Raman Spec.* **2011**, 42, 2154-2164.
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