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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

MASSEY UNIVERSITY

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2012
For Mum and Dad
Abstract

Dipyrin 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.

Metallodipyrin 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.
Acknowledgements

I would like to take the opportunity to thank the large number of people who have contributed to my PhD research and thesis. Firstly, I would like to thank my supervisors Associate Professor Shane Telfer and Dr Mark Waterland for their enthusiasm, encouragement, and patience throughout my research years. Thanks for challenging me when I needed it but most importantly always being there when I needed help or advice. Thanks also for the time and energy you have put into my project.

Thanks also to all past and present members of the Telfer/Waterland research empire and other lab colleagues. Many interesting discussions were had over the past few years, some even related to chemistry. Specifically I must thank Dr Carl Otter for the helpful chemistry discussions relating to my project and Dave Lun for being the all-round go to guy for assistance with lab equipment, mass spectrometry, and many other chemistry problems.

A special mention must also go to Dr Pat Edwards for assistance with specialised NMR experiments, Dr Wayne Campbell and Dr Vyacheslav Filichev for their assistance with establishing the new fluorimeter protocol, Nessha Wise for her assistance with undertaking electrochemistry experiments and Professor Simon Hall for answering many electrochemistry related questions. I must also thank Jamie Withers for assisting me with preparing some of the figures presented in this thesis.

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.

I would like to acknowledge the financial support from Massey University for a Doctoral scholarship and the MacDiarmid Institute to allow me to undertake this project; and the Institute of Fundamental Sciences Postgraduate travel fund, Royal Society of
New Zealand travel grants and Claude McCarthy Fellowship for travel awards to conferences in Dunedin and Japan, and a research visit to the University of Hong Kong.

I have utilised the expertise of many past and present technical and departmental staff from the Institute of Fundamental Sciences and I would like to thank them for their assistance during my research and thesis writing.

Finally, I must thank my family and partner (Kyle) for their support and encouragement over the last few years, and particularly thanks to Mum for flying me home for long weekends on the farm. As many of my friends will know writing a thesis is exceptionally difficult and stressful so thanks for the support when I needed it and the distraction when I needed a break.

Fear is temporary, achievement is permanent
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<tr>
<td>acac</td>
<td>acetylacetonato</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous</td>
</tr>
<tr>
<td>Ar</td>
<td>aromatic</td>
</tr>
<tr>
<td>ATR</td>
<td>attenuated total reflection</td>
</tr>
<tr>
<td>bipy</td>
<td>2,2'-bipyridine</td>
</tr>
<tr>
<td>BODIPY</td>
<td>boron difluoride complex of dipyrrin</td>
</tr>
<tr>
<td>Calcd</td>
<td>calculated</td>
</tr>
<tr>
<td>CD</td>
<td>circular dichroism spectroscopy</td>
</tr>
<tr>
<td>CDCl₃</td>
<td>deuterated chloroform</td>
</tr>
<tr>
<td>conc.</td>
<td>concentrated</td>
</tr>
<tr>
<td>COSY</td>
<td>correlation spectroscopy</td>
</tr>
<tr>
<td>dcb</td>
<td>4,4'-dicarboxy-2,2'-bipyridine</td>
</tr>
<tr>
<td>DDQ</td>
<td>2,3-dichloro-5,6-dicyanobenzoquinone</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DIPEA</td>
<td>N,N-diisopropylethylamine</td>
</tr>
<tr>
<td>dmcb</td>
<td>4,4'-dimethoxycarbonyl-2,2'-bipyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>DSSC</td>
<td>dye-sensitised solar cell</td>
</tr>
<tr>
<td>EDD</td>
<td>electron density difference</td>
</tr>
<tr>
<td>EF</td>
<td>enhancement factor</td>
</tr>
<tr>
<td>en</td>
<td>1,2-diaminoethane</td>
</tr>
<tr>
<td>equiv.</td>
<td>equivalent</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionisation</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FT</td>
<td>fourier transform</td>
</tr>
<tr>
<td>FWHM</td>
<td>full-width half maximum</td>
</tr>
<tr>
<td>hfacac</td>
<td>hexafluoroacetylacetonato</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
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</table>
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 46
- 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)-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:


