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Dipyrrin Complexes as Dyes for Dye-Sensitised Solar Cells

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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 3×10^{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 dipyrrens, described most simply as "half a porphyrin", which possess many of the attractive qualities for DSSC dyes. Although there are no examples of ruthenium-dipyrren 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 dipyrren 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 ^1H 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 dipyrin, thus aiding future studies into the use of dipyrins as dyes for DSSC's. This thesis summarises the findings of the above outlined research project.

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ABBREVIATIONS AND SYMBOLS

acac. acetylacetonone

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

BODIPY. Borondifluoride dipyrin

CH₃OH. Methanol. Also abbreviated to MeOH. Deuterated methanol is represented as MeOD or CD₃OD.

CHCl₃. Chloroform. Deuterated chloroform is represented as CDCl₃

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

DMF. Dimethylformamide

DMSO. Dimethylsulfoxide

dp. Dipyrin

dpm. Dipyrromethane

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.

NEt₃. Triethylamine

NMR. Nuclear magnetic resonance

phen. Phenanthroline (1,10-phenanthroline, unless otherwise stated)

ppm. Parts per million

Ru(II). Ruthenium(II), Ru²⁺

SCN. Thiocyanate

SEM. Scanning electron micrograph

TCO. Transparent conducting oxide

TFA. Trifluoroacetic acid

THF. Tetrahydrofuran

TiO₂. Titanium dioxide

TLC. Thin layer chromatography

TnBA. Tetra-n-butyl ammonium

UV. Ultraviolet

1-T. Transmittance

A. Absorbance

Bu. Butyl group i.e C₄H₉

¹³C. Carbon. In reference to NMR spectroscopy utilising the ¹³C isotope of carbon.

e⁻. Electron

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

hν. Light, photons

I/I₃⁻. 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 = 10⁹ m

P_{max}. The maximum quantity of power supplied (watts)

P_{source}. Quantity of power supplied from the power source (watts)

R. generic functional group

s⁻¹. per second, unit.

V. volts – the unit for voltage

V_{oc}. Open-circuit voltage (V)

ΔE. Change in energy (Joules). Also appears in the text as ΔE_n 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 (%)

λ_{ex}. Excitation wavelength (nm)

λ_{max}. Wavelength maximum or energy maximum (nm)

μm. Micrometres = 10⁶ 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 ($-\text{C}=\text{}$) 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*).