

The Synthesis and Characterisation of Polyhedral Oligomeric Silsesquioxane Bound Chromophores

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Thesis submitted to the Faculty of Science and Engineering of Flinders University in
partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

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September 2008

Adelaide, South Australia

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ABSTRACT

This research involved the synthesis and characterisation of a range of optically active polyhedral oligomeric silsesquioxane (POSS) compounds.

POSS precursor compounds containing functional groups required for subsequent attachment of the desired functional groups have been synthesised. Examples of such precursor compounds include mono-functionalised POSS compounds with periphery aldehyde, azide, amino and pyridyl functional groups.

A variety of POSS compounds, functionalised with a range of optical functionalities, including optical limiters such as fulleropyrrolidine and iminofullerene, and dyes and pigments, including naphthalene, biphenyl, perylene, pyrene and porphyrin have been synthesised.

The reaction of mono-functionalised POSS aldehydes with fullerene (C_{60}) in the presence of N-methylglycine yielded the desired POSS fulleropyrrolidines, whilst reaction of mono-functionalised POSS azide with C_{60} yielded POSS iminofullerenes. All POSS fullerene compounds were characterised by power limiting measurements, exhibiting comparable power limiting to that of parent C_{60} .

The microwave condensation of mono-amino POSS with a range of mono- and bis-anhydrides yielded the POSS imide compounds, which were characterised by UV-Vis and fluorescence spectrophotometry. The perylene POSS imide derivative was further characterised by single crystal x-ray crystallography. The naphtha and biphenyl POSS imides exhibited extremely weak fluorescence, whilst the perylene

POSS imide displayed particularly strong fluorescence, with a quantum yield approaching unity.

The incorporation of a pyridyl group on the periphery of a mono-functionalised POSS cage allowed for the synthesis of the first porphyrin functionalised POSS compound. Mono-porphyrin POSS exhibited comparable absorption properties to other pyridyl ligated ruthenium porphyrins.

Mono-functionalised pyrene POSS compounds were prepared through the reaction of 1-pyrene acid chloride with mono(3-aminopropyl)POSS. This synthetic pathway offered a convenient route to mono-functionalised pyrene POSS, in preference to the multi-substitution associated with Heck coupling. Mono-pyrene POSS was determined to be strongly fluorescent, exhibiting a high quantum yield of fluorescence.

ACKNOWLEDGEMENTS

I would like to thank my supervisors Prof. Janis Matisons and Assoc. Prof. George Simon for the opportunity to undertake this project and their support and assistance. Additionally, I would like to express gratitude to Dr Mark Fisher for his support in the latter stages of the project and the opportunity to work on the biodiesel program, which taught me about chemistry in the real world. I must also thank Dr Stephen Clarke for always making me focus the final hurdle and providing part or my scholarship towards the latter stages the project.

Thanks to Dr Marek Samoc and Dr Anna Samoc at ANU for their help in obtaining the power limiting data and also to Dr Brian Skelton for the x-ray crystallography measurement.

I would also like to thank all the past and present members of the Nanomaterials group at Flinders University. Special thanks must go to Simon Mathew for all his help, ideas and encouragement over my time at Flinders, and for proving that the best ideas are often borne at the pub over a drink. I would also like to say cheers to Rachel Pillar for her help in editing parts of this thesis; it was much appreciated, even if she is a physical chemist.

To my family and Fee, it's been a rough time these past few years but you guys helped me through it, without your love and support there is no way I could have finished this thesis.

Finally, I'd like to dedicate this thesis in part to my late brother in law, Darren. Thanks for the memories mate, I wish you were here to see me finally finish this; it's been a constant source of amusement between us over the years and life isn't the same without you.

‘I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text’

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(D. J. CLARKE)

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ABBREVIATIONS AND PARAMETER DEFINITIONS

ϵ	(epsilon) molar extinction coefficient
λ	(lambda) wavelength
\AA	Angstrom
δ	(delta) chemical shift in ppm
ppm	parts per million
${}^xJ_{A-B}$	coupling constant between nuclei A and B over x bonds in Hz
FTIR	Fourier Transform InfraRed
NMR	Nuclear Magnetic Resonance
UV-VIS	Ultraviolet visible
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
Ph	Phenyl
Cy	Cyclohexyl
Cp	Cyclopentyl
λ_{\max}	wavelength of maximum absorption
λ_{exc}	wavelength of excitation
Φ_F	quantum yield
κ	dielectric constant
M_n	mean molecular weight
<i>o</i>	ortho
<i>m</i>	meta
<i>p</i>	para
vs	very strong
s	strong
m	medium
w	weak