The Synthesis and Characterisation of Polyhedral Oligomeric Silsesquioxane Bound Chromophores

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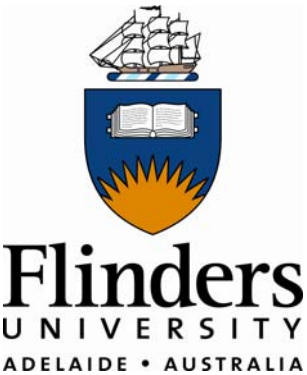
in

CHEMISTRY

Prof Janis Matisons

Prof George Simon



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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.

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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
Å	Angstrom
δ	(delta) chemical shift in ppm
ppm	parts per million
$^{x}J_{A-B}$	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
o	ortho
m	meta
p	para
vs	very strong
s	strong
m	medium
w	weak