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Porphyrins for Surface Modification

A Thesis Presented in Partial Fulfilment of the
Requirements for the Degree of
Doctor of Philosophy
in
Chemistry
at Massey University, Palmerston North,
New Zealand.

Wayne Mason Campbell

2001

MASSEY UNIVERSITY

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Abstract

The controlled synthesis of a variety of benzoic acid porphyrins ranging from monomers to arrays for the modification of TiO_2 and GaAs semiconductors, and sulfur functionalised porphyrin monomers for attachment to GaAs and Au surfaces was achieved. A semi-quantitative study of the photosensitisation of TiO_2 by the porphyrin acids was carried out.

The syntheses of β-styryl linked porphyrin benzoic acids and some *meso*-substituted benzoic acid porphyrins was successfully carried out employing Wittig chemistry and classical porphyrin-forming condensation reactions with appropriate formyl methyl esters. Hydrolysis of the resulting porphyrin esters provided a facile and reliable acid synthesis, particularly where multi-step reactions were necessary. It was also demonstrated that acid functionality on porphyrins could be generated from aldehydes via esters, even though direct oxidation of the aldehydes to acids could not be achieved. The syntheses of "dipole" and "collinear" diporphyrins were achieved, providing two different porphyrin light harvesting arrays for evaluation on semiconductor surfaces. As a result of the synthesis of a new linear diporphyrin Building Block C, an alternative pathway to the controlled syntheses of mixed-metal and mixed-porphyrin arrays was achieved. This provided an alternative strategy for the controlled placement of three different metals into three different porphyrins of a linear triporphyrin, pentaporphyrin and a larger star-shaped nonaporphyrin.

The exploitation of the stepwise controlled synthesis of the triporphyrin systems was expanded to include mixed-porphyrin systems synthesised with a unique tetraester porphyrin phosphonium salt. This phosphonium salt afforded mixed-diporphyrin and mixed-triporphyrin arrays, which were hydrolysed to give "sticky" mixed-diporphyrin and triporphyrin acid arrays.

An alternative milder and higher yielding stepwise Wittig method was developed for the synthesis of a star shaped TXP pentaporphyrin. This new method involving milder base conditions gives advantages over the traditional acid catalysed approach developed in these laboratories. It is now possible to build these arrays in a stepwise manner with

acid labile metals present in the porphyrin moieties. Access to the controlled synthesis of "sticky" mixed-pentaporphyrin arrays was then achieved using this new methodology.

With the synthesis of a variety of unique benzoic acid functionalised porphyrin monomers and multiporphyrin array systems, evaluation of their performance in the dye-sensitised TiO_2 Grätzel cell was carried out. The development of a reliable solar cell testing apparatus and procedures required to assess the solar cell performance of these chromophores is presented. None of the conditions employed have been optimised, but insights into the significance of the porphyrin photoelectrochemical cell variables has been obtained. It was determined that the porphyrin acids are better photosensitisers than their salts, and that Zn(II) metalloporphyrins performed best as dyes. The results also suggest that Cu(II) metalloporphyrins are worth pursuing in future where long term stability of the chromophores is required in solar cells. It was also found that adsorption solvent choice, electrolyte composition and dye concentrations are all critical to cell performance, and should all be optimised in future studies. The tetraaryl β-substituted monoporphyrin acids were found to have a significant advantage over the multiporphyrin arrays and other monoporphyrins synthesised and examined in this work.

A variety of new disulfide porphyrins and some new 2- and 3-thienylporphyrins were successfully synthesised. A new class of terthiophene-appended porphyrins was also synthesised. Using a combination of Wittig chemistry and classical condensation reactions, β-substituted, and bis- and tetra-*meso*-porphyrin variants were synthesised and characterised. Both the bis- and tetraterthienylpoprhyrins were isolated as mixtures of atropisomers.

Acknowledgments

I would like to thank my Supervisors, Associate Professor Dr. David Officer and Professor Dr. Anthony Burrell for their guidance and assistance over the last few years. A special thanks to Bob (David, for hours of proof reading), Geedha and Sophie for friendship and nutrition, and Esther for mountain biking excursions. Also thanks to Dr. Simon Hall for help with electrochemical aspects of the thesis.

Thanks to all the members of the Porphyrin Research Group and Laboratory (past and present) Warwick Belcher, Esther Blandford, Gavin Collis, Roger Edie, Daina Grant, Sanjeev Gambhir, Jo-Anna Hislop, Carolin Huhn, Steven Kennedy, David Lunn, Rekha Parshot, Alex Park, Paul Plieger, Sonya Scott, Emma Smith, Andrew Steedman, Bruno Therrien and Kirstie Wild. They have made it a rewarding and interesting learning experience, ensuring there was never a dull moment to be had. I would also like to acknowledge the other cohabitants of the laboratory, Dr. Dave Harding and his research group and other departmental students.

I am grateful for the assistance of Dr. Pat Edwards (NMR spectroscopy, Massey University), the IFS Mechanical (Barry, Noel and Steve) and Electronic Workshops (Udo, Peter and Keith), and also Terry and Penny from IFS Chemistry Stores. I also would like to take this opportunity to thank all other Institute and Departmental staff members for their help during my PhD and who with their team effort make the place run.

I would like to acknowledge important financial support provided by the Public Good Science Fund (PGSF MAU602).

A big thanks to my flatmates (Anna and Malcolm) who over the last few years who have had to put up with the mood swings associated with the ups and downs of research. Lastly, I would like to acknowledge my family and friends, especially Dad and Nancy for all their support and interest during the last few years.

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Abbreviations

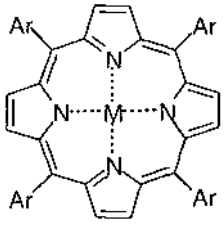
AFM	atomic force microscopy
AM1.0	air mass 1.0 (shortest path length for solar radiation through the atmosphere)
AM1.5	air mass 1.5 (1.5 times the shortest path length for solar radiation through the atmosphere)
AR	analytical reagent
app	apparent
aq.	aqueous
Ar	aryl group
avg	average
Au	gold
BAP	5,15-bis-*aryl*-porphyrin
BAcP	bis-*acetal*-porphyrin
BCP	bis-*carboxy*-porphyrin
BEP	bis-*ester*-porphyrin
BDP	bis-*disulfide*-porphyrin
BFP	bis-*formyl*-porphyrin
BP	3,5-di-*tert*-butylphenyl group
B2TP	bis-2-*thienyl*-porphyrin
B3TP	bis-3-*thienyl*-porphyrin
BTTP	bis-*terthienyl*-porphyrin
Calcd	calculated
CHCA	α-cyano-4-hydroxycinnamic acid
conc.	concentrated
COSY	correlated spectroscopy
d	doublet
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-dichloroethane
DCM	dichloromethane or CH_2Cl_2
DMF	*N*,*N*-dimethylformamide
DMSO	dimethylsulfoxide

dia	circular diameter
DPM	dipyrrylmethane
EI	electron ionisation
eq	equivalent
ES	electrospray
Et	ethyl
Et_2O	diethyl ether
EDW	electron donating group
Et_3N	triethylamine
EWG	electron withdrawing group
FAB	fast atom bombardment
FET	field-effect-transistor
FF	fill factor (ratio of the maximum output of the photovoltaic device, to the product of I_{sc} and V_{oc})
GaAs	gallium arsenide
GP	general-purpose reagent
h	hours
hept	heptet
hex	hextet
HMTA	hexamethylenetetramine
HR	high resolution
HRMS	high resolution mass spectrometry
HOMO	highest occupied molecular orbital
IPCE	incident photon-to-current conversion efficiency
I_{sc}	short circuit current
ITO	indium-tin-oxide (conductive glass coating)
LUMO	lowest unoccupied molecular orbital
LR	low resolution
LRMS	low resolution mass spectrometry
min	minutes
M	mol L^{-1}
M	a metal ion
m	multiplet, milli
MALDI	matrix assisted laser desorption ionisation spectroscopy

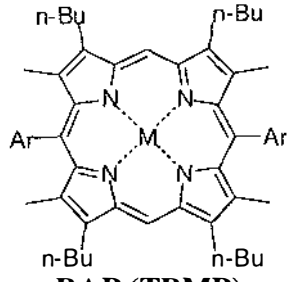
Me	methyl
MeOH	methanol
mp	melting point
MS	mass spectrometry
NMR	nuclear magnetic resonance
[O]	oxidation
oct	octet
P(A-D)	TiO_2 coated ITO glass (batches A-D)
Pc	phthalocyanine
PEC	photoelectrochemical cell
pent	pentet
Ph	phenyl
ppm	parts per million
ps	phosphonium salt
q	quartet
[R]	reduction
R_f	retention factor
RT	room temperature
RO	reverse osmosis
ROSEY	rotating frame overhauser enhancement spectroscopy
sat.	saturated
SC	semiconductor
SEM	scanning electron microscopy
sh	shoulder
SP	"sticky" porphyrin
SS	steady state
STM	scanning tunnelling microscopy
t	triplet
TAcP	tetra-*acetal*-porphyrin
TAP	5,10,15,20-tetra-*aryl*-porphyrin
TBM	tetrabutyltetramethyl
TBMP	2,8,12,18-tetra-*n*-butyl-3,7,13,17-tetramethylporphyrin
TBP	5,10,15,20-tetrakis(3',5'-di-*tert*-butylphenyl)porphyrin
TCA	trichloroacetic acid

TCP	tetra-4'-*carboxy*-porphyrin
T3CP	tetra-3'-*carboxy*-porphyrin
T3,5CP	tetra-3',5'-*dicarboxy*-porphyrin
TEP	tetra-*4'-ester*-porphyrin
T3EP	tetra-*3'- ester*-porphyrin
T3,5EP	tetra-*3',5'-diester*-porphyrin
TFA	trifluoroacetic acid
TFP	tetra-*4'-formyl*-porphyrin
THF	tetrahydrofuran
TiO_2	titanium dioxide
TLC	thin layer chromatography
TMS	tetramethylsilane
TOF	time-of-flight
TOPP	5,10,15,20-tetra(4-octylphenyl)porphyrin
TPP	5,10,15,20-tetraphenylporphyrin
TR	all-*trans*-retinoic acid
TTTP	tetra-*3''-terthienyl*-porphyrin
TXP	tetra-*xylyl*-porphyrin or 5,10,15,20-tetrakis(3',5'-dimethylphenyl)porphyrin
UV-vis	ultraviolet-visible spectroscopy
Xyl	xylyl (3,5-dimethylphenyl group)
V_{oc}	open circuit voltage

TAP and BAP Index



TAP



BAP (TBMP)

TAP	Ar	#
TPP	Ph	**1**
TXP	Xyl	**2**
TBP	BP	**3**
TEP	$-CO_2Me$	**85**
TCP	$-CO_2H$	**8**
T3EP	Est	**93**
T3CP	Acid	**95**
T3,5EP		**74**
T3,5CP		**75**
TAcP		**114**
TFP	$-CHO$	**110**
TTTP		**139**

BAP	Ar	#
BAcP		**62**
BFP	$-CHO$	**76**
BEP	$-CO_2Me$	**60**
BCP	$-CO_2H$	**73**
BDP		**150**
B2TP		**134**
B3TP		**135**
BTTP		**138**

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