

Molecular Design and Reaction Mechanisms

There are four areas of research under the umbrella of this title, which range across synthetic and mechanistic aspects of inorganic coordination chemistry and organic chemistry.

- **Energetic materials** - electrochemical studies toward environmental remediation.
- **Macrocycles** - synthetic organic, coordination chemistry and metallo-supramolecular chemistry.
- **Supramolecular construction** - molecular host-guest chemistry of cucurbit[n]uril and associated assembly processes and physical properties.
- **An analysis of the reaction processes in the above areas**, with a view toward mechanistic understanding and the implementation of synthetic techniques in molecular design.



Dr Lynne Wallace in her laboratory.

Members

Academic Staff:

Dr Lynne Wallace (l.wallace@adfa.edu.au) BSc *Edin.*, PhD ANU

Dr Anthony Day (a.day@adfa.edu.au) BSc, PhD ANU

Dr Mokhesur Rahman (m.rahman@adfa.edu.au) MSc *Rajsh.*, Dipl Chem, Dr rer nat *Regensburg*, MRACI, CChem

Emeritus Professor:

Emeritus Professor Greg Jackson BSc (Hons), PhD *Melb.*, DSc *UNSW*, FRACI, CChem

Research Assistants:

Dr Damian Buck (part time, Feb-Jul 2009) BSc PhD ANU

Dr T.D. Suja (part-time, Jul-Dec 2009) BSc, MSc *Calicut*, PhD *Kerala*

Visiting Fellow:

CAPT Mark Bali (Sept 2009-Feb 2010)

Research Students:

Kirsten Randle - Research Topic - Detection of peroxide based explosives.

CAPT Mark Bali - Research Topic - Neutralisation of explosives (due to start a MSc in Feb 2010).

Feng Wu - Research Topic - Development of new cucurbiturils and biomimetic catalytic processes.

Fanfei Li is jointly supervised by A. Day and G. Collins (Biological Chemistry group) - Research Topic - Dinuclear ruthenium complexes as therapeutic agents.

Research Collaborators:

Dr D. Armitt (DSTO, Weapons Systems Division)

Assoc. Prof. G. Collins (PEMS, UNSW@ADFA)

Assoc. Prof. C. Harb (SEIT, UNSW@ADFA)

Dr P. Kirkbride (Australian Federal Police)

Prof. C. Lennard (University of Canberra)

Dr A. Provatas (DSTO Weapons Systems Division)

Prof. T. Zhu (Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, University of Guizhou, Guiyang, PR China)

Current Research

Aspects of supramolecular chemistry utilizing cucurbit [n]uril

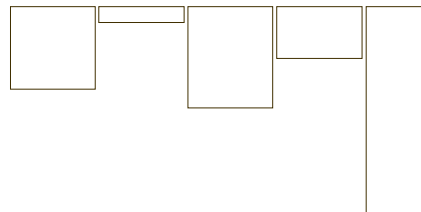
Dr Anthony Day - cross collaboration on some topics with Dr Lynne Wallace and/or Assoc. Prof. Grant Collins

Development of new methods for explosives and contraband detection based on host-guest interactions

Dr Anthony Day, Dr Lynne Wallace, Kirsten Randle, Prof. Chris Lennard, Dr Paul Kirkbride

Electrochemical remediation processes for treatment of wastewater from explosives manufacturing

Molecular Design and Reaction Mechanisms



Dr Lynne Wallace & Dr Anthony Day

NTO (nitrotriazolone) is a new insensitive explosive that may replace RDX, the current military standard, in some applications. Due to its high water solubility, the wastewater from its manufacture cannot be treated by conventional means. We have been investigating alternative remediation methods based on electrochemical treatment for NTO, which may also be applicable for other organic explosives. These electrochemical methods are more environmentally friendly, since no additional chemical loading is required, and the only input is electricity.

Organic power in organic packaging

Dr Anthony Day & Dr T.D. Suja

Synthesis and characterization of new high nitrogen compounds

Dr Lynne Wallace, Dr Anthony Day, Dr Arthur Provas

Insensitive high explosives (IHEs) are an important area of research, due to the increased requirement for safer energetic materials in industrial and defence sectors. Azoxytriazolone (AZTO) is a new chemical species discovered by our research group, and preliminary results indicate it may possess potential as a new IHE. We are studying methods of synthesis of AZTO and other related compounds, and also investigating their solid-state and solution properties.

Synthesis and study of new iridium complexes for use in supramolecular and medicinal applications

Dr Lynne Wallace

Many molecular devices and pharmaceuticals contain components based on transition metals such as iridium or platinum. These transition metal complexes, consisting of organic units bonded to a central metal atom, can be structurally modified to fulfill different purposes. In this project, different synthetic approaches are used to prepare new iridium complexes, and these are studied, using a range of spectroscopic and electrochemical techniques, for their potential in light-activated molecular devices and to determine their interaction with biomolecules.

Synthesis, study and characterization of mono- and di-nuclear cobalt complexes to isolate metallo rotaxanes (a mechanically interlocked metallo architectures)

Dr Mokhlesur Rahman, Dr Anthony Day

Rotaxanes are of interest for their potential use as molecular switch, nano-shuttles, molecular electronics and molecular muscles. Transition metal complexes as stoppers also offer the possibility for synthesis of metallo polyrotaxane. Moreover, having a transition metal within this supramolecular architecture furnishes it with specific photonic, electric and magnetic properties.

Recent Achievements

CAPT Mark Bali is the recipient of the Chief of Defence Force Scholarship for 2010. The prestigious Chief of Defence Force Scholarship is awarded annually to one officer in the ADF for postgraduate research in a field that has strong military relevance.

CAPT Bali is due to start an MSc in Feb 2010 (**A. Day** and **L. Wallace** are his supervisors & Dr D Armit (DSTO) is co-supervisor). Mark has just been appointed as a Visiting Fellow in the meantime (covering the period from Sept 2009-Feb 2010). His research topic will be "Neutralisation of Explosives".

Kirsten Randle was winner of the best oral research presentation at UNSW@ADFA Research Day 2008.

Student Research

Detection of peroxide based explosives

Kirsten Randle (k.randle@student.adfa.edu.au) PhD

Field of Study: Forensic Science/Counter Terrorism

Improvised explosive devices created from peroxide containing materials have increasingly been utilised in recent years by a number of terrorist organizations, particularly in Israel, as well as in the UK and the USA. Peroxide-based explosives can be easily "home-made" using inexpensive, readily available starting materials which can be obtained in most hardware stores. My aim is to develop a sensitive and reliable field test for the detection of these peroxide based explosives and others as Tri-Acetone Tri-Peroxide (TATP) and HexaMethylene Triperoxide Diamine (HMTD). This research focuses on the development of an enhanced visual detection kit using sensitive metal catalysts in conjunction with the ABTS + radical cation and organic colour changing reagent Syringaldazine (SYAZ) in addition to the family of molecules known as cucurbit[n]uril (n=6-10), which have the potential to enhance visual detection.

Development of new cucurbiturils and biomimetic catalytic processes

Feng Wu (f.wu@student.adfa.edu.au) PhD

Field of Study: Chemistry

PhD Opportunities and Scholarships

If you are interested in a PhD or Masters by Research in molecular design and reaction mechanisms:

Contact:

Dr Lynne Wallace (l.wallace@adfa.edu.au)

Dr Anthony Day (a.day@adfa.edu.au)

Dr Mokhlesur Rahman (m.rahman@adfa.edu.au)

Major Facilities

- NMR spectrometer
- HPLC
- GC-MS
- FTIR spectrometer
- UV-vis spectrometers
- Potentiostats

Molecular Design and Reaction Mechanisms

Publications

In Press

Conference – Full Paper, non refereed

Underwood, C., Wall, C., Day, A., Provatas, A. & Wallace, L., 2009, Electrolytic treatment of nitroazole solutions in the synthesis of new high-nitrogen compounds, *PARARI 2009 (9th Australian Explosives Ordnance Symposium)*, 10-12 Nov 2009, Adelaide, Australia, accepted.

2009 publications

Journal - Refereed

Wallace, L., Cronin, M.P., Day, A.I. & Buck, D.P., 2009, Electrochemical method applicable to treatment of wastewater from Nitrotriazolone production, *Environmental Science and Technology*, 43(6), 1993-1998, doi: 10.1021/es8028878.

2008 publications

Journal - Refereed

Limei, Z., Jiannan, Z., Yunqian, Z., Zhu, Q., Xue, S., Tao, Z., Zhang, J., Xin, Z., Wei, Z., Long, L. & **Day, A.I.**, 2008, Opposing substitution in cucurbit[6]urils forms ellipsoid cavities: the symmetrical dicyclohexanocucurbit[6]uril is no exception highlighted by inclusion and exclusion complexes, *Supramolecular Chemistry*, 20(8), 709-716, doi: 10.1080/10610270701747602.

Ni, X., Lin, J., Zheng, Y., Wu, W., Zhang, Y.B., Xue, S., Zhu, Q., Tao, Z. & **Day, A.I.**, 2008, Supramolecular bracelets and interlocking rings elaborated through the interrelationship of neighboring chemical environments of alkyl-substitution on cucurbit[5]uril, *Crystal Growth and Design*, 8(9), 3446-3450, doi: 10.1021/cg800451z.

Zhao, Y., Buck, D.P., Morris, D.L., Pourgholami, M.H., Day, A.I. & Collins, J.G., 2008, Solubilisation and cytotoxicity of albendazole encapsulated in cucurbit[n]uril, *Organic & Biomolecular Chemistry*, 6(24), 4509-4515, doi: 10.1039/b813759e.

Conference Participation

Conference Presentations

Ni, X.-L., Lin, J.-X., Zheng, Y.-Y., Wu, W.-S., Zhang, Y.-Q., Xue, S.-F., Zhu, Q.-J., Zhu, T. & **Day, A.**, 2009, Partially substituted cucurbit[n]uril to new supramolecular forms, *International Symposium on Macrocyclic & Supramolecular Chemistry*, 21-25 June 2009, Maastricht, Netherlands.

Zhao, Y., Pisani, M., Wallace, L., Collins, J.G., & Day, A., 2009, New supramolecular forms to partially substituted cucurbit[n]uril, *1st International Conference on Cucurbituril*, 10-11 July 2009, Pohang, Republic of Korea.

Randle, K., Day, A., Wallace, L., Kirkbride, P. & Lennard, C., 2008, Cucurbituril enhanced detection of peroxide-based explosives, *Australian and New Zealand Forensic Science Society (ANZFSS) Symposium*, 6-9 October 2008, Melbourne, Australia – oral presentation.

Randle, K., Day, A.I., Wallace, L., Kirkbride, P. & Lennard, C., 2008, Detection of peroxide-based explosives, *Australian Energetic Materials Symposium: Abstracts*, December 2008, Flinders University, Adelaide, SA, Australia – oral presentation.

Underwood, C., Day, A.I. & Wallace, L., 2008, Electrosynthetic routes to new high-nitrogen compounds based on triazoles and triazolones, *Australian Energetic Materials Symposium: Abstracts*, December 2008, Flinders University, Adelaide, SA, Australia. Slide presentation available at: http://www.flinders.edu.au/shadomx/apps/fms/fmsdownload.cfm?file_uid=B26F92D6-E4C5-3F41-996C-17D3526381B2&siteName=science_engineering

Grants

UNSW Grants

A. Day, Organic power in organic packaging, Early Career Researcher Grant, UNSW@ADFA, 2009: \$36,436.

L. Wallace & A. Day, Environmentally friendly methods for the synthesis of novel high-nitrogen compounds and remediation of wastewater from explosives manufacture, Defence Related Research Funding Scheme (DRR), 2009: \$15,380.

A. Day, Curcubit[n]uril as an Artificial Muscle Component, Special Research Grant, UNSW@ADFA, 2008.

A. Day, Advanced Forms of Cucurbit[n]uril, Rector's Startup Grant, UNSW@ADFA, 2008.

L. Wallace & A. Day, Further investigations on azoxytriazolone (AZTO), a promising new energetic molecule discovered at UNSW@ADFA, Defence-Related Research Funding Scheme (DRR), 2008.

Visitors

CAPT Mark Bali, Australian Army officer is a Visiting Fellow to PEMS (Sept 2009-Feb 2010). He is currently affiliated with the School of Military Engineering in NSW.

Ruby Oun, University of Strathclyde, Scotland visited during 2009 and was hosted by **Anthony Day**.

Kunihiko Katsuragawa, a Practicum Student visited from mid 2008-January 2009. Kunihiko worked on a project supervised by Anthony Day on "The interaction of organosulfur compounds in the host-guest chemistry of cucurbiturils". He was an exchange student in PEMS under the terms of the Cooperative Agreement for Scholastic Exchange between UNSW@ADFA and the Faculty of Engineering at Toyama University.

Professor Tao Zhu, a visitor and collaborator of **Anthony Day** spent the month of April 2008 in PEMS.