Chemical Research in the MacDiarmid Institute for Advanced Materials and Nanotechnology

In our July issue last year (*Chem. in NZ*, **2006**, *70*, 54-56) we profiled the MacDiarmid Institute and its five thematic areas of research. We now present synopses of Themes III-V, each presented by the academic-in-charge, as these encompass by far the majority of the chemically-based studies that are undertaken. This was set in motion long before the death of Victoria alumnus and Nobel Laureate, Professor Alan MacDiarmid on February 7 last. His death is a great loss to New Zealand and to the international science community. Alan received an honorary DSc from Victoria in 1999 and his Nobel Prize in 2000, allowed the MacDiarmid Institute for Advanced Materials & Nanotechnology to be named after him, and was an active supporter of it. He never forgot his roots as a New Zealander and was scheduled to speak at the AMN-3 International Conference for Advanced Materials and Nanotechnology (organised by the Institute) the week following his death. Autobiographical details are available at the Nobel web site (www.nobel.se) and also at http://www.nzedge.com/heroes/macdiarmid.html

Molecular Materials Research within the MacDiarmid Institute

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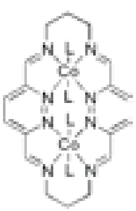
The third theme of The MacDiarmid Institute focuses on polymer and molecular systems. In late 2006 three new researchers began work and what follows seeks to highlight their research as well as describing some of the other research conducted during last year.

Prof Sally Brooker (Otago University) joined the Institute because of her interest in single molecule magnets and spin-crossover systems. Her group has pioneered the design and synthesis of new macrocycle ligands which can be used to encapsulate a number of metals ions of high spin state within a single molecular structure to create a single molecule magnet as illustrated by **1**. These ligands are cousins to the porphyrins, expanded porphyrins, and phthalocyanines. While phthalocyanines have been utilized in making single molecule magnets,[1] Sally's approach uses aggregated metal-oxy species[2] to gather the high-spin ions together and then bind them within the macrocyclic encapsulant to improve solubility and stability. The new ligands offer two important advantages, i) a cavity of specified size can be synthesized so as to capture a specific aggregate size, and ii) the electronic, supramolecular, and solubility characteristics of the system can then be influenced more easily by modifying the donor and peripheral groups on the macrocycles.



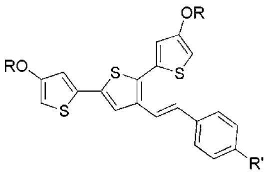
1, L = CNS^-

As well as creating and controlling high-spin systems, the group design and synthesize molecules in which metal spin states may be flipped by stimuli such as light or heat,[3] thus having potential in memory storage. In fact, complex **1** is the first dicobalt complex that undergoes simultaneous magnetic exchange and spin crossover,[4] and the first structurally characterized bimetallic complex in which one metal ion is high spin whilst the other is low spin. The focus of the group is to use the high level of synthetic control to provide a systematic study of molecular behaviour as a function of the ligand employed; useful structure-magnetic behavior correlations are expected.

Dr Jadranka Travas-Sejdic is the Director of the Polymer Electronics Research Centre (PERC) at Auckland University. The centre has considerable experience in conducting polymers (CPs), biosensing,[5] and polymer electronics applications based on such materials. Current research is in the development of biosening platforms that will offer rapid response, require no sample labeling, and provide intrinsic electrical and optical readout.[6] This includes the synthesis and characterization of novel electrically conducting polymers, photoluminescent polymers,[7] and nanostructured polymers and other nanomaterials that may have advantageous properties for biosensing.[8]

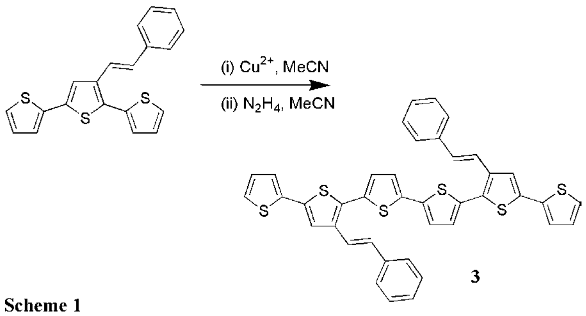
CP nanostructures are emerging as alternatives to silicon and carbon nanotubes for number of application (including chemical and biochemical sensing) due to their unique opto-electrical properties and easy of chemical functionalization. CP nano-wires have been prepared by a number of methods; however, most have shortcomings such as a need for template dissolution, difficulty in postsynthesis alignment and attachment to the electrodes. The group plans to develop simple fabrication methodology to micro- and nano-patterning of CPs on (conductive and non-conductive) surfaces. This is based on the building of hydrophilic/hydrophobic micro- and nano-patterns on surfaces by standard soft lithographic approaches, *e.g.* (macro)molecular self-assembly, that will act as templates for subsequent pattern-directed growth of conducting polymers from both liquid and vapour phase.

Prof David Officer (Director, Nanomaterials Research Centre, Massey University) has been within the Institute since its inception in 2002. His research focuses on the synthesis of thiophene-based polymers, *e.g.* **2**,[9,10] and their application in all plastic solar cells[11] and the group has been able to produce soluble polythiophene systems with electronically functionalized sites. These sites allow tuning of the nature of the excited state in terthiophene monomers as evidenced by fluorescence and ultrafast spectroscopic studies.[12] David is also active with a number of NZ companies, one of which uses ZnS as a base for electroluminescent panel fabrication and the colour durability of these panels is to be assessed. While he has just moved to a chair at the University of Wollongong, he will retain an active interest in the MacDiarmid Institute through s collaborations by remaining a Partner Investigator.

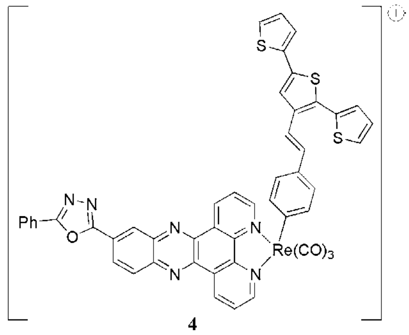


2, R = Me, hexyl; R' = NMe_2 NH_2, OMe, H, CN or NO_2

A/Prof Keith Gordon (Otago University) has been a researcher within the Institute since its inception. His research interests fall into two categories, namely understanding the electronic properties of thiophene-based systems using computational chemistry and spectroscopy[9,12-15] and secondly the design of new materials for organic light-emitting diodes (OLEDs)[16]. The group has been able to show that for substituted terthiophene systems oxidation creates localized reactive sites that result in regiospecific dimerization (Scheme 1) and a subsequent lack of reactivity of the resulting sexithiophene **3**.[15] They were also able to capture the reactive terthiophene radical cations using time-resolved resonance Raman spectroscopy[13] and also succeeded in synthesising the trifunctional OLED material **4** that covalently connected the three essential types of components for OLED operation, *viz.* electron transport, and emission and hole transport.[17] Future work will examine the nature of the electronic interactions between OLED components and, within the Institute, research will focus on the organisation of molecules using the properties of liquid crystals – and the potential use of these assemblages in solar cells and OLEDs. Keith also used resonance Raman excitation profiles to map out the structural changes that occur upon photoexcitiation of metal complexes.[18]



Scheme 1



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A/Prof Simon Hall (Massey University) began working in the Institute in 2002. He is interested in the nucleation and growth of electroactive materials,[19] particularly interpreting current-time transients in terms of nucleation kinetics and transition from 2-D to 3-D growth but is currently working with the start-up company *Anzode* looking to commercialize some of his research into long-life batteries.

Dr Shane Telfer (Massey University) joined the Institute last year to build up molecular materials using transition metal ions. Such ions have wonderful structural and functional properties that make them an attractive. Work is to commence on a Marsden-funded project investigating the crystal engineering of catalytically-active porous materials that include metallotectons – metal-centred building blocks with hydrogen bonding groups on their peripheries − and on use of bio-inspired H-bonding recognition motifs in supramolecular materials chemistry.

A/Prof Alison Downard (Canterbury University) has been with the Institute since 2002 and is interested in the covalent attachment of organic layers to the conducting substrates of nanoscale organic layers by way of radical coupling. This gives materials with potential applications that range from molecular electronics to sensing[20] and anti-corrosion coatings. A key aspect of the grafting methods is the generation of a carbon-centred radical that gives a very stable carbon surface bond and, thereby, attachment of the organic layer.[21] In recent work the group has gained detailed insight into nm scale organic layers grafted to conducting carbon surfaces.[22] that have interesting dynamic behaviours of the layers.[23] They also use the layers for tethering of nanoparticles[24] and pattern nano- and micro-scale organic species on carbon surfaces.[25] Patterned tethering of vertically-aligned carbon nanotube arrays to conducting surfaces using the same chemistry are also to be investigated.

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