

AUSTRALIAN JOURNAL OF CHEMISTRY

AN INTERNATIONAL JOURNAL FOR CHEMICAL SCIENCE

RESEARCH FRONT: Alan Sargeson Special Issue

Foreword

Foreword to Professor Alan M. Sargeson Special Issue

A foreword to the Research Front dedicated to Professor Alan Sargeson.

Paul V. Bernhardt

Aust. J. Chem. **2009**, *62*, 1195.

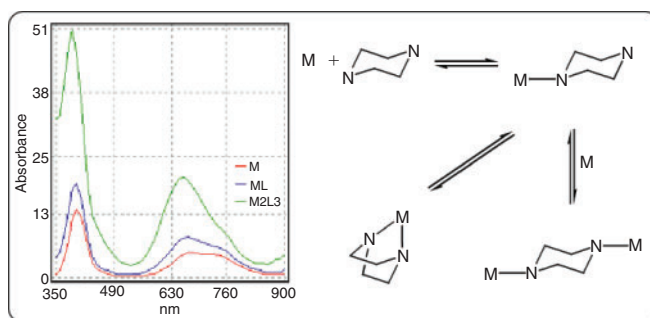
Full Papers

Complexation of Constrained Ligands Piperazine, *N*-substituted Piperazines, and Thiomorpholine

Sarah E. Clifford, Vanny Tiwow, Aleasia Gendron, Marcel Maeder, Monica Rossignoli, Geoffrey A. Lawrance, Peter Turner, Alexander J. Blake, Martin Schröder

Aust. J. Chem. **2009**, *62*, 1196–1206.

Complexation reactions of even simple ligands, which may be unravelled by powerful chemometric data analysis methodologies, can be revealing and the outcomes surprising. The complexation of piperazine, *N*-substituted-piperazines, and thiomorpholine by metal(II) ions is reported, with mechanistic paths defined. X-ray crystal structures of two products show some complexation modes.

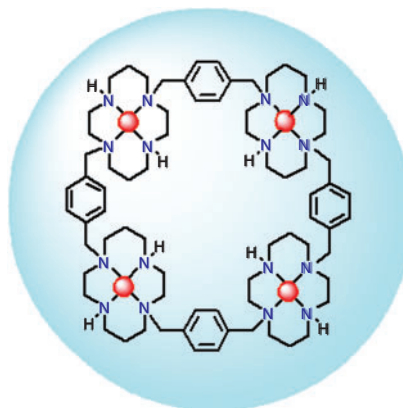


Macrocyclic Ligand Design. A Large Covalently-Linked Ring System Incorporating Four Cyclam Units and its Interaction with Nickel(II), Copper(II), Zinc(II), and Cadmium(II)

Ying Dong, Leonard F. Lindoy

Aust. J. Chem. **2009**, *62*, 1207–1213.

The synthesis and investigation of a unprecedented xylyl-linked cyclic tetracyclam ligand along with its complexation to form tetranuclear Ni(II), Cu(II), Zn(II), and Cd(II) derivatives are described. The study makes available an example of a new category of large cyclic receptors whose cavity can be tuned electronically through variation of the metal centres incorporated in the cavity walls.

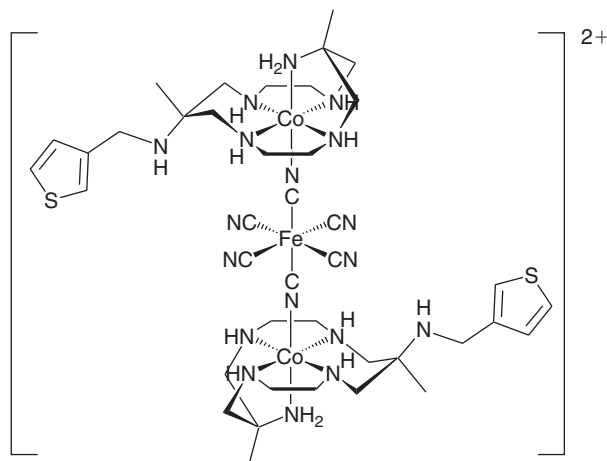


**Macrocyclic Thiophene-Appended
Cyanido-Bridged Co^{III}/Fe^{II}
Complexes: Precursors to
Mixed-valent Poly-thiophene
Hybrid Materials**

Sharizal Hasan, Nathan L. Kilah,
Manuel Martinez, Paul V. Bernhardt

Aust. J. Chem. **2009**, 62, 1214–1220.

A thiophene-appended macrocyclic hexamine bound to Co^{III} in a pentadentate fashion can be assembled into both dinuclear (Co^{III}-Fe^{II}) and trinuclear (Co^{III}-Fe^{II}-Co^{III}) mixed-valent complexes in complex with ferrocyanide. The spectroscopic and electrochemical properties of these complexes have been studied with a view to their incorporation into polythiophene conducting polymers.

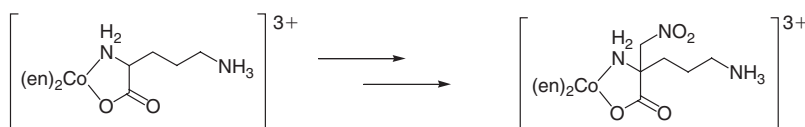


**Reactions of Co(III)-coordinated
Ornithine: Towards Inhibitors of
the Polyamine Biosynthetic
Pathway**

Andrea J. Clarkson, Allan G.
Blackman, Charles R. Clark,
Alan M. Sargeson

Aust. J. Chem. **2009**, 62, 1221–1225.

The incorporation of suicide inhibitors into chemotherapeutic agents which specifically target tumour cells represents a possible method for the effective treatment of cancer. In this paper, we report the syntheses and characterization of Co(III) complexes containing ornithine and its derivatives. Specifically, we show that the [Co(en)₂(2-nitromethylornithineH)]³⁺ ion, which contains the ornithine decarboxylase suicide inhibitor 2-nitromethylornithine, can be easily prepared from the ornithine-containing starting material [Co(en)₂S-ornithineH]³⁺.

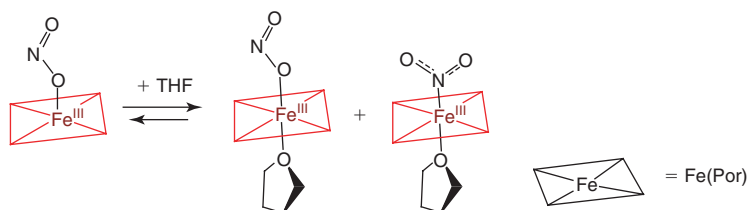


**Reaction of the Five-Coordinate
O-Nitrito Complex Fe(Por)(ONO)
(Por = meso-tetra-arylporphyrinato)
with THF Gives Two Six-Coordinate
Isomers**

Tigran S. Kurtikyan, Astghik A.
Hovhannisyanyan, Alexei Iretskii,
Peter C. Ford

Aust. J. Chem. **2009**, 62, 1226–1230.

The interaction of the nitrite ion with heme proteins plays important roles in mammalian physiology. Here we describe continued spectroscopic studies on the proximal ligand effect on the mode of NO₂⁻ bonding with heme models. When the proximal ligand is a nitrogen base the N-nitrito isomers are more stable, but when it is tetrahydrofuran, a mixture of the linkage isomers Fe(Por)(THF)(η¹-ONO) and Fe(Por)(THF)(NO₂) results.

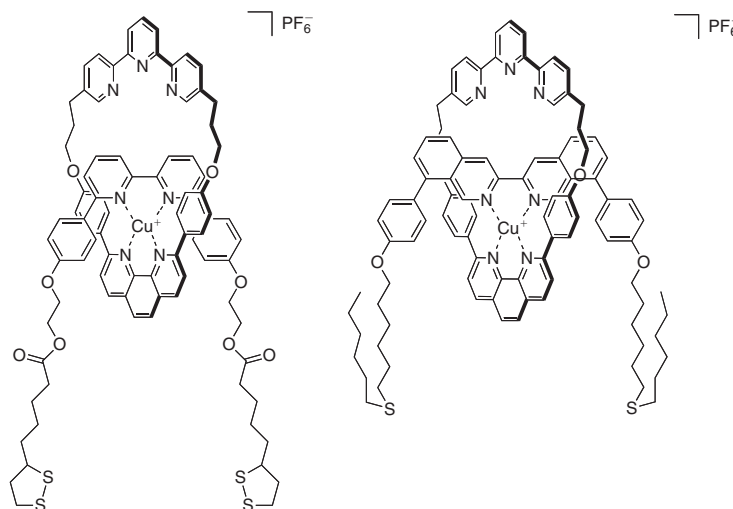


Copper-Complexed Pirouetting [2]pseudorotaxanes with Sulfur-Containing End-Groups Attached to the Thread: Synthesis, Electrochemical Studies, and Deposition on Gold Electrodes

Jean-Paul Collin, Pierre Mobian,
Jean-Pierre Sauvage, Angélique Sour,
Yi-Ming Yan, Itamar Willner

Aust. J. Chem. **2009**, *62*, 1231–1237.

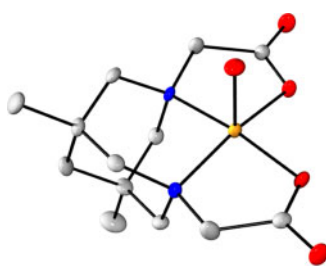
Two copper [2]pseudorotaxanes incorporating a macrocycle with two chelating sites and a thread have been synthesized. One of the threads was a hindering 2,2'-bipyridine functionalized by two thioctic-ended arms. The second thread was an 8,8'-diphenyl-3,3'-biisoquinoline functionalized by two thioether-ended arms. The electrochemical studies of the two copper [2]pseudorotaxanes, both in solution and anchored on a gold surface, showed only fast-moving systems in solution.



Mono- and Dinuclear Copper(II) and Iron(III) Complexes of a Tetradentate Bispidine-diacetate Ligand

Peter Comba, Lena Daumann,
Julie Lefebvre, Gerald Linti,
Bodo Martin, Johannes Straub,
Thomas Zessin

Aust. J. Chem. **2009**, *62*, 1238–1245.



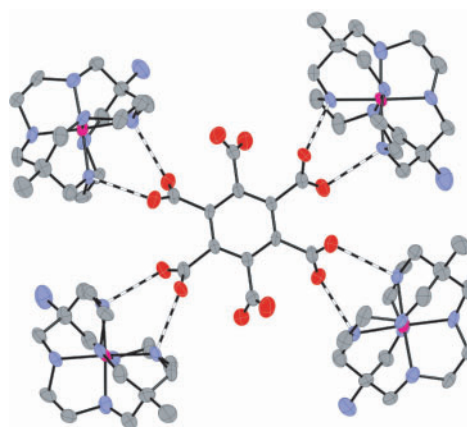
Bispidine-containing complexes have been widely investigated for their interesting structural properties as well as their use as biomimetic compounds and their efficient catalysis. In this article, a new N_2O_2 -type tetradentate bispidine ligand is reported, along with the preparation and characterization of mono- and dinuclear copper(II) and dinuclear iron(III) complexes. Elucidation of the dinuclear copper(II) structure was achieved by combining results from EPR spectroscopy with molecular mechanics calculations.

Variations on a Cage Theme: Some Complexes of Bicyclic Polyamines as Supramolecular Synthons

Ian J. Clark, Alessandra Crispini,
Paul S. Donnelly, Lutz M. Engelhardt,
Jack M. Harrowfield, Seong-Hoon Jeong,
Yang Kim, George A. Koutsantonis,
Young Hoon Lee, Nigel A. Lengkeek,
Mauro Mocerino, Gareth L. Nealon,
Mark I. Ogden, Yu Chul Park, Claudio
Pettinari, Lara Polanzan, Elisabeth
Rukmini, Alan M. Sargeson, Brian W.
Skelton, Alexandre N. Sobolev,
Pierre Thuéry, Allan H. White

Aust. J. Chem. **2009**, *62*, 1246–1260.

Analysis of the crystal structures of a variety of cage amine complexes provides an illustration of the ways in which the lattices of these complexes are determined by labile interactions. The form of these interactions and thus the nature of the complex cations as supramolecular synthons depends on a range of factors, discussed herein.

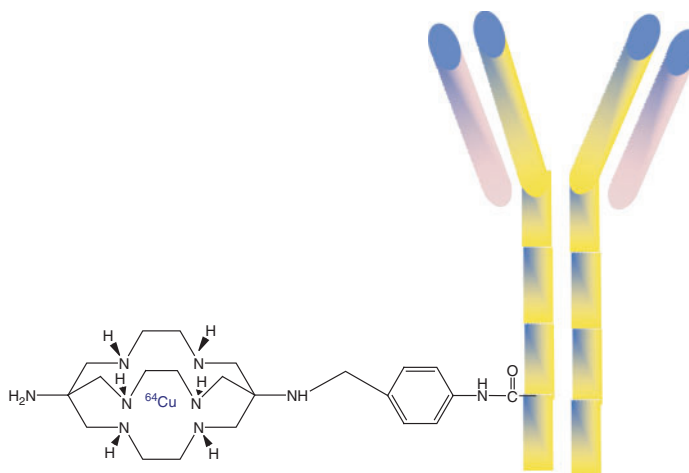


An Investigation into the Potential of SarAr for Use in ^{64}Cu Radioimmunotherapy

Nadine Di Bartolo, Suzanne V. Smith, Eric Hetherington, Alan Sargeson

Aust. J. Chem. **2009**, *62*, 1261–1270.

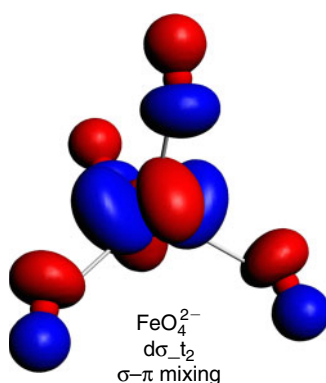
SarAr has been used to produce a ^{64}Cu -radioimmunoconjugate for radiotherapy, and its chemical stability in vivo has been compared with analogues incorporating well-known therapeutic radioisotopes ^{131}I and ^{90}Y . Biodistribution studies show the ^{64}Cu -radioimmunoconjugate is significantly more stable in vivo. Dosimetry calculations show the SarAr ^{64}Cu -labelled immunoconjugates could be effective for radiotherapy with fewer side-effects.



Bridging Kohn–Sham DFT and the Angular Overlap Model. Ligand-Field Parameters and Bond Covalencies in Tetrahedral Complexes

Claus E. Schäffer, Christian Anthon, Jesper Bendix

Aust. J. Chem. **2009**, *62*, 1271–1279.



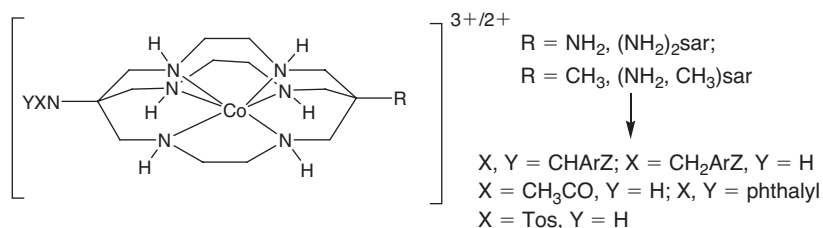
Molecular orbital density functional theory is used to provide a comparison of the valence shells of tetrahedral complexes of the metals of the first transition series. Computational experiments with enforced tetrahedral symmetry find an identity of the valence shell orbital pattern for all the chloride complexes.

Dependence of the Properties of Cobalt(III) Cage Complex as a Function of the Derivatization of Amine Substituents

Alan M. Sargeson, Peter A. Lay

Aust. J. Chem. **2009**, *62*, 1280–1290.

Control of the redox properties of cobalt cage complexes by chemical modifications of substituents is important for their use as electron-transfer agents and such modifications can also be used to change the lipophilicity of the complexes for a variety of biological and other applications. The synthesis and properties of a range of cobalt(III) cage complexes in which the amine groups have been derivatized is useful in controlling a variety of chemical and physical properties, including $\text{Co}^{\text{III/II}}$ redox chemistry, and in providing a range of useful synthons that have the potential for the synthesis of interesting conjugates containing cage complexes. These advances in synthetic chemistry have greatly expanded the diversity of redox chemistry and types of conjugation reactions that can be performed.

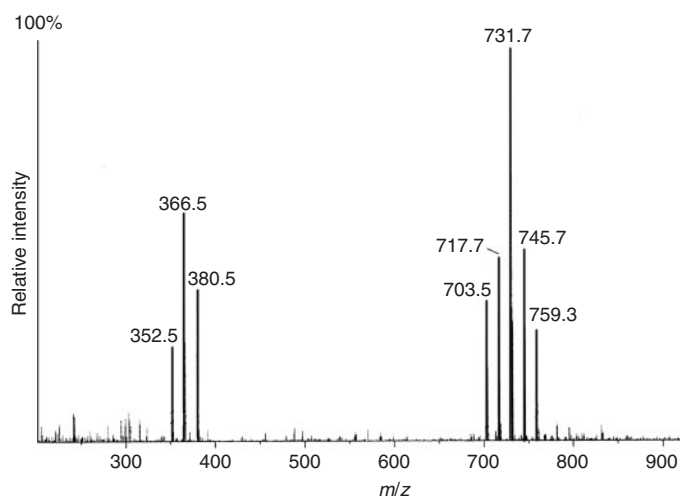


Pseudoisotopic Molecule Mass Spectrometry: A Useful Tool for Studying Assembly and Exchange in Multinuclear Complexes

Alexandra Spyratou, Sarah Clifford,
Xavier Melich, Claire Deville,
Matthieu Tissot, Gregoire Bonvin,
Philippe Perrottet, Alan Williams

Aust. J. Chem. **2009**, *62*, 1291–1299.

Using mixtures of similar ligands with slightly different molecular masses leads to multiplet structure in the electrospray ionization-mass spectrometry spectra, enabling identification of the nuclearity of self-assembled species. The same technique shows the diversity of kinetics and mechanism shown by these complexes.

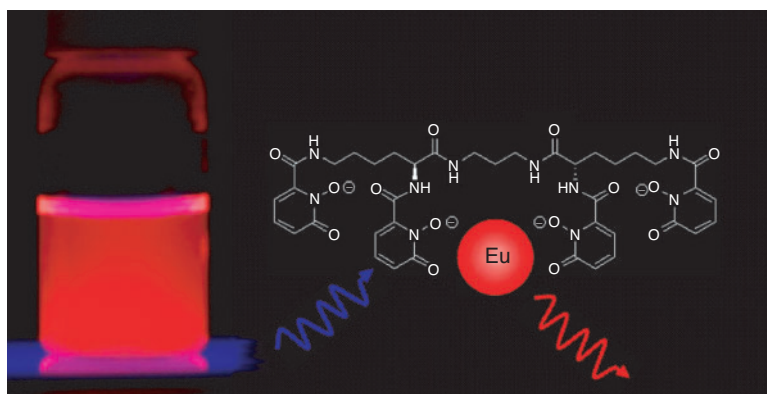


Eu^{III} Complexes of Octadentate 1-Hydroxy-2-pyridinones: Stability and Improved Photophysical Performance

Evan G. Moore, Anthony D'Aléo,
Jide Xu, Kenneth N. Raymond

Aust. J. Chem. **2009**, *62*, 1300–1307.

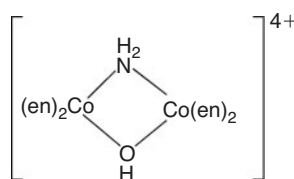
The search for lanthanoid complexes (e.g. Eu(III) and Tb(III)) that demonstrate excellent photophysical properties is an active area of current research, because these luminescent probes are useful as labels for bioassay development. However, several pre-requisites for their successful implementation exist, notably including the often limited aqueous stability and overall brightness of the complexes. Herein, we describe the synthesis, stability, and photophysical properties of a new octadentate ligand based on the 1-hydroxy-2-pyridinone (1,2-HOPO) chelate group that couples excellent aqueous stability with enhanced luminescence performance, and compare this complex to previously reported 1,2-HOPO based Eu(III) agents.



Synthesis and Characterization of Simple Hydroxo- and Amido-Bridged Cobalt(III) Dinuclear Ions Missing from the Alfred Werner Collection

W. Gregory Jackson

Aust. J. Chem. **2009**, *62*, 1308–1317.



Alfred Werner around 1900 synthesized a considerable number of dinuclear bis(ethylenediamine)cobalt(III) bearing one amido or hydroxo bridge, and another such as NO_2^- , SO_4^{2-} , NH_2^- , or OH^- . They all exist in *meso* and racemic forms but two key missing compounds have defied synthesis for a hundred years. Herein we report ways to now make these, opening, the way to a host of derivatives suitable for further fundamental studies, such as reactions of coordinated ligands.

Foreword

**The Inaugural Australian Workshop
on Bioconjugate Chemistry,
UNSW 2008**

Pall Thordarson, Richard J. Payne

Aust. J. Chem. **2009**, *62*, 1318–1319.



The first Australian Workshop on Bioconjugate Chemistry was held in March of last year at the University of New South Wales. Several of the speakers at the Workshop have contributed to the present special Research Front of the *Australian Journal of Chemistry*, highlighting the current burst of activity in this important re-emerging interdisciplinary field of chemistry.

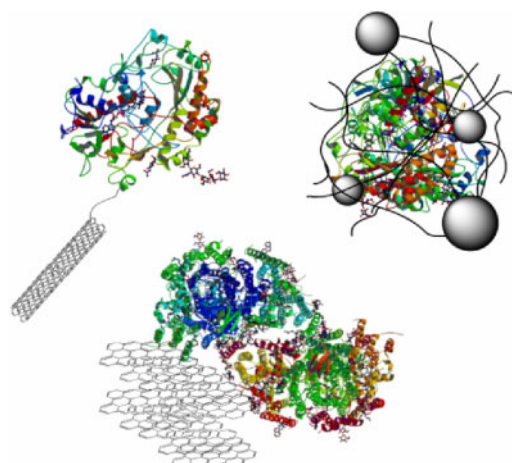
Review

**The Bioconjugation of Redox
Proteins to Novel Electrode
Materials**

*Daniel C. Goldstein, Pall Thordarson,
Joshua R. Peterson*

Aust. J. Chem. **2009**, *62*, 1320–1327.

Developments in the immobilization of redox proteins onto electrode surfaces involve the incorporation of new nano- and meso-structured electrode materials that can efficiently interface with a protein's redox centre. This paper reviews the materials and techniques used to construct these enzyme-electrodes. These advances are improving our understanding of biological molecules and leading towards the production of new bioelectronic devices.



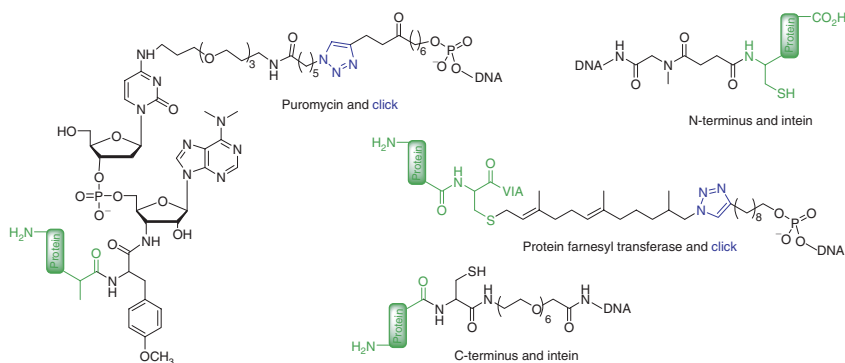
Highlight

**Synthesis and Applications of
Covalent Protein-DNA Conjugates**

Patrick M. Schaeffer, Nicholas E. Dixon

Aust. J. Chem. **2009**, *62*, 1328–1332.

Synthetic protein-DNA conjugates are valuable tools with applications in nano- and biotechnology. Various synthetic methods for their production have been developed during the past three decades. The present article reviews current methodologies for the synthesis of covalent protein-DNA conjugates with particular focus on the regiospecificity and stoichiometry of these reactions.



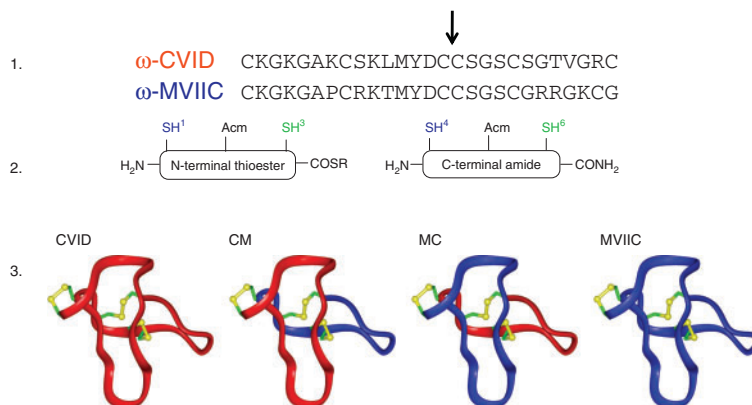
Communications

Rapid Access to ω -Conotoxin Chimeras using Native Chemical Ligation

Gene Hopping, Richard J. Lewis,
Paul F. Alewood

Aust. J. Chem. **2009**, *62*, 1333–1338.

Omega conotoxins, which target calcium channels, have attracted recent interest as a source of novel drugs for the treatment of chronic pain. Grafting different regions of related peptides together to form a single protein chimera is a valuable tool in rapidly elucidating regions of activity or selectivity in peptides and proteins. The contributions to activity of the N- and C-terminal segments of the N-type ω -conotoxin CVID and the P/Q type ω -conotoxin MVIIC were evaluated by employing native chemical ligation to generate novel and potent calcium channel chimeric ligands.

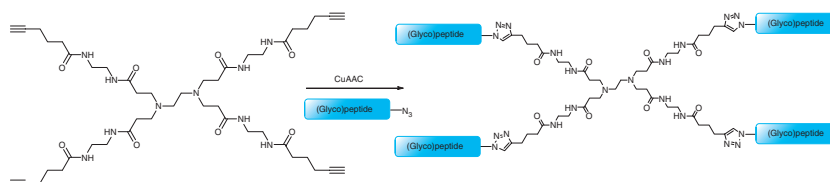


Synthesis of MUC1 Peptide and Glycopeptide Dendrimers

Candy K. Y. Chun, Richard J. Payne

Aust. J. Chem. **2009**, *62*, 1339–1343.

A number of dendrimers possessing multiple copies of peptides and glycopeptides belonging to the MUC1 eicosapeptide tandem repeat sequence have been prepared. Fmoc-strategy solid-phase peptide synthesis was used to construct peptides and glycopeptides, which were conjugated to suitably functionalized dendrimer cores using the copper-catalyzed azide-alkyne cycloaddition reaction to produce multivalent peptide and glycopeptide dendrimers.

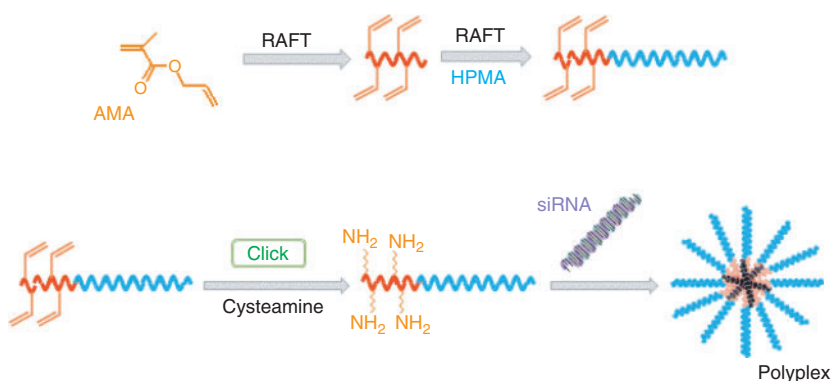


Synthesis of siRNA Polyplexes Adopting a Combination of RAFT Polymerization and Thiol-Ene Chemistry

David Valade, Cyrille Boyer,
Thomas P. Davis, Volga Bulmus

Aust. J. Chem. **2009**, *62*, 1344–1350.

Synthetic polymers are promising candidates for efficient delivery of small interfering RNA (siRNA). A reactive copolymer scaffold of PHPMA was generated by RAFT polymerization and converted to a polycation for complexation with siRNA using thiol-ene chemistry. It can be envisioned that such reactive copolymers of PHPMA could be converted to structures with versatile and more advanced functionalities for delivery of siRNA.

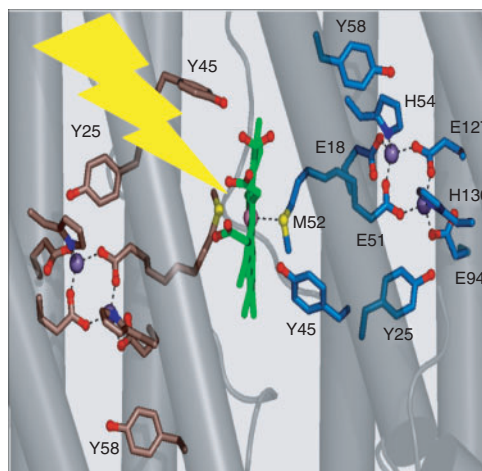


Elucidating Photochemical Pathways of Tyrosine Oxidation in an Engineered Bacterioferritin 'Reaction Centre'

Kastoori Hingorani, Brendon Conlan,
Warwick Hillier, Tom Wydrzynski

Aust. J. Chem. **2009**, 62, 1351–1354.

Upon light excitation of bacterioferritin from *Escherichia coli* that was engineered to undergo photooxidation reactions, a tyrosine radical cation is generated. Site selective mutations of the three tyrosine residues that are within electron tunnelling distance of the photoactive site were studied to determine the photochemical pathways of electron transfer.



REGULAR PAPERS

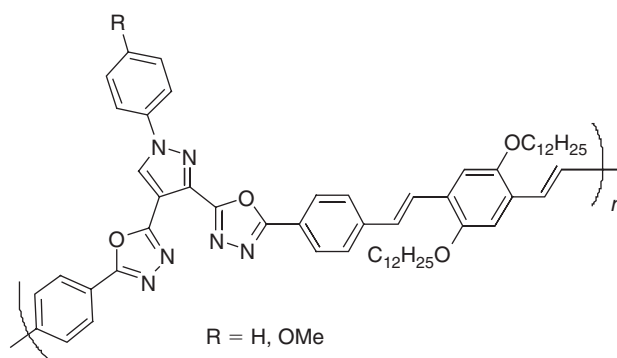
Full Papers

Synthesis and Characterization of Soluble Conjugated Poly(*p*-phenylenevinylene) Derivatives Constituted of Alternating Pyrazole and 1,3,4-Oxadiazole Moieties

En-Ming Chang, Shin-Lin Huang,
Cheng-Tien Lee, Hui-Chang Lin,
Chun-Yen Chen, Yu-Ying Huang,
Shao-Kai Lin, Fung Fuh Wong

Aust. J. Chem. **2009**, 62, 1355–1362.

Two new soluble poly(*p*-phenylenevinylene) derivatives with 1,3,4-oxadiazole and pyrazole rings along the main chain have been synthesized by Heck coupling. The new conjugated polymers are soluble in common organic solvents because of the fully conjugated backbone with dodecyloxy side groups. Spectroscopic studies and characterization of the electronic properties reveal that the new polymers are potential efficient blue-green electroluminescent materials.

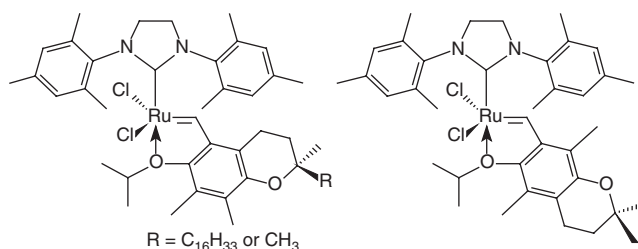


Hindered Rotation in New Air-Stable Ruthenium Olefin Metathesis Catalysts with Chromanylmethylidene Ligands

Agnieszka Hryniewicka, Jacek W. Morzycki,
Leszek Siergiejczyk, Stanisław Witkowski,
Jacek Wójcik, Adam Gryff-Keller

Aust. J. Chem. **2009**, 62, 1363–1370.

Three new ruthenium complexes with chromanylmethylidene ligands were synthesized and dynamic NMR analysis of these compounds was carried out. The complexes may potentially serve as latent catalysts for olefin metathesis – they promote the simple ring-closing metathesis reactions very slowly at room temperature, but are much more active at slightly elevated temperature.



Efficient Synthesis of Dendritic Architectures by One-Pot Double Click Reactions*Xing Quan Xiong**Aust. J. Chem.* **2009**, 62, 1371–1377.

Dendrimers have emerged as attractive nanometer-scale materials for various applications. Herein, we provide a simple and efficient approach for the preparation of dendrimers with peripheral hydroxy end-groups by double click reactions with a one-pot technique. The dendrimers are characterized by various techniques, e.g., ^1H NMR, ^{13}C NMR, MS, and SEC.

