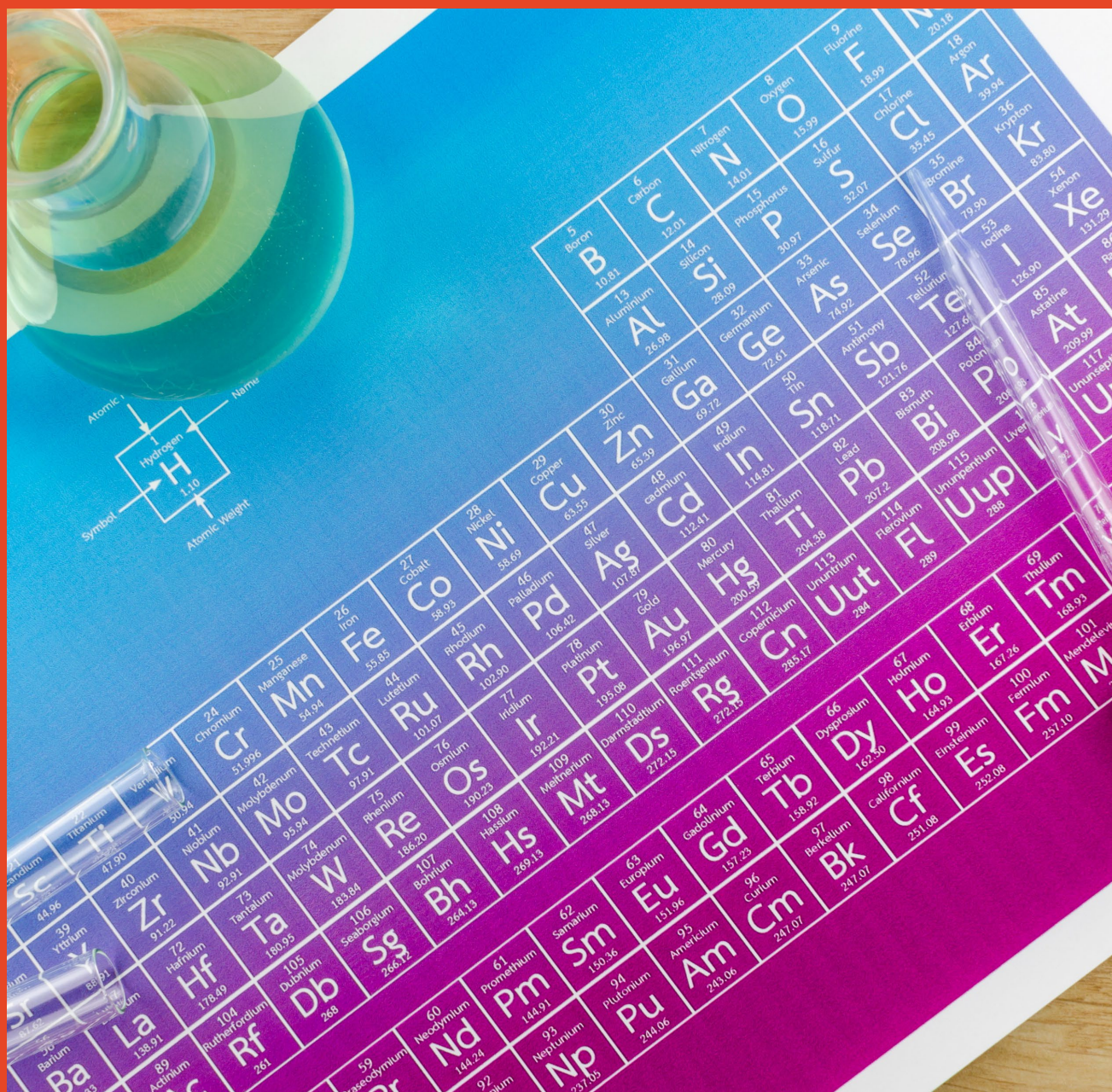




THE UNIVERSITY OF
SYDNEY

Francis Lions Lecture 2025

Professor Penelope J. Brothers



Wednesday 17th September 2025

Chemistry Lecture Theatre 4

Francis Lions

Francis Lions (1901–1972) was a brilliant scholar and esteemed academic from the University of Sydney. He graduated with first-class honours and received university medals in both chemistry (1922) and organic chemistry (1923). He travelled to Britain with an 1851 Exhibition Scholarship to study with Professor Robert Robinson at Manchester and afterwards spent a year at Oxford. Upon returning to Australia, Lions joined



the University of Sydney as a lecturer in 1926, later being promoted to Senior Lecturer in 1944 and Reader in 1946. Renowned for his engaging teaching style, he was known to famously lecture without notes.

Lions earned international recognition for his pioneering research in coordination chemistry, particularly in the design of multidentate organic ligands that bind to transition metals. His early work in heterocyclic chemistry laid the foundation for his later innovations, where he envisioned organic molecules that could be “wound around” a metal atom, forming stable complexes through five (quinqedentate) or six (sexadentate) heteroatom centres to form a metal-organic complex. Lions also worked alongside Francis Dwyer, another University of Sydney faculty member, and collectively expanded knowledge in synthesising, and understanding the stereochemical and optical properties of these compounds.

Beyond his scientific endeavours, Lions actively engaged in university affairs, serving as a member of the University Senate and contributing to various initiatives such as the University Health Service. He was also a distinguished sportsman, excelling in swimming, diving, cycling, athletics, and football. As a strong advocate for Australian science, he assumed the role of President of the Royal Society of New South Wales and frequently published his work in the society's journal, along with the Journal and Proceedings of The Australian Chemical Institute.

Previous Lecturers

2000	<u>Professor Alan Sargeson</u> The Australian National University
2001	<u>Emeritus Professor David Black</u> University of New South Wales
2002	<u>Associate Professor Harold Goodwin</u> University of New South Wales
2003	<u>Professor Andy Hor</u> National University of Singapore (currently A*STAR)
2004	<u>Professor Brice Bosnich</u> University of Chicago
2005	<u>Professor Roeland Nolte</u> Radboud University
2006	<u>Professor Ian Rae</u> University of Melbourne
2007	<u>Professor Max Lu</u> The University of Queensland
2008	<u>Professor Sally Brooker</u> University of Otago
2009	<u>Professor Christine McKenzie</u> University of Southern Denmark
2013	<u>Professor Richard Keene</u> James Cook University, Australia
2014	<u>Professor Leone Spiccia</u> Monash University
2015	<u>Professor John Evans</u> Durham University
2016	<u>Professor Richard Robson</u> University of Melbourne, Australia
2018	<u>Professor Sally Brooker</u> University of Otago
2023	<u>Professor Andrew Goodwin</u> University of Oxford
2024	<u>Professor Paul Donelly</u> University of Melbourne

Professor Penny Brothers

*Professor Emerita, Research School of Chemistry,
Australian National University, Australia.*

*Honorary Professor, School of Chemical Sciences,
University of Auckland, New Zealand*

Professor Penny Brothers is a New Zealander educated at the University of Auckland and Stanford University. Now based in Auckland, NZ, she is currently an Emerita Professor at the Research School of Chemistry at the Australian National University. She was Director of the Research School of Chemistry from 2019-2024.



Prior to that she was in the School of Chemical Sciences at the University of Auckland since 1988 and has been a visiting professor at the Universities of California at Davis and at Berkeley, the Heidelberg, Münster, Burgundy, Peking University, the Arctic University of Norway and Los Alamos National Laboratory (as a Fulbright Senior Scholar).

She was a Principal Investigator in the MacDiarmid Institute for Advanced Nanomaterials (NZ), and an Associate Editor of Chemical Communications and a member of the Marsden Fund Council (NZ). She served as President of the New Zealand Institute of Chemistry in 2017.

Her recent research has focussed on the chemistry of boron coordinated to porphyrin and corrole ligands, BODIPY fluorophores for sugar recognition and surface patterning using molecular pentagons.

Tetrapyrroles with unusual geometries: focus on *s* and *p* block complexes

In 1981, the year he won the Nobel Prize, Roald Hoffmann and Kazuyuki Tatsumi published two papers entitled “Metalloporphyrins with Unusual Geometries” that strongly influenced the state of the art in porphyrin and tetrapyrrole research. An unquestioned assumption from that time was that porphyrin coordination chemistry was anchored firmly in the *d* block of the periodic table, not unreasonable given the origins of the field in heme and vitamin B12 featuring iron and cobalt. Surprisingly, the presence of the Group 2 element magnesium in chlorophyll had not inspired chemists to interrogate more deeply the role of main group elements in tetrapyrrole chemistry.

Over the decades since these landmark papers, the emergence of tetrapyrroles bearing coordinated *s* and *p* block main group elements has extended the concepts of unusual geometries well beyond those originally envisaged. The chemistry of the *d* block elements is largely governed by oxidation states and *d*-electron configurations; while in the *s* and *p* blocks the fundamental properties of size and electronegativity hold more sway. Main group tetrapyrrole complexes are examples of “misfit chemistry” in which the poor match between the environment offered by the central element and the requirements of the coordinated elements stimulates unusual chemistry for both partners.

Main group metals range from lightweight lithium to the *p* block heavies thallium, lead and bismuth; all are known to form porphyrin complexes with dramatic out-of-plane metal geometries. The classic *p* block elements carbon, boron, and phosphorus challenge the “metalloporphyrin” paradigm; these small, light non-metals nevertheless exhibit a rich chemistry in a tetrapyrrole setting. The extensive range of diboron porphyrinoids feature tetrapyrroles acting as binucleating ligands, incorporating not one but two elements within the coordination site. Silicon and germanium porphyrinoids demonstrate the interplay between redox properties of the ligand and central element. The underlying themes are the new lessons to be learnt that can be translated into other areas of the chemical sciences.

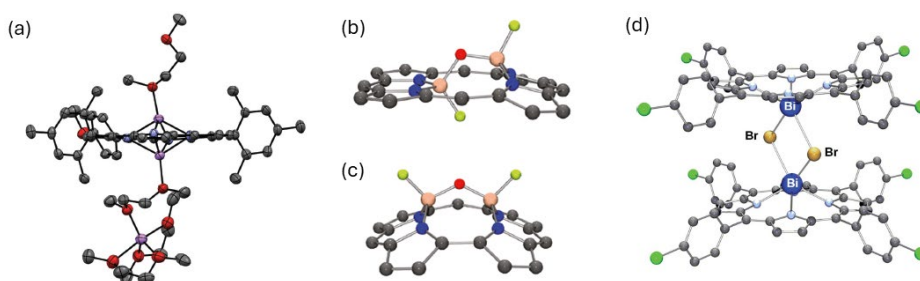


Figure. (a) $[\text{Li}_2(\text{corrole})(\text{DME})]\text{--}[\text{Li}(\text{DME})_4]$, (b) $\text{B}_2\text{OF}_2(\text{porphyrin})$, (c) $[\text{B}_2\text{OF}_2(\text{corrole})]^-$, (d) $[\text{Bi}(\text{porphyrin})\text{Br}]_2$