

On-surface covalent assembly of coordination polymers with integrated read and write functions

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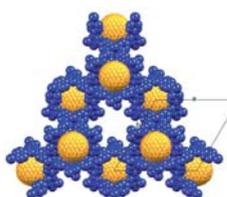
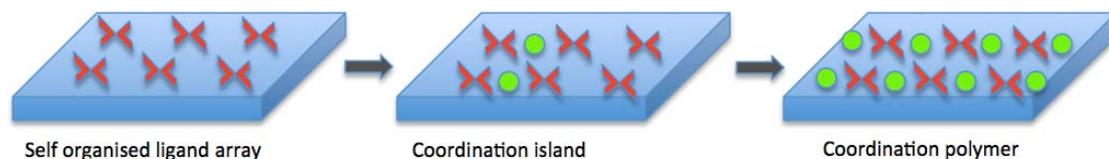
Highly functional supramolecular architectures are the key to biochemical processes such as light harvesting, site and shape selective chemical reactions and the interconversion of energy between different physical or chemical forms. The non-covalent assembly of multiple functional components provides an atom efficient way to access polyvalent structures. Nature has implemented such architectures through a relatively small toolbox of macromolecular building blocks, namely proteins and polysaccharides. With the emergence of synthetic polymer chemistry and of metal organic frameworks, unnatural macromolecular architectures have been developed and established as functional materials in many applications including catalysis and photovoltaics.

Two of the PIs (ECC, CEH) have been concerned with elaborating the structural elements in molecular components which control 2D-pattern formation in self-assembled monolayers at atomically flat surfaces [1-3]. In parallel they have developed synthetic systems to probe the key molecular recognition elements and algorithms controlling the assembly of coordination polymers and 3D molecular frameworks. In particular they studied the influence of the metal-ions used for complexation and the organic linker component upon the resulting architecture of the resultant 2D or 3D frameworks. By judicious selection of heteromultitopic bridging ligands with metal binding sites optimised for different metal ions, an exquisite level of molecular control in the assembly of heterometallic extended 2D and 3D structures with precisely positioned metal ions has been achieved [4,5].

It has recently been demonstrated, that on-surface reactions [6,7] can be used for the synthesis of 2D coordination and covalent polymers [8,9] which exhibit highly interesting electronic [10] and magnetic [11,12] properties arising from the interaction of the substrate and the molecular layer.

In this project, groups from the University of Basel (ECC, CEH) and PSI (TJ) who have investigated similar periodic polymer systems from distinctively different scientific perspectives will join forces. The key expertise of ECC and CEH in the design and synthesis of self-organising materials and of TJ in studying and understanding the structure and properties of self-assembled and self-organised structures will be combined. It is this multidisciplinary and multicultural approach that makes the project appropriate for the the SNI doctoral programme. The added value of the proposal is multifold: We aim to understand the growth, topology, topography and morphology of surface-templated coordination polymers as they evolve from 2D monolayer islands to multilayers and surface supported bulk-like structures. This will be studied and compared with the wealth of bulk properties known from previous work.

Substrates will include low reactivity metals such as gold, as well as oxygen terminated metals and metal oxides and ionic crystal carpet layers which can modulate the interaction between the substrate and the coordination polymer layers. New generations of organic ligands will be designed to be commensurate with the selected surface chemistry and topography. In addition to the established solution casting methods of monolayer preparation, we will also investigate CVD and MOCVD techniques as well as sublimation for delivering the metal centres to self-assembled monolayers of ligands.



The host-guest properties of the surface metallopolymers will be investigated. Guest molecules such as C_{60} which have been established both in 3D bulk

[13,14] as well as in 2D layers [15,16] will be delivered by solution casting or co-sublimation to assess the full complexity of the materials structure and to investigate the property tuning possible in such novel systems.

A jointly supervised PhD student, with a masters degree in nanosciences or chemistry will first gain experience in the preparation of coordination polymers in the Housecroft/Constable group while attending selected lectures in preparation for this project. In this period, combinatorial studies of the metal and ligand toolbox will be made as a close collaboration of the two groups to optimise in-situ preparation parameters.

After one year, we plan that the student is introduced to the multi-chamber in-situ preparation and characterization system in the TJ group and starts to explore the best growth conditions and substrates for the surface template formation of tpy based coordination networks. The focus of the research is on the characterization of sub-monolayer and monolayer thick coordination networks by high resolution Scanning Tunneling Microscopy and Spectroscopy. In conjunction with X-ray photoelectron spectroscopy revealing the chemical species involved in the formation of the coordination network [17,18], the network architecture and morphology (defect densities, crystallographic parameters, etc.) will be assessed in the initial phase of surface templated growth. Important factors are: the substrate type and its surface termination (N, S, O on metals), the coordination metal (to be deposited separately or to be provided by diffusion from the substrate) as well as the molecular linker. These studies will provide unique mechanistic and structural insights into the growth of 3D coordination networks. An important issue will be the discussion of the different formation mechanisms 'in-situ and on-surface' and 'in-solution' on physico-chemical grounds. This also links up to earlier work in the nanolab where 'in-situ and on-surface' supramolecular chemistry has been discussed in comparison with the corresponding in-solution behavior [19,20].

In the third year, the focus of the project will be the assessment of the physico-chemical properties of the periodic structures beyond their coordination architecture. This will involve the substitution of molecular linkers with selected functional groups containing photonic or redox active units and the study of the correspondingly modified properties both in the Chemistry and in the Physics Department as well as at the Paul Scherrer Institut where unique and highly sensitive photon methods are available in the form of X-ray Absorption Spectroscopy [21], Near Edge X-ray Absorption Fine Structure [22], Surface XRD and also – if needed – 'ambient' XPS to compare coordination networks prepared in solution, 'in-situ and on-surface'.

References

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CURRICULUM VITAE

Catherine Elizabeth Constable-HOUSECROFT



Title: Professor
Date of Birth: 23 February 1955
Nationality: British
Place of Birth: Bradford, West Yorkshire
Marital Status: Married to Professor Edwin C. Constable; no children

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Education: University of Durham
1976 B.Sc. Honours (First Class) Chemistry
1979 Ph.D. (Prof. K. Wade)
University of Cambridge 1989 M.A.
University of Basel 1994 Umhabilitatiert

Employment: 1979-1983 Chemistry teacher, Oxford Girls' High School, Oxford, UK
1984-1985 Postdoctoral Associate, Department of Chemistry, University of Notre Dame, IN 46556, USA
1985-1986 Assistant Professor, Department of Chemistry, University of New Hampshire, USA
1986-1994 College Lecturer in Chemistry, Newnham College, Cambridge, UK; Royal Society Research Fellow, University of Cambridge, UK; Lecturer in Inorganic Chemistry, University of Cambridge, UK
1994-1994 Privat Dozentin, Department of Chemistry, University of Basel, CH-4056 Basel, Switzerland
1998-present Titular Professor, Department of Chemistry, University of Basel, CH-4056 Basel, Switzerland
2000-2002 Professor of Chemistry, School of Chemical Sciences, University of Birmingham, UK

Editorial work: Associate Editor (1990-1999) *Coordination Chemistry Reviews*, Elsevier, Oxford
Volume Editor, *Comprehensive Organometallic Chemistry*, 2nd Ed. 1995, Pergamon, Oxford
Executive Editor, *Polyhedron*, Elsevier, Oxford (1997-present)
Volume Editor, *Comprehensive Organometallic Chemistry*, 3rd Ed., 2007, Elsevier, Oxford

Summary: Catherine Housecroft is Professor of Chemistry at the University of Basel. She is co-director of a highly active research group with Edwin Constable, and has a broad range of interests spanning organometallic and coordination chemistries. Current research is focused towards the application of coordination chemistry to sustainable energy and functional coordination polymers. She has published over 300 research papers and 55 review articles, in addition to a number of chapters in edited books and reference works. She is an internationally recognized author of undergraduate textbooks: *Chemistry* (coauthored with her husband Edwin Constable) and *Inorganic Chemistry* (with Alan Sharpe) are both in their fourth editions.

Edwin Constable

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Employment

S.E.R.C. Post-Doctoral Research Fellow, University of Cambridge	1980-1982
University Demonstrator, University of Cambridge	1983-1987
University Lecturer, University of Cambridge	1987-1993
Ordinarius for Inorganic Chemistry, University of Basel.	1993-2000
Professor of Inorganic Chemistry, University of Birmingham	2000-2001
Head of School of Chemistry, University of Birmingham	2001-2002
Ordinarius for Chemistry, University of Basel	2002-
Vice Rector for Research and Talent Promotion, University of Basel	2011 -

Education

St Catherine's College Oxford, BA (Hons) Chemistry. First class	1974-1978
Linacre College, Oxford, D. Phil Chemistry, D. Phil Chemistry. "Heterocyclic Synthesis"	1978-2000

Selected academic awards and honours

Howard Memorial Lecturer, Sydney, 1997
Erskine Fellow, University of Canterbury, Christchurch, New Zealand, 2003
Visiting Fellow at the Research School of Chemistry, Australian National University, Canberra, 2005, 2006
William Evans Fellow, University of Otago, Dunedin, New Zealand, 2007
ERC Advanced Grant Awardee, Project LiLo 2011
Royal Society of Chemistry Sustainable Energy Award 2011

Professional summary

Professor Edwin (Ed) Constable has been involved in supramolecular chemistry since its inception and has published over 500 research papers and many books. His h-Index is 62. He studied chemistry at St. Catherine's College, Oxford, completing his Part II studying acridine intercalators. His doctoral studies were also in Oxford, where he worked on the design of metal complexes for solar cells. He then moved to Cambridge where he held sequentially an 1851 Research Fellowship, a University Demonstratorship and Lectureship and was a Fellow of Darwin and Robinson Colleges. In 1993 he accepted a call to the Chair of Inorganic Chemistry in Basel where he has remained with the exception of a period at the University of Birmingham 2000-2001.

He has been Research Dean of the Faculty and is currently Vice-Rector for Research. His interests lie in metallosupramolecular and materials chemistry, especially in the use of metal ions for the assembly of novel architectures incorporating specific electronic or photophysical properties. He is a highly cited researcher and is involved in industrial collaborations, national and EU funded programs in interfacial and heterogeneous chemistry for nanoscale electronic, catalytic and electrocatalytic devices. Interest centres upon the development of new dyes for the dye-sensitized nano crystalline solar cell and new materials for OLEDs and related lighting technologies. He received an ERC Advanced Grant (2011-2016) for his project LiLo (Light-In, Light-Out) relating to sustainable materials chemistry and is actively involved in the Swiss Nanoscience Institute. He has a strong record of funding in pure and applied science projects and a long-standing interest in the use of homogeneous and heterogeneous systems for solar energy conversion and for water activation chemistry. He runs the research group jointly with his wife, Professor Catherine Housecroft.

Curriculum Vitae of Thomas A. Jung

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ASSIGNMENT: Honorary Professor in "Nanoscale Science" at the University of Basel (2009)
Group leader 'Molecular Nanoscience' at PSI and at the 'Nanolab' of the University of Basel (1999-current)

IBM Zurich Research Laboratory, Rueschlikon Switzerland (Jul 1994 – Dec 1996)

IBM T.J. Watson Research Center, Yorktown Heights NY (Sep 1992 – Jul 1994)

Paul Scherrer Institute Zurich, now: CSEM Zurich (Feb 1992—Aug 1992)

Research Assistant, University of Basel, Switzerland (Oct 1987—Jan 1992)

EDUCATION: PhD in Condensed Matter / Surface Physics, University of Basel, Switzerland (1992)

'Physik Diplom' specializing in Biophysics and Solid State Physics, Swiss Federal Institute of Technology, Zurich, Switzerland (1987).

ACHIEVEMENTS:

Responsibility for currently about 12 scientific and technical coworkers. Conducted key research in different fields and with significant citation record. Secondary impact of this research in the open press, and in more than 5 issued patents. Successful collaboration with companies and corporations including Nanonis, Sony, IBM, Straumann and Roche.

Experienced Lecturer in nanoscale science, surface science and introductory physics, both in the classroom and in laboratory sessions. Educated numerous PhD and diploma students, proven successful by their professional careers. Visiting scientist at the University of Wisconsin at Madison, USA and visiting professor at Kyoto University, Japan.

Referee for highly ranked scientific journals and granting agencies. Co-organizer of scientific workshops and conferences. Member of the American Physical Society, the American Association for the Advancement of Science and the Swiss Physical Society. Active member of the committee of the Swiss Physical Society (1997--2004); President of the Swiss Physical Society (1999--2002).

Scientific advisor to the European Commission through the Scientific Committee for New and Emerging Health Risks (SCENIHR), in particular for 'Nanoparticles and Nanotechnologies'. Coorganiser of the CMD-18 in Montreux and the International Young Physicists Tournament (IYPT) in Switzerland, a 'World Year of Physics' activity. Active promoter for the role of science in the society.

WEBSITES:

<http://lmn.web.psi.ch/molnano/>

<http://www.physik.unibas.ch/dept/pages/en/personnel/jung.htm>

<http://monet.physik.unibas.ch/que/nanolab/>

PERSONAL INFO:

Born in Zurich, Switzerland, December 20th 1962.

Swiss citizenship, married, 4 children.

Native speaker of German, fluent in English, oral knowledge of French, some Dutch.

Interests: Travelling, literature, music; Sports: Mountaineering, skiing, cycling.