

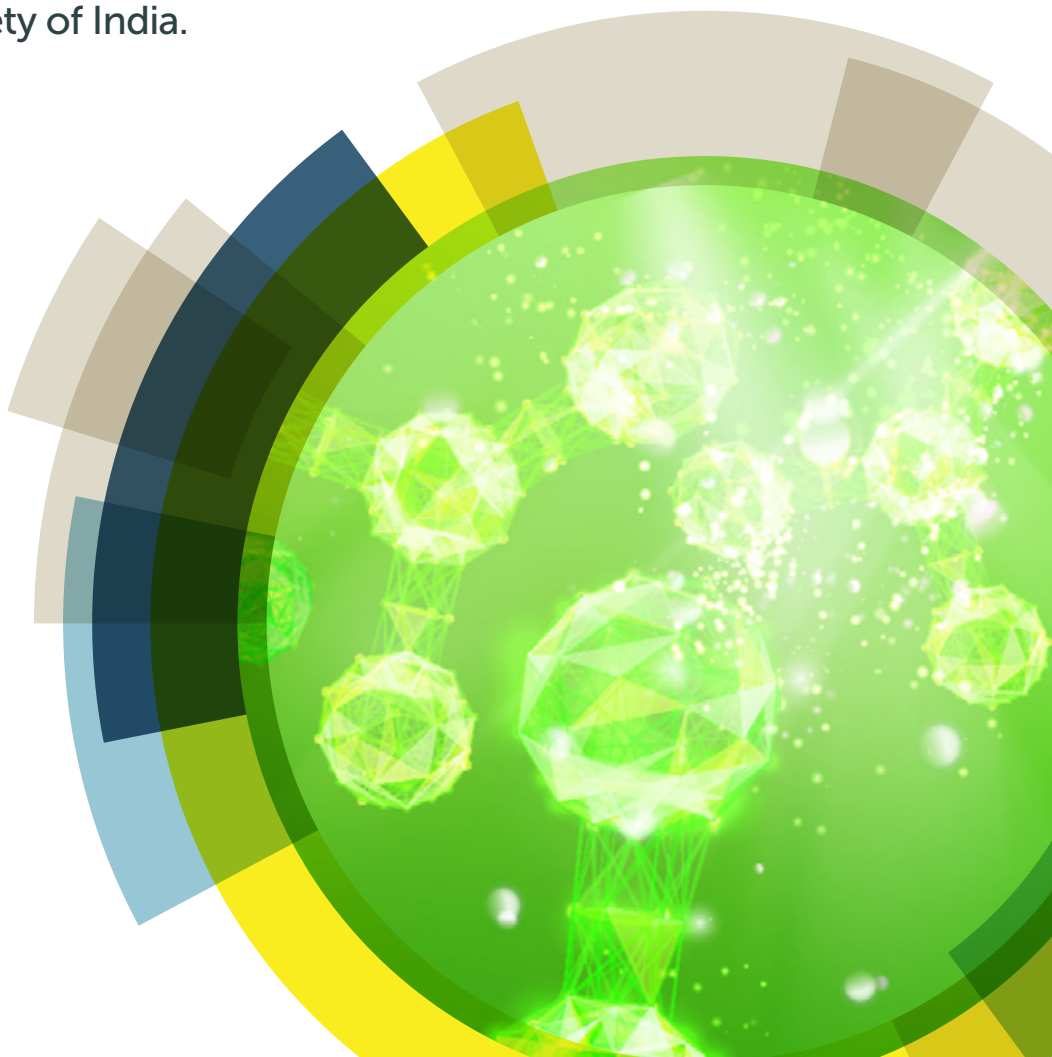


21 June 2016, Edinburgh, UK

# UK-India Symposium on Functional Materials

Organised by the Royal Society of Chemistry,  
University of Edinburgh and  
Chemical Research Society of India.

## Book of Abstracts



# Join the world's leading chemistry community

Affiliate membership of the Royal Society of Chemistry is offered to full paying non-member delegates of this conference, at no extra cost\*.

**As a member we can help you:**

**Get funding** – with travel grants and bursaries to attend the right conferences and events

**Tap into a global network** – that offers opportunities to promote and share your work, ideas and expertise

**Plan and manage your career** – with specialist advice, events and development opportunities such as Chartered status

**Be the first to know** – about the latest innovations and research in your field with access to our top quality publications and other major publishers content

**To take advantage of this offer look out for the electronic membership invitation, or simply speak to a member of staff at the conference.**

Find out more about membership, go to [www.rsc.org/join](http://www.rsc.org/join) or contact [membership@rsc.org](mailto:membership@rsc.org)

\*Duration of membership is until 31 December 2016.  
This offer is valid until 31 May 2016.



---

## Speaker biographies

---



**Dr Michael Shaver**

*EaStCHEM School of Chemistry, University of Edinburgh*

Dr Michael Shaver is a Chancellor's Fellow and Reader in the School of Chemistry at the University of Edinburgh. He is a synthetic polymer chemist with a focus on improving the sustainability of functional materials. He received his PhD from the University of British Columbia, was an NSERC Postdoctoral Fellow at Imperial College London, started his independent career at the University of Prince Edward Island before moving to Edinburgh in 2012. He is the Editor-in-Chief of the journal Green Materials and the 2015 winner of the MacroGroup UK Young Researcher Medal.



**Professor Uday Maitra**

*Department of Organic Chemistry, Indian Institute of Science, Bangalore*

After his BSc from Presidency College, Calcutta and MSc from IIT Kanpur, Uday Maitra got his PhD from Columbia University working with Prof. Ronald Breslow. Following a postdoctoral stay at the University of California at Berkeley with Prof. Paul Bartlett, he returned to India, and after a year at IIT Kanpur moved to IISc Bangalore in 1989. His research interests are in the Chemistry of Bile acids; Hydrogels, Metallohydrogels and Organogels; Nano/hybrid materials; Enzyme sensing, etc. He is also greatly interested in Chemistry Education and is a regular participant in a variety of outreach programmes for high school and undergraduate students. He has received a number of awards and honours including the S.S. Bhatnagar Award in Chemical Sciences in 2001, and is an elected fellow of the Indian Academy of Sciences and the Indian National Science Academy.



**Professor Sandeep Verma**

*Department of Chemistry and Center for Nanoscience and Soft Nanotechnology*

Sandeep Verma obtained Ph.D. in medicinal chemistry from University of Illinois Medical Center, Chicago, USA, in 1994. He subsequently held postdoctoral positions at Johns Hopkins University Medical Institutions, Baltimore, USA, and Max-Planck-Institute for Experimental Medicine, Göttingen, Germany, prior to joining Department of Chemistry, IIT Kanpur, in 1997, where he is presently an endowed Chair Professor and Head of Chemistry Department. His research interests include peptide/protein assemblies for disease modeling, surface chemistry of metal complexes and bioimaging. He is a recipient of Shanti Swarup Bhatnagar Prize in Chemical Sciences (2010), DAE-SRC Outstanding Investigator Award (2012), and J C Bose National Fellowship (2013), to name a few. He is an elected Fellow of Indian National Science Academy, Indian Academy of Sciences, National Academy of Sciences, India, and Royal Society of Chemistry (UK). He is an Associate Editor of Journal of Chemical Sciences (Springer) and serves on the Editorial Advisory Boards of Chemical Communications (RSC, UK), Cell Chemical Biology (Cell Press) and Journal of Peptide Science (Wiley).



**Professor Cait MacPhee**

*School of Physics & Astronomy, University of Edinburgh*

Cait MacPhee is a Professor of Biological Physics at the University of Edinburgh. She completed her degree and PhD in Australia in the biosciences, gradually moving across to physics during the course of her career. After a postdoc in Oxford Cait took up her first academic post in the Cavendish Laboratory at the University of Cambridge in 2002. In 2005 she moved to the School of Physics and Astronomy at the University of Edinburgh, where she was appointed to a Chair in 2011. She has interests in protein structure-function relationships, biomolecular self-assembly, protein evolution, nanobiotechnology, primary school education, and encouraging women in physics. In 2016 Cait was awarded a CBE for services to women in physics. She is married with two children (currently aged 9 and 10). Cait tweets as @sciorama.



**Professor Tanusri Saha-Dasgupta**

*S.N.Bose National Centre for Basic Sciences*

Tanusri Saha-Dasgupta obtained her PhD degree from Calcutta University, India in 1995 on the topic of Transport, Phase Formation and Statistical Physics in Disordered Solids. She was a Post-doctoral Fellow in ONERA, Paris during 1995-96, Research Scientist at CNRS, Cergy-Pontoise, France during 1996-97, Research Scientist at Max-Planck Institute, Stuttgart during 1996-99, before returning back to India as a Research Associate in IISc, Bangalore in 1999. She joined S.N.Bose National Centre in 2000, and is now a Senior Professor in the same Institute. She so far has produced 9 PhD students and published about 170 research papers in various International journals. She is a fellow of American Physical Society, Indian National Academy of Sciences, National Academy of Sciences, India, West Bengal Academy of Sciences, recipient of Swarnajayanti Fellowship, DAE-Raja Ramna lecture award, P.Sheel Memorial lecture award, MRSI-ICSC Superconductivity & Materials Science Annual Prize, and headed the Max-Planck India partner group. She is also the coordinator of Thematic Unit of Excellence on Computational Materials Science set up within S.N.Bose National Centre. She works in the area of computational condensed matter physics, related to the application of first principles electronic structure calculations both in bulk and nanoscale. Saha-Dasgupta is also engaged in various International research program, which includes Indo-German, Indo-Dutch, Indo-Russian, Indo-Austrian, Indo-European, Indo-US, Indo-Russian, Indo-Dutch, Indo-Austrian and Indo-Swedish programs.



**Eli Zysman-Colman**

*EaStCHEM School of Chemistry, University of St Andrews*

Eli Zysman-Colman obtained his Ph.D. from McGill University in 2003 under the supervision of Prof. David N. Harpp as an FCAR scholar where he conducted research in physical organic sulfur chemistry. He then completed two postdoctoral fellowships, one in supramolecular chemistry with Jay Siegel at the Organic Chemistry Institute, University of Zurich as an FQRNT fellow and the other in inorganic materials chemistry with Stefan Bernhard at Princeton University as a PCCM fellow. He joined the department of chemistry at the Université de Sherbrooke in Quebec, Canada as an assistant professor in 2007. In 2013, he moved to the University of St Andrews where he is presently reader in optoelectronic materials. His research program focuses on the rational design of: (I) luminophores for energy-efficient visual displays and flat panel lighting based on organic light emitting diode (OLED) and light-emitting electrochemical cell (LEEC) device architectures; (II) light harvesting dyes for dye-sensitized solar cells (DSSCs) and organic photovoltaics; (III) sensing materials employed in electrochemiluminescence; and (IV) photoredox catalysts for organic reactions.

**Professor Satish Patil**

*SSCU, Indian Institute of Science, Bangalore*

Prof. Satish Patil holds a Master degree in Chemistry from Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. He finished his PhD under the supervision of Professor Ullrich Scherf at Bergische Universität Wuppertal, Germany in 2004. Thereafter, he worked as a California Nanosystems Institute (CNSI) Postdoctoral Fellow from 2004-2006 in the Group of Professor Fred Wudl at the University of California, Los Angeles. In June 2006, he joined as an Assistant Professor at Indian Institute of Science, Bangalore. In 2012 he was promoted to Associate Professor. His present research is focused on  $\pi$ -conjugated organic materials for energy generation and storage applications.

**Mark Symes**

*School of Chemistry, University of Glasgow, Glasgow, UK*

Mark Symes was born in London in 1982 and graduated from the University of Cambridge in 2005. After a PhD at the University of Edinburgh with David A. Leigh (FRS), he undertook postdoctoral studies at the Massachusetts Institute of Technology (2009-2010). In late 2010, he returned to the UK and became a postdoctoral researcher at the University of Glasgow. This didn't put them off though, and he joined the faculty at Glasgow in 2013. His research interests span energy conversion, small molecule activations, electrochemistry and coordination chemistry, as well as new materials for all the above. He lives in Scotland with his wife Katherine and son Charlie.



**Professor Andy Mount**

*EaStCHEM, School of Chemistry, The University of Edinburgh*

Professor Andy Mount is Professor of Physical Electrochemistry and Dean of Research in the College of Science & Engineering (CSE) at the University of Edinburgh. His research interests include fundamental and applied electrochemistry, sensing and analysis and the development and application of healthcare and low carbon clean energy technologies; he plays a leading role in several major multidisciplinary collaborations across Scotland, the UK and Europe. As Dean of Research he is now leading the development of CSE research and impact strategy. He is a Fellow of the Royal Society of Chemistry (RSC), Chair of the RSC Faraday Standing Committee on Conferences, which organizes the highly successful Faraday Discussions conferences and journal series, and a member of RSC Faraday Division Council. He is also member of the Scottish Science Advisory Council.



**Professor Vinod K. Singh**

*Indian Institute of Science Education and Research*

Professor Singh did M.Sc. (Chemistry) from BHU, Varanasi in 1980 and Ph.D. at Malti-Chem Research Center Nandesari, Baroda under the guidance of Dr. Sukh Dev. He spent two years (1985-1987) in Canada at University of Calgary and University of British Columbia and three years at Harvard University (Advisor: Professor E. J. Corey, Nobel Laureate) in U.S.A, as a post-doctoral fellow. After a brief stint as a senior scientist at Neurogen Corporation, USA, Professor Singh joined IIT Kanpur as an Assistant Professor (Chemistry) in 1990 and rose to a level of Professor.

Professor Singh's research work falls in the area of synthetic organic chemistry, more specifically, asymmetric synthesis. He has developed several new chiral ligands/catalysts for enantioselective reactions. He has accomplished total synthesis of several bioactive natural products. His work has been recognized in the form of several awards and honors such as Distinguished Alumnus Award by BHU (2012), Goyal Award (2011), Shanti Swarup Bhatnagar prize (2004), and Swarnajayanti Fellowship Award (1998), among others. He is Fellow of all the Science Academy of the country. He has been honored with Padma Shri (2014), a civilian award by the Government of India.

Professor Singh is a Regional Editor of an Organic Chemistry journal - Tetrahedron Lett. He has been a Member of Scientific Advisory Council to the Prime Minister (SAC to PM: 2009-2014). He is currently on deputation as a Founder Director of IISER Bhopal since 12th June 2008. He is a Mentor Director of IISER Berhampur.

---

## Catalyst Driven Advances in Sustainable Polymer Synthesis

---

Dr Michael P Shaver

*EaStCHEM School of Chemistry, University of Edinburgh*  
*michael.shaver@ed.ac.uk*

Catalysts offer chemists the ability to control various aspects of polymerisation reactions to afford new materials with defined properties and tangible benefits. Our research group sits at the interface between inorganic and polymer chemistry, using coordination chemistry inspiration to offer insight into controlled radical polymerisations and ring opening polymerisations. This talk will focus on our work in biodegradable materials and controlled radical polymerisation. Highlights include: monomer design in ring-opening polymerisation, post-polymerisation modification of aliphatic polyesters, tacticity control in complex macrostructures and new iron-based catalysts for atom transfer radical polymerisation that are the fastest reported to date and operate by a unique dual-control mechanism.

---

## Soft Functional Materials from Metallohydrogels

---

Uday Maitra,\* Tumpa Gorai, Raju Laishram, Mitasree Maity

*Department of Organic Chemistry, Indian Institute of Science*

*Bangalore 560012, India*

*Email: maitra@orgchem.iisc.ernet.in*

Functional molecular gels are being increasingly investigated owing to their potential applications in various fields such as biomaterials, sensing, optoelectronics etc. Among many known gelators, bile acid derivatives are known to form self-assembled fibrillar networks (SAFINs), eventually leading to the immobilization of solvent molecules around them. We have recently developed a variety of gels from bile acid derivatives, and with metals salts derived from them. The use of these novel soft materials for the design of nanostructured materials, luminescent hydrogels and enzyme sensors will be presented in this lecture. The progress we have made in understanding the 'structures' of the gels will also be discussed.

### References

1. Chakrabarty, A., Marre, S., Landis, R.F., Rotello, V.M., Maitra, U., Del Guerzo, A., Aymonier, C. J. Mater. Chem. C, 2015, 3, 7561-7566.
2. Laishram, R., Bhowmik, S., Maitra, U. J. Mater. Chem. C, 2015, 3, 5885-5889.
3. Maity, M., Maitra, U. J. Mater. Chem. A, 2014, 2, 18952-18958.
4. Sajisha, V.S., Maitra, U. RSC Adv., 2014, 4, 43167-43171.
5. Bhowmik, S., Gorai, T., Maitra, U. J. Mater. Chem. C. 2014, 2, 1597-1600.
6. Kandaneli, R., Sarkar, A., Maitra, U. Dalton Trans. 2013, 42, 15381-15386.
7. Bhowmik, S., Maitra, U. Chem. Commun, 2012, 48, 4624.
8. Banerjee, S., Kandaneli, R., Bhowmik, S., Maitra, U. Soft Matter 2011, 7, 8207.
9. Bhowmik, S., Banerjee, S., Maitra, U. Chem. Commun. 2010, 46, 8642.

This work was supported by grants from the Department of Science & Technology, New Delhi, and from the Indo-French Centre for the Promotion of Advanced Research, New Delhi.



---

## **Modified Purine Nucleobases as Key Components in Cell Imaging, Surface Modifications and Lithium Ion Batteries**

---

V Venkatesh, R Kamal Saravanan, N Nagapradeep and Sandeep Verma  
*Department of Chemistry and Center for Nanoscience and Soft Nanotechnology*  
*Indian Institute of Technology Kanpur, Kanpur 208016 (India)*  
*sverma@iitk.ac.in*

Purine nucleobases, critical components of nucleic acids, have a key role in structure and genetic information storage. Given their versatile heterocyclic skeleton, we and others have exploited them for the construction of a variety of molecular frameworks, branching out into applications involving gold-nanocluster based cell nucleus imaging, sw/mw-CNT conjugations and surface modifications, and more recently, as a solid electrolyte in lithium ion batteries. We will present a brief overview of our recent results and an insight into future applications of these biocompatible ligands in diagnostics and devices.

---

## Smart proteins for new soft materials

---

Cait MacPhee

*School of Physics & Astronomy, University of Edinburgh, Edinburgh EH9 3FD, UK  
cait.macphee@ed.ac.uk*

Bacteria typically live in social communities called “biofilms” and employ a diverse range of molecules to structure their local environment. These molecules offer opportunities for structuring a range of soft materials including foodstuffs and non-food formulations. I will describe one of these biomolecules, a protein called BslA, that stabilises hydrophobic/hydrophilic interfaces and imparts mechanical stability. Nature has evolved a “smart” protein that carries out its function only in the right place and at the right time, and this offers opportunities for formulating new, smart, materials.

---

# Understanding and Manipulation of Physical and Chemical Processes in Complex Materials: A first-principles Approach

---

Tanusri Saha-Dasgupta

*Department of Condensed Matter Physics and Materials Science, S.N.Bose National Centre for  
Basic Sciences, Salt Lake, Kolkata 700098, INDIA  
tanusri@bose.res.in*

A tremendous progress has been made in recent time in application of materials-specific, computational theory for providing microscopic understanding of complex materials. The chemistry controls the physical properties e.g. electrical, magnetic, and optical properties of materials. At the root of all are the “Electrons”. In this talk, with few examples I will discuss how first-principles electronic structure calculations can be employed for the purpose of microscopic understanding, and importantly for manipulation of properties. Examples discussed will include carbon materials, and hybrid metalorganic materials consisting of both organic and inorganic components.

---

# Design of Thermally Activated Delayed Fluorescence Emitters for Electroluminescent Devices

---

Eli Zysman-Colman

*Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, Fife,  
UK, KY16 9ST*

*eli.zysman-colman@st-andrews.ac.uk*

Artificial lighting represents an almost \$91 Billion worldwide, corresponding to 20% of total worldwide electricity output. The fabrication of solid-state lighting devices that are significantly more energy efficient and lower cost than the current state-of-the-art is particularly germane to addressing issues relating to energy consumption, environmental impact and quality of living. Organic Light Emitting Diodes (OLEDs) and Light-emitting electrochemical cells (LEECs) represent two promising technologies. However, stable and bright white light devices have yet to be fully realized in the latter while the cost is presently too high in the former. One of the main challenges remaining is the development of bright blue emitters that when incorporated produce bright and stable devices of the same colour. In this presentation I will outline our recent efforts towards the rational design of third-generation emitters that emit via thermally-activated delayed fluorescence (TADF).

---

## Triplet Excitons in Organic Semiconductors

---

Satish Patil

*Solid State and Structural Chemistry Unit*

*Indian Institute of Science, Bangalore*

*satish@sscu.iisc.ernet.in*

In bulk heterojunction solar cells, the polymer triplet states are considered a main loss mechanism. The charge-transfer (CT) states can irreversibly recombine to form polymer triplet excitons due to their lower energy relative to the CT states. Triplet excitons can however be used for the generation of photocurrent when energy levels are appropriately aligned. In organic light-emitting diodes, recombination of hole and electron produces 25% of singlet excitons (S1) and 75% of triplet excitons (T1). Only the transitions from singlet excitons can be harvested for light emission as transition from T1 to S0 is spin forbidden and considered as dark states. We are interested to harvest these triplet excitons by careful design of organic molecules and their energy levels. This talk will discuss design rules of such organic materials. In addition, discussion would also be directed towards the performance of materials developed in our laboratory for organic solar cells and light-emitting diodes.

---

# Materials for electrochemical water splitting: a fresh look at some old catalysts and some new(er) catalysts for old applications

---

Mark D. Symes

*School of Chemistry, University of Glasgow, Glasgow, UK*  
*mark.symes@glasgow.ac.uk*

There has been much interest recently in electrocatalytic water splitting for storing intermittent renewably-generated power (e.g. solar) as chemical fuels such as hydrogen. In this talk, I will give an overview of the research in the Symes group that works towards the overall objective of renewably-driven electrocatalytic water splitting. We shall examine electrocatalysis of both water oxidation and proton reduction at low pH using metastable cobalt-based catalyst films that exploit the natural propensity of the first row transition metals and their oxides to dissolve at low pH.<sup>1</sup> Next, we shall explore the role of trace impurities in the electrolyte as a potential source of significant electrocatalytic activity for water oxidation and proton reduction and steps that can be taken to prevent such adventitious contaminants from giving false positive results for electrocatalysis.<sup>2,3</sup> Finally, we will examine ternary metal chalcogenides as highly active proton reduction catalysts, touching on methods by which these catalysts can be prepared and their electrochemical performance.<sup>4</sup>

## References

1. L. G. Bloor, P. I. Molina, M. D. Symes, L. Cronin, *J. Am. Chem. Soc.* 2014, 136, 3304.
2. I. Roger, M. D. Symes, *J. Am. Chem. Soc.* 2015, 137, 13980.
3. I. Roger, M. D. Symes, Manuscript in preparation
4. I. Roger, R. Moca, H. N. Miras, A. Y. Ganin, M. D. Symes, Submitted.



---

## **Novel Electrode Systems for Enhanced Sensing and Analysis**

---

Andy Mount

*EaStCHEM, School of Chemistry, The University of Edinburgh, Edinburgh EH9 3FJ, Scotland  
a.mount@ed.ac.uk*

There is a pressing need for the development of enhanced electrochemical sensor systems of high fidelity, particularly for healthcare and energy applications. This talk will outline progress in two aspects of enhancement, which both present advanced materials challenges; the development and characterisation of novel microfabricated enhanced electrode systems and the design and functionalisation of electrodes with selected materials for specific sensing and analysis. Novel single electrode and multielectrode devices will be presented which have been designed and produced through microfabrication, showing both their predicted and their established enhanced response. Developments in two application areas will then be presented, where specific materials functionalisation has been carried out to produce electrodes tailored to selective sensing. In the first application, progress towards enhanced biosensors which detect disease-relevant markers from real-world biological matrices with enhanced rapidity and sensitivity will be outlined. The second application area addressed will be the development of sensing and analysis systems suited to measurement in the hostile environment of molten salts. These are attractive media for developing chemical and electrochemical processes with potential applications in areas including fuel reprocessing, metal refining, molten salt batteries and electric power cells.

---

## Enantioselective Approach to Isoindolinones and Tetrahydroisoquinolines (THIQ)

---

Vinod K Singh

*IISER Bhopal, Bhopal Bypass Road, Bhauri, Bhopal 462066, MP, India*

*Department of Chemistry, IIT Kanpur, Kanpur 208016, UP, India*

*Email: vinodks@iitk.ac.in*

Enantioenriched isoindolinones and tetrahydroisoquinolines represent an important class of synthetically useful heterocyclic compounds with impressive diversity of biological activities. Although few elegant approaches to these targets have been reported, there was no straightforward synthesis of isoindolinones and tetrahydroisoquinolines (THIQ's) employing a unified strategy from simple and readily available starting materials.

In this talk, I will be delineating our efforts towards enantioselective synthesis of these important classes of compounds employing a metal catalyzed (Cu(I)-PYBOX-diPh catalyzed alkynylation cascade<sup>1</sup> as well as through an organocatalytic Mannich strategy involving remarkably high enantioselective (up to >99% ee) cascades/ sequences.<sup>2</sup> Both the strategies involve one C-C and two C-N bond forming events in one-pot in an operationally simple reaction conditions in good to excellent yields.

### References

1. (a) Bisai, V.; Suneja, A.; and Singh, V.K. *Angew.Chem., Int. Ed.* 2014, 53, 10737. (b) Sivasankaran, D.; Bisai, V.; Unhale, R. A.; Suneja, A.; Singh, V.K. *Org. Lett.* 2014, 16, 6068.
2. Bisai, V.; Unhale, R. A.; Suneja, A.; Sivasankaran, D.; Singh, V.K. *Org. Lett.* 2015, 17, 2102.

---

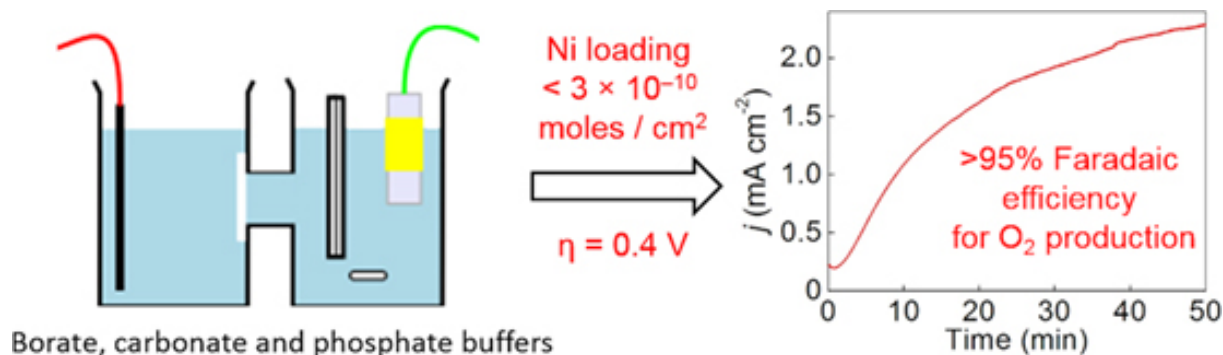
# Efficient Electrocatalytic Water Oxidation at Neutral and High pH by Adventitious Nickel at Nanomolar Concentrations<sup>1</sup>

---

Isolda Roger\* and Mark D. Symes

*WestCHEM, School of Chemistry, University of Glasgow,  
University Avenue, Glasgow, G12 8QQ, U.K*

**ABSTRACT:** Electrolytic water oxidation using earth-abundant elements is a key challenge in the quest to develop cheap, large surface area arrays for solar-to-hydrogen conversion. There have been numerous studies in this area in recent years, but there remains an imperative to demonstrate that the current densities reported are indeed due to the species under consideration, and not due to the presence of adventitious (yet possibly highly active) contaminants at low levels. Herein, we show that adventitious nickel at concentrations as low as 17 nM can act as a water oxidation catalyst in mildly basic aqueous solutions, achieving stable (tens of hours) current densities of 1 mA cm<sup>-2</sup> at overpotentials as low as 540 mV at pH 9.2 and 400 mV at pH 13. This nickel was not added to the electrolysis baths deliberately, but was found to be present in the electrolytes as an impurity by ICP-MS. The presence of nickel on anodes from extended-time bulk electrolysis experiments was confirmed by XPS. In showing that such low levels of nickel can perform water oxidation at overpotentials comparable to many recently-reported water oxidation catalysts, this work serves to raise the burden of proof required of new materials in this field: contamination by adventitious nickel at trace loadings must be excluded as a possible cause of any observed water oxidation activity.



## References

- 1 Roger, I.; Symes, M. D. *J. Am. Chem. Soc.*, 2015, 137 (43), 13980

---

# Nanocomposite films as a gas sensor for organic compounds

---

Shams B. Ali, Dr. Benjamin R. Horrocks and Prof Andrew Houlton

*Bedson Building, Chemical Nanoscience Laboratories, School of Chemistry, Newcastle University, NE1 7RU. s.ali2@newcastle.ac.uk*

**Abstract:** This research concerns the physical and structural properties of carbon nanotube /conductive polymer composites and their use in gas sensors. A good sensor should be sensitive, reliable, low cost, with fast response and a short recovery time<sup>1</sup>. Carbon nanotubes (CNTs) are well-suited because of their unique properties; their small size, hollow centre, large surface area and good electric conductivity. However, it has been shown that pristine carbon nanotubes have a low response for volatile organic compounds – our target analyse - therefore we attempted to improve this property of CNTs by templating pyrrole on CNTs. Polypyrrole is simple to prepare by oxidation of the monomer and its resistance is very sensitive to organic vapours, although much larger than that of CNTs<sup>2</sup>. TEM and AFM of polypyrrole/CNT composites prepared from single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) show polypyrrole coated the CNTs successfully. There are significant changes in the range of diameters of nanotubes for SWCNTs from (7-10) nm to (8-35) nm and from (2-10) to (21-50) nm for MWCNTs. The composites were tested for the variation in their resistance upon exposure to a range of organic vapours (acetone, chloroform) and to water. The sensing devices comprised simple two-terminal devices over which a layer of the composite was applied by drop-coating. We investigated the effect of the CNT: polypyrrole ratio on the sensor response,  $S = (R - R_0)/R_0$  where  $R_0$  is the resistance in an air atmosphere and  $R$  is the resistance at steady-state after exposure to an air/analyte mixture. In general, pure CNTs show a rapid response time, but very low response (typically  $S < 0.1$ ) at room temperature. As the amount of polypyrrole in the composite is increased,  $S$  increases, the response time deteriorates. Interestingly, the response of the composites may even change sign as a function of target analyse concentration; this suggests that a simple mechanism based on swelling and its effect on the percolation behaviour of CNTs in the polypyrrole matrix is insufficient to explain the data.

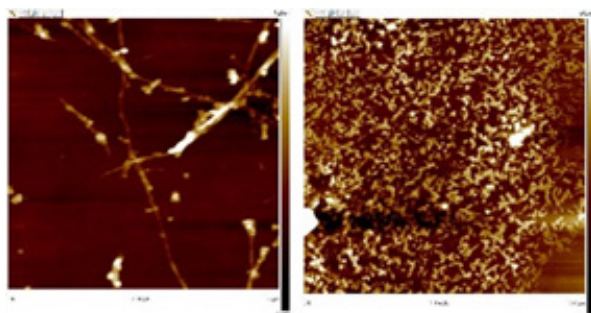


Fig1: AFM height images of (a) height distribution of SWCNTs before templated by Ppy.(b) Height distribution of MWCNTs after templated by Ppy

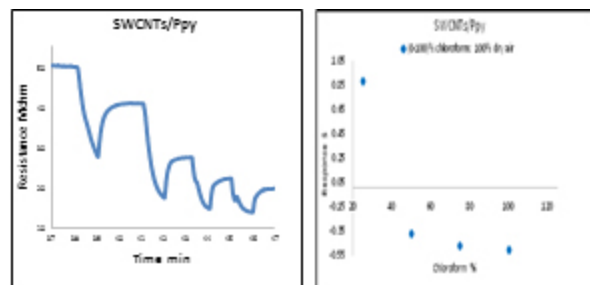


Fig2:(a) show the sensitivity of the electrical resistance  $R$  of SWCNTs/Ppy films to chloroform (0-100)% exposure at 17°C; (b) The device sensitivity  $S = (R - R_0)/R_0$  as a function of chloroform concentration.

## References:

1. King, V.B. (2007) Nanotechnology research advances. New York: Nova Science Publishers.
2. Richard, K., F., Lee, Barry, J., Cox and James, M., Hill (2010) 'The geometric structure of single-walled nanotubes', Nanoscale, 2, pp. 859-872.

---

# Polymer Immobilised Ionic Liquid Phase (PIILP) Stabilised Palladium Nanoparticles: Synthesis and Applications in Catalysis

---

Einas Abood\*<sup>1,2</sup>, Simon Doherty<sup>1</sup>, Julian G. Knight<sup>1</sup>, Ian J. S. Fairlamb<sup>3</sup>

<sup>1</sup>NUCAT, School of Chemistry, Bedson Building,

Newcastle University, Newcastle Upon Tyne, NE1 7RU,

<sup>2</sup>Polymer Research Centre, University of Basrah, Basra, Iraq,

<sup>3</sup>Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

The Doherty group has recently been exploring the concept of Polymer Immobilised Ionic Liquid Phase (PIILP) catalysis, in which the ionic liquid is immobilised in the form of a cation decorated polymer<sup>[1-5]</sup>. This project has developed imidazolium-based heteroatom-modified Polymer Immobilised Ionic Liquids (PIILs), which can immobilise and stabilise Pd-nanoparticles (PdNPs). We have been investigating whether the number and type of heteroatom influence catalyst performance. Preliminary studies revealed that PdNPs generated in situ by reduction of PdCl<sub>4</sub>@NH<sub>2</sub>-PIILP or PdCl<sub>4</sub>@PPh<sub>2</sub>-PIILP are highly active catalysts for the Suzuki-Miyaura cross-coupling between aryl bromides and boronic acids in a 1:1 mixture of ethanol/water. In a comparative study, Pd<sub>0</sub>@PPh<sub>2</sub>-PIILP generated by reduction of PdCl<sub>4</sub>@PPh<sub>2</sub>-PIILP with hydrogen, also gave good conversions under mild conditions; the corresponding TONs matched those obtained with catalyst generated in situ. In stark contrast the corresponding pre-reduced amino-decorated polymer immobilised ionic liquid stabilised palladium nanoparticles, Pd<sub>0</sub>@NH<sub>2</sub>-PIILP, were completely inactive. Kinetic studies, reaction dilution experiments, mercury poisoning, and catalyst loading studies have been employed to investigate the difference between the performance of pre-reduced PdNPs and those generated in situ. The PdNP@PIILP systems have been characterised by a range of techniques including solid state NMR spectroscopy, SEM, TEM, XRD, XPS and BET analysis.

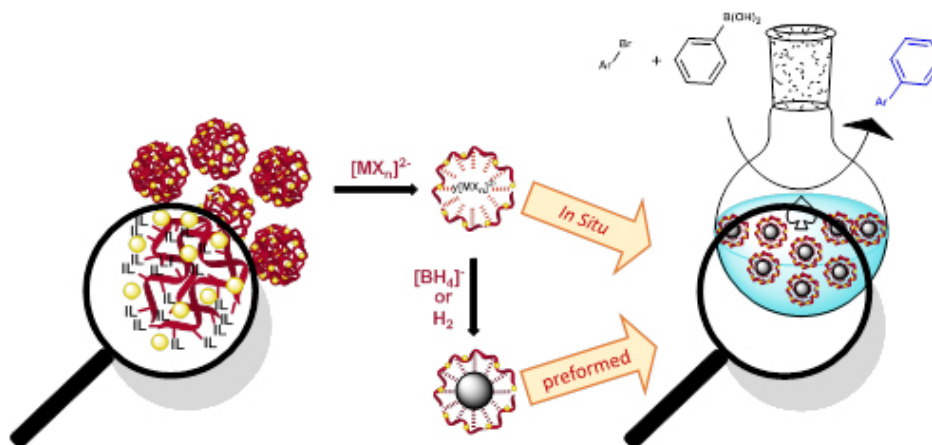


Figure 1. Synthesis of PIILPs Stabilised Nanoparticles

## References

1. S. Doherty, J. G. Knight, J. R. Ellison, D. Weekes, R. W. Harrington, C. Hardacre and H. Manyar, *Green Chemistry*, 2012, **14**, 925.
2. V. P. Chris Hardacre, *Catalysis in Ionic Liquids : From Catalyst Synthesis to Application* RSC, 2014.
3. S. Doherty, J. G. Knight, J. R. Ellison, P. Goodrich, L. Hall, C. Hardacre, M. J. Muldoon, S. Park, A. Ribeiro, C. A. N. de Castro, M. J. Lourenço and P. Davey, *Green Chem.*, 2014, **16**, 1470-1479.
4. S. Doherty, J. G. Knight, N. A. B. Ward, D. O. Perry, D. M. Bittner, M. R. Probert and S. A. Westcott, *Organometallics*, 2014, **33**, 5209-5219.
5. S. Doherty, J. G. Knight, M. A. Carroll, J. R. Ellison, S. J. Hobson, S. Stevens, C. Hardacre and P. Goodrich, *Green Chem.*, 2015, **17**, 1559-1571.

# Synthesis, Properties and LEEC Device Fabrication of cationic Ir(III) complexes Bearing Electron Withdrawing Aryl Ligands

Amlan K. Pal<sup>\*1</sup>, David B. Cordes<sup>2</sup>, Alexandra M. Z. Slawin<sup>2</sup>, Antonio Pertegas Ojeda<sup>3</sup>, Henk Bolink<sup>3</sup> and Eli Zysman-Colman<sup>1</sup>

<sup>1</sup>Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St. Andrews, St. Andrews, Fife, KY16 9ST, United Kingdom

<sup>2</sup>EaStCHEM School of Chemistry, University of St. Andrews, St. Andrews, KY16 9ST, Fife, United Kingdom

<sup>3</sup>Instituto de Ciencia Molecular, Universidad de Valencia, C/J. Beltran 2, 46980 Paterna, Spain

Cationic luminescent Ir(III) complexes bearing cyclometallating C<sup>N</sup> and ancillary N<sup>N</sup> type ligands continue to gain widespread attraction in the fields of photo- and electro-luminescent devices<sup>[1,2]</sup>, photocatalysts<sup>[3]</sup> and biolabelling<sup>[4]</sup>. In this context, our present study involves design and synthesis of four Ir(III) complexes (**1-4**) bearing increasing electron-withdrawing groups on the C<sup>N</sup> ligands (**L1-L4**) (**Figure 1**). The photophysical investigations reveal these complexes as sky-blue-to-green emissive luminophores that do not adhere to the paradigm where increasing electron-withdrawing character translates to bluer emission. We demonstrate how these complexes can act as emitters in light-emitting electrochemical cell (LEEC) devices.

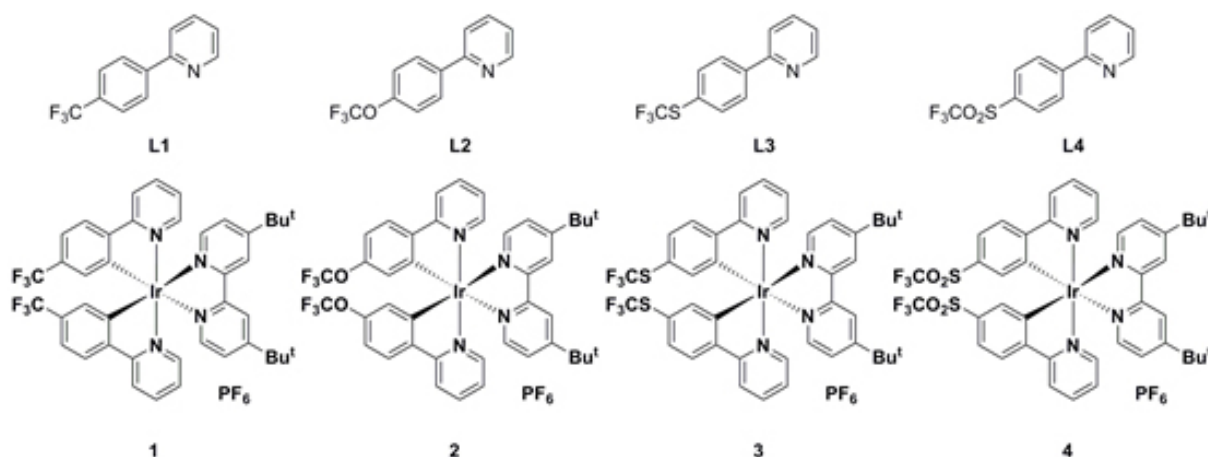


Figure 1. Structures of cyclometallating ligands (**L1-L4**) and cationic Ir(III) complexes (**1-4**) under study.

## References

1. N.M. Shavaleev, G. Xie, S. Varghese, D.B. Cordes, A.M.Z. Slawin, C. Momblona, E. Ortí, H.J. Bolink, I.D.W. Samuel, E. Zysman-Colman. *Inorg. Chem.*, **2015**, 54, 5907.
2. R.D. Costa, E. Ortí, H.J. Bolink, F. Monti, G. Accorsi, N. Armadori. *Angew. Chem. Int. Ed.*, **2012**, 51, 8178.
3. S. Sato, T. Morikawa, T. Kajino, O. Ishitani. *Angew. Chem. Int. Ed.*, **2013**, 52, 988.
3. B. Wang, Y. Liang, H. Dong, T. Tan, B. Zhan, J. Cheng, K.K.-W. Lo, Y.W. Lam, S.H. Cheng. *Chem. Bio. Chem.*, **2012**, 13, 2729.



---

# Investigation of the efficient conversion of photon energy to electricity by newly synthesised well-ordered low band gap semiconducting organic molecules.

---

Boniface Y. Antwi<sup>2\*</sup>, Rupert G. D. Taylor<sup>1</sup>, Richard B. Owoare<sup>2</sup>,  
Robert K. Adaboh<sup>2</sup> and Peter J. Skabara<sup>1</sup>.

<sup>1</sup>*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, United Kingdom.*

<sup>2</sup>*Department of Chemistry, University of Ghana, Legon-Accra, Ghana.*

Demand for carbon free energy has grown over recent years as the world fights against climate change. Current reports show that conventional energy production has environmental and economic challenges associated with it. Consequently, much attention has been directed towards harvesting solar energy for electricity generation. This alternative source of energy is expected to be a sustainable and greener source compared to current methods. Even though progress has been made in this direction, there is much room for improvement. For instance, the prevailing high cost of silicon based solar cells has necessitated varied research into affordable alternative photoactive materials with high power conversion efficiencies. A promising area amongst these is organic photoactive materials (both polymers and small molecules). They have unique properties such as, flexibility, large area applicability, ease of processing and low cost. Research shows that, efficiency of these materials correlates with mobility of photo-generated charge carriers. Ultrafast photo-induced charge transfer (< 100 fs) is best achieved in the bulk-heterojunction solar cell architecture with networked domains (10-20 nm in size) of donor and acceptor materials. The ability of an acceptor material to form networked domains is much desired and pursued in current global research. These domains form from the self-assembling of molecules into perfect crystals. It is therefore inferred that, crystalline molecules enhance charge carrier mobility prior to recombination in organic solar cells. Therefore, it is imperative that, newly synthesised donor molecules crystallise for efficient charge transfer.

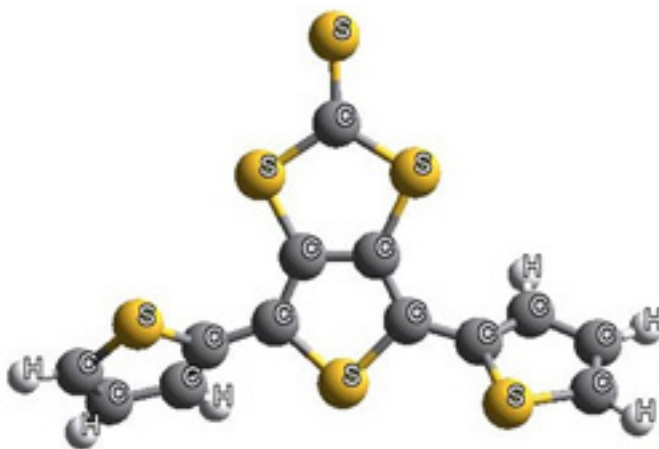


Figure 1: Terthiophene building block. 1

In all, our work seeks to explore the unique features of terthiophene (Figure 1) derivatives and their self-assembling properties, without sacrificing spectral absorption abilities in the synthesis of novel low band gap semiconducting molecules for application in organic solar cell technology.

## Keywords

energy, solar, photovoltaic, semiconductor, and molecules.

## References

1. Skabara P. J., Serebryakov I. M., Roberts D. M., Perepichka I. F., Coles S. J., and Hursthouse M. B., *J. Org. Chem.* 1999, 64, 6418-6424.

---

# BiVO<sub>4</sub>-TiO<sub>2</sub> Composite Films Formed Using the SILAR Method for Photocatalytic Textile Pollutant Degradation

---

Gylen Odling\* and Neil Robertson

*University of Edinburgh, Joseph Black Building, David Brewster Road, Edinburgh, EH9 3HX*

Contamination of drinking water sources is becoming increasingly problematic in the modern world[1]. Photocatalysis has received much attention as a potential method of removing small amounts of highly toxic organic and inorganic compounds from contaminated drinking water in recent years[2]. While titanium dioxide (TiO<sub>2</sub>) is the most popular photocatalytic material to date, fast charge recombination has been noted to reduce the photocatalytic efficiencies significantly[3].

We have used a simple sequential ionic layer adsorption reaction (SILAR) approach to create composite photocatalyst films comprised of BiVO<sub>4</sub> nanoparticles upon a porous TiO<sub>2</sub> scaffold. These composites have demonstrated improved activity for the degradation of model textile pollutant (Rhodamine 6G, Rh6G) under visible light. We also describe a system of BiVO<sub>4</sub> deposited in the same manner upon ZrO<sub>2</sub>, which we use to explore the nature of charge separation in the composites (Figure 1).

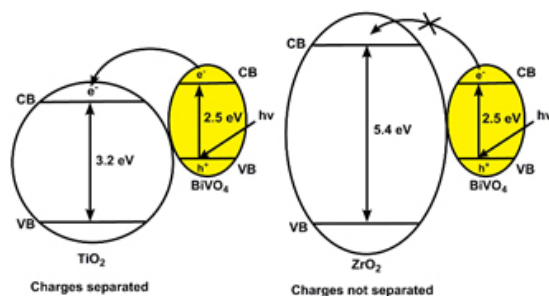


Figure 1. Charge separation in BiVO<sub>4</sub>-TiO<sub>2</sub> and the BiVO<sub>4</sub>-ZrO<sub>2</sub> comparison system.

Photoluminescence studies have determined that a cascade of charge separation steps from the pollutant excited state to the TiO<sub>2</sub> conduction band are responsible for the visible light activity of BiVO<sub>4</sub>-TiO<sub>2</sub> composites (Figure 2).

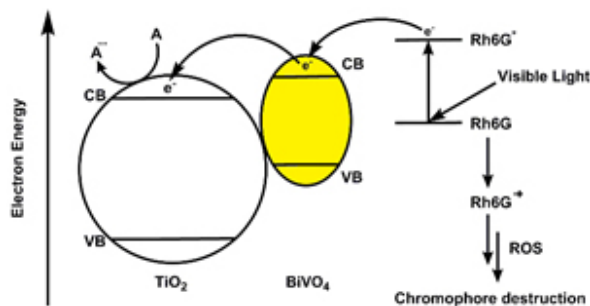


Figure 2. Mechanism determined by photoluminescence studies.

## References

- 1 World Health Organisation Water Fact Sheet No. 391, WHO, 2014.
- 2 S. Banerjee, S. C. Pillai, P. Falaras, K. E. O'Shea, J. A. Byrne and D. D. Dionysiou, *J. Phys. Chem. Lett.*, 2014, **5**, 2543–2554.
- 3 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, **95**, 69–96.

---

## The facile synthesis of $[\text{Co}(\text{bipyridine})_2(\text{X})]^+$ species ( $\text{X}$ = catecholate or benzenedithiolate) and their electronic and solvatochromic properties

---

Giacomo Cioncoloni\*, Hans M. Senn, Stephen Sproules,  
Claire Wilson and Mark D. Symes

*WestCHEM, School of Chemistry, University of Glasgow, Glasgow, G12 8QQ, UK*  
*g.cioncoloni.1@research.gla.ac.uk, mark.symes@glasgow.ac.uk*

Complexes of Co(III) containing more than one type of chelating ligand are targets that can be challenging to synthesize on one hand, and yet are of great fundamental interest on the other. Herein, we describe the synthesis of the complexes  $[\text{Co}(2,2'\text{-bipyridine})_2(\text{catecholate})]^+$  (**1**),  $[\text{Co}(5,5'\text{-dimethyl-2,2'-bipyridine})_2(\text{catecholate})]^+$  (**2**) and  $[\text{Co}(5,5'\text{-dimethyl-2,2'-bipyridine})_2(\text{benzene-1,2-dithiolate})]^+$  (**3**) for the first time. The electronic properties of complexes **2** and **3** were studied in some detail, by both experimental and theoretical methods. Spectroscopic studies showed that complex **2** displays intriguing solvatochromic properties as a function of solvent polarity and hydrogen-bond donation ability, but that the benzenedithiolate analogue **3** (which is a much weaker acceptor of hydrogen bonds from the solvent) is only very weakly solvatochromic. Furthermore, we show that complex **2** has potential as a molecular probe that can allow the composition of mixed solvent systems to be determined as a function of its absorbance spectrum. As the general synthetic procedure followed to obtain these complexes is both high-yielding and straightforward, we hope that this route will serve to expedite the synthesis of this fascinating class of molecules, allowing a variety of more elaborate structures to be accessed.

---

## Large thermoelectric power factors in polycrystalline SnSe

---

Srinivasarao Popuri<sup>1\*</sup>, Michael Pollet<sup>2</sup>, Rodolphe Decourt<sup>2</sup>,  
Finlay Morrison<sup>3</sup> and Jan-Willem Bos<sup>1</sup>

<sup>1</sup>*Institute of Chemical Sciences and Centre for Advanced Energy Storage and Recovery, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS*

<sup>2</sup>*ICMCB-CNRS, University of Bordeaux,*

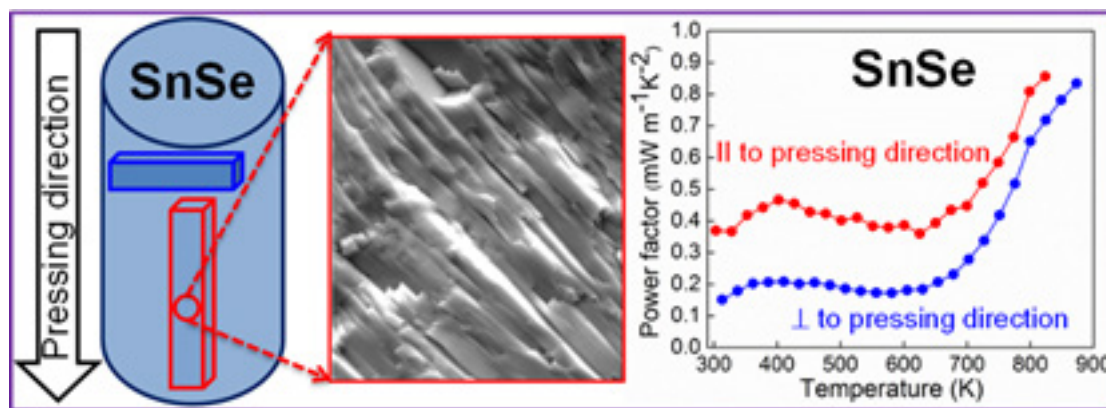
*87 avenue du Dr. A. Schweitzer, Pessac F-33608, France*

<sup>3</sup>*EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK*

There is an ongoing search for more efficient, durable and affordable thermoelectric materials so that the large scale application of thermoelectric generators becomes viable. Tin monoselenide (SnSe) has recently attracted attention due to the realization of an unprecedented figure of merit,  $zT = 2.6$  at 923 K.<sup>[1]</sup> Here,  $zT = S^2T/\rho\kappa$ , where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity and  $\kappa$  is thermal conductivity ( $T$  is the absolute temperature). This has resulted in a large amount of research trying to translate this performance into polycrystalline samples, as these are preferable for thermoelectric device applications.<sup>[2]</sup>

We have used solid state reactions and induction heating hot pressing at moderate temperatures to synthesize and consolidate polycrystalline SnSe samples, respectively. This avoids issues related to non-stoichiometry and has resulted in the isolation of near stoichiometric SnSe<sup>[3]</sup>. These samples have low electrical resistivity values, and afford thermoelectric power factors  $S^2/\rho = 0.9 \text{ mW m}^{-1} \text{ K}^{-2}$  at 750 K. The electrical resistivity and thermal conductivity are anisotropic with respect to the hot-pressing direction with a factor of 2 difference observed. The large power factors and low thermal conductivities give rise to  $zT > 1$  at ~850 K in p-type polycrystalline SnSe<sup>[4]</sup>.

In this poster contribution, we will discuss the impact of processing on the thermoelectric properties of SnSe.



### References:

- 1 L.D. Zhao, S.H. Lo, Y.S. Zhang, H. Sun, G.J. Tan, C. Uher, C. Wolverton, V.P. Dravid, M.G. Kanatzidis, *Nature*, 2014, 508, 373.
- 2 C. L. Chen, H. Wang, Y. Y. Chen, T. Day and G. J. Snyder, *J. Mater. Chem. A*, 2014, 2, 11171.
- 3 Q. Zhang, E. K. Chere, J. Sun, F. Cao, K. Dahal, S. Chen, G. Chen and Z. Ren, *Adv. Energy Mat.*, 2015, 1500360.
- 4 S. R. Popuri, M. Pollet, R. Decourt, F. D. Morrison, N. S. Bennett and J. W. G. Bos, *J. Mater. Chem. C*, 2016, 4, 1685.

---

## Peptide hydrogel materials for cell therapy

---

Anitha C. Kumar<sup>\*1,3</sup>, Harikrishna Erothu<sup>3</sup>, Giuseppe Battaglia<sup>2</sup> and Paul D. Topham<sup>3</sup>

<sup>1</sup>*Chemical Engineering and Applied Chemistry, Aston University, Birmingham, West Midlands, United Kingdom.*

<sup>2</sup>*Department of Chemistry, University College London, London, United Kingdom.*

<sup>3</sup>*Department of Chemistry, Acharya Nagarjuna University, Guntur, Andhra Pradesh, India.*

Mankind has been trying to replace damaged or lost cells with new ones for centuries. Here, we propose the use of polymer-peptide hydrogels for cell therapy. Peptides are biocompatible, biodegradable and can produce suitable gelatinous environments for cell growth at extremely low concentrations (1% peptide)<sup>1</sup>. Polymers can be used to controllably adjust the balance of physical and chemical properties of the final biohybrid<sup>2</sup>. The tri-peptide Arginine-Glycine-Aspartic acid (RGD) is a well-studied cell binding motif for specific transmembrane proteins and is involved in cellular adhesion to the extracellular matrix<sup>3</sup>. There is continuous interest in the development of RGD-based therapeutics. Here, we use the phenylalanine (F) amino acid moiety to direct self-assembly and poly(ethylene oxide) (PEO) for maintaining hydrophilicity of the peptide macromolecules<sup>4</sup>. These materials will supra-molecularly selfassemble to form nanoscale fibres, which entangle to form a 3-dimensional scaffold able to accommodate large volumes of water (known as a supramolecular hydrogel)<sup>5-7</sup>. Importantly, all components of the bio-hybrids are FDA

approved. To synthesise the materials, solid phase peptide synthesis using a Wang resin is employed. The synthesis and characterisation of RGD-based peptides and their gelation properties will be explored and discussed.

### References:

- 1 Dave J. Adams and Paul D. Topham. *Soft Matter* 2010, 6, 3707-3721.
- 2 Stupp S.I. *Nano Letters* **2010**, 10, 4783-4786.
- 3 Weide T.; Modlinger A.; Kessler H. *Top. Curr. Chem.* **2007**, 272, 1-50; Ruoslahti E. *Annu. Rev. Cell Dev. Biol.* 1996, 12, 697-715.
- 4 Gwen F. Chimonides.; Arun A. Sohdi.; Mohammad R. Khaleghi.; Claire R. Hurley.; Dave J. Adams and Paul D. Topham *Journal of Polymer Science, Part A: Polymer Chemistry* **2013**, 51, 4853-4859.
- 5 Lange R and Vacanti J. P. *Science* **1993**, 260, 920-926.
- 6 Liora Almany and Dror Seliktar *Biomaterials* **2005**, 26, 2467-2477.
- 7 Tessmar J.K. and Gopferich A. M., *Adv. Drug Delivery Rev.* **2007**, 59, 274-291.

---

## New Tools for Visualising Nanoparticle Drug Delivery for Healthy Remyelination

---

Sally Vanden-Hehir<sup>1\*</sup>, Dr Anna Williams<sup>2</sup>, Prof Valerie Brunton<sup>3</sup> and Dr Alison Hulme<sup>1</sup>

<sup>1</sup>*EaStCHEM School of Chemistry, University of Edinburgh;*

<sup>2</sup>*MRC Centre for Regenerative Medicine, University of Edinburgh;*

<sup>3</sup>*Institute of Genetics and Molecular Medicine, University of Edinburgh*

Biodegradable polymeric nanoparticles (NPs) are becoming increasingly popular for targeted drug delivery. Recent work in the Williams group (Scottish Centre for Regenerative Medicine)<sup>[1]</sup>, has shown that NPs can be used for drug delivery to the central nervous system to promote remyelination in multiple sclerosis disease models. However, as yet no direct link between the observed biological effect and nanoparticle delivery has been established.

The most commonly used degradable polymer is poly lactide-co-glycolide (PLGA) which is an FDA approved polyester which degrades slowly in vivo via hydrolysis to give sustained drug release<sup>[2]</sup>. Functionalisation of PLGA NPs with antibodies allows targeting of the NPs to specific cells in the brain. PLGA NPs loaded with the protein leukaemia inhibitory factor have been shown to promote remyelination by increasing the rate of maturation of oligodendrocyte precursor cells to oligodendrocytes which are responsible for producing myelin. 1

Raman spectroscopy provides near label free imaging conditions and is sub-optical in resolution<sup>[3]</sup>. Introducing a bio-orthogonal label into the PLGA will allow the NPs to be visualised via Raman spectroscopy, enabling them to be tracked for the first time and questions about their uptake, distribution and degradation to be answered. To allow incorporation of the bio-orthogonal label, the polymer PLGA has been synthesised and fabricated into NPs using the both the emulsion-evaporation and nanoprecipitation methods. The PLGA was characterised by NMR, IR, Raman and SEC; and the NPs have been visualised by TEM. Double emulsion techniques have allowed the incorporation of BSA as a model protein, and we are currently investigating surface functionalisation.

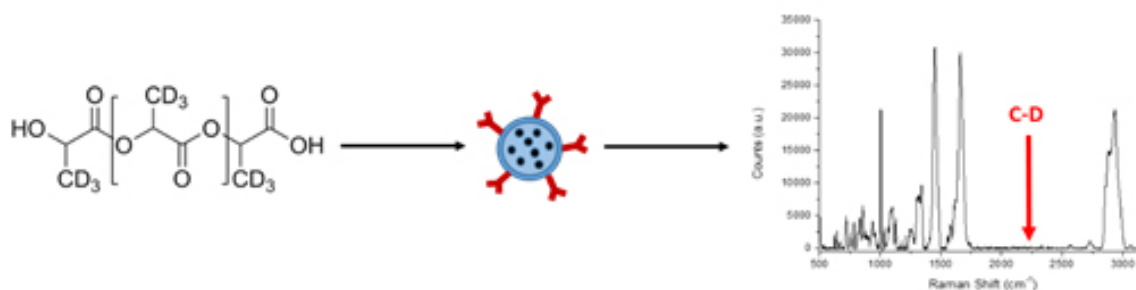


Figure 1: Deuterated PLGA will be used to form nanoparticles which can then be imaged using Raman spectroscopy.

### References

- 1 Ritchenn S. et al. *Biomaterials*, 2015, **56**, 78
- 2 Lee B. K. et al. *Chem. Eng. Sci.*, 2015, **125**, 158
- 3 Tipping W. et al. *Chem. Soc. Rev.*, 2016, **45**, 2075



---

# Selective Chemical Vapour Deposition of Nanoscale Arrays of Antimony Telluride

---

Chitra Gurnani<sup>1a,2</sup>\*, Sophie L. Benjamin<sup>1a</sup>, C. H. (Kees) De Groot<sup>1b</sup>, Andrew L. Hector<sup>1a</sup>, Ruomeng Huang<sup>1b</sup>, William Levason<sup>1a</sup> and Gill Reid<sup>1a</sup>

<sup>a</sup>*School of Chemistry, University of Southampton, SO17 1BJ, UK.*

<sup>b</sup>*School of Electronics and Computer Science, University of Southampton, SO17 1BJ, UK.*

<sup>2</sup>*School of Natural Sciences, Mahindra Ecole Centrale, Hyderabad-500043, India.*

Metal chalcogenide alloys are increasingly demonstrating potential as building blocks for future-generation nano-electronics<sup>[1]</sup>. In particular, the Group 15 chalcogenides  $M_2E_3$  ( $M = Bi, Sb$ ;  $E = Te, Se$ ) are versatile semiconductor materials with narrow bandgaps, and are of considerable interest as thermoelectric materials for near room temperature applications. It has been demonstrated that nanostructuring of these materials can lead to a significant increase in thermoelectric efficiency. Additionally, there has been considerable interest in developing methods to deposit individual nanocrystals of  $M_2E_3$  with specific orientations as topological insulators<sup>[2]</sup>.

We have successfully deposited high quality, nanoscale arrays of single nanocrystals of  $Sb_2Te_3$ , which are readily obtained by selective chemical vapour deposition from the single source molecular precursor,  $MeSb(Te^iBu)_2$ .<sup>[3]</sup> We have demonstrated highly-selective growth onto the conductive TiN regions of lithographically patterned TiN/ $SiO_2$  and etched TiN/TiN substrates. Single crystals grow reproducibly in confined regions of 100 nm diameter with pitch down to 500 nm. This selectivity is shown to prevail over different surface combinations, with different pitches, geometries and hole diameters. The effect of both pitch array and hole diameter on the crystal size will be discussed. Furthermore, we have explored the origins for this selectivity by comparison with our previous work on selective deposition of binary chalcogenides such as  $SnSe_2$ ,  $Ga_2E_3$ ,  $TiSe_2$ ,  $Bi_2Te_3$ .<sup>[4]</sup> These key findings and the underlying possible mechanisms with respect to both the substrate and material properties such as electrical resistivity will be discussed.

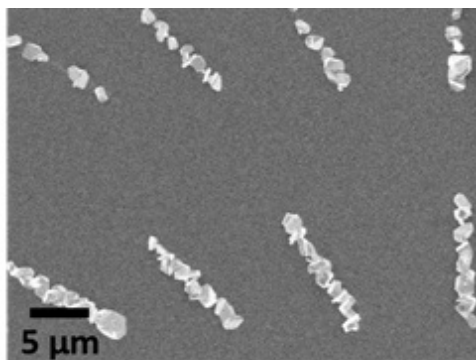


Fig (a):  $Sb_2Te_3$  single crystals grown within 10  $\mu m$  long, random oriented trenches with width of 100 nm (top) and 200 nm (down)

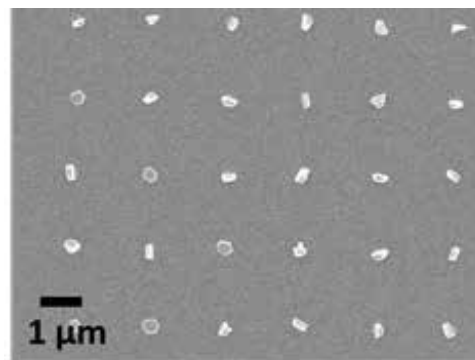


Fig (b):  $Sb_2Te_3$  single nano-crystal arrays grown selectively onto the etched TiN/TiN substrates with circular holes (diameter 100 nm and pitch is 500 nm)

## References:

- 1 M.-R. Gao, Y.-F. Xu, J. Jiang, and S.-H. Yu, *Chem. Soc. Rev.*, 2013, **42**, 2986.
- 2 H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang and S.-C. Zhang, *Nat. Phys.*, 2009, **5**, 438.
- 3 S. L. Benjamin, C. H. de Groot, A. L. Hector, R. Huang, E. Koukharenko, W. Levason and G. Reid, *J. Mater. Chem. C*, 2015, **3**, 423.
- 4 (a) C. H. de Groot, C. Gurnani, A. L. Hector, R. Huang, M. Jura, W. Levason and G. Reid, *Chem. Mater.*, 2012, **24**, 4442  
(b) S. L. Benjamin, C. H. de Groot, C. Gurnani, A. L. Hector, R. Huang, E. Koukharenko, W. Levason and G. Reid, *J. Mater. Chem. A*, 2014, **2**, 4865.

---

# Solid State Packing Control in Materials for Solar Cells

---

Flavia Pop\* and David B. Amabilino

*School of Chemistry, The University of Nottingham, NG72RD Nottingham, UK*

Diketopyrrolopyrroles (DPPs) are promising building blocks for organic electronics in general due to their optical properties, good thermal and photochemical stability, good electron affinity for tuning the frontier energy levels, and excellent planarity for enhancing intermolecular interactions and increasing charge carrier mobility<sup>[1]</sup>. DPPs have huge chemical versatility<sup>[2]</sup> which makes them easy to incorporate in various materials or to be exploited as small molecules for molecular and supramolecular materials, and consequently used for photovoltaic applications<sup>[3]</sup>.

This work presents thiophene based DPP chromophores whose structure and stereochemistry are defined to ensure high specificity in intermolecular interactions in the solid state (Figure 1). These specific functions are addressed through the nitrogen atom and the aromatic rings of the DPP core to control the solubility of the molecule and the packing of the material, and ultimately improve the electron transport and charge collection. Insights of the electronic properties of those chromophores were obtained by solution and solid absorption spectroscopy, cyclic voltammetry and spectroelectrochemistry. Studies in solid state *via* single crystal X-ray diffraction shows unique organisation of the molecules driven by intermolecular hydrogen bonding, as well as important changes in the geometry of the molecule due to other intra- and inter-molecular interactions.

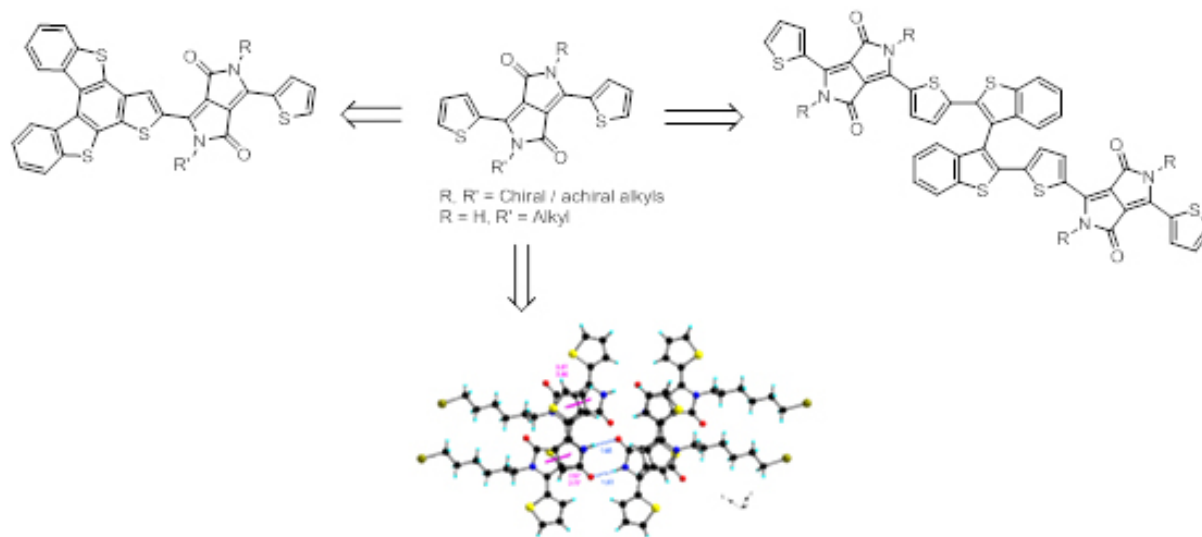


Figure 1

## Acknowledgement

We thank Stephen Davies for the electrochemistry and spectroelectrochemistry, William Lewis for single crystal X-ray diffraction measurements and the EPSRC for funding of this research.

## References:

- 1 a) Hendricks, K.H.; Li, W.; Heintges, G. H. L.; van Puijsen, G. W. P.; Wienk, M. M.; Janssen, R. A.J. *J. Am. Chem. Soc.* **2014**, 136, 11128–11133; b) Xiao, P.; Hong, W.; Li, Y.; Dumur, F.; Graff, B.; Fouassier, J. P.; Gigmes, D.; LaLevee, J. *Polymer* **2014**, 55, 746–751.
- 2 Kaur, M. and Choi, D. H. *Chem. Soc. Rev.* **2015**, 44, 58–77.
- 3 (a) Li, Y.; Sonar, P.; Murphy, L.; Hong, W. *Energy Environ. Sci.* **2013**, 6, 1684–1710; (b) Chandran, D. and Lee, K.-S. *Macromol. Res.* **2013**, 21, 272–283.

---

# High Efficiency Perovskite Solar Cells using Novel Spirofluorene-Xanthene (SFX) and Diacetylene bridged Triphenylamine (DATPA) based Hole Transport Materials

---

Aruna Ivaturi, Michal Maciejczyk, Rosinda Fuentes, Neil Robertson

*School of Chemistry and EaStCHEM, University of Edinburgh,  
King's Buildings, West Mains Road, Edinburgh EH9 3JJ, Scotland, UK  
Aruna.Ivaturi@ed.ac.uk, Neil.Robertson@ed.ac.uk*

As one of the top ten science breakthroughs of 2013, perovskite solar cells have shown potential both in the rapid efficiency improvement (from 3.8% in 2009 to the latest record of 22.1% in 2016) and in cheap material and manufacturing costs. Technology benchmarking and market analysis reveal that by 2025 the PSCs market is expected to reach \$214 million. <sup>[1]</sup> Spiro-MeOTAD has been the most promising hole transport material (HTM) in these devices. However, its high price and tedious multistep synthesis hinders progress of this technology towards commercialization. Considering this, a series of novel cost effective Spiro analogues based on spiro[fluorene-9,9'-xanthene] derivatives (SFX-HTMs), and triphenylamine moieties bridged with a diacetylene group (DATPA-HTMs) with electron-donating substituents and with different alkyl chain have been synthesized. The series of DATPA-HTMs with electron-donating substituent exhibited promising performance when tested in PSCs. <sup>[2]</sup> The alkyl chain in DATPA-HTMs has been varied to explore the effect on charge mobility, material processing, stability and interfacial charge transfer dynamics. SFX derivatives (SFX HTMs SFX-TAD, SFX-TCz, SFX-TPTZ and SFX-MeOTAD) with different oxidation potentials have been fully characterized by spectroscopic methods, elemental analysis and mass spectrometry. Intermolecular interactions were studied by X-ray single crystal and powder diffraction. High thermal stability of materials was revealed with differential scanning calorimetry. Based on these results, SFX-MeOTAD with appropriate energy levels for PSCs was tested in the devices. Device studies have shown competing efficiencies to commonly used Spiro-MeOTAD. Detailed cost analysis revealed that SFX-MeOTAD is more than five times cheaper than Spiro-MeOTAD, demonstrating great potential for use of the SFX family as cost effective and versatile hole conductors facilitating commercialization of perovskite solar cells. <sup>[3]</sup>

## References:

- 1 "Perovskite Photovoltaics 2015-2025: Technologies, Markets, Players", <http://www.prnewswire.com/>
- 2 A. Abate, M. Planells, D. J. Hollman, V. Bharti, S. Chand, H. Snaith, N. Robertson, *Phys. Chem. Chem. Phys.* **2014**, 17, 2335
- 3 M. Maciejczyk, A. Ivaturi, N. Robertson, *J. Mater. Chem. A* (**2016**), 4, 4855.

# Interplay of composition, microstructure and performance in Ce-Zr mixed oxide nanopowders for solid oxide fuel cell anode materials

Richard T. Baker<sup>1\*</sup>, Rodolfo. O. Fuentes<sup>1,2</sup>, Shidong Song<sup>1,3</sup> and Jonathan Kearney<sup>1</sup>

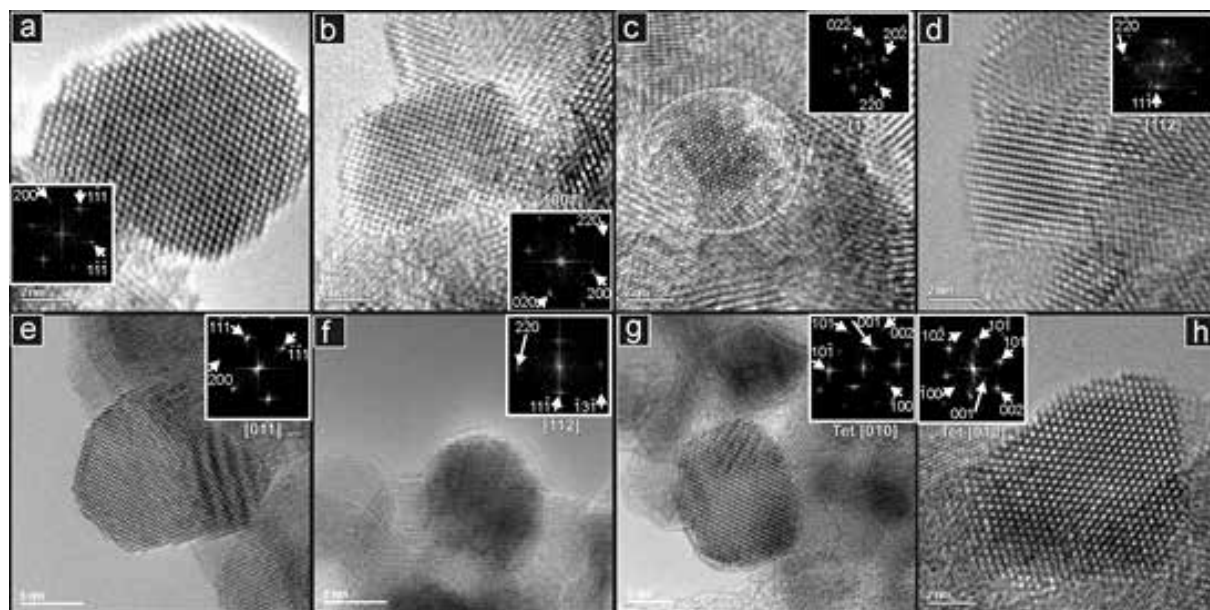
<sup>1</sup>*School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK.*

*<sup>2</sup>now at: Dept. of Solid State Physics, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina.*

<sup>3</sup>now at: School of Chemical and Environmental Engineering,  
China University of Mining and Technology, Beijing 100083, P.R. China.

Solid Oxide Fuel Cells (SOFCs) are of considerable interest for the efficient generation of electrical energy with lower environmental impact than conventional technologies. SOFCs are of particular interest because they are able to operate on fuels other than hydrogen, including hydrocarbons and oxyhydrocarbons. This opens the possibility of their application, not only within the hydrogen economy, but also for the more sparing use of fossil fuels, in the short to medium term, and of biofuels and fuels from waste, in the longer term. However, for such applications, suitable catalysts are required to catalyse the fuel and oxidant half-reactions, which take place at the anode and cathode, respectively. Mixed oxides of Ce and Zr are promising candidates for the anode catalyst because of their ability to activate hydrocarbons, their ability to store and supply oxygen and their thermal stability.

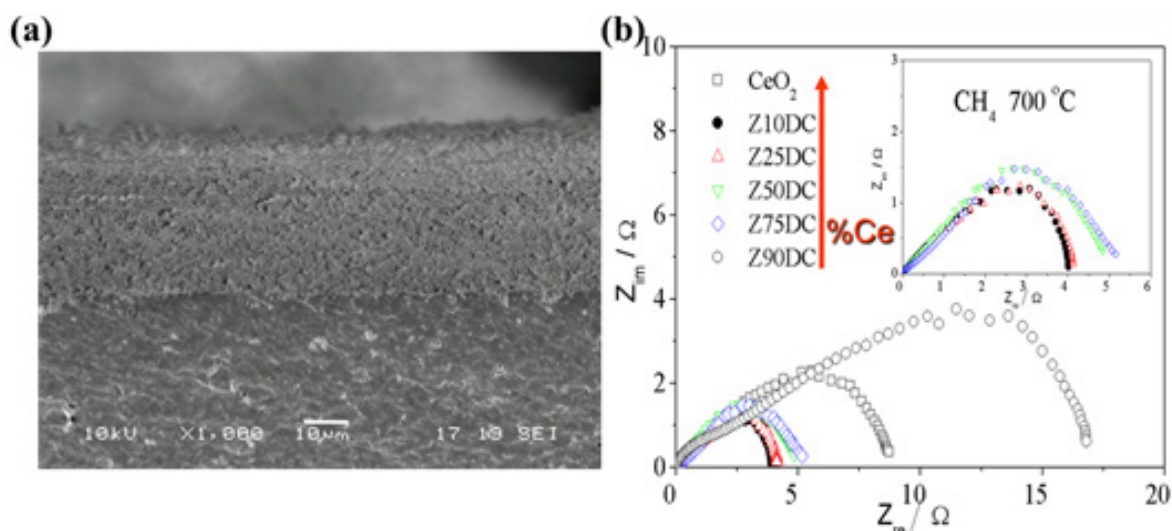
In this work, we used a solution-based, low temperature citrate complexation method to synthesise the compositional series,  $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$  with  $x=0.10, 0.25, 0.50, 0.75$  and  $0.90$ . Our method yielded high purity, nanoparticulate products of reproducible particle size range. The products were fully characterised by XRD, gas adsorption (BET) and electron microscopy (SEM, TEM and HRTEM) equipped with elemental analysis (EDS)<sup>[1]</sup>. The redox and catalytic activities of all members of the compositional series were then compared using temperature programmed and microreactor studies<sup>[2]</sup>. Finally, the electrochemical behaviour of the samples was studied by incorporating the powders into working electrochemical cells and applying the technique of impedance spectroscopy<sup>[3]</sup>.



**Figure 1.** HRTEM images of individual nanocrystals with corresponding DDPs inset:  $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_2$  shows only diffraction patterns consistent with either the cubic Fluorite structure or the tetrahedral structure (**a-d**);  $\text{Ce}_{0.10}\text{Zr}_{0.90}\text{O}_2$ , which shows some diffraction patterns which can be indexed to both Fluorite and tetrahedral phases (**e,h**) but others which can be indexed only to the tetrahedral phase (**g,h**).

XRD patterns showed the crystal phase to change from the cubic fluorite structure to a tetragonal phase with increasing Zr content. This trend was confirmed in digital diffraction patterns obtained from high resolution TEM images of individual nanocrystals of each composition. HRTEM Images for the end-members of the series, with  $x=0.10$  and  $0.90$ , are given as examples in Figure 1. These images confirmed the particle sizes to be of the order of 5 nm for all compositions, as was estimated by the application of the Scherrer equation to the XRD peak widths, and they show the nanocrystals to have well-ordered lattice structures.

Temperature programmed reduction experiments indicated that the compositions with  $x=0.25$  and  $0.10$  contained both the largest amounts, and the most labile, oxygen, and were therefore the more promising samples. Catalytic activity studies confirmed this: these two compositions became active at lower temperatures than all other compositions.



**Figure 2.** (a) Cross-sectional SEM image of a typical porous anode structure deposited on a dense electrolyte for impedance measurements; (b) Impedance spectra for anodes containing the five Ce-Zr compositions and pure  $\text{CeO}_2$  operating in 5% methane at  $700^\circ\text{C}$ . The width of the features along the  $Z'$  axis gives the polarisation resistance of the anode. The lowest (best) values were obtained for  $\text{Ce}_{0.90}\text{Zr}_{0.10}\text{O}_2$  and  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  (numbers in the legends indicate mole% Zr).

In detailed electrochemical studies, the polarisation resistance of anodes fabricated using each of the oxide compositions – as shown in Figure 2a – was measured in a number of fuel atmospheres and over a range of operating temperatures. Again, as seen in Figure 2b, the compositions with  $x=0.10$  and  $0.25$  showed the lowest resistances and were therefore the most promising anode materials. The agreement between the chemical and electrochemical techniques supports the use of this methodology in the search for SOFC anode materials.

This work was performed as part of the Supergen Fuel Cell Consortium (Phase One)<sup>[4]</sup>.

#### References:

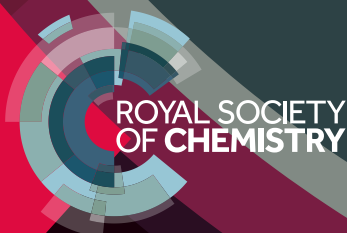
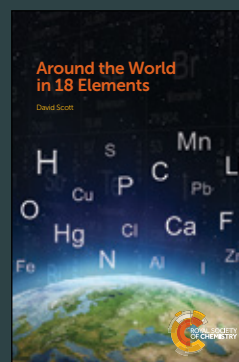
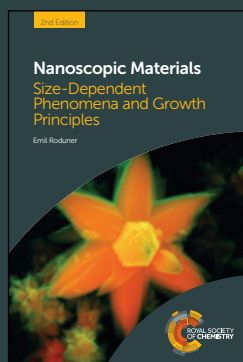
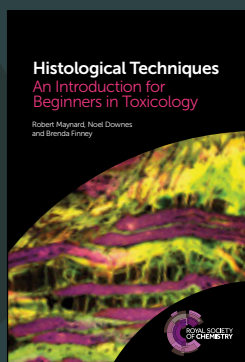
- 1 R.O. Fuentes, R.T. Baker, *J. Phys. Chem. C* (2009) **113**, 914.
- 2 J. Kearney, J.C. Hernández-Reta, R.T. Baker, *Catal. Today* (2012) 139.
- 3 S. Song, R.O. Fuentes, R.T. Baker, *J. Mater. Chem.* (2010) **20**, 9760.
- 4 The work presented here was funded by the Engineering and Physical Research Council through the Supergen Fuel Cell Consortium (Phase One).

Notes

# 35%

## discount on all books for Royal Society of Chemistry members

Choose from over 1,000 high-quality interdisciplinary, professional, expert books that detail the latest research advances and highlight technology, reference information, opinions and perspectives in modern science.





# Make the most of our publications

As one of the world's leading academic publishers, we produce more than 40 peer-reviewed journals and two magazines, and have over 1,500 books covering everything from medicinal chemistry to nanoscience.

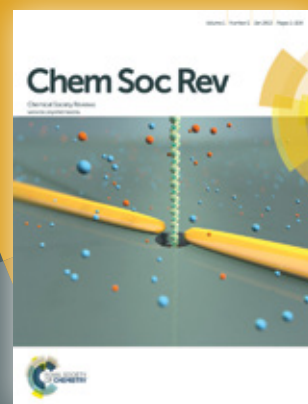
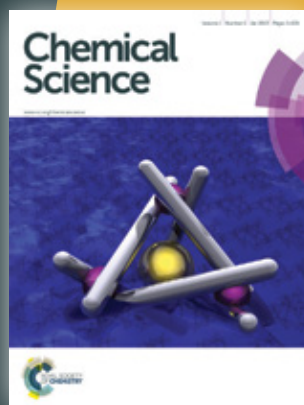
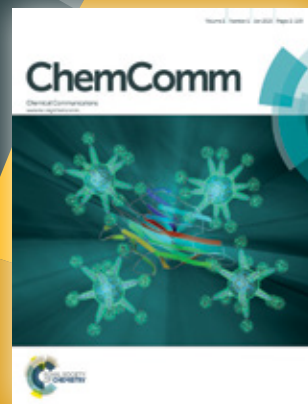
## The 2014 Journal Citation Reports® reinforces our exceptional standards\*:

- Of the top 20 journals in the multidisciplinary chemistry category, six are from the Royal Society of Chemistry, two of which are top 10. No other publisher has more.
- 85% of our journals now have an Impact Factor above 3.

With content valued by the global scientific community, access is a highlight for our members.

## As a member you get free access to:

- One online journal of your choice
- A further 15 free downloads – choose journal article or eBook chapters
- The entire RSC Journals Archive – 260,000 articles across all areas of the chemical science from 1841 – 2007
- Additionally, for just £50 a year (excluding VAT) you can subscribe to any of our other journals online



\* Data based on 2014 Journal Citation Reports®, (Thomson Reuters, June 2015)