View Article Online / Journal Homepage / Table of Contents for this issue
Dynamic Article Links

Chem Soc Rev

Cite this: *Chem. Soc. Rev.*, 2012, **41**, 7333–7334

www.rsc.org/csr

EDITORIAL

From serendipity to design of polyoxometalates at the nanoscale, aesthetic beauty and applications†

Leroy Cronin*[a] and Achim Müller[b]

DOI: 10.1039/c2cs90087d

Polyoxometalate cluster science has come a long way since the first description of molybdenum blue in 1778 by the famous Swedish chemist Scheele. Interestingly, it was considered as an extremely exciting discovery even at that time as the corresponding paper was translated from the Swedish into French and included under the title "*Sur la Mine de Plomb ou Molybdène*" in the series of "*Observations sur la Physique, sur l'Histoire Naturelle et sur les Arts*" by M. L'Abbé Rozier and M. J. A. Mongez le jeune, which collected important scientific publications of the time. Some time later, in 1826, Berzelius described the yellow precipitate that is produced when ammonium molybdate is added in excess to phosphoric acid, which is now known as the textbook example $(NH_4)_3[PMo_{12}O_{40}]_{aq}$. Since this time the advances have been growing at an ever increasing rate. Polyoxometalates, a class of soluble metal oxides occupying a middle region between the monomeric metalates and the infinite metal-oxides, span a wide range of size, nuclearity, composition and physical properties that is quite breathtaking. In addition, the related research is highly interdisciplinary. The developments in polyoxometalate chemistry have been particularly remarkable and rapid since the early 1980s, facilitated by developments in instrumental analytics, and characterized by the explosion in published structural data whereby many hundreds, if not thousands, of new polyoxometalate clusters are added to the literature every year.

So, what represents the state of the art, and what are the options for the future? This themed issue of *Chemical Society Reviews* dedicated to Polyoxometalate Cluster Science answers these questions

[a] *School of Chemistry, WestCHEM, University of Glasgow, Glasgow, G12 8QQ, UK. E-mail: lee.cronin@glasgow.ac.uk*
[b] *Fakultät für Chemie, Universität Bielefeld, Postfach 100131, 33501 Bielefeld, Germany. E-mail: a.mueller@uni-bielefeld.de*

† Part of a themed issue covering the latest developments in polyoxometalate science.

Leroy Cronin

Lee Cronin is the Gardiner Professor of Chemistry at the School of Chemistry, University of Glasgow. Lee was an undergraduate and DPhil student at the University of York, research fellow at the University of Edinburgh and an Alexander von Humboldt Research Fellow at the University of Bielefeld. From 2000 to 2002 he was a lecturer at the University of Birmingham, and moved to the University of Glasgow in 2002. In 2006 he was promoted to Professor. In 2011 he was awarded the RSC Bob Hay Lectureship and 2012 the RSC Corday Morgan Medal and Prize. The work of Cronin and his research group spans a range of fields with creative studies over the entire discipline of chemistry with some focus in the field of inorganic chemistry, specifically the self-assembly and self-organization of inorganic molecules and the engineering of complex systems leading to the emergence of system-level behaviours.

Achim Müller

Achim Müller studied Chemistry and Physics at the University of Göttingen where he got his PhD and Habilitation. In 1977 he obtained a chair of Inorganic Chemistry at the University of Bielefeld where he is now working with his research group. His research is highly interdisciplinary and ranges from molecular physics, via transition metal chemistry, biochemistry and nanoscience to philosophy and history of science. Prof. Achim Müller is a member of several National and International Academies and was honoured with numerous awards (honorary doctor degrees, professorships and memberships) and prizes, the most recent being the Centenary Medal of the Royal Society of Chemistry.

in many ways, and we are very pleased that most of the key research groups working in the field have contributed splendid articles to this issue which can be considered as a major contribution to this area. Work on the exploration and development of transition metal substituted polyoxometalates as water oxidation catalysts gives a key example of the breadth and depth of the area as highlighted by Craig Hill (only the corresponding authors are mentioned here and below) in his article DOI: 10.1039/c2cs35292c. Some of these clusters represent probably the most effective catalysts known. As a testament to the diversity of the field, Eugenio Coronado discusses the fact that magnetic polyoxometalates are ideal candidates to move beyond molecular magnetism, *e.g.* to molecular spintronics and quantum computing, in DOI: 10.1039/c2cs35205b, while Tianbo Liu refers to a new dimension of how macroions and amphiphiles show extraordinary self-assembly/organisation behaviour, in DOI: 10.1039/c2cs35176e. In the contribution by Josep Poblet and Carles Bo, DOI: 10.1039/c2cs35168d, it is shown how structures, properties and reactivities can be explored by theoretical methods to yield new insights, a feat that was barely possible a few years ago. Whereas Ulrich Kortz describes the use of diphosphonate ligands for the syntheses of a large number of very interesting clusters in DOI: 10.1039/c2cs35153f, Anna Proust gives an overview about the functionalization and post-functionalization of polyoxometalates grafted with a range of organic ligands and functional units as a promising strategy for the development of materials in DOI: 10.1039/c2cs35119f, and Yu-Fei Song and Ryo Tsunashima explore the development of devices like batteries and catalysts in DOI: 10.1039/c2cs35143a. Ira Weinstock describes how polyoxometalates can be used to effectively coat or decorate a variety of nanoparticles based on the combination of different classes of nanomaterials in DOI: 10.1039/c2cs35126a. Pierre Mialane explores the diversity in structure and properties of 3d transition metal cation substituted polyoxotungstates in DOI: 10.1039/c2cs35148j, while Guo-Yu Yang reviews in a similar context recent advances in paramagnetic-TM-substituted polyoxometalates (TM = Mn, Fe, Co, Ni, Cu) in DOI: 10.1039/c2cs35133a but with special emphasis on the integration of transition metal clusters. May Nyman and Peter Burns compare transition metal and actinyl polyoxometalates showing how uranyl based architectures can be obtained with an extraordinary diversity of structures in DOI: 10.1039/c2cs35136f. A logical building block strategy is described by Emmanuel Cadot in DOI: 10.1039/c2cs35145e to access a variety of interesting polyoxothiometalates using mainly $\{Mo_2S_2O_2\}$ and $\{Mo_3S_4\}$ units. Achim Müller and Pierre Gouzerh in DOI: 10.1039/c2cs35169b review how linking metal oxide building blocks in a constitutional dynamic library to giant clusters can lead to adaptive chemistry, while in contribution DOI: 10.1039/c2cs35190k Lee Cronin builds on these foundations and shows how dynamic libraries with adaptive options can be related to polyoxometalates with novel properties as well as the fabrication of interesting materials.

This themed issue spans the whole range of possibilities offered by polyoxometalates: beautiful molecules with transferable building blocks, designer surfactants, nanomagnets, organic–inorganic hybrids and related materials, catalysts for energy conversion, a fascinating class of actinide clusters, adaptive and "emergent" chemistry and not to forget new theoretical aspects. We would like to thank all the authors for their contributions.

As guest editors, we believe this issue represents a perfect snapshot of the field going forward. It should serve as a reference to those who wish to learn more about this area of science and also help new researchers become inspired, interested, and involved in the subject. Polyoxometalates have come a long way in more than two hundred years, from Scheele's molybdenum blue to their involvement in modern nanotechnologies, and we look forward with a great deal of enthusiasm and excitement to see how this area will develop in future.