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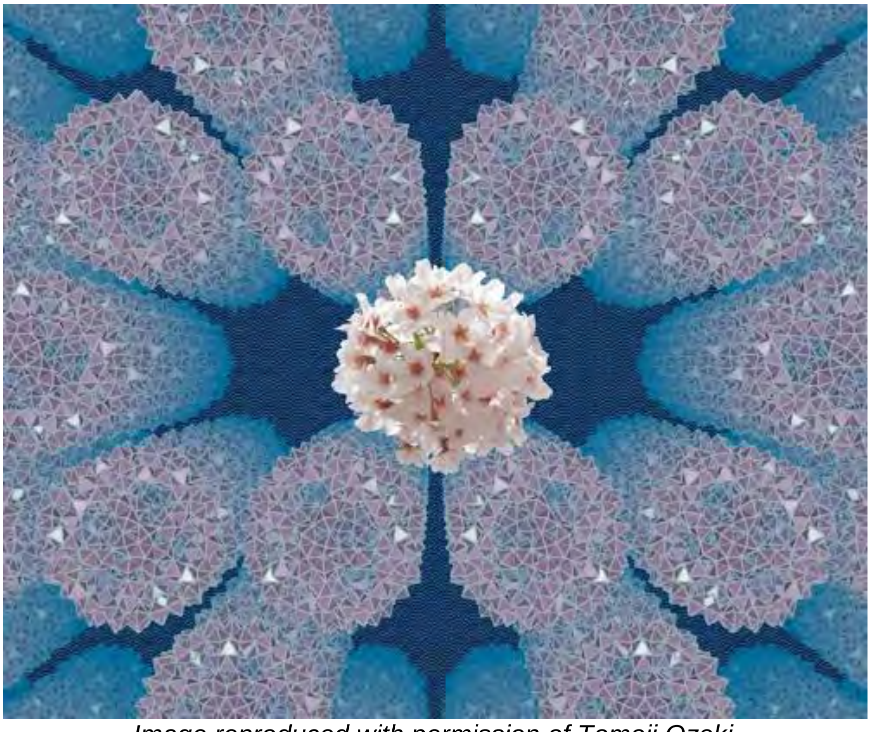

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EDITORIAL

Pushing the frontiers in polyoxometalate and metal oxide cluster science

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De-Liang Long and Leroy Cronin

Polyoxometalates (POMs) constitute a group of soluble metal oxides characterized by a vast compositional range and unusual structural diversity, holding a special position between monomeric oxometalate units and infinite metal oxide frameworks. Although it is now almost two hundred years since the work of Berzelius who published the first polyoxometalate paper in 1826 which described the yellow precipitate produced when ammonium molybdate was added in excess to phosphoric acid and Scheele who first described molybdenum blue in 1778, there continues to be remarkable advances and surprises in their fundamentals and applications. Indeed, there has been an explosion in the number of new POM compounds and their subsequent applications, reaction mechanisms and physical properties. The contemporary interest in POMs can be traced to the seminal work in determining large POM cluster structures in the late 1980s and early 1990s, and this great explosion of structural data was greatly assisted by the wide-spread availability of area detector X-ray diffractometers, not to mention the increase in computing power facilitating fast structure refinement. More recently, a great deal of work has been done on the modifications of traditional POM clusters and their derivatives, including highly innovative work that has explored the development of organic soluble polyoxometalate hybrids. Also the chemistry of POMs has been expanded considerably in terms of utilising them as building blocks for complex materials, as well as advances in electrochemically, magnetic and catalytically active systems. In fact, it is fair to say that POM chemistry has become one of the most popular research areas in inorganic chemistry, with currently more than 1500 papers published each year and this appears to be growing almost exponentially at present along with a global community of POM researchers, which is also reflected by the growing number of conferences and meetings.

This special themed issue of *Dalton Transactions* dedicated to polyoxometalate cluster science showcases a range of recent studies from the entire cross-section of polyoxometalates spanning topics ranging from the discovery of new POM clusters, reactivity, catalysis, electrochemical/photochemical properties and the mechanism of self-assembly. Work on the **extension of traditional POM classification** has been performed by Huang on the synthesis of lanthanide–antimony oxohalide nanoclusters (DOI: 10.1039/C2DT30563A) and by Nicholson on "Reverse Keggin-ion" structures (DOI: 10.1039/C2DT30341H). Attempts at targeting new POM structures are made by our group employing a strategy using **cation exchange to induce structural transformations** in which a missing dodecavanadomanganate(IV) was discovered and verified by crystal structure determination and mass spectrometry (DOI: 10.1039/C2DT30627A) and in addition, a new structure conformation of POM sandwich clusters was observed (DOI: 10.1039/C2DT30616F). One other fundamental way to produce **new types of POM derivatives** is to substitute part of the POM with hetero elements. Creative work has been carried out on organometallic Rh- and Ir-POMs of which reactivity has been screened by mass spectrometry (DOI: 10.1039/C2DT30655G). **Physical property** studies on substituted POM clusters of other hetero elements like Ru(II), In(III) and V(V) *etc.* are also addressed by individual groups (DOI: 10.1039/C2DT30475A, DOI: 10.1039/C2DT30467H, DOI: 10.1039/C2DT30355H and DOI: 10.1039/C2DT30466J). **Covalent modification of POMs** by grafting functional organo groups is a fantastic strategy to make new POM compounds, POM hybrid materials and biologically compatible inorganic clusters. Typical work in this area is presented by Wei (DOI: 10.1039/C2DT30471F) in the alkylimido adaptation of hexamolybdates and by us (DOI: 10.1039/C2DT31008B) in the systematic study on Anderson type clusters which also sets this work into its historical context. POMs can also be viewed/utilized as anionic ligands forming **complexes or complex clusters** with transition metal ions and very interesting work on this subject can be found in the POM-based nickel cluster by Long (DOI: 10.1039/C2DT12507B), and the manganese cluster by Fang (DOI: 10.1039/C2DT30451A). An important contribution is presented by Kato (DOI: 10.1039/C2DT30915G) on the unusual **diplatinum(II) POM complex** and its photocatalytic performance for hydrogen evolution. **POM hybrids and crystal engineering** is currently one of the biggest areas of POM chemistry. Metal complex cations and POM anions form composites that exhibit unprecedented physical and chemical properties and these have been demonstrated by a number of contributions from research groups all over the world. Significant work is the study of solution chemistry of photoactive Ru(II) complexes (DOI: 10.1039/C2DT30503H) and solvent dependent charge transfer of

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pyridyltetrathiafulvalene nickel complexes with POM anions (DOI: 10.1039/C2DT30398A) is also included. The incorporation of d- and f-metal ion complex cations with POM anions to form composites or extended frameworks is a fast growing area and is also well represented in this issue: (DOI: 10.1039/C2DT12508K, DOI: 10.1039/C2DT30517H, DOI: 10.1039/C2DT30481C, DOI: 10.1039/C2DT30393K, DOI: 10.1039/C2DT30559C, DOI: 10.1039/C2DT12382G, DOI: 10.1039/C2DT30582H and DOI: 10.1039/C2DT30537B). Also, the **'nano' assembly mechanism and 'nano' manipulation** of POM clusters are investigated by Wu (DOI: 10.1039/C2DT30641G), Li (DOI: 10.1039/C2DT30421J), Weinstock (DOI: 10.1039/C2DT30592E), Kögerler (DOI: 10.1039/C2DT30502J) and Nomiya (DOI: 10.1039/C2DT30456B), and a very interesting study demonstrates how POM compounds can be used to form **new types of batteries** by Yoshikawa (DOI: 10.1039/C2DT30603D). **Theoretical study** has been carried out by Su (DOI: 10.1039/C2DT30449J) on multistep-redox-triggered chiroptical and nonlinear optical properties of POM clusters as well as a theoretical study on electronic structures by Bo on large POM clusters $\{Mo_{132}\}$ and $\{W_{72}Mo_{60}\}$ which reveals the archetypal nature of polyoxometalates (DOI: 10.1039/C2DT30737E). An **electrochemical study** by Bond is also in the issue (DOI: 10.1039/C2DT30558E) together with a large number of **catalytic studies**. For instance work has been conducted on pollutant dye degradation (DOI: 10.1039/C2DT00001F and DOI: 10.1039/C2DT30304C) and catalytic oxidation and epoxidation (DOI: 10.1039/C2DT30424D and DOI: 10.1039/C2DT30492A), promotion of oximation of aldehydes (DOI: 10.1039/C2DT30092C), hydrolysis of DNA model substrates (DOI: 10.1039/C2DT30588G), photocatalytic H_2 production (DOI: 10.1039/C2DT30663H) and electrocatalytic properties (DOI: 10.1039/C2DT30534H). Furthermore there are two reviews on specific catalytic topics presented by Ye Wang (DOI: 10.1039/C2DT30637A) on POM catalysts for transformations of cellulose into platform chemicals and Xun Wang (DOI: 10.1039/C2DT30470H) on the controlled assembly and catalytic properties of surfactant-encapsulated POM composites.

So where next for polyoxometalates and the frontiers of metal oxide cluster science? It would appear that the transformation from structure based studies to advanced mechanism, derivatisation, and application is continuing at great pace and the development of advanced new strategies for nanoscale 'designer' POM structures with pre-defined properties is a real prospect. We would like to thank all the authors for their contributions and congratulate them on the quality of their work. This issue represents a perfect snapshot of the field going forward and should also 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 the last 200 hundred years from the molybdenum blue of Scheele to the development of polyoxometalate based nanotechnologies today and we look forward with a great deal of enthusiasm and excitement to see how this area will develop in future.