

Editorial

Innovative Inorganic Synthesis

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External Editor: Reshef Tenne

Received: 7 October 2014 / Accepted: 15 October 2014 / Published: 17 October 2014

I am delighted to introduce this Special Issue of *Inorganics*; the first themed issue of the journal and one dedicated to Innovative Inorganic Synthesis. Synthesis is the crucial creative step by which new compounds are made. It is also the means by which important chemicals are formulated and processed from initial laboratory experiments to industrial scale production. Inorganic compounds demonstrate huge diversity and so vastly different approaches are required to achieve a multitude of synthetic targets from delicate complexes to robust extended solids. Unifying this cornucopia of concepts and techniques are principles of inspiration and design; if realising new compounds is a process of discovery, then devising the successful synthesis route is a process of invention. This Special Issue provides examples of the inventive strategies exploited to prepare inorganic compounds. Insightful review papers and original research articles highlight some of the most recent developments in *innovative inorganic synthesis*.

Nanomaterials chemistry is an area that has emerged and flourished over the last two decades. As the types of materials that exist at the nanoscale have become more numerous, so the library of preparative methods has expanded to meet the challenge of their successful synthesis. An important consideration as such synthesis approaches mature is the need to employ techniques that are environmentally benign and sustainable. In the first of two contributions to this issue, Annika Betke and Guido Kickelbick demonstrate very elegantly how reactive milling can be exploited to prepare surface-functionalised nanoparticles (in this case titania) without the use of solvents [1]. Their study illustrates how ball milling can be used to achieve both physical size reduction and the chemical grafting of species to the titania surface in a simultaneous process. In fact, they show that both surface and bulk reaction chemistry occurs in parallel, with the phase behaviour of the titania particles sensitive to the milling conditions. Such synthetic control could prove to be especially important in the tuning of photocatalytic properties and in the subsequent design of polymer composite materials. By contrast to this arguably “top down” approach of reactive milling, the same authors reveal that a

variation of wet chemical nanomaterial synthesis can be employed in the successful “bottom up” production of zinc oxide, magnetite and brushite nanoparticles [2]. Their design of a novel microjet reactor for the processing of these oxide based materials takes a lead from biomaterials synthesis and allows for the continuous flow manufacture of the candidate materials. Both the size and morphology of the products can be manipulated through the available process parameters (such as temperature and flow rate). In a similar vein, Murukanahally Kempaiah Devaraju, Itaru Honma and colleagues at Tohoku University present results of their work using a supercritical water/ethanol mixture as a reactive medium to produce ternary lithium cobalt phosphate [3]. The method produces not only phase-pure material but also nanoparticles that can be controlled in terms of size and shape via choice of precursor, reaction time and temperature. Such characteristics prove important in the electrochemical performance of the materials and their potential as cathodes in reversible lithium ion batteries.

Molecular chemistry meets that of extended solids in the design of molecules for functionalization of solid state materials via surface grafting. In their paper, Ahmed Mohamed and co-workers consider the synthesis of diazonium tetrachloroaurate(III) complexes as suitable precursors for surface grafting to create organic monolayers [4]. Typically, the low stability of diazonium salts at room temperature (which are often explosive) coupled with difficulties of isolation and purification enforce approaches where the precursor is prepared and reacted onwards without intermediate isolation. With careful chemical design approaches, however, it is possible to stabilise the diazonium species and complexation is one possibility. In this contribution, a simple but highly effective synthesis procedure is described to yield stable diazonium tetrachloroaurate(III) complexes.

Two other original papers describe very different aspects of progressive synthetic coordination chemistry. In the first, Stephen Liddle and colleagues report the synthesis of several rare earth bis(iminophosphorano)methanediide complexes [5]. To maximise the chances of avoiding salt occlusion and ligand scrambling, a synthetic approach in which iodide precursors were employed in salt metathesis was pursued rather than following an alkane elimination route. The successful synthesis of the various members of this lanthanide series has facilitated a study of how varying the size of the central metal impacts on the structure and reactivity of the methanediide complexes. Meanwhile, Dai Oyama and his team from Fukushima University utilise a phenomenon, which they term as a “Molecular Sieve Effect” in their report on the synthesis of a series of new ruthenium complexes containing the triphenylphosphine ligand [6]. They capitalise on the ability of the tridentate 2,6-di(1,8-naphthyridin-2-yl)pyridine (dnp) ligand not only to stabilise resulting ruthenium complexes but also to improve the stereospecificity of the reactions dramatically. The coordinated dnp thus behaves like a “molecular sieve” in ligand replacement reactions by directing selected ligands into either equatorial or axial positions in the octahedral complexes. Density Functional Theory (DFT) approaches were used to help rationalise this phenomenon; a concept that could be developed (for examples, using thiocyanate, SCN^- ligands) in the design of new photosensitizers for dye-sensitized solar cells (DSCs).

The Special Issue also contains three comprehensive review papers, which highlight extremely topical areas in which innovative inorganic synthesis either takes centre stage or contributes significantly to a major scientific challenge. Andreia Valente and M. Helena Garcia discuss the urgent and always relevant issue of how chemistry can respond to the global challenges in public health [7].

Ruthenium chemistry is again highlighted as an important area, this time in the battle against cancer. The authors describe how the continued evolution of macromolecular drugs based on the enhanced permeation and retention (EPR) effect is the key to success and moreover, how advances in chemical synthesis play a central role in the production of new and more effective medicines. Multi-nuclearity is an important concept in developing such drugs and achieving both higher cytotoxicity and selectivity. These properties are often molecular weight-dependent and hence it is vital to develop facile and effective strategies for the coordination of drugs to the carriers. This is where synthesis design can be crucial. In a rather different context, Theresia Richter and Rainer Niewa provide a definitive commentary on the current state of the art of ammonothermal chemistry [8]. They describe not only how nitrogen-containing solids such as nitrides, imides and amides might be synthesised but also how ammonia at elevated temperature and pressure (either sub- or supercritical) can be utilised as a solvent in the preparation of hydroxides and chalcogenides. The technique proves to be an extremely useful one in growing crystals (for example of the important III-V semiconductor gallium nitride, GaN) via the judicious choice of starting materials and mineralisers. Three regimes can thus be induced, creating reactions that are driven in ammonobasic, ammononeutral or ammonoacidic conditions. Although the mechanistic steps of reaction and crystal growth are not yet understood in each of these cases, some of the intermediate species that exist can be identified. Finally, Roberto Rosa, Chiara Ponzoni and Cristina Leonelli offer a detailed insight into how microwave methods can be used to synthesise inorganic solids, nanoparticles and materials in solution, via either solvothermal or solution-based combustion techniques [9]. The authors demonstrate how microwave driven hydrothermal synthesis, for example, can be implemented in the formation of numerous oxide and chalcogenide nanostructures with sizes and shapes tunable via experimental conditions. Similarly, the relatively new procedure of solution combustion synthesis by microwaves is revealed to be a means to produce metal, binary oxide and complex oxide nanopowders from the reaction of a metal-containing precursor (such as a nitrate, commonly) with an organic fuel in a homogeneous solution. Developed originally as a concept from a process performed in the solid state, solution combustion syntheses are proving highly effective routes to deliver nanomaterials of controllable size and shape.

Hence overall and in summary, this Special Issue highlights just some of the diverse and creative ways in which novel synthesis forms the foundation in the constant evolution of inorganic chemistry. From the design and controlled coordination of ligands to individual metal centres through the connection of building blocks using weak interactions to the crystal engineering and microstructural construction of materials, the unceasing importance of fresh ideas in synthesis is only too evident as chemistry progresses.

I would like to take this opportunity to thank all of the authors who have contributed such a fine collection of work to this Special Issue. I would also like to thank the editorial staff and publishing staff who, with all their continued hard work, have enabled this issue to be realised.

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