

Preface

Some time ago, relatively recently, the field of coordination polymers exploded. Or rather, it underwent a ‘rapid expansion’, much like the Universe did after the Big Bang. Where once there was an occasional paper or two, there are now whole journals devoted to crystal engineering, of which coordination polymers are a major subdiscipline. No longer are these materials the vaguely defined ‘insoluble material’ that forms at the bottom of your vessel and spells death for your reaction. Rather, they are now the quarry that needs to be coaxed into crystalline form, or probed with X-rays and gases and magnets and lasers. They have gone from ‘polymeric rubbish of unknown composition’ to ‘materials of the future’.

There are a number of reasons for being where we are now. Conceptual leaps were made in the early–mid-1990s in their deliberate design, allied with similar advances in related areas such as organic crystal engineering (aided by the blossoming of the Cambridge Structural Database as a research tool), and metallosupramolecular chemistry (and indeed supramolecular chemistry as a whole). Advances in X-ray diffraction equipment, and our ability to display these materials graphically, also helped; two-dimensional drawings became three-dimensional objects, and we learned to look beyond the local molecular connectivity to the crystal as a whole. Supramolecular chemistry taught us to be ambitious – no longer did we assemble things an atom at a time, but rather used whole molecules as our building blocks, and hoped that we had designed them as well as Nature designed her atoms so that they would self-assemble into the polymer we intended. Sometimes it worked, sometimes it didn’t; every time we learnt something. Indeed, the same holds true today.

The next step, of course, was then to use that knowledge. New materials were made that had lots of holes in them, or were acentric or chiral or heterogeneous catalysts, or any combination of these. Magnetochemists had been using coordination polymers for some time, but even here they benefited from this new thinking. Soon Prussian Blue, cadmium cyanide, copper adiponitrile

nitrate and copper tetracyanotetraphenylmethane were just part of the cosmic background.

So given that this is now a vast and important field, it seems timely for a book dedicated entirely to coordination polymers. This book does not seek to review the entire field comprehensively, in its vast breadth and depth. It simply could not, or at least not in a single volume. Rather, it is written with the eye of an eagle, taking in the whole landscape but also focusing in on particular areas that seem (to us) to be important at the time. The aim is to give the reader a flavour of each field, introduce them to the important concepts and developments, and to reinforce this with selected examples that are, in our subjective view, important, illustrative or occasionally even anomalous. The aim is to cover all aspects of coordination polymers, or as many as we can practicably in a forum such as this.

For practical reasons, however, we have largely restricted ourselves to coordination polymers of transition metals (plus Zn, Cd and Hg) and lanthanoids and have ignored the s- and p-block metals. Similarly, we have chosen to include only ligands that are organic in nature (with a few notable exceptions, such as cyanide). More ‘inorganic’ materials such as those containing single-atom bridges (e.g. halides, oxides and sulfides) or e.g. phosphate-derived materials are largely ignored; sometimes this distinction is, unfortunately, subjective but nonetheless it is a necessary one. Exceptions will arise from time to time in our discussion (e.g. the chapter on organic–inorganic hybrids), but usually only when there is also a more ‘organic’ bridging ligand also present, or a point to be made by widening our metal or ligand vocabulary.

The book has been subtly divided into sections. After the introductory chapter, there follows three chapters that deal with aspects of the *design* of coordination polymers, including nets, interpenetration and all the other factors that need to be taken into account (or explain why the design failed). Then follows a series of *analysis* chapters, where we survey the results reported to date for coordination polymers constructed using both transition metals and lanthanoids, and also the related areas of organometallic networks and organic–inorganic hybrid materials. Finally, we end with a series of chapters on the *applications* of these new materials, including long-range magnetism, spin-crossover materials, porosity (including gas sorption), catalysis, non-linear optical activity and chirality.

We hope that this book acts as both an important introduction to the field for graduate students and a valuable resource and overview for more experienced researchers. Where necessary, we have tried to take a tutorial approach, but we always urge the interested reader to consult the references closely; each is a treasure trove of information from which we have distilled only a portion. There exists such a vast field of knowledge that only selected examples can be mentioned that clearly demonstrate the principles and applications. We acknowledge the work of the many hundreds of researchers who we cannot explicitly mention in the space of these pages but who have contributed to the knowledge pool of the field.

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