

Preface

“Organizing molecules into predictable arrays is the first step in a systematic approach to designing (...) solid-state materials.”

(M. C. Etter et al., J. Am. Chem. Soc., 1987, 109, 7786.)

Making crystals by design is the paradigm of crystal engineering, the modern discipline at the intersection of supramolecular and materials chemistry. The *engineering* idea is that crystals with desired properties can be constructed from the convolution of the physico-chemical properties and intermolecular bonding capacity of the building blocks with the periodicity and symmetry of the crystal. Such a “bottom-up” approach from molecules and ions to aggregates requires crystal-oriented synthetic strategies.

Crystal syntheses do not differ, in their essence, from classical chemical experiments in which molecules are modelled, synthetic routes devised, products characterized and their properties evaluated. However, this typical chemical approach needs, in a sense, to be repeated twice: first, in order to prepare the building blocks (whether molecules or ions), and then to arrange the building blocks in a desired way via nucleation, precipitation and crystallization to attain and/or control crystal properties. Obviously, crystallization invariably implies the need to characterize the solid product, often in the form of a polycrystalline powder, for which routine analytical and spectroscopic laboratory tools are much less useful than in the case of solution chemistry.

The ultimate product of a crystal making exercise is a crystal, therefore understanding and reproducing the crystal-making process requires a good knowledge of solid-state techniques, such as differential scanning calorimetry, thermogravimetry, solid-state NMR, variable temperature X-ray powder diffraction, etc., which are not used routinely in traditional academic chemistry laboratories.

Crystal makers need to master both covalent chemistry in solution, in order to prepare building blocks, and supramolecular chemistry in the solid state, in order to assemble building blocks in crystals. This also applies to the study of coordination networks, where the knowledge of coordination chemistry and metal-ligand bonding is fundamental.

Furthermore, the intriguing possibility that the same building block may lead to different crystal structures, i.e. crystal polymorphs, with their different physico-

chemical properties, needs to be taken into account. Scientists engaging in crystal engineering endeavors must be well aware of this phenomenon and of its – at times dramatic – implications for the “making crystal by design” initial assumption. It is essential to understand why a crystallization process leads to one crystal form or another, and whether these crystal forms interconvert, in order to be able to reproduce the experimental conditions and product selection on a laboratory or plant scale.

When planning this book we were led by awareness that crystal makers come mainly from two traditionally distinct and often separate backgrounds. On the one hand, synthetic chemists, who know well how to make molecules, often possess a limited perception of how their molecules will behave once put together with billions of identical molecules in a crystal, and find problematic the characterization, handling, representation and modelling of crystalline solids. On the other hand, solid-state scientists, of whom crystallographers and solid-state theoreticians represent the most abundant populations, know how to use sophisticated techniques and computational methods for the investigation, characterization and evaluation of crystalline solids but may have limited experience in the handling of complex molecules in laboratory preparations.

With these ideas in mind we have asked a number of highly qualified researchers from different branches of the field to take part in the preparation of a book that could collect the experience of theoreticians, synthetic-solution and solid-state chemists, crystallographers and spectroscopists with a common focus on the project of *making crystals by design*.

This book should serve both as a state-of-art overview of “what’s going on” in frontier areas (theoretical evaluation of noncovalent interactions, hydrogen-bonded crystals, coordination networks, solid-state reactivity and reactions taking place in the solid state, crystal polymorphism, etc.) and as an entry point to the fundamental methods and techniques required for a successful investigation of crystalline solids (crystallography, solid-state NMR spectroscopy, atomic force microscopy etc.).

The response has been extraordinary and we are proud to present to the readership a handbook, which is also a research book, written by a consortium of top-notch scientists but with the main objective of serving as an introductory overview, seen from its various angles, of this burgeoning field. Clearly, the book has no pretensions of exhaustiveness: our main objective has been that of providing an Arianna’s thread to beginners and advanced levels students (as well as to lecturers for their teaching) to guide their way in this cross-disciplinary area of chemical science. If the reading of these chapters stimulates a few young scientists to choose and pursue their focused directions of research in the domain of *crystal making* we shall be successful. The increasing presence of *molecular materials*, *supramolecular solid-state chemistry* or *crystal engineering* topics in postgraduate high level courses (Masters and PhD), suggests that this book could also be a useful tool for teachers.

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