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The Fields of Crystal Engineering and Ionic Liquids Are Actually Quite Similar

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I was recently asked if I would help the *Australian Journal of Chemistry* to put together a Research Front in the area of Crystal Engineering. Professor Ken Seddon (Queen's University of Belfast) and Professor Doug MacFarlane (Monash) were interested in expanding interest in this topical area among the readership of the Journal. Although I edit the American Chemical Society journal *Crystal Growth & Design* (http://pubs.acs.org/journal/cgdefu), which includes coverage of this exciting area, I found the invitation too interesting to resist, primarily because of the irony inherent in my interests in ionic liquids and their design; supposedly the antithesis of crystal engineering.

The fields of Crystal Engineering, the study and engineering of the crystalline solid state of materials, and Ionic Liquids, the study and engineering of the liquid state of salts that typically melt below 100°C, would seem at first glance polar opposites, and yet it was at the intersection of these two fields that I found myself as both were emerging onto the scientific scene. In the mid 1990s, there was a renaissance in the study of the solid state and even though the term 'Crystal Engineering' was coined by G. M. J. Schmidt[1] in the 1970s, it was the work in 1980s and 1990s, by such scientists as Etter,[2] Desiraju,[3] Zaworotko,[4] and many others, that brought fascination with the idea that by studying and understanding weak interactions responsible for crystal packing, one could design new solids from basic building blocks leading to designer solids with specific chemical and physical properties.

During this time period, Seddon's work on the nature of liquid salts as solvents[5] was gaining serious attention in industry. The pioneering work of Wilkes and Zaworotko[6] (yes the same one) had set the stage for air stable room temperature liquid salts to find numerous applications and Seddon's use of these caught the imagination of many scientists and engineers.[7] Since the mid 1990s an excess of 15000 papers have appeared using the term 'Ionic Liquids' and only a few have noted the true relationship between this field and Crystal Engineering (one of those by Doug MacFarlane[8]). Nonetheless, they are quite related. Each seeks to understand the weak interactions between molecules or ions; each seeks to use that knowledge to design materials with a specific set of properties, and each seeks to find new technological uses of the resulting materials.

Perhaps, I was simply in a position to see the commonality of both, when in September 1996, I was invited by Mike Zaworotko, a fellow graduate of The University of Alabama in Jerry Atwood's Group, to discuss chemical crystallography[9] at a NATO Advanced Summer Institute on Crystal Engineering that he was organizing with none other than Ken Seddon.[10] During this meeting, Seddon presented some work on what I thought was a fascinating set of materials; liquid salts which at room temperature might be used as solvents in a context of Green Chemistry.

There were two roads forward for me from this meeting that have led to my desire to understand the control and design of both the solid and liquid states. First, Professor Zaworotko and I began organizing Crystal Engineering symposia,[11–13] leading to the founding of a new journal with the title *Crystal Engineering*[14,15] (Elsevier) in 1998. In 2000, I was then asked by the American Chemical Society to found a new journal more generally related to both the design of the crystalline state, but also to the growth of the crystalline state. The first issue of *Crystal Growth & Design* was published in January 2001[16] with Professor Ken Seddon as one of the first Associate Editors. *Crystal Growth & Design* is now entering its 10th year of publication[17] (http://pubs.acs.org/page/cgdefu/anniversary/10/index.html).

Concurrently, I went back to the laboratory and worked with my group to utilize these fascinating liquid salts in the field of separations; our first publication appearing in 1998.[18] In 2000, Professors Seddon, Volkov, and I organized a NATO Advanced Study Institute in this new field,[19] and the rest as they say is history. Myriads of meetings, books, publications, and patents have appeared in the past decade.

I have been privileged to watch both fields grow and enjoy the excitement of the scientific communities in both areas. As Editor of *Crystal Growth & Design*, I have watched our understanding of the solid state flower and the ability to predict the solid state in such critical fields as the control of polymorphs, expand in leaps and bounds. As an organizer of meetings, books,[20] etc. in the field of Ionic Liquids, I have been fascinated with the new thinking that has accompanied such as simple a thought as using a liquid salt as a solvent or material.

Even in the task set for me here in organizing this Research Front, I could not resist the temptation to link these fascinating fields. I invited one of the leading experts in the crystallization of ionic liquids and their use in preparing crystalline solids, Professor Anja Mudring, to prepare a tutorial review in this area. Her article, 'Crystallization of Ionic Liquids: Theory and Techniques,'[21] is an excellent review of what we know and what we need to find out about the control of the solid states

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obtained from and with ionic liquids. This work continues to draw followers from both the fields of Crystal Engineering and Ionic Liquids, and I predict much commonality will be found.

In inviting key authors for this Research Front, I also wanted to showcase the truly international nature of Crystal Engineering and you will note authors from five continents (as I count continents anyway!), Africa, Asia, Europe, North America, and South America. The articles are equally as diverse with contributions working to understand or control many of the different types of interactions in the solid state (e.g. ionic: 'Crystal engineering studies of ionic crystals of pyridine and carboxylic acid derivatives containing amide functional groups'[22]; π: 'Pb···π aryl interactions as supramolecular synthons'[23]; hydrogen bonding and weaker: 'Understanding supramolecular interactions provides clues for building molecules into minerals and materials: a retrosynthetic analysis of copper-based solids'[24]) to those trying to use the arrangements of molecules in the solid state to control reactivity ('Solid-state synthesis of coordination polymers for [2+2] photoreactions by grinding,'[25] 'Single-crystal to single-crystal transformations – guest removal and substitution in a robust solvent-templated metallocyclic compound'[26]).

Still, what I have not yet seen with any great regularity is the interaction of both the Crystal Engineering and Ionic Liquids communities at a higher level of understanding, nor recognition of how similar the work often is. It seems appropriate to point out as we enter a new decade, that even now we still have not quite reached the ability to design either the solid sate or the liquid state to our satisfaction. While we could bemoan this fact and give up; I would suggest that the fascination is in the chase! Our understanding of both solids and liquids and our ability to model and predict both are growing at a tremendous rate. The future certainly looks bright for both fields!

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