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Introduction to the special issue on crystal engineering

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This special issue on crystal engineering is part of a renewed commitment from IUCr for *Acta Crystallographica Section B* to publish high-quality results in the area of crystal engineering. This commitment is reflected by the recent addition to the journal's subtitle, '*Structural Science, Crystal Engineering and Materials*', and it has been stated previously in an *Editorial* from the Section Editors (Blake & de Boissieu, 2013).

Crystal engineering has always been well within the scope of *Section B*, and the journal has played a key role in developing the research area. A search of *Web of Science*™ (Thomson Reuters) for *Section B*'s most-cited articles identifies some highly influential crystal engineering papers. For example, the 1976 paper from Leiserowitz on the packing modes of carboxylic acids (Leiserowitz, 1976) appears at No. 12 (860 citations), and the work of Desiraju and Gavezzotti on the aromatic hydrocarbons (Desiraju & Gavezzotti, 1989) appears at No. 39 (350 citations). A review article from Aakeröy (1997) stands out at No. 24 (450 citations) as an overview of crystal engineering at the time. The specialist crystal engineering journals appeared shortly after this, so it might be viewed as something of a 'watershed' article as far as *Section B* and crystal engineering are concerned. At No. 9 (1400 citations) is the paper of Etter *et al.* (1990) on graph-set notation, and there are also three articles on the Cambridge Structural Database (CSD; Allen, 2002) in the top ten. These papers prove that *Section B* has contributed significantly to the foundation on which the research field of crystal engineering now stands.

Research in crystal engineering is intimately tied to publication of crystal structures, and IUCr journals have always led the way in this area. It is worth remembering that the publication of crystallographic data in electronic (CIF) format originates from *Acta Cryst.* (McMahon, 1993). An even more important contribution is the IUCr *checkCIF* validation system (Spek, 2009), which has become a worldwide standard. Probably every chemical crystal structure that is published today has passed through the *checkCIF* system at some stage. The importance of *checkCIF* for crystal engineering should not be underestimated because it raises the base level of crystal structures in the literature and databases, thereby helping to ensure a sound crystallographic basis from which crystal engineering can grow.

Given its history and the crucial role that IUCr journals play in chemical crystallography, it is curious that *Section B* has not maintained a status as the premiere journal for publication of crystal engineering results. Any objective measure, such as number of papers published or impact factor, will show that *Section B* lags behind the specialist crystal engineering journals in this area. Whatever the reasons for this, it explains why *Section B* is making a new effort to reach out to the crystal engineering community. In the course of preparing this issue, I have corresponded with many researchers engaged in crystal engineering research. The response towards *Section B* remains positive. There is a general appreciation of the scientific standards that are upheld by *Acta Cryst.*, and an understanding that IUCr journals play a crucial role in enabling crystallographic research. Here, the word *crystallographic* is chosen carefully: the community recognizes *Section B* as a forum for publication of crystallographic results, but crystal engineering is not the same as chemical crystallography. Probably, this is where *Section B* has lost ground. The journal's emphasis, or at least the community's perception of it, has remained on the more fundamental chemical crystallographic aspects of crystal engineering, while the field has moved further towards the design of specific properties and applications. The current challenge for *Section B* is to remind the crystal engineering community that it provides an attractive forum for publication of cutting-edge results in crystal engineering, as well as the more fundamental results in chemical crystallography. I hope that this special issue will serve as something of a reminder.

The contents of the issue continue to emphasize the fundamentals of crystal engineering, but they also give a clear indication of two main areas where crystal engineering is now being applied, namely pharmaceutical solids and metal-organic frameworks (MOFs). The latter topic provides the *Feature Article* from Dey *et al.* (p. 3), which highlights synthesis strategies, structural diversity and properties of MOFs with particular respect to application perspectives. The syntheses and structures of several new coordination polymers and MOF compounds are reported in the papers by Munn *et al.* (p. 11), Cañadillas-Delgado *et al.* (p. 19), Monteiro *et al.* (p. 28) and Hau *et al.* (p. 37).

In the pharmaceutical area, the emphasis is on modifying or controlling solid forms, usually with the intention of optimizing physicochemical properties for active pharmaceutical ingredients (Frampton, 2013). The papers by Surov *et al.* (p. 47), Aitipamula *et al.* (p. 54), Bisht *et al.* (p. 63), Madusanka *et al.* (p. 72) and Sanphui *et al.* (p. 81) focus on this highly active topic. The paper by Madusanka *et al.* (p. 72) is notable for its inclusion of five molecular crystal structures established from powder X-ray diffraction (PXRD) data. Here, this special issue introduces a new innovation: the structures determined from PXRD data have been validated during the review process by energy minimization using dispersion-corrected density functional theory (DFT-D) calculations. We have chosen to apply these methods on the basis of a validation study published in *Section B*, which shows that these calculations reproduce very closely the geometries of correct crystal structures, and can reveal incorrect structures by the fact that they undergo unusually large deformations on minimization (Van de Streek & Neumann, 2010). The calculations provide an orthogonal assessment to the *checkCIF* system, which considers expectations from established crystal structures (*e.g.* bond lengths, close contacts, nature of displacement ellipsoids *etc.*) and compares to (processed) experimental data (*e.g.* compares *R* factors, checks for unresolved twinning *etc.*). The results of the DFT-D minimizations are provided with each published CIF, in order that they can be compared to the experimental structures in the context of the published validation paper. For all of the structures, the deviations on minimization fall within the expected range for correct crystal structures, and the calculations therefore provide additional confidence that the established structures are correct. We hope that this validation tool might be applied more widely within IUCr journals in the future.

Amongst the more fundamental papers in this issue, the paper of Galek *et al.* (p. 91) provides a new example of the invaluable contribution of the CCDC to crystal engineering. It has already been noted that articles on the CSD provide three of the top ten most-cited *Section B* papers, so it is especially pleasing that this type of research still finds its natural home in *Section B*. There are several papers that focus on 'classical' crystal engineering topics: the relationship between molecular structure and crystal structure [Omondi *et al.* (p. 106), Soliman *et al.* (p. 115)], crystallographic identification of subtly different solvates [Gao *et al.* (p. 126)], assembly of ternary co-crystals [Boardman *et al.* (p. 132)], halogen bonds within crystals [Lieffrig *et al.* (p. 141), Saccone *et al.* (p. 149)], and hydrogen-/halogen-bond competition [Durka *et al.* (p. 157)]. The latter is a nice example where a comprehensive set of technical tools is applied to a fundamental crystal engineering matter. Similarly, the paper of Lombardo *et al.* (p. 172) considers crystal morphology and periodic bond chain theory as 'top–down' tools to identify important structural motifs in crystals, in contrast to the more common 'bottom–up' approach that is applied to many crystal-structure descriptions. Finally, the paper of Molčanov *et al.* (p. 181) considers the influence of crystal structure and intermolecular interactions on spin coupling of π-stacked radical anions.

The hope from IUCr journals is that this special issue will help to initiate renewed growth of *Section B* as a forum for publication of cutting-edge crystal engineering results. The journal is committed to the task, but ultimately it will require support from the community. I thank the authors in this issue for their contributions. I encourage all researchers in the area of crystal engineering to consider *Section B* for publication of their next research paper.

References

Aakeröy, C. B. (1997). *Acta Cryst.* B**53**, 569–586.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Blake, A. J. & de Boissieu, M. (2013). *Acta Cryst.* B**69**, 311–312.
Desiraju, G. R. & Gavezzotti, A. (1989). *Acta Cryst.* B**45**, 473–482.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Frampton, C. S. (2013). *Acta Cryst.* C**69**, 1205–1206.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
McMahon, B. (1993). *Acta Cryst.* C**49**, 418–423.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Van de Streek, J. & Neumann, M. A. (2010). *Acta Cryst.* B**66**, 544–558.