Design of crystalline molecular networks with charge-assisted hydrogen bonds

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Empirical guidelines for steering molecular assembly into prescribed crystal architectures *via* hydrogen bonding continue to emerge, with recent developments demonstrating that charge-assisted hydrogen bonds introduce both strength and compliance that can facilitate solid state design.

Materials based on molecular components promise precise control of properties and function because the building blocks can be manipulated using the vast tools of synthetic chemistry. The design and synthesis of crystalline organic materials often are thwarted, however, by the delicate and non-covalent nature of the intermolecular forces responsible for crystal packing, which is crucial to solid-state properties that rely on collective interactions. Sometimes the most innocent modification of a molecular constituent may produce an unanticipated solid-state structure. Furthermore, comprehensive crystal structure prediction of the lowest energy crystal forms through computational methods—complete with space group, lattice parameters, and atomic positions—remains elusive in general,[1,2] although it is advancing rapidly.[3,4]

The current limitations of computational methods have prompted many organic solid-state chemists to deploy empirical strategies for crystal synthesis based on the use of generalized models of molecular packing modes surmised from selected sets of existing crystal structures. This approach, often referred to as crystal engineering, has enabled solid-state chemists to create well-defined lattice architectures with network topologies and lattice metrics prescribed by molecular building blocks adorned with multiple structure-directing functional groups arranged according to well-defined molecular symmetries. Although crystal engineering strategies usually do not result in precise control of atomic positions,[5] often the control of network architecture coupled with systematic adjustment of lattice metrics is sufficient for the design of functional molecular materials. In this respect, hydrogen bonding, a long-standing favorite for crystal design,[6,7] has proven particularly useful. Substantial progress also has been made in the design of metal–organic frameworks,[8–11] but this article focuses on hydrogen-bonded networks.

One sensible tactic for regulating solid-state structure and properties involves the use of structurally robust one-dimensional (1D) and two-dimensional (2D) hydrogen-bonded networks. Persistent *n*-dimensional networks inherently simplify crystal synthesis by reducing the degree of freedom for crystal packing, effectively restricting crystal design to the remaining 3-*n* dimensions. In order to manipulate solid-state properties these networks must be able to withstand modifications introduced by synthetic chemistry. These may involve swapping hydrogen-bonding components that preserve the generic features of the network or altering pendant substituents that do not participate directly in hydrogen bonding (Fig. 1).

Some of the strongest hydrogen bonds are "charge-assisted," wherein the molecular components carry ionic charges. The enhancement of hydrogen bond strength by ionic charge has long been recognized. For example, Gilli, *et al.* classified charge-assisted hydrogen bonds (CAHBs) in crystals according to whether they were *negative charge assisted* (*e.g.*, $-O-H\cdots O^-$), *positive charge assisted* (*e.g.*, $=O\cdots H^+\cdots O=$), or *resonance assisted* where the two oxygens (or two nitrogens) are connected by a system of p-conjugated double bonds.[12] Taylor and Kennard found that N–H donors with formal positive charge tend to form shorter bonds than uncharged N–H groups, and that the negatively

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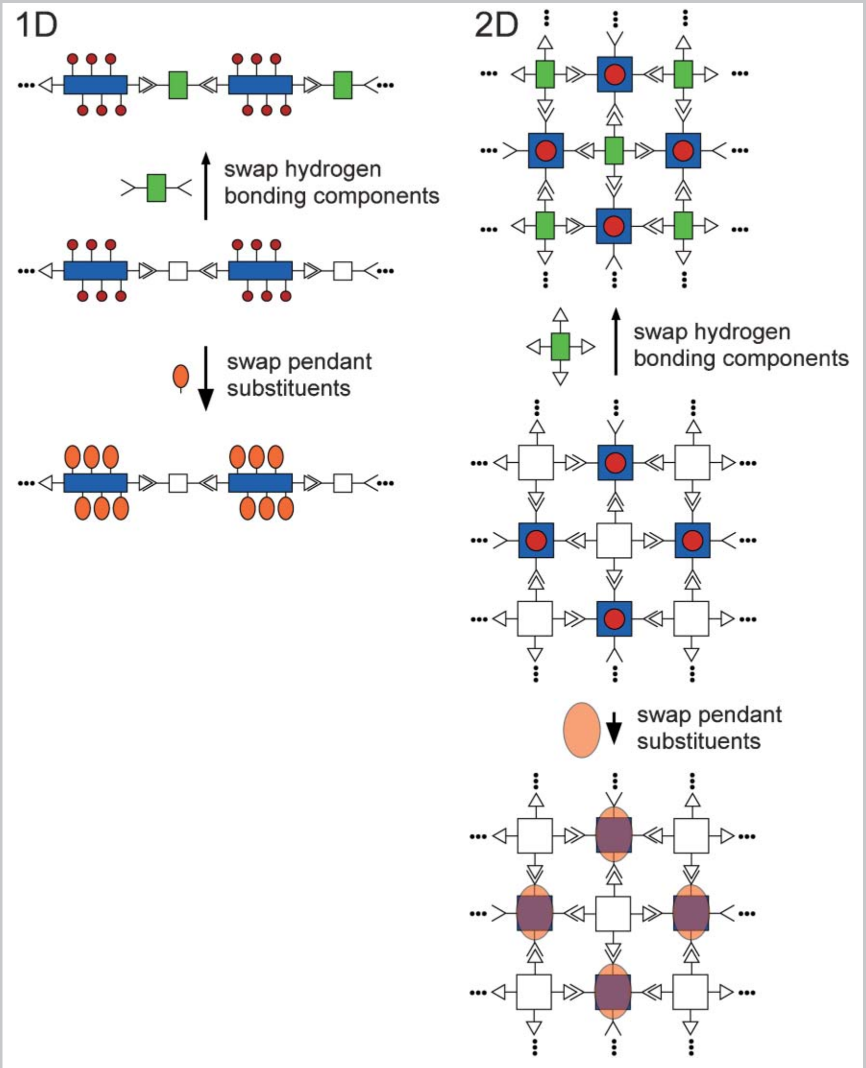

Fig. 1 Schematic representations of hypothetical binary 1D and 2D networks assembled through complementary hydrogen bonding. The networks can be modified by substituting one or both of the hydrogen bonding components or by exchanging pendant groups attached to the network. In the case of the 2D network depicted here, the substituents projecting from the network surface can be altered (red circles to orange ovals).

charged carboxylate ion is a stronger acceptor than uncharged amides, ketones, and carboxyls.[13] This is illustrated by the so-called "Speakman salts," which contain strong hydrogen bonds between a carboxylic acid and a carboxylate ion.[14]

It is quite natural to link robustness to bond strength, and strong hydrogen bonds have the potential to override the multitude of other intermolecular forces in the crystal lattice (*e.g.*, van der Waals, dipole–dipole, multipolar) that otherwise can frustrate rational crystal design. On the other hand, modifications to the backbone of *n*-dimensional networks naturally will alter packing requirements, whether within the network or between pendant substituents, which could exert "strain" on the network. Consequently, networks may be more robust if they are somewhat compliant, that is, if they can deform, with minimal energetic penalty, to accommodate packing requirements while retaining their hydrogen-bonding connectivity and dimensionality. Borrowing from the parlance of materials science, such networks—strong yet pliable—could be regarded as "tough," a characteristic associated with the capacity of a material to undergo strain without fracture. In this respect, hydrogen bonds may prove ideal as they are intrinsically flexible. Although linear hydrogen bond geometries generally are preferred, particularly for strong hydrogen bonds,[6] D–H···A bond angles range widely, implying shallow potential wells that are tantamount to compliant structures. Furthermore, some networks constructed from hydrogen bonds can deform readily while maintaining linearity of their hydrogen bonds, as illustrated below.

During the past decade many compounds with rather sophisticated crystal architectures directed by CAHBs have been reported, some which are depicted in Fig. 2. Because space limitations do not permit an exhaustive overview here, the examples in Fig. 1 are restricted to networks that have been *assembled by design* using (+)N–H···O(−) and (+)N–H···N(−) hydrogen bonds. Amino acids and crystalline phospholipids, which exhibit (+)N–H···O(−) hydrogen bonds, are not discussed here, but the interested reader is encouraged to explore these and compounds with other types of CAHBs, such as (+)O–H···O(−) and (+)C–H···O(−).[15]

One of the more prolific series of CAHB building blocks is the family of bis(amidinium) dications (BA^{2+}), for which N–H substituents protruding from the flanks of an organic core form hydrogen-bonded networks with a variety of complementary anionic acceptors.[16,17] For example, **A** and **B** in Fig. 2 illustrate 1D networks constructed with the [2,2′-(1,2-ethanediyl)pyrimidinium^{2+}] cation (**EBA**$^{2+}$) and the [1,1′-ferrocenedicarboxylate^{2-}][18] and [dicyanoaurate^{-}]$_2$ anions,[19] respectively. The short Au···Au distance of 3.3 Å in **B**, enforced by the span of the N–H hydrogen-bond donors, produced strongly luminescent crystals. Expanding the separation between the Au centers to 4.2 Å by inserting the longer 2,2′-(1,4-phenylene)pyrimidinium^{2+} dication (**PBA**$^{2+}$ in example **C**) reduced the luminescence intensity, as anticipated. This elegant example demonstrates that the structure-directing character of CAHBs and well-defined molecular metrics can be combined to manipulate solid-state properties in a rational manner while retaining the overall architecture of the 1D network. Cyanometallate anions, specifically Pt(CN)$_4^{2-}$, also form 3-D networks with bipyridinum dications, generating a CdSO$_4$-like lattice with channels.[20]

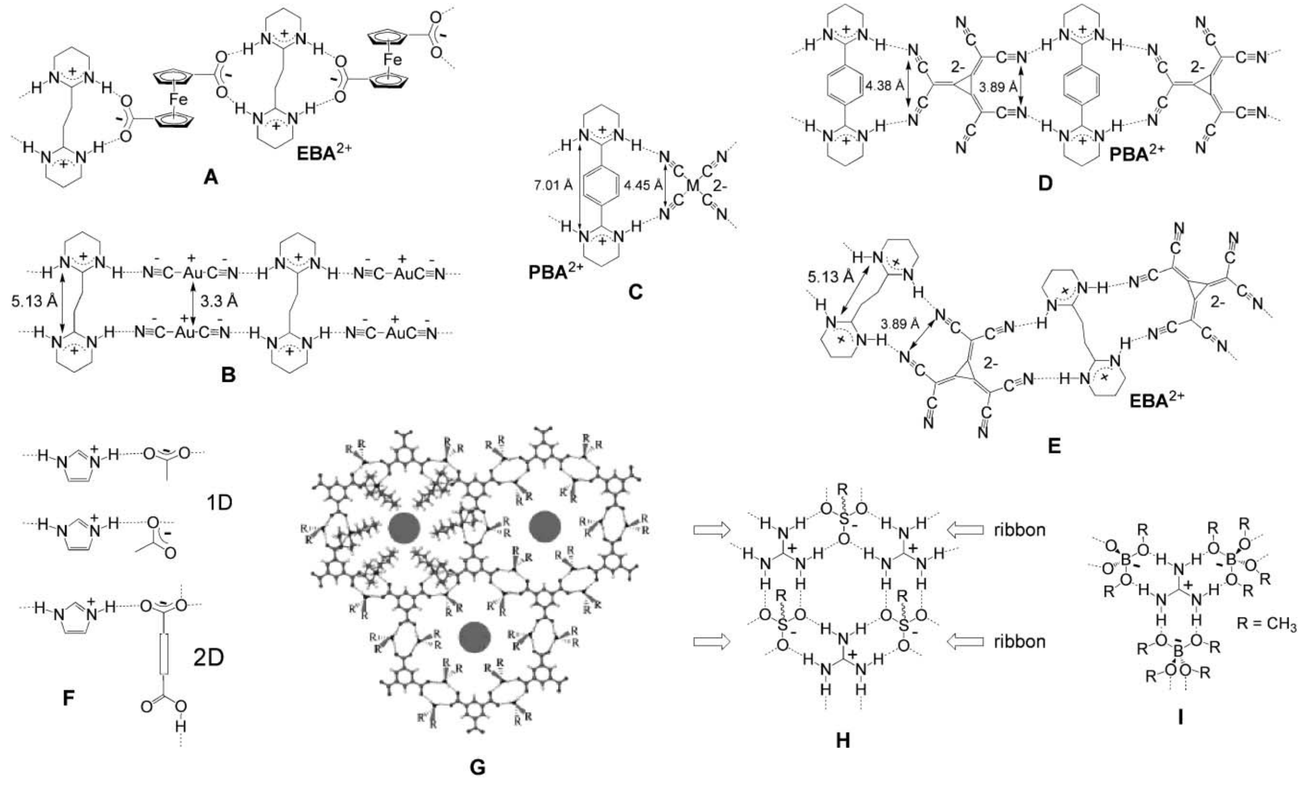

Fig. 2 Various charge-assisted hydrogen bonding motifs observed in molecular crystals. See text for explanations.

The BA^{2+} dications form networks with various other polycyanometallates,[9,21] as exemplified by motif C in Fig. 1. This motif can be transposed to 1D networks with the polycyanoanion depicted in example **D**, which contains geminal cyano groups that are isometric with the vicinal cyano ligands in the polycyanometallates.[22] Metric control exerted by the dications is apparent here as well. The span of the N–H donors of $\mathbf{PBA}^{2+}$ is compatible with both the geminal and non-geminal pairs of cyano acceptors, resulting in the formation of linear chains held together by charge-assisted hydrogen bonds. In contrast, the shorter span of the N–H donors in $\mathbf{EBA}^{2+}$ permits hydrogen bonding with only the non-geminal pairs of cyano acceptors, thus steering assembly into the zigzag 1D chains (**E**).

Charge-assisted (+)N–H···O(−) hydrogen bonds also promote the formation of 1D chains comprising imidazolium and arenecarboxylate ions (**F**). If dicarboxylic acids are used, the 1D chains can be stitched into 2D sheets by Speakman-type $–COO^{-}\cdots HOOC–$ hydrogen bonds.[23] The imidazolium–carboxylate hydrogen bond also has been used to construct a series of isostructural layered materials containing different transition metal ions.[24]

2D honeycomb networks assembled by (+)N–H···O(−) hydrogen bonds have been observed for the 1:3 complexes of the trimesate trianion and dicyclohexylammonium or di-*tert*-butylammonium ions, in which pairs of ammonium cations bridge carboxylate substituents on different trimesate ions (**G**).[25,26] Notably, the 2D sheets pucker to different extents in these structures through deformations of the (+)N–H···O(−) hydrogen bonds, reflecting an intrinsic compliance that enables the network to accommodate differently sized alkyl groups and include solvent molecules while retaining the original hydrogen bond connectivity and the generic honeycomb architecture.

The significance of compliant networks constructed with CAHBs is amply illustrated by the comprehensive series of lamellar inclusion compounds based on the guanidinium ion and numerous organomonosulfonates and disulfonates synthesized in our laboratory. The guanidinium ions (**G**) and the sulfonate group (**S**) form a quasihexagonal (6,3) 2D net in which each ion participates in six (+)N–H···O(−) hydrogen bonds (**H**).[27] The organic substituents attached to the sulfonate moiety project from the sheet surface, serving as pillars that support inclusion cavities between the sheets (Fig. 3). The **GS** sheet is remarkably persistent, appearing in hundreds of compounds derived from a broad range of organosulfonates.[28–30]

Although the tenacity of the **GS** sheet undoubtedly can be attributed to its large number of CAHBs, the network also derives its robustness from accordion-like puckering about the hydrogen bonds that fuse the edges of immutable 1D ribbons. This well-behaved deformation permits the lattice to shrink or expand perpendicular to the ribbons so that the organic constituents can achieve dense packing without disruption of the hydrogen-bond connectivity (the puckering angles range from 180°, which corresponds to a flat sheet, to a highly puckered 70°). The puckering occurs with retention of the linearity of the hydrogen bonds, implying a shallow potential well and a negligible energetic penalty associated with this deformation. This combines synergistically with the

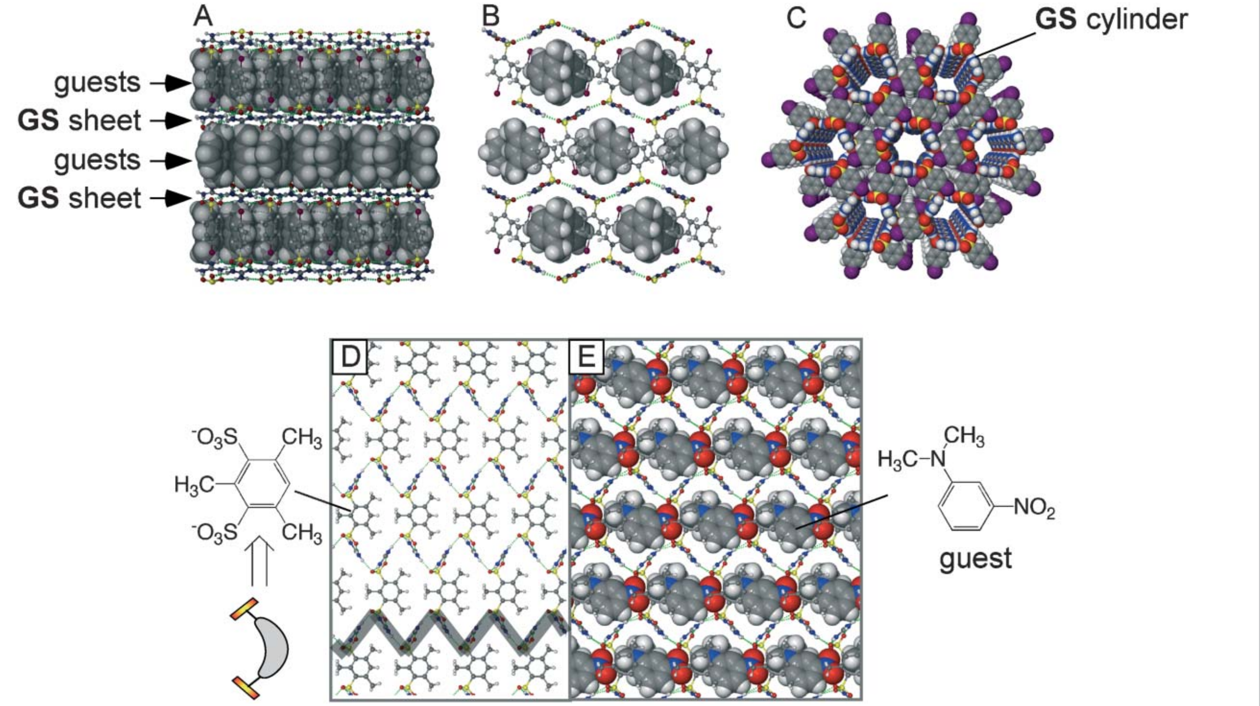

Fig. 3 (A, B) The lamellar inclusion compound [guanidinium][4-bromobenzenesulfonate]·(toluene) as viewed parallel and transverse to the major ribbons respectively. The host framework is rendered as wire-frame and the included guests as space-filled. The puckering of the compliant GS sheet (example H in Fig. 2) is evident in (B). (C) The hexagonal packing observed for the cylindrical inclusion compound [guanidinium][4-bromobenzenesulfonate]·2/3(*o*-xylene). The supramolecular connectivity of the **GS** sheet is identical in both the lamellar and cylindrical architectures. (D, E) Banana-shaped organodisulfonates force the **GS** sheet to pucker like an accordion while promoting formation of polar host frameworks, which have channels that can be occupied by guest molecules to produce materials with second harmonic generation activity.

exceptional strength of the (+)N–H···O(−) hydrogen bonds, bestowing structural toughness to the **GS** sheet. Consequently, lattice metrics in the third dimension and inclusion cavity size and character can be adjusted systematically and reliably by choice of the organosulfonate with retention of lamellar architecture.[31]

The peculiar compliance of the **GS** sheet also enables synthesis of polar host frameworks constructed from "banana-shaped" *m*-arenedisulfonates, which enforce puckering of the **GS** sheets through geometric constraints (Fig. 3). Inclusion of acentric guest molecules in these frameworks produced materials with second harmonic generation activity. Remarkably, the unique characteristics and structural consistency of the **GS** sheet enabled prediction of the space group symmetry and lattice metrics for these compounds using simple geometric principles,[32] a rare occurrence for molecular crystals.

The elastic nature of the **GS** sheet also is apparent for certain combinations of organomonosulfonates and guest molecules that coerce curvature of the sheet into cylinders. These cylinders pack on a hexagonal lattice through weak van der Waals forces between the organic groups projecting from the outer surface of the cylinders, crystallizing in either trigonal $P\bar{3}$ or hexagonal $P6_3/m$ space group symmetry.[33] Interestingly, guanidinium-tetralkoxyborates (**I**) assemble *via* charge-assisted hydrogen bonds into the highly symmetric (10,3)-*a* net ($P\bar{4}3m$ space group). The topology of this network is a consequence of the 3-connecting symmetry of the **G** ion, and the flexibility of the hydrogen bonds permits the network to conform to the highly restrictive symmetry requirements of the special positions in the cubic space group.[34] Notably, high space group symmetries are rare for molecular crystals—only 1.2% and 0.5% of molecular crystals crystallize in trigonal/hexagonal and cubic space groups, respectively.

Such high symmetry structures suggest an interesting link to soft matter phases—surfactant assemblies and block copolymers—which form either lamellar, hexagonal, or cubic phases, the latter two requiring curvature of elastic interfaces between immiscible components. The purposeful design of molecular crystals with tough hydrogen-bonding networks capable of organizing into high symmetry structures through compliant hydrogen-bond networks could strengthen the link between molecular crystals and soft matter.[35]

Collectively, these examples illustrate that CAHBs are effective for crystal design, often producing predictable crystal architectures while enabling manipulation of key structural features. The exceptional strength of these hydrogen bonds and their natural flexibility can conspire to produce "tough" supramolecular networks that can withstand strains created by competing packing interactions in the crystal lattice. This combination of strength and softness may prove to be a potent strategy for the systematic engineering of solid-state structure in molecular crystals.

Notes and references

1 J. D. Dunitz, *Chem. Commun.*, 2003, 545.
2 J. D. Dunitz and A. Gavezzotti, *Angew. Chem., Int. Ed.*, 2005, **44**, 1766.
3 S. L. Price, *Cryst. Eng. Commun.*, 2004, **6**, 344.
4 S. L. Price, *Adv. Drug Delivery Rev.*, 2004, **56**, 301.
5 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
6 M. C. Etter, *Acc. Chem. Res.*, 1990, **23**, 120.
7 J. Bernstein, M. C. Etter and L. Leiserowitz, *Struct. Correl. 1994*, 1994, **2**, 431.
8 D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, 2004, **43**, 5033.
9 N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2005, **38**, 176.
10 K. Uemura, R. Matsuda and S. Kitagawa, *J. Solid State Chem.*, 2005, **178**, 2420.
11 O. R. Evans and W. Lin, *Acc. Chem. Res.*, 2002, **35**, 511.
12 P. Gilli, V. Bertolasi, V. Ferretti and G. Gilli, *J. Am. Chem. Soc.*, 1993, **116**, 909.
13 R. Taylor and O. Kennard, *Acc. Chem. Res.*, 1984, **17**, 320.
14 J. C. Speakman, *Struct. Bonding*, 1972, **12**, 141.
15 D. Braga, A. Angeloni, F. Grepioni and E. Tagliavini, *Chem. Commun.*, 1997, 1447.
16 O. Felix, M. W. Hosseini, A. De Cian and J. Fischer, *New J. Chem.*, 1998, 1389.
17 S. Ferlay, V. Bulach, O. Felix, M. W. Hosseini, J.-M. Planeix and N. Kyritsakas, *CrystEngComm*, 2002, **4**, 447.
18 D. Braga, L. Maini, F. Grepioni, A. De Cian, O. Felix, J. Fischer and M. W. Hosseini, *New J. Chem.*, 2000, **24**, 547.
19 C. Paraschiv, S. Ferlay, M. W. Hosseini, V. Bulach and J.-M. Planeix, *Chem. Commun.*, 2004, 2270.
20 P. C. Crawford, A. L. Gillon, J. Green, A. G. Orpen, T. J. Podesta and S. V. Pritchard, *CrystEngComm.*, 2004, **6**, 419.
21 S. Ferlay and M. W. Hosseini, *Chem. Commun.*, 2004, 788.
22 D. Shacklady, S.-O. Lee, S. Ferlay, M. W. Hosseini and M. D. Ward, *Cryst. Growth. Des.*, 2005, **5**, 995.
23 J. C. MacDonald, P. C. Dorrestein and M. M. Pilley, *Cryst. Growth Des.*, 2001, **1**, 29.
24 J. C. MacDonald, P. C. Dorrestein, M. M. Pilley, M. M. Foote, J. L. Lundburg, R. W. Henning, A. J. Schultz and J. L. Manson, *J. Am. Chem. Soc.*, 2000, **122**, 11692.
25 D. J. Plaut, K. M. Lund and M. D. Ward, *Chem. Commun.*, 2000, 769–770.
26 R. E. Melendez, C. V. K. Sharma, M. J. Zaworotko, C. Bauer and R. D. Rogers, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2213.
27 V. A. Russell, M. C. Etter and M. D. Ward, *J. Am. Chem. Soc.*, 1994, **116**, 1941.
28 V. A. Russell, C. Evans, W. Li and M. D. Ward, *Science*, 1997, **276**, 575.
29 K. T. Holman, A. M. Pivovar, J. A. Swift and M. D. Ward, *Acc. Chem. Res.*, 2001, **34**, 107.
30 N. J. Burke, A. D. Burrows, M. F. Mahon and S. J. Teat, *CrystEngComm*, 2004, **6**, 429.
31 K. T. Holman, S. M. Martin, D. P. Parker and M. D. Ward, *J. Am. Chem. Soc.*, 2001, **123**, 4421.
32 K. T. Holman, A. M. Pivovar and M. D. Ward, *Science*, 2001, **294**, 1907.
33 M. J. Horner, K. T. Holman and M. D. Ward, *Angew. Chem.*, 2001, **40**, 4045.
34 B. F. Abrahams, M. G. Haywood and R. Robson, *J. Am. Chem. Soc.*, 2005, **127**, 816.
35 M. A. Horner and M. D. Ward, *CrystEngComm*, 2004, **6**, 401.