



Mechanical property design of molecular solids



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ABSTRACT

The current emphasis of *crystal engineering*, which has evolved over the past three decades through crystal packing analysis and identification of crystal design strategies, has shifted from structure to properties, i.e., design of molecular solids with targeted combination of properties. Amongst the panoply of chemical, physical, and biological properties that these materials exhibit, a comprehensive understanding of the mechanical properties is perhaps the most challenging as it involves connecting molecular level structural features to macroscopic mechanical behavior. However, the adoption of the nanoindentation technique, with which it is possible to measure—both quantitatively and accurately—the mechanical response of even small single crystals, in crystal engineering, has paved the way for substantial progress in the recent past. In this review, we summarize some recent results with an emphasis as to how one can design and control properties of molecular solids such as elastic modulus and hardness. This review closes with an enumeration of the key challenges that lie ahead. Such studies show a big scope for studying mechanical properties of organic crystals as a function of crystal structure, and in turn to understand their structure-property relationship for designing future smart materials. This emerging research field has prospects and a potential to play an important role in the future development of crystal engineering.

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1. Introduction

Crystal engineering is a multidisciplinary field with strong roots in chemistry and materials science [1,2]. This broad subject, with its emphasis on the design of new molecular solids with desired properties based on an understanding of intermolecular interactions in terms of crystal packing, has evolved over the past three decades into a formidable research domain of its own standing. The first phase of this evolution involved detailed understanding of the intimate connection between intermolecular interactions and crystal packing [3–6]. Next, the concept of the supramolecular synthon as the fundamental building block, where one functional group in a molecule recognizes another of the same or different molecules in a specific pattern, as the basis for designing solids was recognized and implemented [7,8]. It is then reasonable to expect that the natural progression of this evolution will involve a distinct third—and perhaps final—phase wherein the understanding that is developed hitherto is utilized for designing materials with specific targeted

properties. The basic assumption here is that if one can control the crystal structure, then they can also, in principle, control the properties of the resulting solids too. In essence, this stage involves a shifting of the ‘engineering’ emphasis from structure to property [2,9]. Indeed, the design of functional materials with specific physical and chemical properties that are targeted towards particular applications has gained considerable ground in the recent past. Examples include design and synthesis of metal organic frameworks (MOFs) for gas adsorption and catalysis, polymers for optimized photochemical and photophysical characteristics, active pharmaceutical ingredients (APIs) with enhanced biodissolvability and pharmacokinetics, and biomaterials with excellent biocompatibility [10–15].

The emphasis of this review is on design of new molecular solids with targeted mechanical performance(s). Understanding of the mechanical behavior of materials, a domain specialization of metallurgists and mechanical engineers hitherto, has become a topic of interest for chemists in the recent past [16–25]. This is due to the realization of the importance of the mechanical properties of molecular solids in determining/realizing the application potential of a number of exciting solids such as organic semiconductors, artificial muscles and thermosensitive and mechanochromic organic solids [26–33]. In the case of APIs, which are often subjected to a wide variety of mechanical operations during tablet

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formulation such as grinding, milling and crushing, detailed knowledge of the mechanical properties is essential so that they can suitably be exploited during the manufacturing in the pharmaceutical industry [20,21,34–38]. Such knowledge is essential from the scientific point of view as well; an example is stress induced polymorphic phase transitions in APIs during the mechanical operations [23,39,40]. In the context of biomaterials, the importance of mechanical properties is underlined by the recent realization that spider silks, in particular dragline silk, have exceptional combination of extensibility (ductility) and high tensile strength [41,42]. Synthesis of such stiff/hard/tough solids that are also biocompatible requires detailed understanding as to how those properties are connected to the underlying crystal structure.

While the importance of the study of mechanical behavior of molecular solids has long been recognized by chemists, they generally did not have the necessary tools that would yield quantitative scientific measurements to pursue it at their disposal. Hence, chemists had no choice but to rely on qualitative assessments. This situation has changed significantly in the recent past with the realization that nanoindentation, a somewhat recent mechanical property measurement technique that is widely applied on small volume materials such as thin films, can be gainfully used to study molecular single crystals, which too are often available only in small sizes, as well [20,27,38,43]. This, in turn, has enabled establishment of structure-property correlations in the molecular solids. Primers on the nanoindentation technique and the utility of it in crystal engineering are already written by some of us [20,43–50]. Therefore, we focus on design of molecular solids for specific and targeted mechanical performances. This is accomplished by summarizing some of the recent advances that have been made by us as well as by others.

2. Mechanical property design

The three basic mechanical properties of a material are its stiffness, strength and toughness, which characterize its resistance to elastic and plastic deformations, and cracking respectively. The simplest measures of these properties are the Young's modulus, E , hardness, H , and fracture toughness, K_{IC} . In the following, we will summarize as to the basic set of guidelines that have been hitherto arrived at for obtaining molecular materials with specifically enhanced properties.

2.1. Elasticity

Elastic deformation of a crystalline material primarily depends on the type, number, and strength of the intermolecular interactions (or bonds in the case of atomic solids such as metals) and the packing efficiency within the crystal structure—a crystal with a higher packing, all else being identical, typically tends to exhibit higher stiffness [51,52]. This mode of deformation, which occurs first upon stressing the solid, is fully reversible, i.e., the initial shape is completely regained upon unloading. In metallic and ionic materials, the macroscopic deformation is a result of the stretching of the atomic bonds, but bond breaking, which is irreversible, does not take place during elastic deformation [54]. In the context of polymers and molecular materials, the intermolecular interactions, which are considerably weak vis-a-vis those in metals, can break and reform readily during such deformation [18,20,27]. This imparts considerable elastic flexibility to organic solids with their E being orders of magnitude smaller than those of metals and ceramics [54]. This low stiffness is advantageous when highly flexible materials are required; the best examples for this are the natural fibers like muscle protein titin, spider silk and cytoskeleton micro-tubules [28,30,41,42,55,56]. However, and from a synthetic

crystal engineering perspective, “What are the structural parameters that will impart considerable elasticity to molecular materials?” is a question that requires a satisfactory answer. For that, a set of guidelines or principles need to be established, which in turn can be utilized for design of elastic materials. In this context, it is noteworthy that there are many molecular crystals which show molecular movements not just under mechanical loading but also under some physico-chemical conditions. Terao et al. showed reversible bending in mixed crystals of diarylethylene derivatives under UV light source which is repeatable many times without any breakage [57]. Henke et al. reported flexible MOFs that exhibit structural transition upon adsorption of different guest molecules [58].

Imparting both flexibility and crystallinity to the same organic solid remains a great challenge because crystallinity typically correlates with brittleness, i.e., the ease with which the solid can break apart without undergoing much deformation. For example, similar to ordered molecular crystals, liquid crystals are flexible in nature, but are more amorphous [59]. Ghosh and Reddy demonstrated the first example of excellent shape recovery during flexing of the cocrystal solvate of caffeine-4-chloro-3-nitrobenzoic acid [51]. They attributed such behavior to the weak, dispersive, and interlocking nature of the C—H... π interactions that are ubiquitous in the structure. Subsequently, Takamizawa et al. demonstrated that such 'organo-superelasticity' also occurs in a pure organic crystal of terephthalamide, over a large number of mechanical loading cycles [53]. Mukherjee and Desiraju, who observed that the crystals of 4-bromo-3-chlorophenol are highly flexible, attributed it to the comparable hydrogen and halogen bonding in different directions [52]. These above examples suggest that considerable elastic deformation can be obtained in crystals with isotropic molecular packing.

However, no general crystal engineering rules were put forth for the design of the elastic molecular crystals. Ghosh et al. addressed this through the examination of the mechanical behavior of a family of seven halogenated *N*-benzylideneaniline crystals with the objective of identifying the common structural features that make these crystals highly flexible [60]. For this purpose, they synthesized long acicular crystals of the molecular series **EC1** to **EC7** from corresponding dichlorobenzaldehyde and halogen-substituted aniline by slow evaporation of methanol (Fig. 1a). All the crystals in this series were found to be highly flexible. Even when the crystals break into two pieces when the applied force is high (Fig. 1b(i)), the broken halves are themselves elastically bendable with excellent shape recovery. These qualitative results were further confirmed by quantitative mechanical tests on a nanoindenter, wherein instead of indenting, they have conducted tests on the long and slender crystals in the three-point bend configuration. Representative load-displacement (P - h) curves obtained on an **EC6** crystal are shown in Fig. 2a. The load-unload cycles yield zero displacement upon complete unloading showing the ability of the crystals for shape recovery and hence elastic nature of the series of molecular crystals examined. However, considerable hysteresis in those cycles can be noted. These quantitative tests also confirm the maximum elastic strain that these crystals can accommodate is much larger than other comparable materials. This elastic behavior of this family of crystals is then attributed to the following common characteristics within their crystal structures. The molecules in these crystals are interconnected through a multitude of weak C—H...N and C—H...Cl hydrogen bonds (Fig. 1c). These bonds, being weak, break readily upon the application of load, but reform during unloading. (This is the reason for the observation of a large hysteresis in the load-unload cycles. Such hysteresis can be exploited in energy harvesting applications.)

Thus, the following two structural features are essential for obtaining highly elastic crystals. The first is that they should contain multitude of isotropic weak, dispersive hydrogen bond (C—H...Cl, C—H...Br) and halogen bond (Cl...Cl, Cl...Br, Br...Br)

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