Preface to the Special Issue

The origin of our understanding of the crystalline organic solid state can be traced to concepts of molecular structure developed by scientists in the early and middle 1800s. To this day, Pasteur's laborious separation of enantiomorphic crystals of tartaric acid in 1848 stands as a classic example of the relationship between molecular symmetry and crystal properties. The advent of X-ray crystallographic methods in the early 1900s and its application to the determination of solid-state structure enabled detailed understanding of the structure of molecules in the solid state and the packing arrangements of molecules in the crystal lattice. The relation between structure and function became increasingly recognized in the mid-1900s, with advances in polymer synthesis and the determination of the crystal structure of deoxyribonucleic acid. It was only a matter of time until the influence of molecular packing and solid-state structure of molecular crystals on the physical properties and chemical reactivity of these materials was demonstrated. The pioneering work by Gerhardt Schmidt and Mendel Cohen at the Weizmann Institute in the early 1960s on the photodimerization of specific polymorphs of *trans*-cinnamic acids is generally regarded as the birth of "crystal engineering", which is still the mainstay of research in the organic solid state. These and further studies of solid-state reactivity by other research groups provided important illustrations of the unique ability to direct molecular reactivity by controlling reaction geometries in organic crystals. Interest in crystal engineering has intensified over the past two decades with the design and synthesis of new materials exhibiting properties such as conductivity, superconductivity, ferromagnetism, and nonlinear optical effects, characteristics generally associated with more familiar nonmolecular materials. The impact of solid-state structure and crystal engineering principles on pharmaceutical chemistry—where crystallization, morphology, and polymorphism are crucial materials issues—has been well established and continues to be felt in that industry.

From the standpoint of materials design, interest in crystalline organic solids remains strong because of our ability to manipulate solid-state and crystal properties by judicious design or choice of molecular constituents from a nearly unlimited number of candidates. Of course, for many of us the elegant and beautiful symmetries of these materials is sufficient grounds for our interest. This is exemplified by the hexameric 1,3-cyclohexanedione–benzene inclusion complex discovered by Peggy Etter and illustrated on the cover of this issue. However, research concerning the organic solid state and the factors governing molecular organization is also increasing our understanding of biologically relevant molecules such as peptides and proteins, aiding the synthesis of new materials for nonlinear optics and other electronics applications and advancing the design of crystallization processes.

The contributions contained in this issue exemplify the interest, breadth, and diversity of the organic solid state. The topics contained in many of these reports were of great interest to Peggy Etter. Codification and prediction of crystal packing, hydrogen bonding in the solid state, organic crystals for second harmonic generation, and synthesis of cocrystals represent fundamentally and technologically important research areas. Emerging research areas are also represented, including crystal nucleation and growth phenomena, scanning tunneling and atomic force microscopy of organic crystals, topochemical synthesis studies, and conducting and magnetic materials. Related materials design concepts are also illustrated by contributions describing well-defined functional polymers and hybrid materials based on organic constituents and inorganic matrices. The diversity of these contributions is typical of materials chemistry—broad in scope and sometimes difficult to define. But it is clear that the investigation, design, and synthesis of organic solid-state materials will be a vital component of materials research for the foreseeable future.

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