Crystalline Molecular Machines

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Molecular Crystals on the Move: From Single-Crystal-to-Single-Crystal Photoreactions to Molecular Machinery**

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The physical and chemical properties of molecular crystals can be traced back to their molecular and macroscopic properties.[1,2] The nature of their components and packing structures are just as important as the symmetry of the ensemble and the direction of measurement, or anisotropy. For this reason, photoreactive molecular crystals are very appealing from a materials-science perspective. As their composition and structure evolve as a function of reaction progress, their physical and material properties are affected in a predetermined and often controllable manner. It has also been suggested that the properties of materials can be modulated with amphidynamic crystals,[3] which are specifically designed with static and mobile components that are capable of responding to the presence of external fields. Thus, the conjunction of anisotropic physical properties, controllable chemical process, addressable dynamics, and collective phenomena suggest many challenges and opportunities for the development of crystalline molecular machines.

Key to the use of photoresponsive molecular crystals as addressable functional materials is our ability to understand and control their chemical reactivity. While it is sometimes assumed that reactions in crystals are forbidden, this notion can be readily challenged. In fact, more than 160 years of observations[4] involving hundreds of reactive crystals[5] have led to significant advances in our understanding of solid-state reactivity[6] and crystal design.[7] However, while it is widely appreciated that reactions in crystals tend to be highly selective, the effects of product accumulation on the subtle balance of the original lattice architecture have not been addressed in as much detail.

Since the first documented examples,[4,8] chemists have shown that most photoreactive crystals tend to collapse and degrade as the reaction proceeds. In a pioneering study, McBride and co-workers estimated that the local stress accompanying the decarboxylation of diacyl peroxides in crystals reaches values in the range of 40–60 kbar, which is close to the pressure needed to convert graphite into diamond.[9] Whereas the magnitude of the local stress depends on the structural mismatch between reactants and products, little is known about the relaxation mechanisms. In some cases, the difference between reactants and products is so small that three-dimensional order is preserved with relatively minor adjustments in the unit cell (Figure 1). These

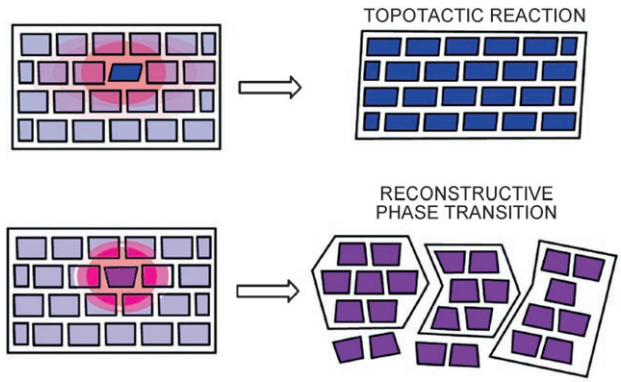

Figure 1. Representation of a) a topotactic (single-crystal-to-single-crystal) reaction and, b) a solid-to-solid reconstructive reaction. Different mechanisms for release of local stress in the lattice of the reactant may determine the mechanical outcome.

reactions are said to be single-crystal-to-single-crystal, or topotactic. Other reactions involve molecular changes that are sufficiently large to cause the original structure to collapse.[10] Those changes that occur above the eutectic temperature of the two-component (reactant and product) phase diagram cause the crystal to melt. At lower temperatures, reconstructive phase transitions occur,[11] and single crystals turn opaque as product-rich domains of relatively small size separate and scatter light. Some examples observed by atomic force microscopy (AFM) show crystal disintegration, phase rebuilding, and phase transformations.[10] In some cases the product is formed in an amorphous phase.[11]

In a recent publication, Irie and co-workers reported that structural changes taking place in crystal-to-crystal photochemical reactions may lead to useful mechanochemical action at the micron scale (Scheme 1).[12] Their observations

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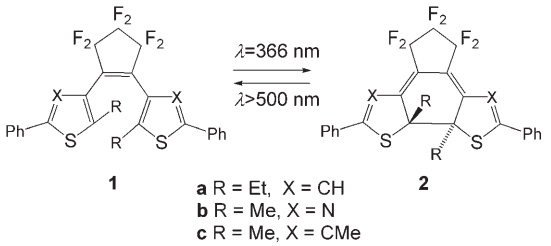


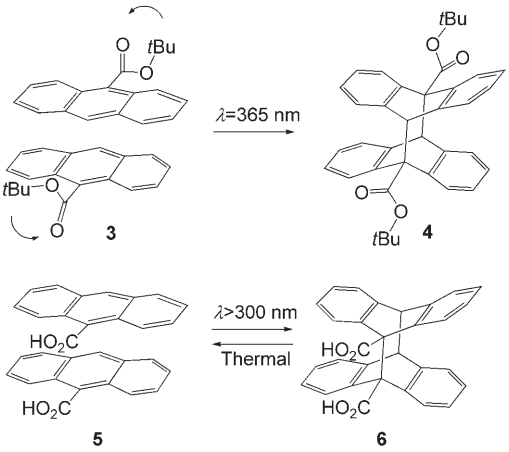
Scheme 1. Photomechanically responsive diarylethenes **1a–c** and their reversible conversion into tetraenes **2a–c**.

include: a) small single-crystalline microplates (ca. 10–100 μm) of photochromic diarylethene **1a** that change shape from squares to parallelograms on exposure to UV light, b) small rectangular prisms of **1b** that expand by as much as 7% along their longest dimension, and c) rodlike crystals ($225 \times 5 \times 6.5\ \mu m^3$) of **1b** that bend towards the source of light when one end is fixed onto a glass surface. Prior to these studies, Irie et al. had used AFM to document changes of surface morphology in relatively large (ca. $10 \times 10 \times 0.5\ mm^3$) specimens of compound **1c**.[13]

The ring-closing reaction of **1** causes a change in the electronic structure which results in the deep blue to purple color of **2**. The overall change in structure is small enough for the reaction to be topochemically allowed when the aryl groups adopt the antiparallel conformation required in the product. Experiments with **1c** had shown that 1-nm steps are formed on the crystal (100) surface when irradiated with 366-nm light, and that the steps disappear upon illumination with light at wavelengths above 500 nm. It was shown that each 1-nm step requires reaction to depths of about 600 molecular layers.[13] A key observation was that the step formation in **1c** requires an induction period, suggesting that reconstruction of the lattice requires a critical concentration of reacted molecules before collective reorganization can take place.

Given the volume and concentration dependence of step formation of the surface of **1c**, and recent reports indicating that single-crystal-to-single-crystal reactions are more likely with nanocrystalline specimens,[14,15] it is likely that the novel behavior of **1a** and **1b** may partially reflect properties characteristic of smaller crystal sizes. Key observations with **1a** and **1b** include their photomechanical reversibility, the need of an induction period for the changes in crystal shape to take place, a photostationary state with as much as 70% of the closed-ring isomer present (**2**), and changes in crystal dimensions that appear to have no hysteresis. The physical properties that change as a function of composition and variations in the crystal structure can be monitored by optical (order parameter and shift in λ_{max}) and thermal (melting point) measurements. These properties also confirmed that the smaller photomechanically responsive crystals have the same morphology as well-characterized macroscopic specimens. Notably, rodlike crystals of **1b** mounted at one end on a glass surface bent reversibly towards the light source, and away from it, upon exposure to ultraviolet and visible light, respectively. This behavior was ascribed to a gradient in the extent of photoisomerization, so that shrinkage of the irradiated part of the crystal causes bending. In a nice demonstration of photomechanical work, or photoactuation, Irie et al. attached a gold microparticle about 90 times heavier than the single crystal to the moving end. They showed that illumination of the photochromic rod resulted in displacement of the load of up to 30 μm; a process that was reproducibly repeated with no observable fatigue for no less than 80 cycles.[12]

Auguring that the remarkable properties of **1a** and **1b** might not be exceptional, Bardeen et al. described analogous effects with 200-nm-diameter nanorods of 9-*tert*-butylanthracenecarboxylate **3**[15] and 9-anthracenecarboxylic acid **5** Scheme 2.[16] Both samples were prepared by solvent annealing in Al_2O_3 templates.[17] Crystals of **3** were shown to expand



Scheme 2. Photoresponsive anthracene carboxylates.

irreversibly by as much as 15% along the long axis in a single-crystal-to-single-crystal process that forms dimer **4**. Notably, isomorphous micrometer-size specimens of **3** fragmented upon light exposure, showing that relaxation processes in these crystals are indeed size-dependent. The identity of "as-formed" and recrystallized samples of photodimer **4** was confirmed, demonstrating that the chemical reaction in crystals of **3** drives a reconstructive phase transition.[11] In a more recent report, exposure of **5** to UV light resulted in formation of the thermally unstable *syn* 4+4 photodimer **6**, which spontaneously reverts to the starting anthracene carboxylic acid.[16] When long (60 μm) nanorods of **6** were briefly exposed to 365-nm light while suspended in a 50% solution of phosphoric acid in water, the nanorods could reversibly flex and then revert back to their original shape in the dark. By monitoring the recovery of anthracene emission it was established that thermal recovery occurs within a few minutes. Shorter recovery times could display the locomotive behavior of an artificial flagellum.

The experimental observations demonstrate single-crystal-to-single-crystal reactions are capable of dissipating the stress generated at specific reaction sites through the entire specimen. The nature of these relaxation processes may be dependent on the size and micro- or nanorheological properties of the ensemble.[13,16] This fact would be consistent with a state of matter in transition between discrete supramolecular

aggregates and macroscopic crystalline specimens. The independent reports by the groups of Irie and Bardeen suggest many promising opportunities in the fields of functional materials and artificial molecular machinery.

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