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All-in-One: Thermally Twistable, Photobendable, Elastically Deformable and Self-Healable Soft Crystal

Poonam Gupta,[a] Durga Prasad Karothu,[b] Ejaz Ahmed,[b] Pance Naumov*[b] and Naba K. Nath*[a]

Abstract: The first example of a smart crystalline material, the 2:1 cocrystal of probenecid and 4,4′-azopyridine, which responds reversibly to multiple external stimuli (heat, UV light, and mechanical pressure) by twisting, bending and elastic deformation without fracture is reported. This material is also able to self-heal on heating and cooling, thereby overcoming the main setbacks of molecular crystals for future applications as crystal actuators. The photo- and thermomechanical effects and self-healing capabilities of the material are rooted in reversible *trans–cis* isomerization of the azopyridine unit and crystal-to-crystal phase transition. Fairly isotropic intermolecular interactions and interlocked criss-crossed molecular packing secure high elasticity of the crystals.

Nature has always amazed materials scientists with its highly sophisticated biomolecular systems, and some of these structures have already been translated by researchers and engineers into useful advanced technologies.[1] Particularly appealing are the mechanisms for motion or dispersal found in plants and insects, the basic kinematic traits of which can be replicated by the motility of the recently discovered *dynamic crystals*, which are able to jump,[2–6] bend,[7–14] twist,[15,17] crawl,[18] roll,[19] and even walk[18] when they are excited by heat or light.[20–23] The kinematic effects of these advanced crystalline materials comply to many of the requirements for micromachinery gears, such as those used in microrobotics and microfluidics. Moreover, when impacted by external force (application of localized pressure) many mechanically complaint molecular crystals dissipate the applied stress and undergo reversible (elastic)[24–26] or irreversible (plastic)[27] bending without disintegration.

Amidst the rapid rise of the adaptive crystalline materials, the recent research efforts revolve around optimization of their performance aimed to accomplish fast, reversible and fatigueless response to applied stimuli after prolonged operation. The capability of recovery after damage during operation, akin to the biological systems, is as equally as important if these materials are to be considered for future applications. Yet, due to difficulties with predictability of molecular packing, intermolecular interactions and crystal habit, combining multiple mechanical responses to different stimuli in a single molecular crystal remains as one of the most formidable challenges.[28] Several recent reports of self-healing molecular crystals[29–31] open prospects for further exploration into the self-repairing mechanisms in crystals. Here we report the first example of a molecular material, a cocrystal of 4,4′-azopyridine and the uricosuric agent probenecid (Figure 1a), that responds reversibly to *three* different external stimuli—heat, light and mechanical force. Molecular crystals of probenecid are known to be plastically bendable, and cocrystallization with 4,4′-azopyridine was carried out to introduce an additional property of photoinduced mechanical effects in the same system. The crystals twist and untwist when they are heated or cooled, bend reversibly when they are exposed to UV light, and deform elastically when they are subject to mechanical force. Perhaps most importantly, these crystals can also self-heal during heating and cooling, thus displaying the most diverse set of functions in a single soft crystalline material reported to date.

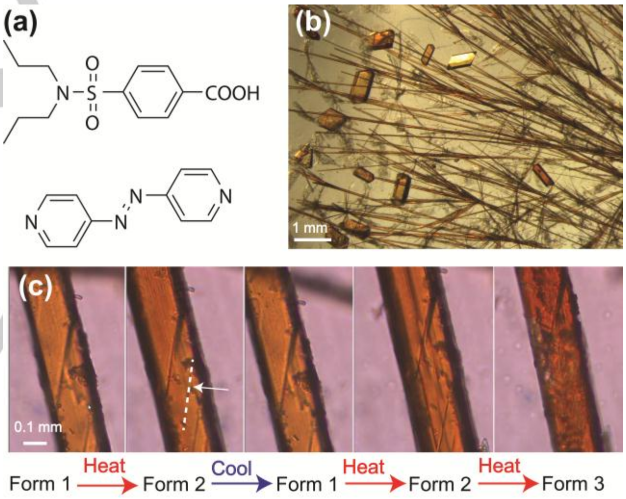

Figure 1. (a) Molecular structures of probenecid and 4,4′-azopyridine, (b) optical microscopic image showing the crystal habits of the two polymorphs of the cocrystal, form 1 (acicular crystals) and form 3 (blocky crystals), and (c) thermal microscopy images showing progression of the habit plane (phase front) during the reversible phase transition form 1 → form 2 and during the irreversible phase transition form 2 → form 3. The habit plane is highlighted with broken white line, and is more easily visible in Supporting Information Videos S1 and S2.

Cocrystallization of 4,4′-azopyridine with probenecid in 1 : 2 molar ratio by slow evaporation from acetonitrile afforded orange crystals with acicular and blocky habit (Figure 1b; for synthesis characterization and crystal morphology, see Supporting Information, Scheme S1, Figure S1). Single crystal X-ray diffraction analysis confirmed that the two crystalline habits correspond to different polymorphs, hereafter referred to as form 1 (acicular crystals) and form 3 (blocky crystals). To our surprise, these two polymorphs exhibited very different response to heating, application of mechanical stress and exposure to UV light: in contrast with form 3, which was unaffected by these

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stimuli, the single crystals of form 1 responded to each in three distinct ways. When heated on a thermal stage coupled with a microscope at a rate of 20 ºC min^{-1}, crystals of form 1 underwent two thermal events. Between ~62 and 64 ºC a phase front (habit plane) was observed to propagate through the crystal (Figure 1c; Supporting Information, Figure S2, Videos S1 and S2). Upon subsequent cooling below ~58 ºC, the phase front moved in the opposite direction. This was occasionally accompanied by rapid and reversible distortion or motion of the crystal (Supporting Information, Figure S2 and Video S2). On further heating above ~76 ºC, progression of a phase front was observed again, however it occurred without any observable macroscopic motion of the crystal (Figure 1c; Supporting Information, Figure S2, Video S1 and S2). When cooled from 76 ºC to room temperature, the crystal did not display any of the events observed during heating, indicating that the change around 76 ºC is irreversible. The rate of progression of the first transition was calculated from the progressing habit plane to be approximately 2.5 mm s^{-1}, and it is much slower compared to the rate of phase transitions associated with the thermosalient crystals (typically on the order of several m s^{-1})[4–6], however it is much faster than the mechanically inactive second transition (0.08 mm s^{-1}).

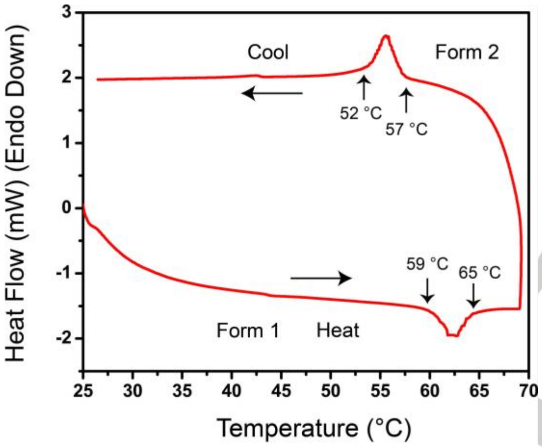

Figure 2. Heating-cooling cycle in the DSC thermogram of the cocrystal showing effects due to the reversible phase transition between forms 1 and 2.

Differential scanning calorimetry (DSC) carried out on crystals of form 1 at 5 ºC min^{-1} showed endothermic peaks at 59–65 ºC (Figure 2) and 76–86 ºC (Figure S3) corresponding to the two phase transitions. The first phase transition, from form 1 to another polymorph, form 2, occurs at 59–65 ºC on heating and at 57–53 ºC on cooling. The second transition (~76 ºC) from form 2 to form 3 is irreversible, and no phase transition was observed on cooling of form 3 (Supporting Information, Figure S3).

The mechanical response observed with thermal microscopy prompted us to further investigate the heat-induced reshaping of crystals of form 1. The thermomechanical response of 35 crystals was inspected by heating to 68 ºC each crystal in turn on its wider face, (001) (for face indexing, see Supporting Information, Figure S4) and subsequent cooling to room temperature. A total of 14 crystals were found to twist, occasionally by lifting at one end off from the base. The crystals retained their twisted shape as long as they were kept above the phase transition temperature; they untwisted and recovered their original shape after they were cooled below the phase transition (Figure 3; Supporting Information, Figure S5, Videos S3, S4 and S5). None of these 14 crystals was found to splinter or crack during twisting, and the macroscopic integrity and crystallinity was preserved even after cooling. The other crystals were found to exhibit other mechanical effects (Supporting Information, Figure S6, S7, Video S6).

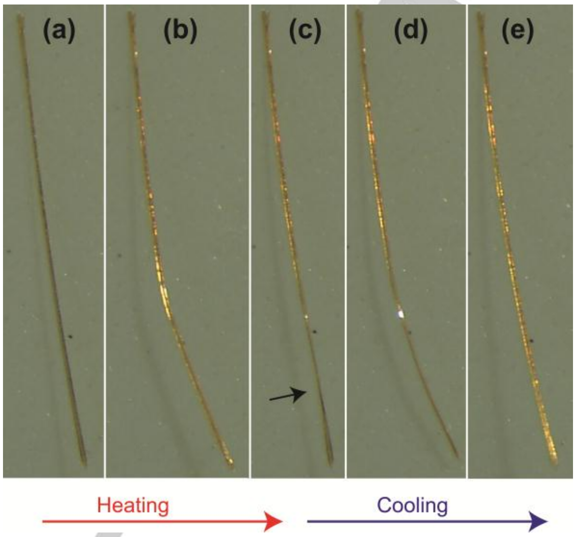

Figure 3. A cocrystal (size: length, 6.12 mm; width, 0.26 mm; thickness, 0.12 mm) twists when heated, whereupon one end lifts off the base (pointing toward the reader), and untwists after cooling, regaining its original shape. The black arrow indicates the region where the twisting occurs.

To gain mechanistic insight into the origin of the mechanical effects, the structure of form 1 was determined by using X-ray diffraction analysis (Supporting Information, Figure S8 and Table S1). A crystal of form 1 was transformed to form 2 *in situ*, by heating to 63 ºC with a stream of nitrogen gas on the diffractometer. Although the heating caused some deterioration of crystal quality, the diffraction quality was sufficient to determine the structure of form 2 at 63 ºC. The same crystal was further heated above 76 ºC, however the crystal quality of form 3 obtained *in situ* was insufficient for structure solution. Therefore the same crystal was cooled to room temperature, and the structure determination showed that it is in form 3. The calculated powder diffraction pattern of thus obtained form 3 was identical to that of form 3 obtained by crystallization (Supporting Information, Figure S9). Form 1 crystallizes in the monoclinic space group $P2_1/c$ with one molecule of probenecid and half molecule of 4,4′-azopyridine in the asymmetric unit whereas, the structure of form 2 is triclinic, space group $P\bar{1}$ with two molecules of probenecid and two half-molecules of 4,4′-azopyridine molecules in the asymmetric unit (Supporting Information, Table S1). The structure of form 3 is triclinic, space group $P\bar{1}$ with one molecule of probenecid and half molecule of azopyridine in the asymmetric unit.

The basic building block of both polymorphs consists of one azopyridine molecule bonded by O—H···N and auxiliary C—H···O hydrogen bonds to two probenecid molecules, one on either of its two termini (Supporting Information, Figure S10). These hydrogen-bonded entities are stacked over one another by C—H···O and C=O···π interactions and form infinite stacks along the *b* axis. The molecular stacks are closely packed and form infinite 2D layers. The resulting 2D layers are criss-crossed and interact through C—H···O hydrogen bonds.

On heating and cooling over the transition 1 ↔ 2 the molecular arrangement changes by small reorganization of the 2D layers. The interplanar angle between the two nearly perpendicular probenecid benzene rings decreases from 89.3(3)º in form 1 to 85.4(2)º in form 2, while the angle between the two azopyridine planes expands from 84.7(3)º in form 1 to 87.4(9)º in form 2 (Figure 4a). The centroid-to-centroid disposition in the stacking direction of the criss-crossed 2D layers changes from 0.0(6)º in form 1 to 6.0(4)º in form 2 (Figure 4b). Apart from these major changes, the transition to form 2 is also associated with a change in conformation of the *n*-propyl chains in one of the symmetry-independent probenecid molecules. These changes in molecular packing result in expansion along the *a* axis of 5.2%, expansion along the *b* axis of 1.6% and contraction along the *c* axis of –2.8% when the crystal transitions from form 1 to form 2. These changes in molecular packing and conformation during the phase transition generate anisotropic strains and result in macroscopic distortion that ultimately appears as twisting of the crystal (Figure 4c,d). Consistent with most single-crystal-to-single-crystal phase transitions that are not accompanied by observable mechanical effects, the second phase transition, 2 → 3, which was not accompanied by mechanical effects, is related to significant structural change (for the structure of form 3, see Supporting Information, Figure S11).

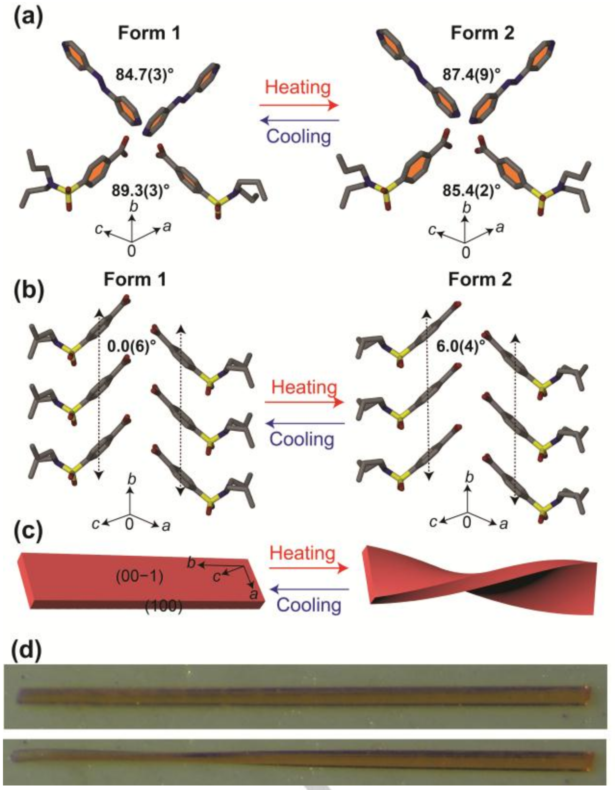

Figure 4. Crystal structures of forms 1 and 2, and proposed mechanism for the mechanical effect that accompanies the reversible phase transition 1 ↔ 2. (a) Subtle changes in the angles between the aromatic rings of two criss-crossed probenecid molecules and between the molecular planes of two criss-crossed azopyridine rings. (b) Change in the angle between the centroid-to-centroid π···π stacking direction of the criss-crossed 2D layers of about 6º during the transition. (c,d) Non-uniform strain generated during the transition results in reversible twisting of the crystals, shown here with a cartoon (c) and twisting of actual crystal (d) (size: length, 5.90 mm; width, 0.36 mm; thickness, 0.15 mm).

In many cases it was observed that the bi- or multi-furcate branches of the split crystal advance towards each other after the phase change and tend to rejoin. To inspect the details of this phenomenon, several well-shaped single crystals were examined with temperature-controlled optical microscopy. A crystal was first heated over the transition 1 → 2 and cooled below the transition 2 → 1 at rate of 5 ºC min^{-1}. (Supporting Information, Video S7), during which a small crack appeared on the (001) face of the crystal. The crystal visibly separated around its central cracked section (Figure 5a; Supporting Information, Video S8) during a second heat cool cycle. The cracked crystal was heated above 1 → 2, whereupon the crack disappeared without any visible trace of the original crack (Supporting Information, Videos S8 and S9). Another instance showed that two planks that separated out of the crystal were rejoined by heating, thereby partially recovering the original crystal (Supporting Information, Figure S12, Video S10). These experiments indicate that after the crystal is cracked by heating—at least macroscopically—it appears to heal when cycled thermally in the temperature range 52–68 ºC. Although the effects are clearly facilitated by heating and the phase transition, these observations resemble the recently reported examples of self-healing crystals.[29–31]

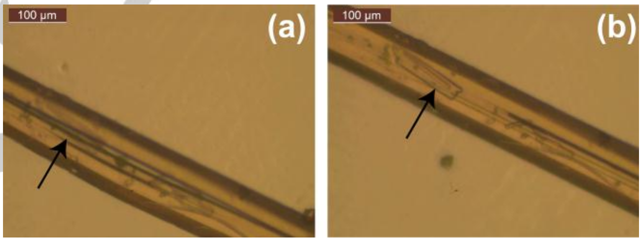

Figure 5. Thermally-assisted self-healing effects. A crystal, cracked during first heat-cool cycle over the phase transition 1 ↔ 2 (a) partially heals on second heating as seen by the regained translucency under microscope (b). The black arrow shows the region where crack occurred and disappeared.

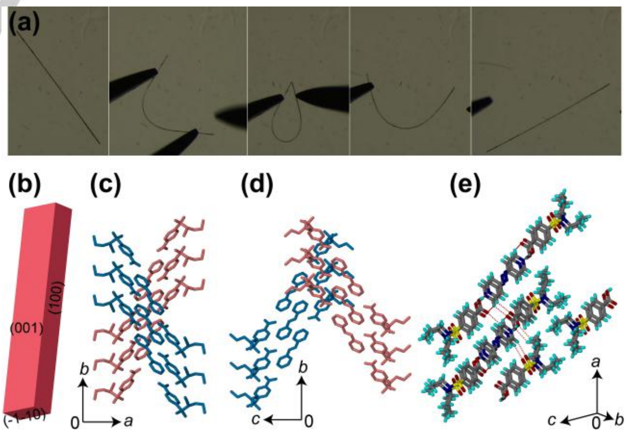

Figure 6. (a) Slender crystals of form 1 can be elastically bend up to 360º to form a loop. (b) Indices of the prominent faces of the crystal. (c–e) View of the molecular packing as seen normal to the (001) face (c), the (100) face (d) and the $(\bar{1},\bar{1},0)$ face (e), showing the interlocked molecular packing.

In addition to these properties, the cocrystals are also extraordinarily elastic. Crystal of form 1 (typical size: 7.5 mm × 0.3 mm × 0.2 mm) held on the wider face, (001), can be bent up 360º and shaped in a loop without breaking, similar to some previously reported examples[25,26] (Figure 6a; Supporting

Information, Video S11). After the stress is released, the crystals regain their original straight shape. In the crystal structure of form 1, the building blocks of probenecid and azopyridine are connected by weak intermolecular interactions of comparable length, that is, C=O$\cdots\pi$ (~2.8 kcal mol^{-1}), C—H$\cdots$O (~2.8 kcal mol^{-1}) and van der Waals interactions (~0.9 kcal mol^{-1} per atom pair) in all three directions. The criss-crossed 2D layers consisting of hydrogen-bonded probenecid/azopyridine units are interconnected by weak intermolecular C—H$\cdots$O hydrogen bond (Figure 6c–e). Such interlocked molecular packing and isotropic intermolecular interactions in crystal structures were earlier related to the elastic bendability of other molecular crystals,[20,21] and could be the main contributor to the extraordinary elasticity observed with the cocrystal in this work.

In addition to the other mechanical properties described above crystals of form 1 also display rapid and reversible bending under UV light owing to the ability of the azopyridine molecule[32] to undergo photoinduced *trans-cis* isomerization (Supporting Information, Figure S13). Crystals of form 1 of size in the range 6.0–9.0 mm × 0.2–0.5 mm × 0.08–2.0 were irradiated on their (001) face for 1 s with UV light from a mercury-xenon lamp with a heat filter, and the photomechanical response was recorded with a camera attached to a microscope. The crystals bent away from the light source with a speed of 0.15–2.15 mm s^{-1}, reaching maximum deflection of 0.08–1.14 mm within 0.49–0.57 s when exposed to UV light with power 580.0 mW cm^{-2}. After the irradiation was terminated, the crystals instantly regained their original straight shape within 0.39–0.44 s with a speed of 0.2–2.66 mm s^{-1}. To check the dependence of the maximal deflection on the UV excitation power, 14 crystals were irradiated on their wider face with UV light with excitation power ranging from 58.5–580 mW cm^{-2} in 10 different steps at a distance of 2 cm from the UV light output (Supporting Information, Video S12). It was found that, at least within the range of excitation powers used in the experiment, the maximum deflection increases with increasing UV excitation power (Supporting Information, Figure S14). The crystals retained their macroscopic integrity and were actuated several times without any detectable damage and loss of crystallinity, even when they were exposed to the highest attainable power of the UV light for more than 10 minutes.

In summary, we have demonstrated the first example of a multifunctional molecular crystal which combines three functionalities and can respond to multiple external stimuli—heat, light and mechanical force. The mechanical response of this material is not only rapid, but it is also reversible and occurs with short recovery times, and thus meets the main requirements for a multifunctional, soft molecular crystalline material. An additional trait of this material is the ability to heal by heat, which turns this and related cocrystals into prospective candidates for robust and durable singe crystal actuators.

Acknowledgements

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Keywords: actuators • azobenzene • photomechanical effects • self-healing • single crystal

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COMMUNICATION

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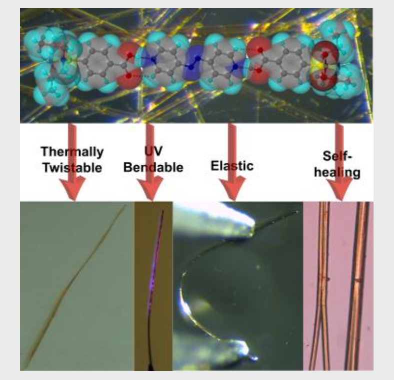

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