



The world of exotic crystals:

Raman spectro-microscopy for probing local structure

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In this article, we review briefly the recent progress on mechanically responsive molecular crystals which defy the common perception that “crystals are rigid”. Crystals which respond to different external stimuli are emerging fast and may find applications in miniature technologies, sensors, flexible devices, and soft-robotics. Here, we present some early examples of molecular crystals from our group, along with other examples of our choice, to emphasize on the use of Raman spectromicroscopy technique for characterizing crystals, polymorphic forms and strained crystals in the context of structure-property correlation and crystal engineering.

What are crystals?

Broadly, solids can be classified into three sets; namely crystalline, polycrystalline and amorphous (Figure 1a). In amorphous materials, the substituent elements, such as atoms, molecules or ions are not organized in a definite lattice pattern, thus lack long-range internal order. On the other hand, a crystal or crystalline solid material constitutes a lattice that extends in three dimensions, made up of atoms, ions or molecules. Crystalline materials are omnipresent around



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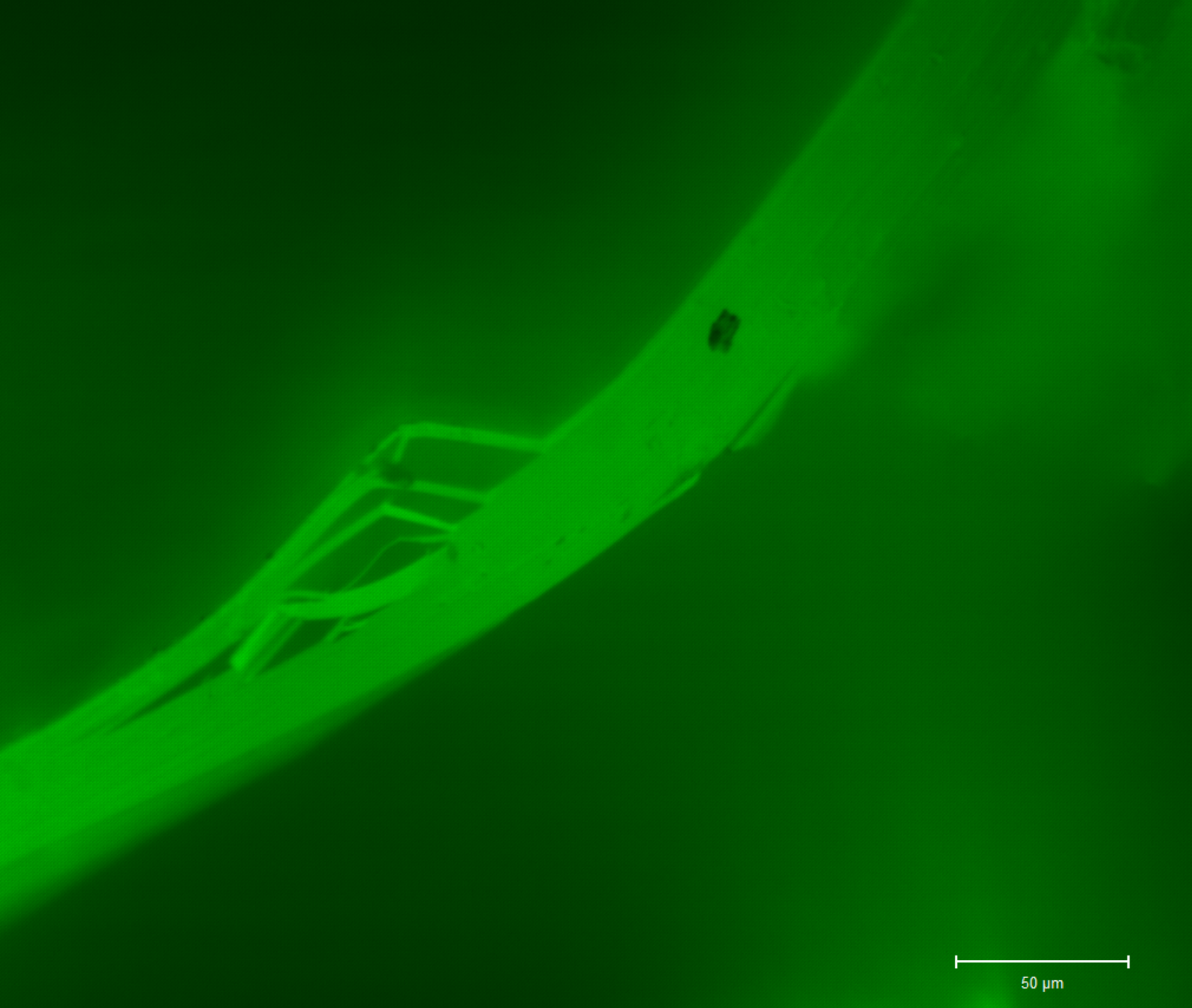


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us, such as in the form of semiconductors, pharmaceuticals, solar cells, batteries, biominerals, rocks and soils. Common examples of crystals in our daily life include table salt and sugar. Polycrystalline materials are constituted by many small crystalline domains, called “grains”, separated by grain boundaries (Figure 1a). The grains, typically with sizes varying from nanometers to millimeters, have random crystallographic orientations.

Most chemical and physical properties of solids depend immensely on the way their constituents are organized in a three-dimensional space (Figure 1b,c). Our ability to manipulate the organization of constituents in crystals can provide immense opportunities to produce materials with improved properties. A subject which deals with this idea is termed as “crystal engineering”, which studies the design and synthesis of crystal structures with desired properties

through deliberate control of intermolecular interactions making up the structure ^[1] ^[2]. In order to be able to engineer the properties of crystals, we have to understand the nature of interactions, their directionality and the influence of the same on the emergent properties of crystals.

The phenomenon of polymorphism

Materials can crystallize in more than one form in the solid state, which is termed as



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physics to analyze electron-phonon interactions and quantum confinement in semiconductor nanostructures using Raman micro-spectroscopy.

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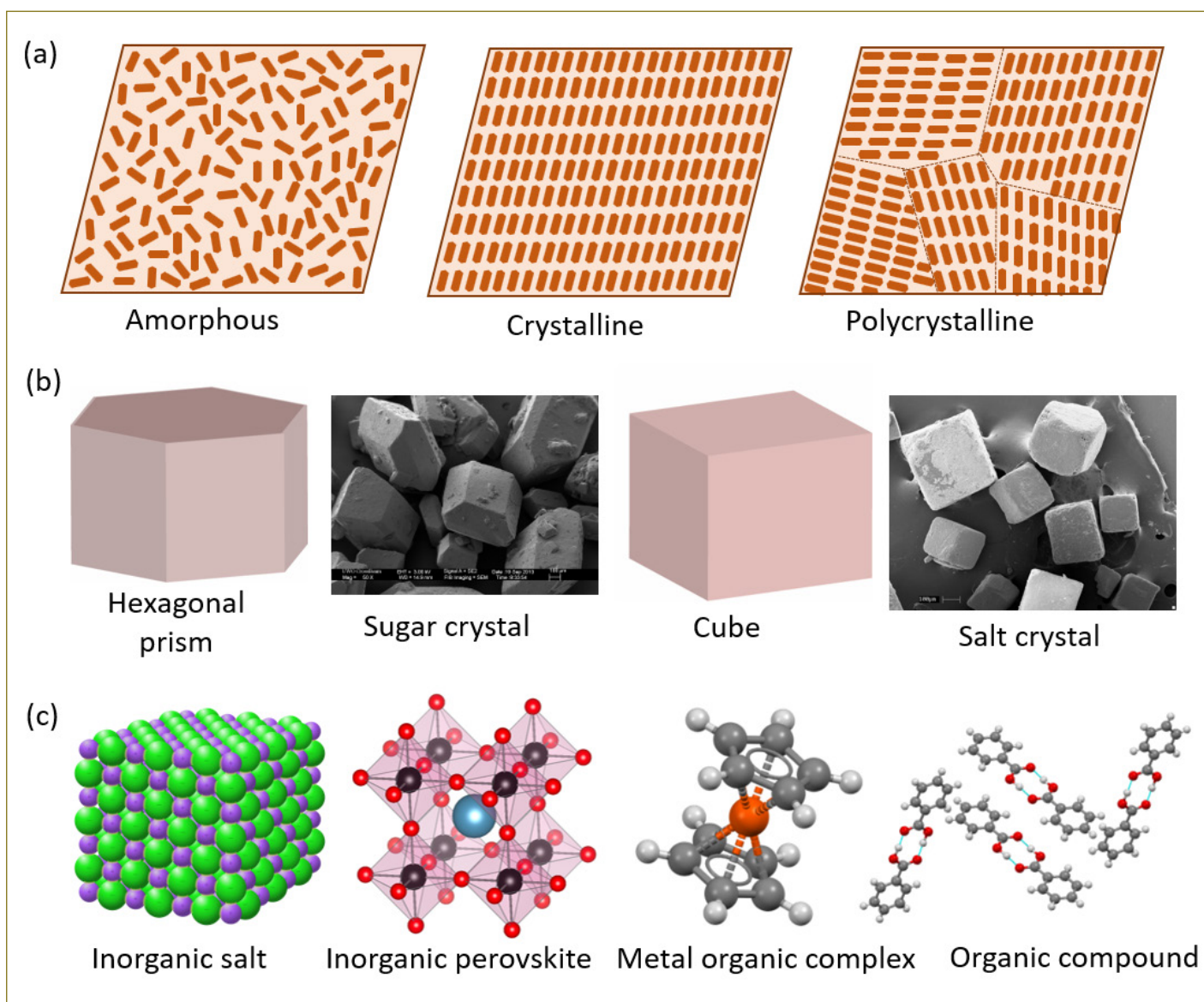


Figure 1. (a) The three general types of solids: amorphous (with no particular ordered arrangement of constituents); single crystal (with long range order or periodicity); polycrystalline (with multiple ordered domains called grains separated by a grain boundary). (b) Different shapes of crystals: hexagonal prism as found in sugar crystals (picture courtesy: UWO Nanofabrication Facility); cube as found in salt crystals (picture courtesy: NISE Network). (c) Structure of different solid crystals viz inorganic salt (NaCl); inorganic perovskite with formula ABO₃; organic-inorganic hybrid (ferrocene); and hydrogen bonding in organic crystal (benzoic acid, C₆H₅COOH).

polymorphism (Figure 2a)^[3]. The phenomenon of polymorphism has far reaching consequences in the pharmaceutical industry as various physical properties like density, tabletability, solubility, melting point and hygroscopicity are affected by this. This can in turn impact the marketability of a drug substance. Hence, the selection of a desired solid state form for the processing and final product development has become a vital step in drug marketing. Similarly, polymorphism can affect optical, electrical, mechanical and many other properties that are relevant to the performance of devices. An interesting outcome of polymorphism is found in crystals of 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile or

ROY, which has a record number of known polymorphs that appear with different colour and morphologies. Not only that, but a new form has also been predicted to become the most stable among all known polymorphs above 10 GPa pressure^[4].

Another historically relevant example is the photoreactivity of trans cinnamic acid. The molecule can crystallize in three forms, α , β and γ . In the α and β forms, the molecules adopt a crystal structure with a short axis of around 4Å. When irradiated, they undergo [2 + 2] photodimerization. While in the γ form, the molecules pack in such a manner that they are >4.7Å apart, hence no reaction occurs in the presence

of light^[5]. Polymorphism is also utilized to tune functionalities of semiconductors, as in the example of 2-dimensional quinoial terthiophene, where polymorphic transitions were used to tune the electron mobility by five orders of magnitude.^[6]

If a crystal is rigid and static, how can it bend?

When we think of crystals, the idea which comes to mind is that they are static, brittle and "dead". This preconception is mainly due to the fact that most crystals are rigid, consisting of discrete species tightly bound to each other and balanced by attractive and repulsive forces. Most crystals possess tightly packed molecules with no space or

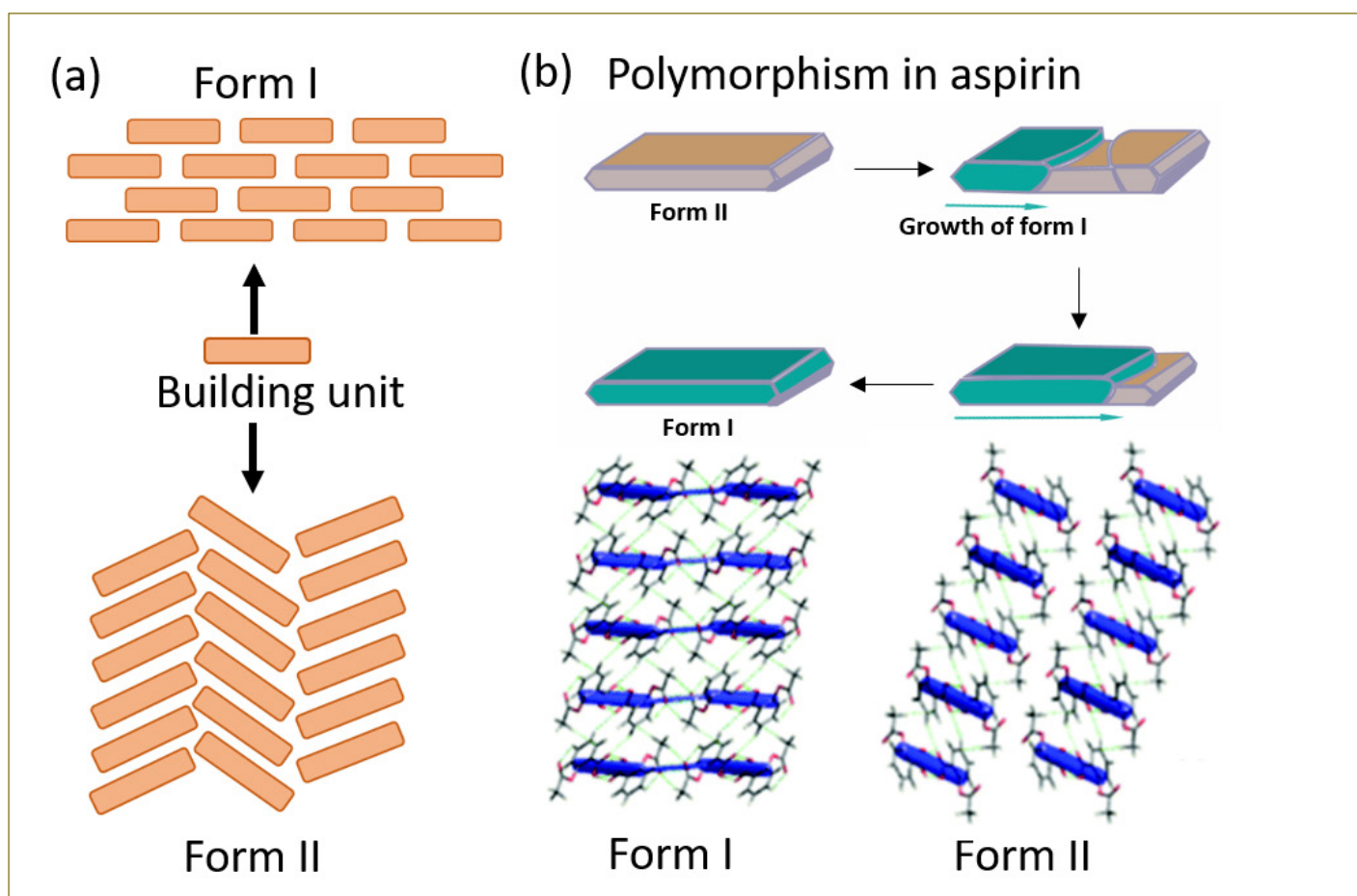


Figure 2. The phenomenon of polymorphism. (a) Schematic of polymorphism arising from a single constituent or building block. (b) Polymorphism in aspirin. Schematic of intergrowth polymorphism in aspirin (adapted from ref 63) and the two different packing arrangements in the two polymorphs of aspirin (adapted from ref 64).

scope for significant local molecular movements. But there are now many examples which defy this common perception. For instance, it has been shown over past two decades that crystals can bend like a copper wire or steel rod to produce permanently bent shapes (plastic deformation) or spring back to their original shape (elastic recovery) upon release of external stress, respectively^{[7] [9]}. Crystals have been shown to display a wide range of exotic properties, such as shape-memory effects^[9], twisting^[10], jumping^[11], curling^[12], rolling^[13], hopping^[14] and so on^[15].

Bending (also known as flexure) is a well-known mechanical property in applied mechanics, whereby objects respond to a load applied on it. Bending is commonly found in rod or sheet shaped metals, alloys, rubber, etc. There are two main types of flexural responses encountered in materials: elasticity and plasticity. Elastic materials change their shape when mechanical stress is applied and subsequently return to their original shape upon removal of the stress (Figure 2a). Plastic materials, on the other hand, show change in shape irreversibly when a stress is applied and require external

stress to be brought back to their original shape.

Molecular crystals can bend, twist, and do more!

Elastic and plastic flexing in molecular crystals might have been beyond the imagination of scientists some years ago, but have now become a rapidly growing active field of research (Figure 3). The very first examples of plastically bendable molecular crystals were reported by Reddy *et al.* from Desiraju's group, from a screening of over 60 molecular crystals. This allowed establishing a causative correlation between bending and crystal packing^[16]. There remained little doubt that mechanical properties of crystals can be directly correlated to their underlying structure, or crystal packing, direction of intermolecular interactions and anisotropy. Anisotropy means that crystals exhibit different properties in different directions. In case of some crystals like hexachlorobenzene, the needle-shaped crystals snap readily when stress is applied on the (100) face, but upon application of force on the (001) face, they are able to bend up to 360° without fracturing^[17]. The plastic deformation accompanied by preservation of a

great deal of macro-scopic integrity in these crystals provides an opportunity for use as mechano-responsive functional materials in the scale of micrometers to millimeters^[18].

The mechanical behavior of the crystals can be examined in many ways; one of the simplest and most popular ways is to apply mechanical stress using a pair of forceps and a metal needle (Figure 3a) while viewing them under a microscope. Elastic and exceptional mechanical flexibility in organic crystals was first reported in a cocrystal solvate of caffeine and 4-chloro-3-nitrobenzoic acid by Ghosh and Reddy^[19]. The needle shaped crystals underwent bending repeatedly, before finally breaking when pushed beyond their elastic limit. However, the two broken halves underwent excellent shape recovery while maintaining good structural integrity, which was comparable to that of pristine crystals.

Most of the mechanically compliant crystals reported in literature correspond mainly to the two ends of the spectrum, that is either fully elastic or fully plastic bending types^{[10] [20] [21]}. However, in recent years, intermediate type examples have also been

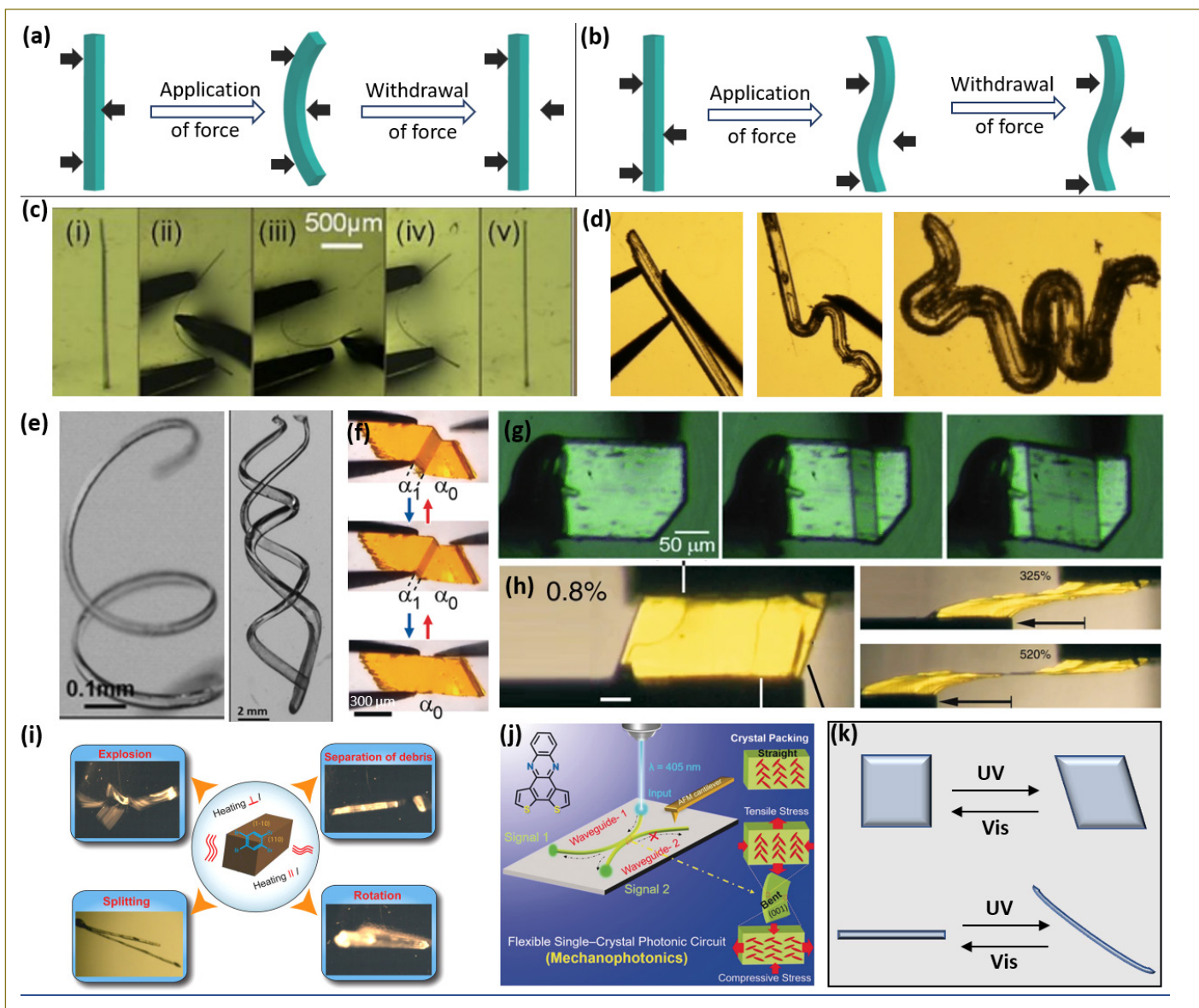


Figure 3. Mechanical properties of molecular crystals. (a) Schematic of elastic (reversible) bending. (b) Schematic of plastic (irreversible) bending. (c) Demonstration of elastic bending of naphthalenetetracarboxylic diimide derivative crystal (adapted from ref 21). (d) Demonstration of plastic bending of hexachlorobenzene crystal (adapted from ref 36). (e) Different crystal shapes achieved by applying mechanical stress on a plastic crystal of BH_3NMe_3 crystal (adapted from ref 26). (f) Ferroelasticity, (g) Superelasticity and (h) Superplasticity observed in different organic crystals (from ref 27, 28, 29). (i) Thermosalient crystals (adapted from ref 11). (j) Crystals used as circuits for mechanophotonics (adapted from ref 34). (k) Photomechanical bending of organic crystals (adapted from ref 32).

reported^[22]. One such example, dimethylammoniumperhenate single crystals, was reported from Reddy's group which exhibits elasto-plastic bending behaviour at room temperature^[23]. Up to a stress of 1%, the crystals bend and unbend elastically, but beyond that the elastic recovery is accompanied by some amount of permanent (plastic) deformation. Interestingly, at elevated temperatures (around 115 °C) the crystals exhibit exceptional malleability due to a polymorphic transformation to a so called, "plastic crystal phase" where molecules gain orientational (dynamic) disorder.^[24] "Plastic crystals" or "orientationally disordered crystals" display exceptional plasticity, comparable to plastic metals (for e.g. gold and silver) closer to their melting temperatures. The orientationally

disordered molecules or ions easily allow local molecular movements (as compared to their ordered phases) thus it is possible to mold them into a range of desired shapes, yet with high crystallinity (Figure 3e). The orientationally disordered plastic crystals thus hold a great potential for technologies, as reported by Harada and coworkers from Japan^[25].

In general, the orientationally disordered plastic crystals, consisting of globular, cylindrical or disc shaped molecules, show exceptional mechanical properties. In the solid state, due to their unique shapes, their molecules or ions are capable of undergoing rotations leading to orientational disorder, while preserving order in the long

range^[26]. Hence, these materials can show huge temperature changes pertaining to the order-to-disorder phase transition when small pressures are applied to them near room temperature. This unique property makes them very attractive for producing barocaloric effects (where materials show heating or cooling in response to variation in external pressure) for refrigeration technologies that are environmentally friendly alternatives for traditional fluorine-based technologies^[24].

Takamizawa *et al.* reported the phenomenon of ferroelasticity and superelasticity in organic crystals of 5-chloro-2-nitroaniline^[27] and 4,4'-dicarboxydiphenyl ether^[28] respectively. Superelasticity is a

mechanical elasticity phenomenon involving a phase transition whereby the newly formed daughter phase is less stable, and the structure returns to the mother phase when the stress is withdrawn^[29]. Ferroelasticity, on the other hand, may or may not involve a phase transition whereby the daughter phase remains after withdrawal of external force, but it can also return to the mother phase when the external force is applied in the opposite direction.

In the field of smart electronics, stimuli-responsiveness of materials is the key. While many kinds of materials like polymers, gels, etc. have been utilized for such purposes, the response is usually not very fast. Such shortcomings may be addressed by employing crystals which have long-range order and the response times could be relatively quick. Stimuli-responsive crystals have potential for uses in numerous applications like sensors, actuators, wearables, and biomedical devices due to their ability to respond to external stimuli like heat, light, electricity, humidity, chemical treatment and mechanical treatment. Such stimuli-based responses have already been successfully manifested to carry out structural transformations and reactions in the solid state^[30]. Naumov *et al.* reported many kinds of dynamic aspects of crystalline molecular solids^[15] [31]. A study by Irie *et al.*^[32] in 2007 reported an organic molecular crystal (diarylethene derivative), which on exposure to ultraviolet light changed from a square shape to a lozenge shape in about 25 μ s; and switched back to its original state on irradiation with visible light. Photomechanical molecular crystals that expand under illumination could additionally be used as photon-powered actuators^[33]. The groups of Chandrasekhar and Zhang independently reported the application of elastically and plastically bendable crystals as optical waveguides and lasing materials^[34] [35]. Since emission and mechanical properties of organic crystals depend directly on the molecular level packing and interactions, crystal engineering approach can be used to regulate these properties simultaneously. The technological advancement of organic crystals would push forward the rapid progress of biocompatible and all-organic actuators and broaden their applications in industry.

Insights into the bending mechanism

The most fascinating aspect of single crystals is that they allow determination of their internal structure from diffraction techniques. Hence drawing correlations between their observed property and underlying structure is possible. Based on recent observations, structural models for the different types of

bending behaviours have been put forward.^[16] [36] [19] [37]

In case of plastically bendable crystals, presence of slip planes between molecular layers with adequate intra-layer local molecular movements, provide a basis for bending of the single crystals^[38] [39]. While plastic bending of molecular crystals can be rationalized based on anisotropic packing (although with few exceptions^[40]) and the availability of slip systems, elastic properties, on the other hand largely depend on structural buffers that allow local molecular movements but provide resistance to slip (or permanent deformation)^[41]. In elastically bendable crystals, the applied external stress prompts local molecular movements leading to build up of elastic strain, which enables the crystals to spring back to their original shape upon release of the stress. Here, absence of facile slip planes and presence of mechanical and/or energetic resistance is critical to prevent plastic deformation thus extending the elastic regime of the crystals^[42]. Typically, moderately strong interactions that operate at long range can act as “*structural buffers*” as they can be ruptured or restored during elastic bending^[42] [43]. Achieving a fine balance between weak and strong interactions with adequate local flexibility of structure could be one design approach for imparting exceptional elasticity in molecular crystals. The increasing number of elastic crystals in the literature suggest that small elasticity to the tune of 1-3 % strain is achievable in many crystals.

Towards finding the cause and effect of bending

The initial qualitative mechanistic models which have been proposed to explain the mechanism of bending have been based on structural features of unperturbed crystals. Although it is possible to obtain structural information from deformed regions of crystals from diffraction experiments, due to the large diameter of X-ray beams (typically ranging from 100 - 300 μ m) and the averaging nature of the technique, overlap of diffraction peaks from different regions of anisotropically strained crystals is inevitable. As a result, the fine details of the structural changes that occur at atomic scale are blurred due to large errors in atomic coordinates. Hence, visualization of the inhomogeneous molecular distribution in the crystal lattice from the bent state is quite challenging. To understand the local atomistic scale changes, light-matter interaction based spectroscopic tools like micro-IR and micro-Raman are indispensable.

Elastic and Inelastic Scattering of light

Blue and orange sky (Figure 4a) caused by light scattering is a very clear example of elastic scattering by the gas molecules present in the atmosphere which makes light/photons scatter without any change in the energy of incident photon of electromagnetic radiation from the Sun. The other type of scattering known as inelastic scattering causes a change in energy of the incident photon and is reflected in terms of the vibrational energy of atoms, molecules, matter, etc., and is also known as Raman scattering (Figure 4b). This weak radiation, in presence of elastically scattered radiation, was discovered by Sir C.V. Raman^[44] [45], an Indian Physicist, in 1928 by use of a benzene flask, a direct vision pocket spectroscope and an ordinary light source, in the initial experiment (Figure 4c). After the discovery of Raman effect, a spectroscopy based on this effect, named as Raman spectroscopy has become widely accessible. With the advancement in lasers and modern charged couple devices (CCDs) the modern Raman spectrometer, has become a powerful tool, particularly as it can be easily integrated with other techniques, such as indenters for in-situ studies. With time, advancements in the instrumental capabilities have added additional features to the traditional Raman spectroscopy which include, Raman microscopy, surface enhanced Raman spectroscopy, etc. The Raman spectroscopic technique is non-destructive and provides finger-print of any form of matter. Raman spectroscopy not only probes strong and weak interactions via perturbed vibrational properties but also allows understanding physical processes like quantum confinement^[46] [47], electron-phonon interaction^[48] [49]^[50] and physical and chemical perturbations under pressure^[51], temperature^[52] and doping^[53] in materials.

Raman spectro-microscopy^[54] integrates microscopic spatial assessments of sample by integrating the generic Raman spectroscope with confocal optical microscope, which can acquire spatial information amalgamated with chemical specificity of the materials to present a subtle-scale analysis of wide range of materials. Amongst all the classes of materials present in nature, the analysis of crystalline materials has always been an intriguing arena amongst the scientific community, because of their applications in wide range of devices like photosynaptic^[55] device, liquid crystal displays^[56], and opto-electronics. Crystal engineering to tweak mechanical, chemical, physical and optical properties of organic, inorganic or metal-organic crystals has been widely used in past few decades^[57]. Superior characterization tools, such as Raman

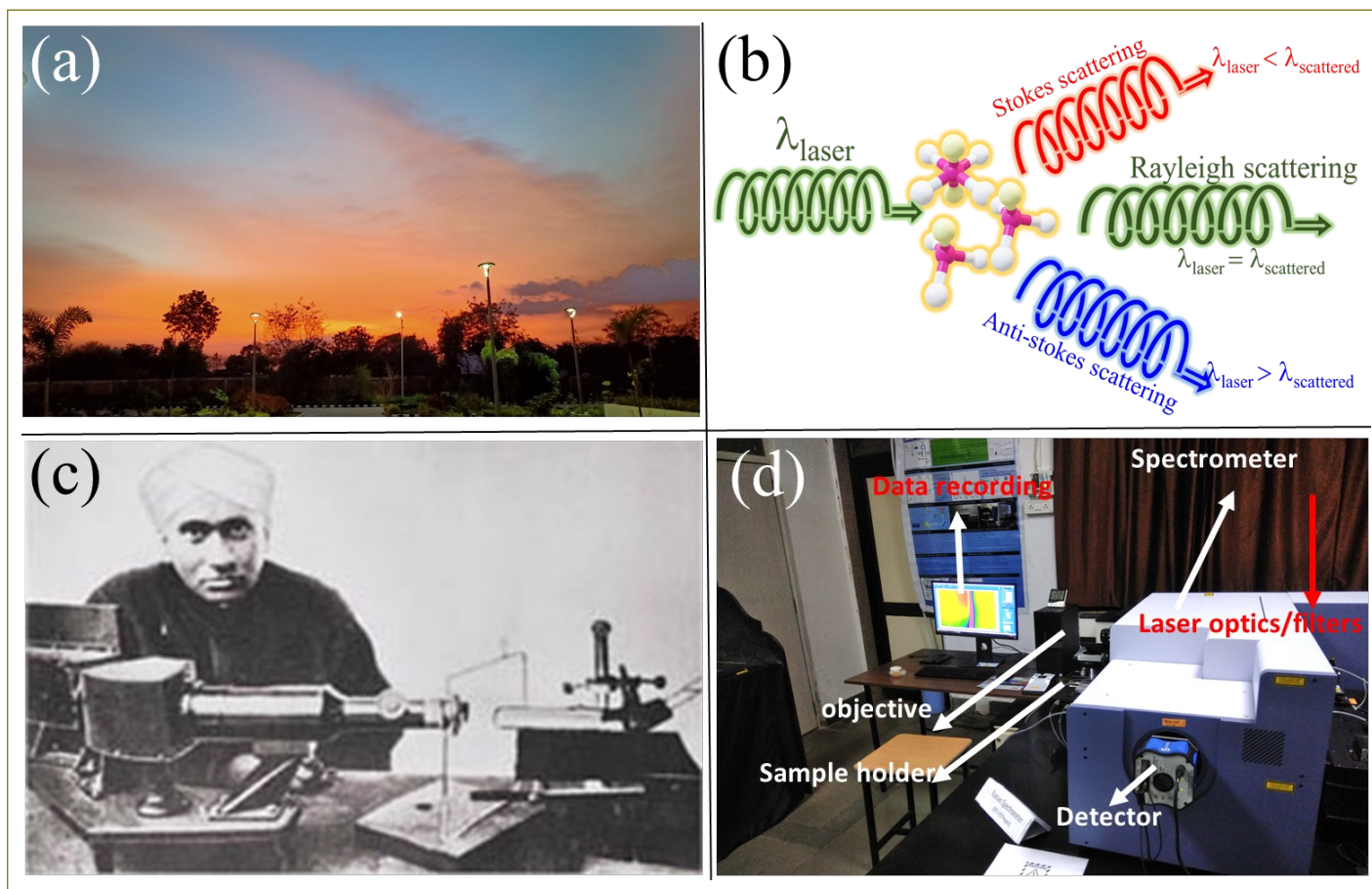


Figure 4. (a) Blue and orange sky due to Rayleigh scattering. (b) Schematic representation of elastic (Rayleigh) and inelastic (Raman) scattering mechanism. (c) Sir C.V. Raman with the first Raman spectrometer (image courtesy: The Indian Association for the Cultivation of Science). (d) Modern Raman spectrometer equipped with advanced lasers and CCD detectors.

spectro-microscopy, are thus a requisite for elevated and deeper analysis of molecular perturbations, to shift the entire paradigm of engineered crystals. The crystals of inorganic materials, for example, SrTiO_3 , BaTiO_3 etc., have been explored for their flexoelectric^[59] and piezoelectric^[29] properties enabled through strain gradient, and by changing the length scale of the material to nano-regime, respectively.

Probing flexible crystals by Raman spectro-microscopy

Recent studies on organic molecular crystals (OMCs), amongst various classes of crystals, have led to many serendipitous discoveries of dynamic mechanical behavior^[59]. The flexible^[60], twistable, and self-healing^[61] crystals in presence of different stimuli show exceptional mechanical responses and it is extremely challenging to study the associated local structural changes, post-deformation. Although the Raman spectro-microscopy is remarkable for analysis of local level perturbations in crystals,^[62] it has not yet been utilized to its full potential for studying dynamic crystals. A few reports which provide valuable insights

for the analysis of mechanical properties via Raman microscopy are presented below.

Recently, Das *et al.*^[23] studied the structural changes at different stress conditions in an elasto-plastic, mechanically bendable heavy transition metal based molecular single crystal of an oxyacid salt. Raman spectro-microscopy, revealed blue shifts in Raman spectra of the crystal (Figure 5a) which provided valuable insights into the level of perturbations caused in bonds by the reorientations and slippage of molecules across the slip planes as the stress gradually progresses from elastic to plastic deformation state. Analysis of Re-O symmetric stretch vibration of pristine crystal (968 cm^{-1}) showed that this peak is minimally blue-shifted in elastic state ($\sim 968.9\text{ cm}^{-1}$) while it is significantly blue-shifted in plastic state (969.6 cm^{-1}). Similarly, the N-H asymmetric vibration at 908.6 cm^{-1} also shows similar trend when moved from elastic (909.5 cm^{-1}) to plastic state (910.6 cm^{-1}). Interestingly, the rocking vibration of the ammonium ion at 335.6 cm^{-1} , about the central N atom that involves in forming tetramer unit (shown in Figure 5b), is unperturbed for the elastic state, but perturbed in plastic state. This

indicates that the N-H...O contacts, that form the tetrameric units, are intact within the elastic limit (which involves minimal local movements/rotations) but are strained in plastic state (local movements/rotations plus slippage of molecules). This example revealed the increase in molecular changes/displacements and structural perturbations as strain progresses from elastic to plastic state, demonstrating the unique advantage of Raman spectro-microscopy. The mechanistic insights into the bending mechanism, established via several experiments, including Raman spectro-microscopy, thus conclude that during the elastic deformation, the structural changes are gradual from the outer arc (expansion $\theta_1 > \theta$) to the inner arc (compression $\theta_2 < \theta$), as shown in Figure 5b.

Another analysis by Panda *et al.*^[36] reported the hexachlorobenzene (HCB) crystals capable of undergoing exceptional plastic deformation while retaining the macroscopic integrity of the monoliths (Figure 5c-e). A micro-Raman spectroscopy was performed to understand the mechanism of bending at molecular level (Figure 5f, g). The Cl...Cl halogen interactions in the deformed

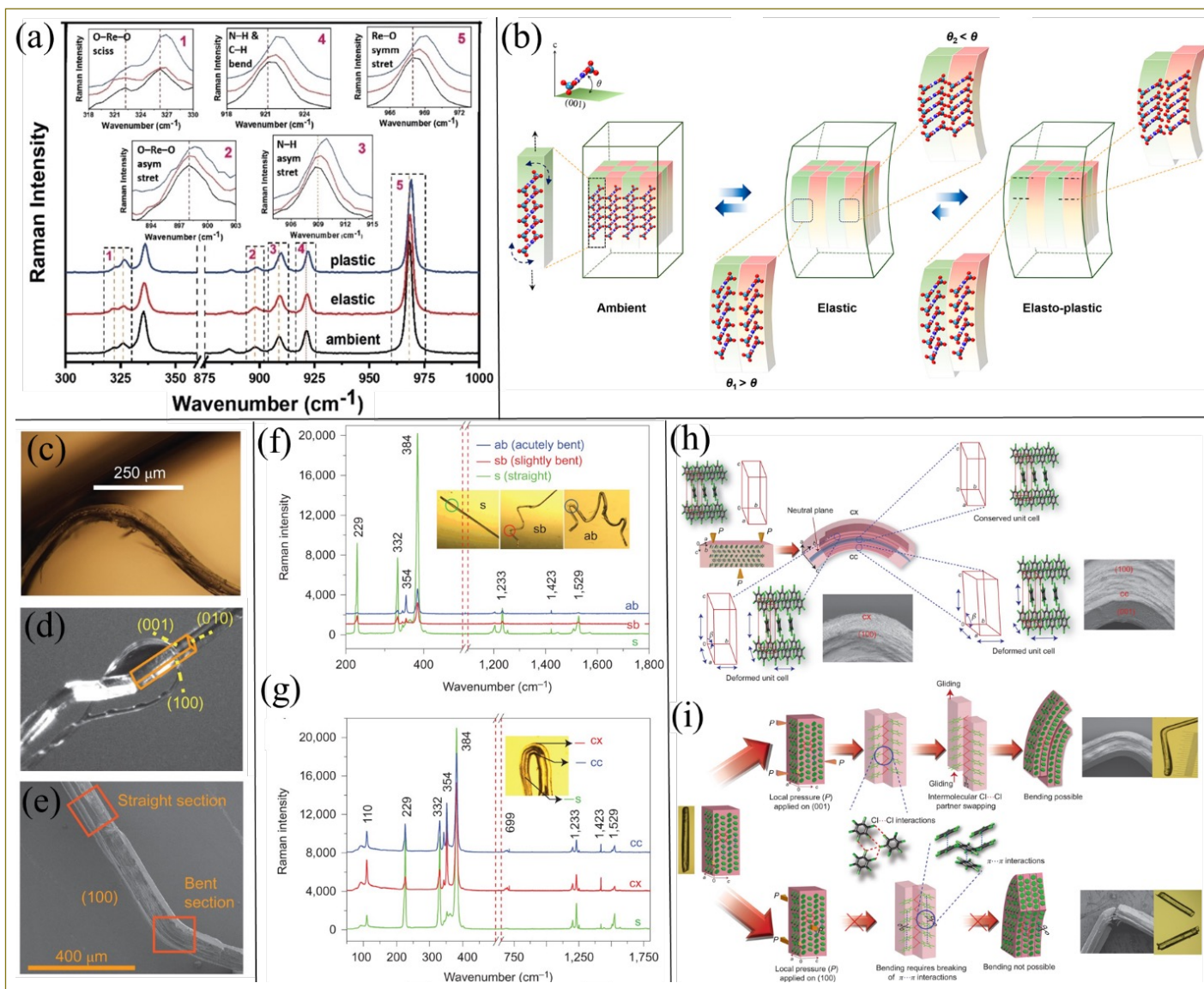


Figure 5. (a) Micro-Raman spectra of pristine (ambient), elastic and plastic states of crystal (adapted from ref 23). (b) Schematic showing proposed elasto-plastic bending mechanism, involving both molecular rotations and slippage (adapted from ref 23). (c,d) Optical micrographs of hexachlorobenzene (HCB) crystal (adapted from ref 36). (e) SEM image showing bent and straight regions in HCB crystal. (f) Raman spectra from acutely bent, slightly bent and straight crystals. (g) Raman spectra from convex, concave and unbent region of acutely bent crystal. (h) Observed changes in unit cell parameters in bent crystals. (i) Mechanism showing anisotropic mechanical deformation in HCB crystals. (Figure 5(c-i), adapted from ref 36).

HCB are affected by the sliding of crystal layers and splaying of molecules, thereby affecting the strength of intermolecular interactions (Figure 5i). The intensities of in-plane $\delta(\text{C}-\text{Cl})$ vibration at 332 cm^{-1} and out of plane vibration of $\text{C}-\text{Cl}$ at 229 cm^{-1} consistently decrease with crystal bending (Figure 5g). It was also observed that, these modes were much more sensitive to tensile stress (cx side) than to compression (cc side), in consonance with weakened $\text{Cl}\cdots\text{Cl}$ on the cx side, making the crystal's length change swiftly in the outward direction than inwards due to counterbalance of inwards compression by repulsive interactions. Based on the above observations combined with the micro-IR spectroscopy, a mechanism was proposed which explains the plastic bending of HCB crystals. Panda *et al.* concluded,

that the “application of three-point local pressure on 001 face results in formation of ridged layers, which glide on top of each other simultaneously being stretched on the cx side and slightly compressed on the cc side”^[36] (Figure 5h). The weakened and even broken $\text{Cl}\cdots\text{Cl}$ interactions are reformed after the gliding owing to the adaptability of these soft crystals, preserving the crystal integrity. These weak interactions from the (001) plane thus facilitate gliding via providing smoother interface between layers. Whereas, the application of stress on the (100) face would lead to breaking of $\pi\cdots\pi$ interactions, thus resulting in fracture (Figure 5i). Overall, Raman spectroscopy provides insights into the molecular level perturbations in the layers of crystals experiencing tensile and compressive strains.

Raman microscopy to probe intergrowth polymorphism in pharmaceutical drugs

In pharmaceutical industry, the separation and purity of drug polymorphs is a major challenge^[63]. Raman microscopy, being a non-destructive and sensitive technique, is effective to probe subtle inter- and intra-molecular structural differences in polymorphic crystals or solid forms. Any solid form or polymorphic transformations can be effectively identified as this technique acts as fingerprint with an ability to establish even small changes corresponding to noncovalent interactions that occur in crystals when subjected to various stresses, like pressure, heat or chemical^[63].

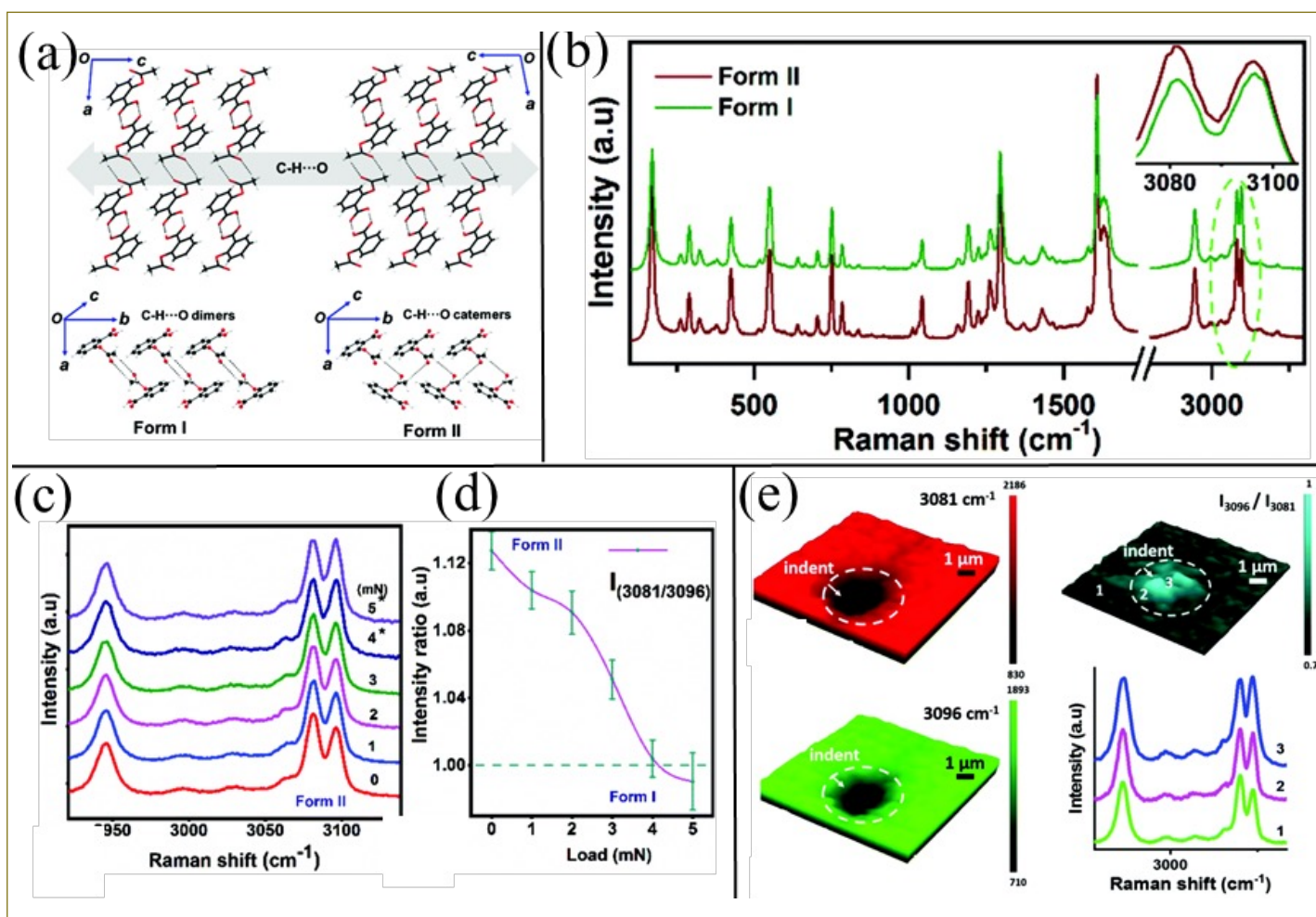


Figure 6. (a) Crystal structure of aspirin polymorphs, (b) Raman spectra from two forms of aspirin crystal. (c) Raman spectra as a function of normal load, depicting C–H stretching modes. (d) Intensity ratio of 3081 cm^{-1} and 3096 cm^{-1} bands. (e) Raman mapping from a 5 mN nanoindented aspirin form II. Figure is adapted from reference 64.

A study by Manimunda *et al.*^[64] probed indentation induced phase transformation in polymorphic single crystals of aspirin. Figure 6a shows the structure of the two forms, I and II, which differ in terms of the interlayer hydrogen bond forming dimers (forming form I) or catemers (forming form II). The transformation to form I from form II is driven by shear stress. The full range Raman spectra of form I and II, (Figure 6b) look similar for both the forms, except the change in relative intensities of the peaks in the regions 3000–3150 cm^{-1} . The stress dependent form transformation was studied using the in-situ Raman microscopy during indentation at different indentation loads, as shown in Figure 6c. Above 5 mN indentation load, the change in relative intensity of 3081 and 3096 cm^{-1} occurs (Figure 6d), indicating the perturbed aromatic C–H stretching mode.

Figure 6e, shows the load dependent change in spatial Raman intensity map of 3081 cm^{-1} (stretching modes of aromatic C–H and C–OH of COOH) and 3096 cm^{-1} peak (aromatic C–H stretching modes)

confirming the phase transformation in form II due to the indentation load of 5 mN. The Raman map at 5 mN load shows a higher intensity ratio (I_{3096}/I_{3081}), within the indentation zone and thus confirming the polymorphic transformation from form II to form I. The above study paves the way for analysis of various medicinal drugs to understand molecular and mechanical properties through enabling complete mechanical diagnosis of the material at the subtle scale along with establishing its structure property relationship.

Summary and future perspectives

The variety of dynamic and exotic molecular crystals that can respond to various external stresses or stimuli are attractive and have great technological prospects. Single crystals, due to their near-defect-free structures with excellent internal order, could be valuable for achieving highest theoretical performances of, for instance, electron transport, photon transport, etc., but their fragile and rigid nature has remained a great challenge for their utility in devices. The

advent of dynamic and adaptive crystals brings new opportunities for future. Raman spectro-microscopy can be expanded using its nature of detecting subtle changes in interactions, by combining it with scanning probe microscopic techniques like atomic force microscopy and scanning tunneling microscopy to understand the nature of mechanical properties. Nonetheless, the structure-property relationship analysis of organic crystals is an intriguing arena of research wherein, in-situ nanoindentation based Raman spectro-microscopy can yield a wealth of information and is yet to be explored in greater depth. The field is completely open for scientists and researchers for utilizing basic and advanced Raman spectro-microscopic techniques to reveal various latent information about crystals. To improve the understanding, Raman can be combined with various other complementary techniques to explore further. This approach will help in understanding the crystals better to make them more application oriented.

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