Large Local Internal Stress in an Elastically Bent Molecular Crystal Revealed by Raman Shifts

Atiqur Rahman, Srijan Mondal, Mantu Modak, Ashi Singh, Hanuman Singh, Navdeep S. Thayat, Jack K. Clegg, Himanshu K. Poswal, V. Haridas, Sajesh P. Thomas*

Dedicated to Prof. Arunachalam Ramanan on the occasion of his retirement.

ABSTRACT: The structural dynamics involved in the mechanical flexibility of molecular crystals are not well understood yet. Here, we report an elastically bending lipidated molecular crystal that shows systematic shifts in characteristic vibrational frequencies across the bent crystal region - revealing the nature of structural changes during bending and the local internal stress distribution. The elastic flexibility is rendered by intermolecular N−H···O hydrogen-bonded chains along with strong yet flexible alkyl-chain hydrophobic interactions in this crystal structure. The blue shifts in the bond stretching modes (such as C=O and C−H modes) in the inner arc region and red shifts in the outer arc region of the bent crystals observed via micro-Raman mapping are counterintuitive to the bending models based on intermolecular hydrogen bonds. Correlating these shifts with the trends observed from high-pressure Raman studies on the crystal reveals the local stress difference between the inner arc and outer arc regions of the bent crystal to be ~2 GPa, more than an order of magnitude higher than the previously proposed value in elastically bending crystals. High local internal stress can have direct ramifications on the properties of molecular piezoelectric energy harvesters, actuators, semiconductors, and flexible optoelectronic materials.

Mechanical flexibility in molecular crystals[1,2] has potential applications in functional molecular materials,[3,4] sensors,[5] mechanical actuators,[6] and wearable devices.[7] Examples of flexible crystals formed by organic molecules,[8–13] metal-organic complexes,[14] coordination polymers[15–18], etc. are increasingly being reported lately. Among the diverse classes of molecular crystals that are reported for their mechanical flexibility, examples of peptides and peptide analogues are relatively rare. Elastically flexible peptide crystals are particularly significant (such as the ones reported by Gazit et al),[19] owing to their biocompatibility and potential applications in biomedical and bioengineering devices.[20] Herein, we report elastic bending in single crystals of a lipidated molecule containing an amide group (compound **1**; Figure 1a) with a multi-pronged study of the structural changes in the bent crystal region. The structural factors that render elastic flexibility to crystals and the atomistic picture of the intermolecular dynamics in the bent crystal region are a topic of fundamental interest within the emerging field of 'crystal adaptronics'.[21] Hence, several spatially resolved studies on mechanically bent molecular crystals have been attempted. Micro-focus synchrotron X-ray diffraction studies on the elastically bent crystals have shown stretching in the outer arc and compression of the inner arc regions,[14,15,22] along with molecular re-orientations. These structural changes can lead to variations in the physical properties of the crystals at the bent region- such as the variation in melting point [23] and the change in magnetic ordering temperature.[24] Spatially resolved photoluminescence (PL) studies on bent crystals have revealed shifts in emission wave lengths and changes in intensities in the bent region.[12,25,26] Micro-Raman spectroscopy is another important tool employed to probe the local structural changes across the bent region of
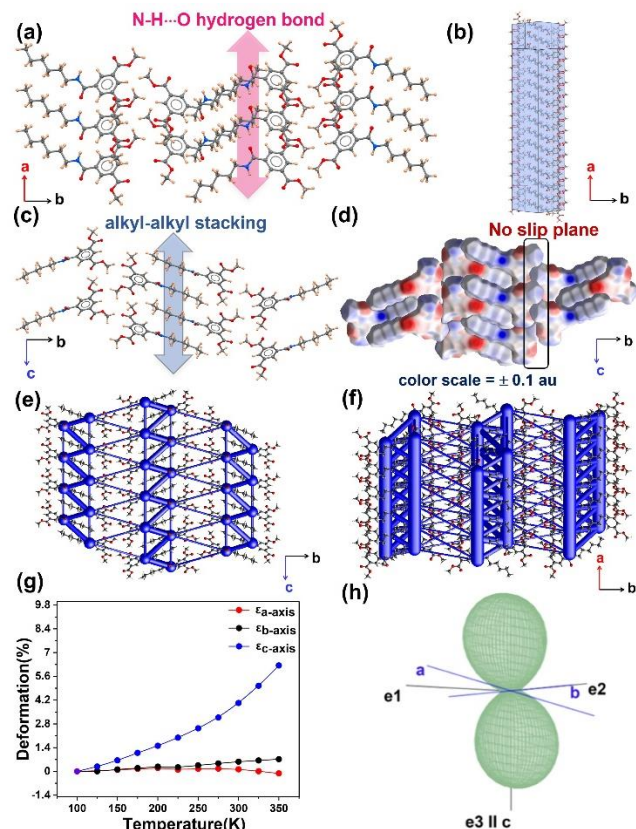
flexible crystals.[22,27–29] Shifts and broadening in the Raman peaks in the elastically bent crystal
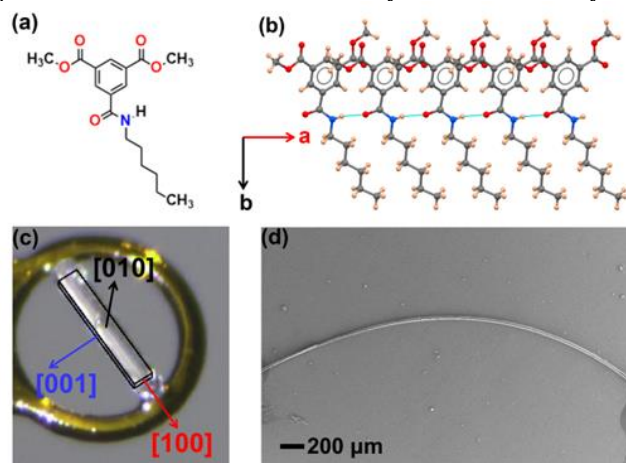
Figure 1. (a) Molecular structure of **1**, (b) N–H···O hydrogen-bonded chains along the bending direction, (c) face indexed image of **1** highlighting the crystallographic directions, and (d) SEM image of a bent crystal.

regions have been reported.[27,28,30] On the other hand, some recent studies reported no significant frequency shifts in the vibrational modes in an elastoplastic molecular crystal and a plastically flexible coordination polymer.[22,31] These distinct trends in the spectral features imply a significant gap in our understanding of the vibrational frequency shifts associated with the local structural changes in the bent crystal regions. Here we report systematic trends in characteristic vibrational frequency shifts in the elastically bent region of the crystal **1** (Figure 1). In combination with high-pressure Raman studies,

these frequency shifts have been utilized here to gain insights into the distribution of local stress/pressure experienced by molecules in the bent region. To our knowledge, there is no report of such systematic frequency shifts of characteristic peaks or the estimates of local stress in the bent region for

Figure 2. (a) Strong N–H···O hydrogen bonding interaction along [100] direction, (b) BFDH morphology of crystal **1**, (c) alkyl-alkyl stacking along [001] direction, and (d) Electrostatic potential map showing the absence of slip plane. (e,f) Energy frameworks viewed down [100] and [001] directions respectively. (g) Percentage deformation of the unit cell parameters of **1** with temperature, and (h) thermal expansion plot showing highest thermal expansion along [001] direction.
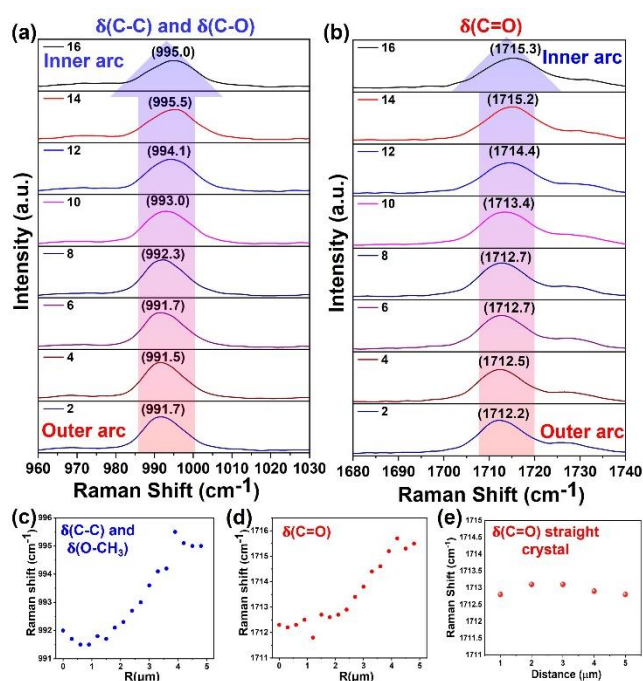
elastically flexible molecular crystals. Such information on the local stress distribution is crucial in understanding the photophysical and electronic properties of flexible functional molecular materials.

Compound **1** was synthesized by a protocol reported by us earlier.[32] It crystallizes in space group $P2_1/n$, with cell parameters $a = 5.0470(2)$ Å, $b = 41.1376(18)$ Å, $c = 8.0726(3)$ Å, $\beta = 102.024(2)°$, Z = 4, and Z' = 1. The crystals exhibit an acicular habit with the needle growing along a-axis ([100] direction). Analysis of intermolecular interactions shows that the N–H···O hydrogen bonding molecular pair forms the strongest motif (-73.5 kJ mol⁻¹) that leads to catemer chains - favoring crystal growth along [100] direction (Figure 1b). Notably, this supramolecular motif is stabilized by a dispersion contribution of -65.1 kJ mol⁻¹, compared to the electrostatic term of -39.0 kJ mol⁻¹ (and an exchange-repulsion of 30.7 kJ mol⁻¹) - indicating the dominant role of hydrophobic interactions involving the alkyl tails. In directions perpendicular to the needle direction, the interactions are weaker leading to an anisotropic interaction topology as manifested in their energy frameworks (Figures 2e-2f). The major interactions along [010] direction are characterized by the molecular pairs (Figures S5, dimers 8,9) showing C–H···O=C weak hydrogen bonds (-11.5 kJ mol⁻¹ and -9.5 kJ mol⁻¹) in which dispersion term contributes more (-6.4 kJ mol⁻¹ and -7.0 kJ mol⁻¹). The packing along [001] direction is mainly stabilized by a number of C–H···H–C interacting molecular pairs (with interaction energies -44.0 kJ mol⁻¹, -34.4 kJ mol⁻¹ and -33.2 kJ mol⁻¹ – for dimers 2,3,4 given in Figure S5) with dispersion forming the major contributions. The electrostatic potentials mapped on Hirshfeld surfaces of the molecules and their packing show the absence of slip plane along the bending direction (Figure 2d). This feature, along with the strong interaction anisotropy could be among the major factors that support the reversible bending of the crystal along [100] direction. To probe how the interaction anisotropy manifests in the thermal expansion of the crystal, we collected variable temperature XRD data from 100 K to 350 K at intervals of 25 K. Owing to the strong interaction anisotropy along the a-axis, no considerable expansion occurs along that direction. Whereas the hydrophobic interactions formed by the alkyl chains along c-axis allow the highest extent of thermal expansion along [001] direction (Figures 2g-2h). The flexibility of the hexyl chain along the [001] direction between two antiparallel tails (Figure 2c) is evident in the atomic displacement parameters from the variable temperature XRD models (Figure S7). The higher contribution of the dispersion components associated with the inter-chain hydrophobic interactions (See dimer 2 and 3 in Figure S5) may have a role in preventing the long-range sliding of the supramolecular chains formed along [100] direction. A detailed analysis of the electron density features of the weak C–H···O and hydrophobic interactions in **1** has been given in Figure S3 and Table S2.

To probe the spectroscopic features associated with the structural perturbations and the local stress in the bent crystal region, we performed micro-Raman spectroscopic line mapping across an elastically bent crystal of **1**. It is generally understood from heuristic models that elastically bending crystals undergo compression in the inner arc region and elongation in the outer arc region of the bent crystals.[10,33] Such a model implies the shortening of intermolecular interactions in the inner arc region and elongation in the outer arc region – which would in principle lead to frequency shifts in bond vibrational modes. When intermolecular interactions such as hydrogen bonds become stronger and shorter, the corresponding intramolecular bonds become weaker – as per the n→σ* electron transfer model of hydrogen bonds (as illustrated in Figure 4a). This would imply red shifts in the inner arc region and blue shifts in the outer arc region for the peaks corresponding to the intramolecular bonds. However, a few spatially resolved micro-Raman studies on flexible crystals show no such conclusive trend in the frequency shifts.[22,27,29,31] Interestingly, here we observed significant blue shifts of around 2 - 4 cm⁻¹ from the inner arc to the outer arc of the bent crystal of **1** (Figure 3), contrary to the above-mentioned n→σ* model. To our knowledge, this is the first observation of such clear and systematic shifts in characteristic bond stretching frequencies (such as C=O vibrational modes) on a bent crystal. Notable shifts were observed for peaks at 225 cm⁻¹, 305 cm⁻¹, 801 cm⁻¹, 992 cm⁻¹, 1126 cm⁻¹, 1324 cm⁻¹ and 1713 cm⁻¹. Whereas peaks at 1349 cm⁻¹, 1444 cm⁻¹ and 1595 cm⁻¹ showed small shifts (see Figure S11). Across a bent crystal of thickness ~ 7μm, the C=O bond stretching peak at 1712.9 cm⁻¹ showed a significant shift

of 3.1 cm^{-1} from the outer arc to the inner arc (Figure 3d). Similarly, the peak at 992.4 cm^{-1} (corresponding to C−C and O−CH$_3$ bonds bending modes) exhibited a shift of 3.3 cm^{-1} from outer arc to inner arc (Figure 3c). Shift in peaks corresponds to C−H bending modes (1323 cm^{-1}) also showed a shift of ~ 2.7 cm^{-1} (Table S6). These peaks were assigned based on the vibrational frequencies simulated at B3LYP/6-311G(d,p) level, and in comparison to the reported Raman studies on similar lipidated molecular crystals[34–36] (see Supporting Information Table S8). Given that the spectral resolution of measurements was 1 cm^{-1}, we further examined how significant are the observed shifts in the bent crystal region. To test this, we performed micro-Raman line mapping across a straight, unstrained crystal of **1**. The standard deviation in the C=O stretching frequencies estimated from a line mapping across the thickness of 5 μm from a straight crystal was found to be 0.15 cm^{-1} (Table S7). This further validates the significance of the shifts we observed across the bent crystal region due to the local stress. To put this into perspective, Raman shifts in silicon


Figure 3. (a,b) Raman spectra showing shifts from outer arc to inner arc region in C−C/C−O bending and C=O stretching modes. (c-d) Raman shifts with distance from outer arc to inner arc region of the bent crystal, and (e) that for a straight crystal.

crystal as small as 0.05 cm^{-1} have been shown to be a significant indicator of the local stress by Batchelder et al.[37]

Intriguingly, the observed trend of shifts in micro-Raman spectra are contrary to those reported by Mishra et. al on the elastically bending crystals of halogenated aniline derivatives[28] (red shifts and broadening in the inner arc and blue shift in the outer arc). They proposed a model based on inhomogeneous spatial separation of molecules with the outer and inner arcs of the bent crystal showing states of tension and compressive stress, with a crude estimate of local stress by employing finite element analysis.[28]

To rationalize the observed trend of blue shifts in the inner arc of **1** in terms of intermolecular changes during crystal bending, we surveyed reports of high-pressure Raman spectroscopic experiments on molecular crystals (including

those with C=O groups) which revealed a systematic trend of blue shifts at high pressures (Table S9). It may be understood that at high pressures, due to the compression of the lattice and
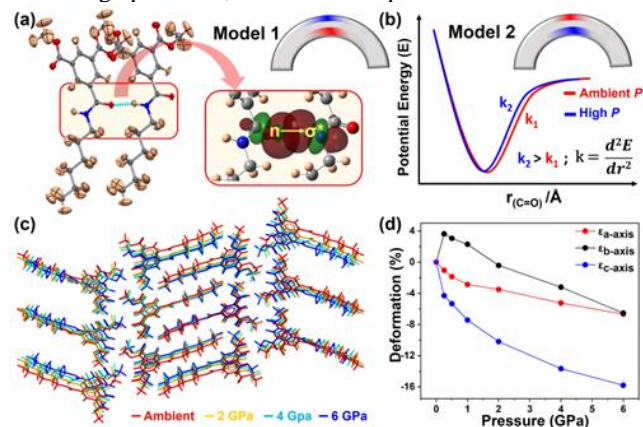
Figure 4. (a) Schematic representation of n→σ* model of intermolecular hydrogen bond (Model 1), and (b) the steepening of potential energy curve under applied stress and an increase in the force constant of intramolecular bonds (Model 2) – in relation to the Raman shifts in the bent crystal regions. (c) An overlay of the simulated crystal structures of **1** at high pressure, showing the compression along the alkyl···alkyl stacking. (d) Percentage deformation in unit cell parameters with pressure (simulated).

the associated change in electrostatic environment around the molecules (causing stress on bonds), a steepening of This leads to blue shifts in their interatomic potential energy wells can lead to increase in the effective force constant of bonds. characteristic peaks (as in Model 2 in Figure 4b). Hence, it is evident that the blue shifts in the inner arc region of bent crystal **1** corresponds to a high local stress relative to the unbent crystal. To visualize the structural changes upon an applied stress, we further employed high-pressure simulations using quantum periodic calculations at hydrostatic pressure points from ambient to 6 GPa (Figures 4c,4d). Compressibility is lowest along [100] and highest along [001], which correlate with the crystal packing features (Figures 2c, 4c-4d). To correlate the structural changes with the local stress experienced in the bent region of the crystal, we set out to perform a high-pressure Raman experiment on **1**. To our knowledge, local stress (local pressure upon bending) in flexible molecular crystals, has not been quantified yet. Towards this goal, here we analysed Raman spectra obtained for a crystal of **1,** from ambient pressure to ~10 GPa using a diamond anvil cell. In this study, we mainly focused on the two characteristic peaks at 992.4 cm^{-1} and 1712.9 cm^{-1}. Figure 5d shows the linear trend in blue shifts on these peaks with respect to pressure with a slope of 1.19 cm^{-1} GPa^{-1} for C=O peaks and 1.77 cm^{-1} GPa^{-1} for C−C peaks (Figure 5c-5d). By combining these linear trends with the micro-Raman mapping, a blue shift of ~3.1 cm^{-1} in C=O stretching mode from the inner to outer arc region of the bent crystal translates to a local stress gradient with a pressure difference of ~2.6 GPa between the inner and outer arc regions. Similarly, the bending modes at 992.4 cm^{-1} and 800.7 cm^{-1}, show shifts of ~3.3 cm^{-1} and 4.8 cm^{-1} respectively, indicating a pressure difference of ~1.9 - 2.2 GPa and from the inner to outer arc region of the bent crystal (Figure S15). Although the hydrostatic pressure exerted on the crystal in a diamond anvil cell is distinct in nature from the more directional local stress in an elastically bent crystal, it can reasonably mimic the spectral shifts due to bending. This approximation is supported by the following observation:

although the stress upon bending is directional in nature, its local distribution is largely homogeneous if we consider a
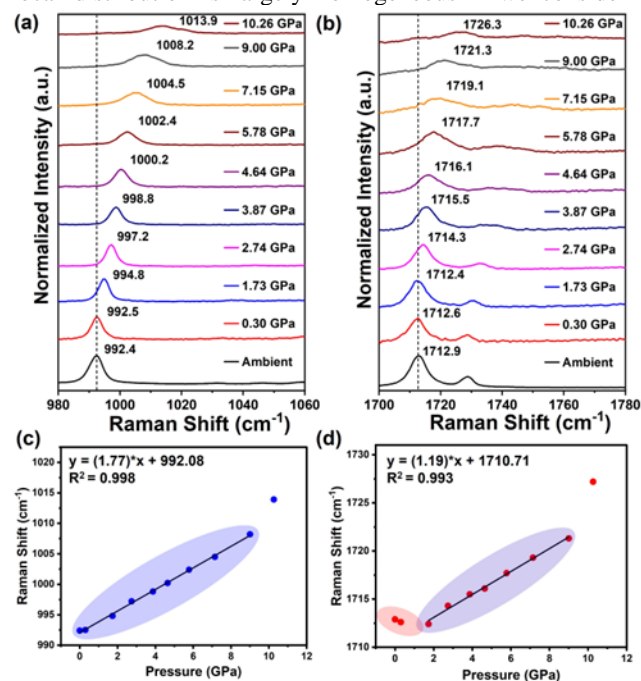
Figure 5. (a,b) High-pressure Raman spectra showing shifts in peaks of C–C bending and C=O stretching modes respectively from ambient pressure to 10.26 GPa. (c,d) Raman shifts with pressure showing a linear trend (which is used in this study to estimate the local stress in the bent crystal of **1**).

small volume element within a bent crystal – as shown using finite element analysis by Mishra et al in their elastically bent crystal. [28] However, the values of local pressure gradient estimated by our study are significantly higher than the semi-quantitative estimate by Mishra et al (0.1 GPa stress at the outer arc region). Intriguingly, the C=O peaks at the low-pressure points (such as 0.3 GPa), show an irregular trend, and even imply a slight red shift (Figure 5d).We conjecture that at lower pressure points the intermolecular dynamics and frequency shifts tend to obey Model 1 ($n \rightarrow \sigma^*$ model; Figure 4a) whereas, at higher pressure further lattice compression leads to a trend as per Model 2 and blue shifts (Figure 4b).

In summary, the approach of combining micro-Raman mapping in our elastically flexible crystals with high-pressure Raman spectroscopy brings out a reasonable estimate of the local internal stress experienced by molecules in the bent crystal region. Our study clearly indicates an elevated local pressure experienced by the molecules in the inner arc region of an elastically bent crystal and a reduced local pressure at the outer arc region- with their difference being around 2 GPa. Such an insight could be useful in the design of peptide based biocompatible sensors and actuators. Understanding the intermolecular dynamics and the local stress in the flexible crystals can have direct implications in the context of functional molecular materials in relation to their photoluminescence properties, electronic band gaps, as well as piezoelectric properties.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is provided as a separate document.

Accession codes

CCDC 2306814 and 2323708 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033

AUTHOR INFORMATION

Corresponding Author

* **Sajesh P Thomas** – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India; https://orcid.org/0000-0003-3552-8625 ; E-mail: sajesh@iitd.ac.in

Auhors

Atiqur Rahman – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India; School of Chemistry and Molecular Biosciences, The University of Queensland, Qld, Australia, 4072

Srijan Mondal – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India

Mantu Modak – High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Center, Mumbai 400085, India

Ashi Singh – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India

Hanuman Singh – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India

Navdeep S Thayat – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India

Jack K Clegg – School of Chemistry and Molecular Biosciences, The University of Queensland, Qld, Australia, 4072

Himanshu K. Poswal – High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Center, Mumbai 400085, India; Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

V Haridas – Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016, India; Department of Chemistry, Indian Institute of Technology Palakkad, Kerala, 678623, India

Notes
The authors declare no competing financial interest.

REFERENCES

(1) Thompson, A. J.; Chamorro Orué, A. I.; Nair, A. J.; Price, J. R.; McMurtrie, J.; Clegg, J. K. Elastically Flexible Molecular Crystals. *Chem. Soc. Rev.* **2021**, *50* (21), 11725–11740.

(2) Naumov, P.; Chizhik, S.; Panda, M. K.; Nath, N. K.; Boldyreva, E. Mechanically Responsive Molecular Crystals. *Chem. Rev.* **2015**, *115* (22), 12440–12490.

(3) Annadhasan, M.; Agrawal, A. R.; Bhunia, S.; Pradeep, V. V.; Zade, S. S.; Reddy, C. M.; Chandrasekar, R. Mechanophotonics: Flexible Single-Crystal Organic Waveguides and Circuits. *Angew. Chemie Int. Ed.* **2020**, *59* (33), 13852–13858.

(4) Chinnasamy, R.; Ravi, J.; Vinay Pradeep, V.; Manoharan, D.; Emmerling, F.; Bhattacharya, B.; Ghosh, S.; Chandrasekar, R. Adaptable Optical Microwaveguides From Mechanically Flexible Crystalline Materials. *Chem. - A Eur. J.* **2022**, *28* (40).

(5) Lan, L.; Yang, X.; Tang, B.; Yu, X.; Liu, X.; Li, L.; Naumov, P.; Zhang, H. Hybrid Elastic Organic Crystals That Respond to Aerial Humidity. *Angew. Chemie Int. Ed.* **2022**, *61* (14), e202200196.

(6) Sahoo, S. C.; Sinha, S. B.; Kiran, M. S. R. N.; Ramamurty, U.; Dericioglu, A. F.; Reddy, C. M.; Naumov, P. Kinematic and Mechanical Profile of the Self-Actuation of Thermosalient Crystal Twins of 1,2,4,5-Tetrabromobenzene: A Molecular Crystalline Analogue of a Bimetallic Strip. *J. Am. Chem. Soc.* **2013**, *135* (37), 13843–13850.

(7) Yang, X.; Lan, L.; Li, L.; Liu, X.; Naumov, P.; Zhang, H. Remote and Precise Control over Morphology and Motion of Organic Crystals by Using Magnetic Field. *Nat. Commun.* **2022**, *13* (1), 2322.

(8) Reddy, C. M.; Gundakaram, R. C.; Basavoju, S.; Kirchner, M. T.; Padmanabhan, K. A.; Desiraju, G. R. Structural Basis for Bending of Organic Crystals. *Chem. Commun.* **2005**, *1* (31), 3945–3947.

(9) Reddy, C. M.; Kirchner, M. T.; Gundakaram, R. C.; Padmanabhan, K. A.; Desiraju, G. R. Isostructurality, Polymorphism and Mechanical Properties of Some Hexahalogenated Benzenes: The Nature of Halogen···halogen Interactions. *Chem. - A Eur. J.* **2006**, *12* (8), 2222–2234.

(10) Ghosh, S.; Mishra, M. K.; Kadambi, S. B.; Ramamurty, U.; Desiraju, G. R. Designing Elastic Organic Crystals: Highly Flexible Polyhalogenated N-Benzylideneanilines. *Angew. Chemie Int. Ed.* **2015**, *54* (9), 2674–2678.

(11) Thomas, S. P.; Shi, M. W.; Koutsantonis, G. A.; Jayatilaka, D.; Edwards, A. J.; Spackman, M. A. The Elusive Structural Origin of Plastic Bending in Dimethyl Sulfone Crystals with Quasi-Isotropic Crystal Packing. *Angew. Chemie Int. Ed.* **2017**, *56* (29), 8468–8472.

(12) Bhattacharya, B.; Roy, D.; Dey, S.; Puthuvakkal, A.; Bhunia, S.; Mondal, S.; Chowdhury, R.; Bhattacharya, M.; Mandal, M.; Manoj, K.; Mandal, P. K.; Reddy, C. M. Mechanical-Bending-Induced Fluorescence Enhancement in Plastically Flexible Crystals of a GFP Chromophore Analogue. *Angew. Chemie Int. Ed.* **2020**, *59* (45), 19878–19883.

(13) Samanta, R.; Das, S.; Mondal, S.; Alkhidir, T.; Mohamed, S.; Senanayak, S. P.; Reddy, C. M. Elastic Organic Semiconducting Single Crystals for Durable All-Flexible Field-Effect Transistors: Insights into the Bending Mechanism. *Chem. Sci.* **2022**, *14* (6), 1363–1371.

(14) Worthy, A.; Grosjean, A.; Pfrunder, M. C.; Xu, Y.; Yan, C.; Edwards, G.; Clegg, J. K.; McMurtrie, J. C. Atomic Resolution of Structural Changes in Elastic Crystals of Copper(II) Acetylacetonate. *Nat. Chem.* **2018**, *10* (1), 65–69.

(15) Thomas, S. P.; Worthy, A.; Eikeland, E. Z.; Thompson, A. J.; Grosjean, A.; Tolborg, K.; Krause, L.; Sugimoto, K.; Spackman, M. A.; McMurtrie, J. C.; Clegg, J. K.; Iversen, B. B. Coordination Sphere Flexibility Leads to Elastic Deformation in a One-Dimensional Coordination Polymer Crystal. *Chem. Mater.* **2023**, *35* (6), 2495–2502.

(16) Liu, X.; Michalchuk, A. A. L.; Bhattacharya, B.; Yasuda, N.; Emmerling, F.; Pulham, C. R. High-Pressure Reversibility in a Plastically Flexible Coordination Polymer Crystal. *Nat. Commun.* **2021**, *12* (1).

(17) Bhattacharya, B.; Michalchuk, A. A. L.; Silbernagl, D.; Rautenberg, M.; Schmid, T.; Feiler, T.; Reimann, K.; Ghalgaoui, A.; Sturm, H.; Paulus, B.; Emmerling, F. A Mechanistic Perspective on Plastically Flexible Coordination Polymers. *Angew. Chemie Int. Ed.* **2020**, *59* (14), 5557–5561.

(18) Đaković, M.; Borovina, M.; Pisačić, M.; Aakeröy, C. B.; Soldin, Ž.; Kukovec, B. M.; Kodrin, I. Mechanically Responsive Crystalline Coordination Polymers with Controllable Elasticity. *Angew. Chemie Int. Ed.* **2018**, *57* (45), 14801–14805.

(19) Adler-Abramovich, L.; Arnon, Z. A.; Sui, X. M.; Azuri, I.; Cohen, H.; Hod, O.; Kronik, L.; Shimon, L. J. W.; Wagner, H. D.; Gazit, E. Bioinspired Flexible and Tough Layered Peptide Crystals. *Adv. Mater.* **2018**, *30* (5), 1–6.

(20) Nguyen, V.; Zhu, R.; Jenkins, K.; Yang, R. Self-Assembly of Diphenylalanine Peptide with Controlled Polarization for Power Generation. *Nat. Commun.* **2016**, *7* (1), 13566.

(21) Ahmed, E.; Karothu, D. P.; Naumov, P. Crystal Adaptronics: Mechanically Reconfigurable Elastic and Superelastic Molecular Crystals. *Angew. Chemie Int. Ed.* **2018**, *57* (29), 8837–8846.

(22) Bhattacharya, B.; Michalchuk, A. A. L.; Silbernagl, D.; Yasuda, N.; Feiler, T.; Sturm, H.; Emmerling, F. An Atomistic Mechanism for Elasto-Plastic Bending in Molecular Crystals. *Chem. Sci.* **2023**, *14* (13), 3441–3450.

(23) Ahmed, E.; Karothu, D. P.; Pejov, L.; Commins, P.; Hu, Q.; Naumov, P. From Mechanical Effects to Mechanochemistry: Softening and Depression of the Melting Point of Deformed Plastic Crystals. *J. Am. Chem. Soc.* **2020**, *142* (25), 11219–11231.

(24) Kenny, E. P.; Jacko, A. C.; Powell, B. J. Mechanomagnetics in Elastic Crystals: Insights from [Cu(Acac)2]. *Angew. Chemie Int. Ed.* **2019**, *58* (42), 15082–15088.

(25) Hayashi, S.; Koizumi, T. Elastic Organic Crystals of a Fluorescent π-Conjugated Molecule. *Angew. Chemie Int. Ed.* **2016**, *55* (8), 2701–2704.

(26) Hayashi, S.; Ishiwari, F.; Fukushima, T.; Mikage, S.; Imamura, Y.; Tashiro, M.; Katouda, M. Anisotropic Poisson Effect and Deformation-Induced Fluorescence Change of Elastic 9,10-Dibromoanthracene Single Crystals. *Angew. Chemie Int. Ed.* **2020**, *59* (37), 16195–16201.

(27) Wang, K.; Mishra, M. K.; Sun, C. C. Exceptionally Elastic Single-Component Pharmaceutical Crystals. *Chem. Mater.* **2019**, *31* (5), 1794–1799.

(28) Mishra, M. K.; Mishra, K.; Syed Asif, S. A.; Manimunda, P. Structural Analysis of Elastically Bent Organic Crystals Using in Situ Indentation and Micro-Raman Spectroscopy. *Chem. Commun.* **2017**, *53* (97), 13035–13038.

(29) Panda, M. K.; Ghosh, S.; Yasuda, N.; Moriwaki, T.; Mukherjee, G. D.; Reddy, C. M.; Naumov, P. Spatially Resolved Analysis of Short-Range Structure Perturbations in a Plastically Bent Molecular Crystal. *Nat. Chem.* **2015**, *7* (1), 65–72.

(30) Wei, C.; Bai, L.; Wei, C.; Bai, L.; An, X.; Xu, M.; Liu, W.; Zhang, W.; Singh, M. Article Atomic-Resolved Hierarchical Structure of Elastic p -Conjugated Molecular Crystal for Flexible Organic Photonics Atomic-Resolved Hierarchical Structure of Elastic p - Conjugated Molecular Crystal. *CHEMPR* **2022**, *8* (5), 1427–1441.

(31) An, L.-C.; Li, X.; Li, Z.-G.; Li, Q.; Beldon, P. J.; Gao, F.-F.; Li, Z.-Y.; Zhu, S.; Di, L.; Zhao, S.; Zhu, J.; Comboni, D.; Kupenko, I.; Li, W.; Ramamurty, U.; Bu, X.-H. Plastic Bending in a Semiconducting Coordination Polymer Crystal Enabled by Delamination. *Nat. Commun.* **2022**, *13* (1), 6645.

(32) Naik, S.; Haridas, V. Micro-Urchin from Synthetic Self-Assembling Molecules. *RSC Adv.* **2013**, *3* (44), 21356–21359.

(33) Ghosh, S.; Mishra, M. K.; Ganguly, S.; Desiraju, G. R. Dual Stress and Thermally Driven Mechanical Properties of the Same Organic Crystal: 2,6-Dichlorobenzylidene-4-Fluoro-3-Nitroaniline. *J. Am. Chem. Soc.* **2015**, *137* (31), 9912–9921.

(34) Gaber, B. P.; Peticolas, W. L. On the Quantitative Interpretation of Biomembrane Structure by Raman Spectroscopy. *Biochim. Biophys. Acta - Biomembr.* **1977**, *465* (2), 260–274.

(35)   Orendorff, C. J.; Ducey, M. W. J.; Pemberton, J. E. Quantitative Correlation of Raman Spectral Indicators in Determining Conformational Order in Alkyl Chains. *J. Phys. Chem. A* **2002**, *106* (30), 6991–6998.

(36)   Socrates, G.; Infrared and Raman Characteristic Group Frequencies: Tables and Charts, 3rd ed.; *John Wiley & Sons*, **2001**, *3*, 336.

(37)   Bonera, E.; Fanciulli, M.; Batchelder, D. N. Stress Mapping in Silicon: Advantages of Using a Raman Spectrometer with a Single Dispersive Stage. *Appl. Spectrosc.* **2002**, *56* (5), 560–563.

TOC GRAPHIC:

Local Stress Gradient in an Elastically Bending Lipidated Molecular Crystal Estimated by Raman Shifts

Atiqur Rahman, Srijan Mondal, Mantu Modak, Ashi Singh, Hanuman Singh, Navdeep S. Thayat, Jack K. Clegg, Himanshu K. Poswal, V. Haridas, Sajesh P. Thomas*
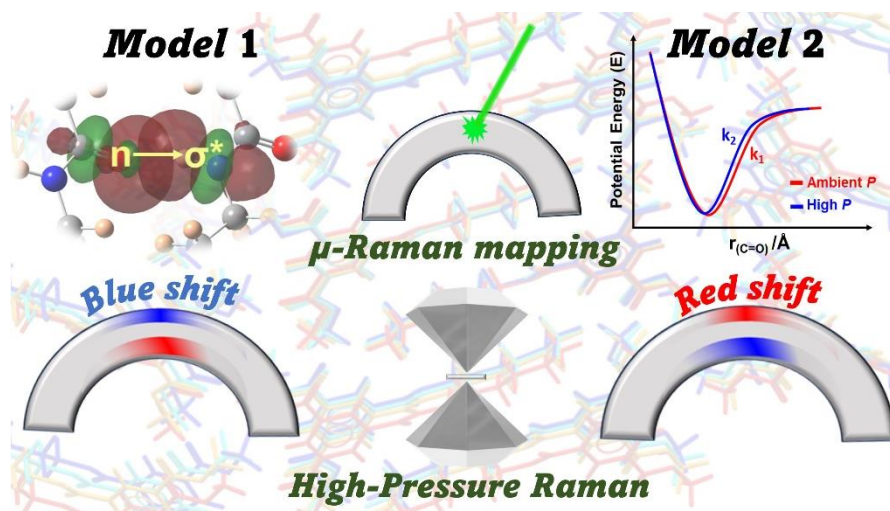
Combining frequency shifts from Micro-raman mapping with high-pressure Raman studies on an elastically bending molecular crystal leads to insights into the local internal stress upon bending- thus solving a long-standing puzzle.