Electronic Supporting Information (ESI)

Structural Analysis of Elastically Bent Organic Crystals by in situ Indentation and micro-Raman Spectroscopy

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S1. Experiments details

Materials. All the chemicals were purchased from Sigma-Aldrich. Commercially available solvents were used as received without further purification.

Single crystal preparation

2,3-dichlorobenzylidine-4-bromoaniline (DCBA): Long and acicular elastic bendable crystals of DBCA in the dimension of 3-5 mm long an 0.02-0.05 mm thick, were prepared by adding one equivalent each of the corresponding 2,3-dichlorobenzaldehyde and 4-bromoaniline in hot methanol followed by slow solution evaporation at ambient conditions. **2,6-dichlorobenzylidine-3,4-dichloroaniline (DCCA):** Similarly, long and acicular elastic bendable crystals of DCCA in the dimension of 3-5 mm long an 0.02-0.05 mm thick, were prepared by adding one equivalent each of 2,6-dichlorobenzaldehyde and 3,4-dichloroaniline in hot methanol followed by slow solution evaporation at ambient conditions.

S2. Single crystal X-ray diffraction experiment

The crystals of DCBA and DCCA confirmed by checking the cell parameters and comparison with the reported structure (see table below) in the CSD.[1] X-ray diffraction was carried out on a Rigaku Mercury 375R/M CCD (XtaLAB mini) diffractometer using graphite monochromatic Mo-K_α radiation. Face indexing of good quality single crystals was performed with the Rigaku CrystalClear 2.0 software[2] and confirmed with the reported face indexing to perform the nanoindentation device (Bruker Nano Surfaces, USA) equipped with micro-Raman spectroscopy on the lateral face of the bent portion of the elastic crystals.

Crystallographic information table

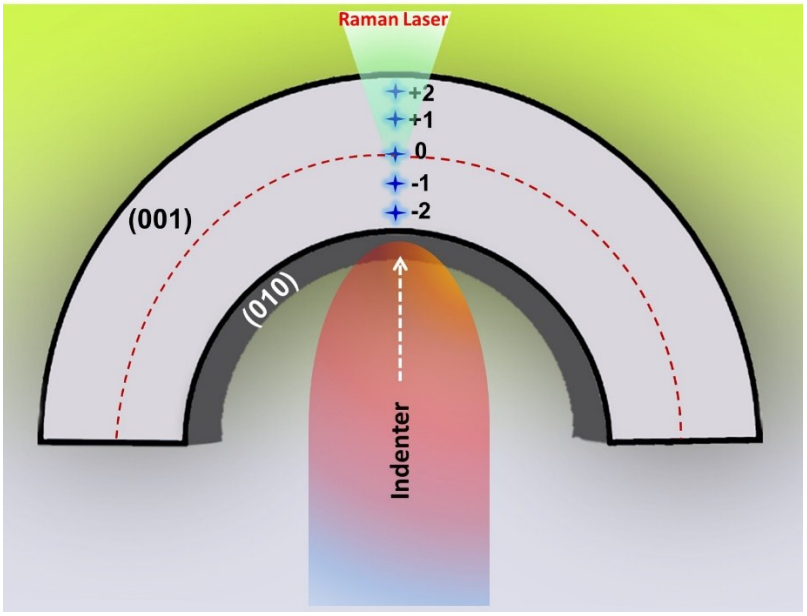
	DCBA	**DCCA**
Formula	$C_{13}H_8BrCl_2N$	$C_{13}H_8Cl_4N$
Molecular weight	329.01	319.94
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
***a* (Å)**	3.913(5)	11.801(3)
***b* (Å)**	11.773(13)	3.913(8)

***c* (Å)**	13.282(15)	27.923(6)
***α* (°)**	86.82(2)	90
***β* (°)**	88.82(2)	95.528(12)
***γ* (°)**	87.15(2)	90
Volume (Å^3)	610.0(12)	1283.3(5)
Z/Z′	2/1	4/1
ρ_{calc} (g/cm^3)	1.791	1.656
Refcode	SUBXIY	SUBYEV

S3. In situ Bending and Raman measurements

A custom built, nanoindentation device (Bruker Nano Surfaces, USA) was used to bend the elastic crystal. A three-plate capacitive transducer with maximum load, displacement range of 500 mN and 150 μm, was used to apply load on (001) and (010) face of the DCBA and DCCA crystal respectively. A diamond flat punch indenter (50 μm diameter) was used as a probe. A constant load of 5 mN was applied on the bendable face (001) of the crystal. The bent state was maintained for 50 seconds to facilitate Raman spectral acquisition. Using a micro Raman spectrometer (Renishaw, U.K), *in situ* Raman spectra were recorded (100-3200 cm^{-1} spectral range) at 5 different locations on the bent section of the lateral (100) and (001) face of DCBA and DCCA crystal respectively. A 785 nm diode laser was used as an excitation source. A 10 sec, spectral acquisition time and 50 μW laser power was used for Raman measurements. The Raman spectra were post-processed using Renishaw in-built Wire 4.1 software.

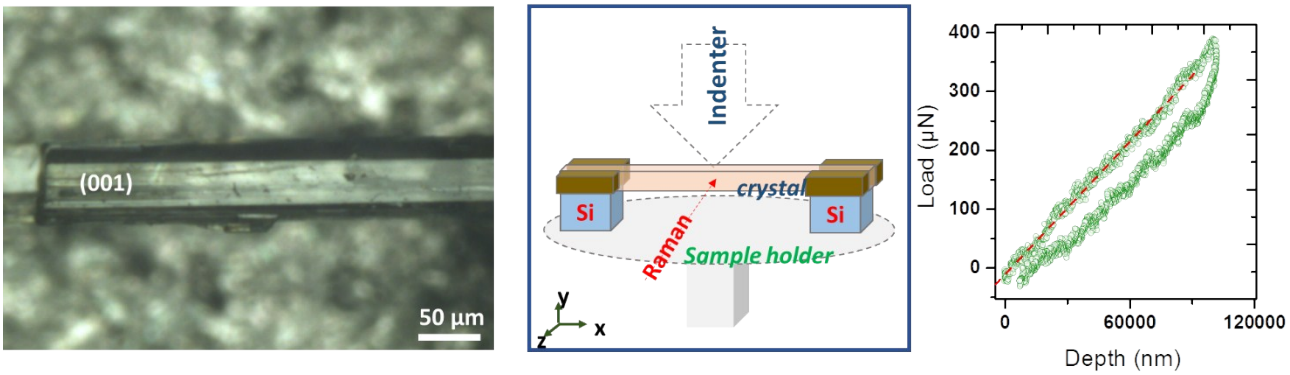
S4: Schematic illustration of elastically bent DCCA crystal. Sample and the indenter was aligned laterally. Raman measurements were done on 5 locations on (001) face, under the bent state.



S5. Finite Element Modeling (FEA) details

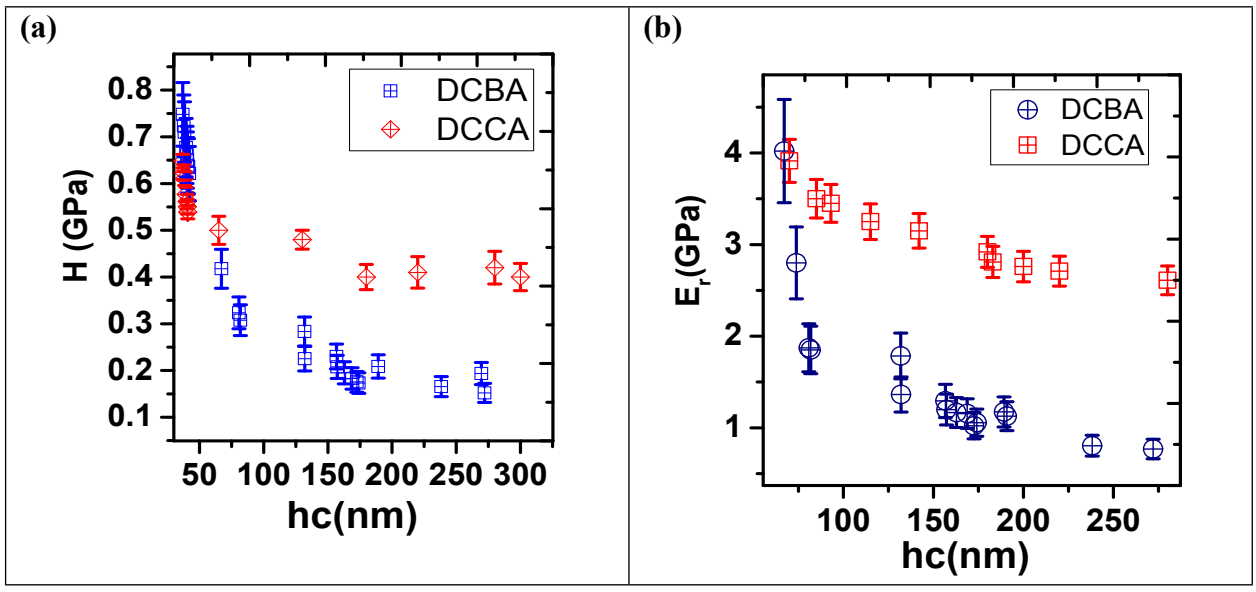
SOLIDWORKS simulation 2016 software was used to calculate the principal stress distribution in elastic crystal beam. Three-point bending analysis was performed on doubly clamped elastic crystal beam. Beam dimensions used for simulation are: length (1.1 mm), Width (50 µm) and height (50 µm). A normal load of 5 mN was applied on clamped beam.

A. (a) Optical micrograph of the DCBA crystal, (b) Schematic representation of three-point bending test, (c) load vs displacement plot.



(a) (b) (c)

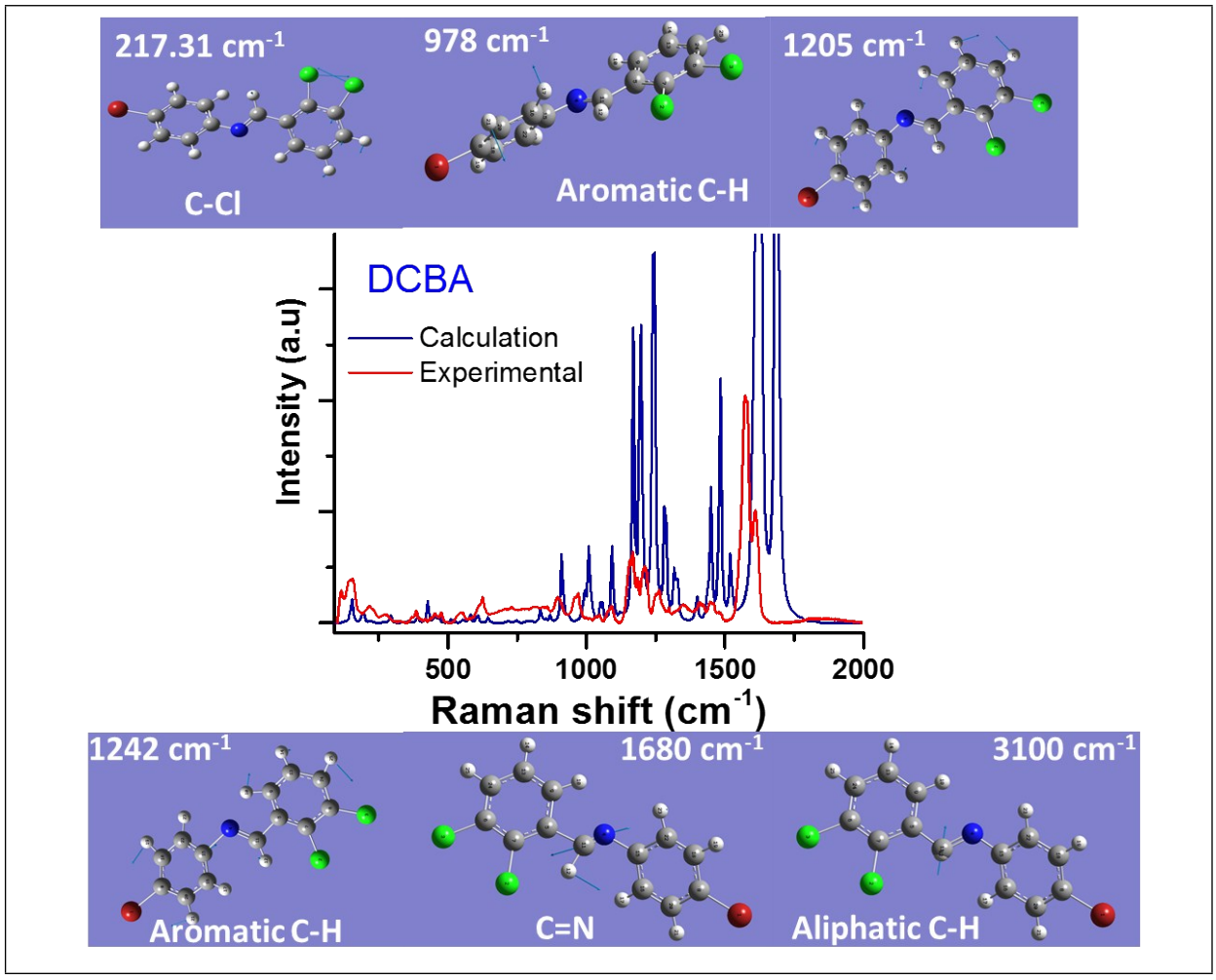
B. Mechanical properties of elastic crystals (a) variation of Hardness with contact depth, (b) Reduced Modulus as a function of contact depth.



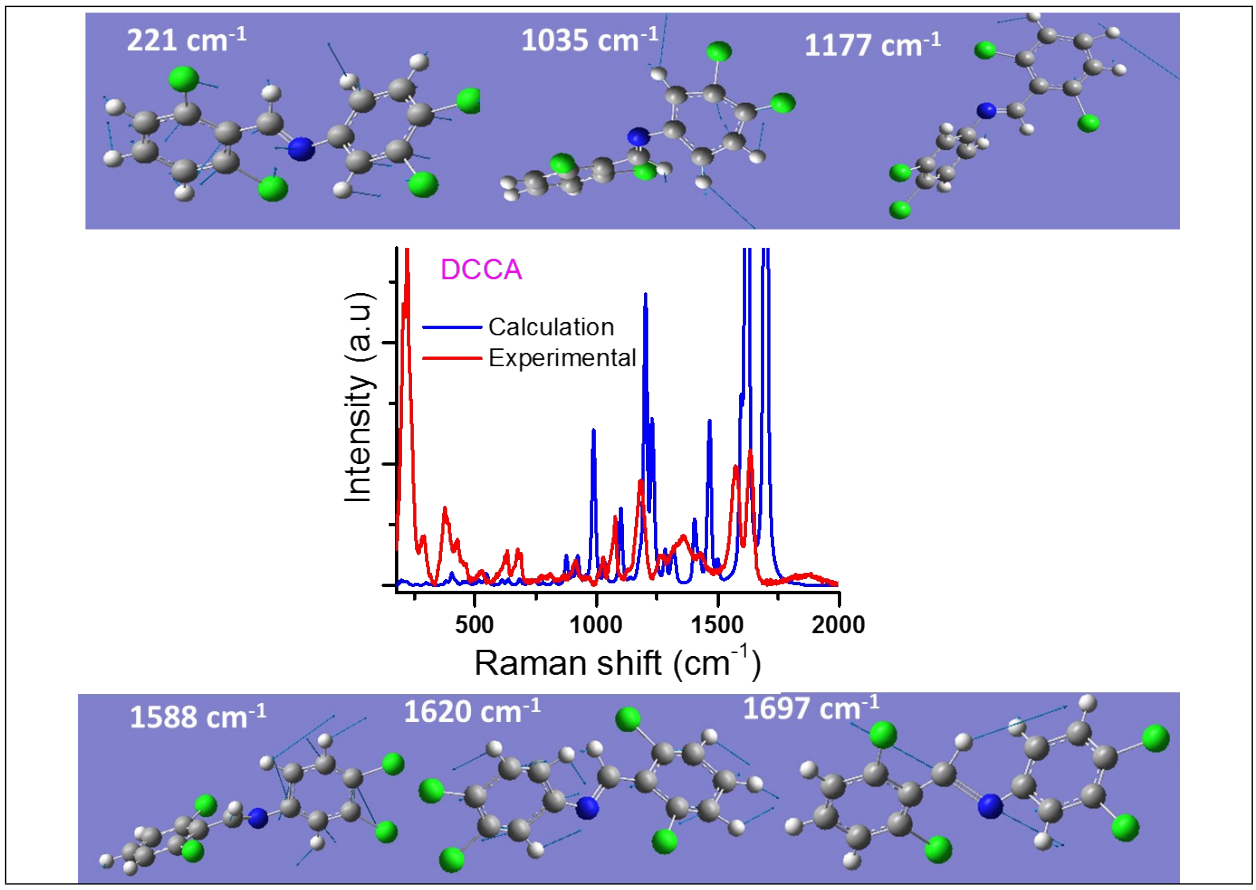
S6: Raman vibrational experimental and computational details

The vibrational computations of DCBA and DCCA molecules was calculated by using Becke-3-Lee Yang Parr (B3LYP) density functional theory(DFT) method with 6311++G(d,p) basis set in ground state using Gaussian-09 program.[3] The positive values of all calculated vibrational wavenumbers show that the optimized molecular structure is stable.

A: Calculated and experimental spectra of DCBA. Inset images show pictorial representation of vibrational modes.



B. Calculated and experimental spectra of DCCA. Inset images show pictorial representation of vibrational modes.



References:

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3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.

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