Hand-twistable Plastically Deformable Crystals of an Organic Small Rigid Molecule

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Supplementary Information:

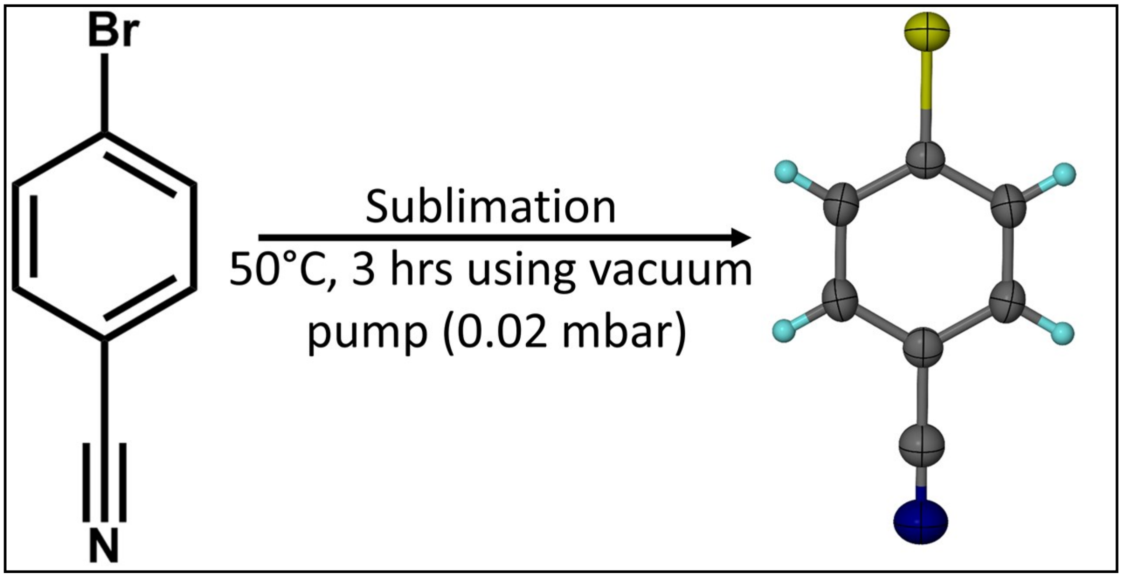
Experimental Information

Materials

4-bromobenzonitrile was purchased from Sigma-Aldrich and used as received without further purification.

Crystallization of 4-bromobenzonitrile

Crystals of 4-bromobenzonitrile were obtained by sublimation at 50 °C for 3 hrs using glass oven under dynamic vacuum (0.02 mbar). For the X-ray diffraction study of 4-bromobenzonitrile, a small colourless block was cut from a long crystal.



Scheme S1: Crystallization of the organic compound 4-bromobenzonitrile.

Preparation of the single crystal of 4-bromobenzonitrile (4-BBN-S)

A very suitable, straight and rectangular crystal of 4-bromobenzonitrile was selected for the single crystal X-ray diffraction (SCXRD) analysis. The crystal was glued on the glass fibre using epoxy and the SCXRD data were collected.

Preparation of the bent crystals of 4-bromobenzonitrile (4-BBN-B)

The same single crystal was bent using mechanical force before data collection (figure S1).

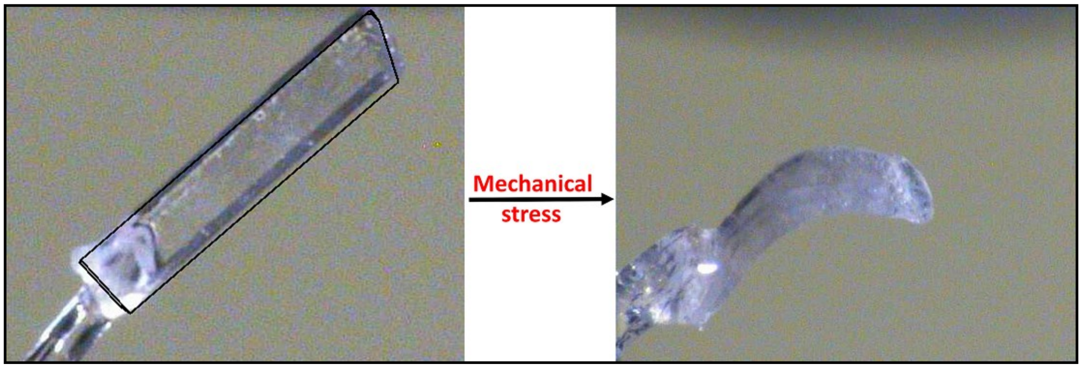


Figure S1: Images showing straight and bent crystal for SCXRD analysis.

Computational Analysis.

Crystal structures of 4-bromobenzonitrile at 273 K were imported from the refined crystal structures. Only the hydrogen atoms in the framework were optimized as part of a periodic system using the CASTEP module of the Materials Studio software suite.[1] The optimizations were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and thresholds for geometry optimization and SCF convergence were chosen as 1×10^{-5} and 1×10^{-6} eV, respectively. Single point energy calculations using the DMol3 module of the Materials Studio software suite were performed using the GGA PBE functional with Grimme's DFT-D dispersion correction, and threshold for SCF convergence were chosen as 1×10^{-6} eV. The electron density data obtained from the DMol3 calculations were used to construct the three-dimensional 0.01 e^{-} $Å^{-3}$ electron density contour used for the molecular electrostatic potential map (obtained from the same calculation).

From the calculation, we found that if we consider only an individual 4-bromobenzonitrile, negative electrostatic potential is observed at the center of benzene ring due to the presence of -CN and -Br groups (Figure S2a). As a result, the molecules should not stack in face to face fashion because of the repulsive interactions. However, on considering the overall packing of 4-bromobenzonitrile, the interactions from neighbouring molecules affect the electron density distribution on the benzene ring i.e. the π-clouds (shifted to negative electron density at the two ends of the molecule (Figure S2b) and as a result the center of the benzene ring becomes slightly positive. Overall, 4-bromobenzonitrile are arranged in polar mode, therefore in order to stabilise the system i.e. to minimise repulsion, the molecules have to stack in an offset manner so that the positive aromatic center interacts with the negative π-cloud on the neighbouring molecule.[2] Hence, the offset π···π stacking[2,3,4,5] is observed in the system.

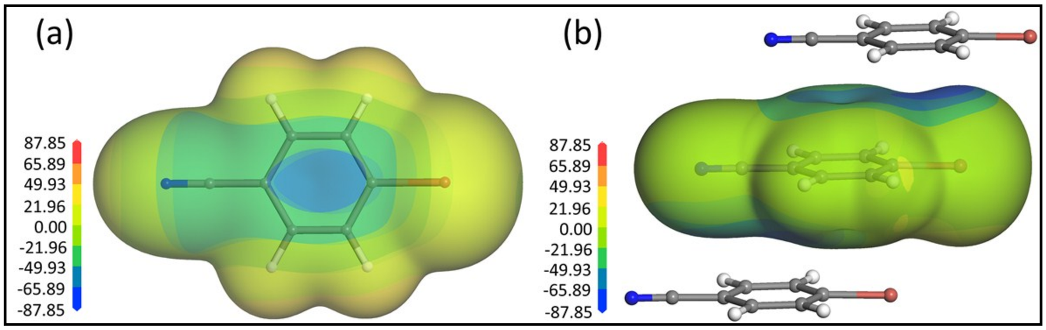


Figure S2: Electrostatic potential mapped onto the electron density isosurface of (a) the molecule and (b) the molecules in the crystal packing showing the offset π···π interactions. Electrostatic potentials are in kcal/mol. Areas of positive and negative potentials are indicates in red and blue respectively.

Table S1. Crystallographic details for straight (**4-BBN-S)** and bent (**4-BBN-B)** crystals.

Identification code	**4-BBN-S**	**4-BBN-B**
Empirical formula	C_7H_4NBr	C_7H_4NBr
Formula weight (g/mol)	182.02	182.02
Temperature/K	273(2)	273(2)
Crystal system	Monoclinic	Monoclinic
Space group	*Cm*	*Cm*
a/Å	9.5310(20)	9.5090(50)
b/Å	8.5593(18)	8.5350(70)
c/Å	4.1352(9)	4.1270(20)
α/°	90	90.00
β/°	90.295(3)	90.311(5)
γ/°	90	90.00
Volume/Å^3	337.34(12)	334.9(3)
Z	2	2
ρ_{calc} (g/cm^3)	1.792	1.805
μ/mm^{-1}	5.990	6.033
F(000)	176	176
Crystal size/mm^3	0.91 × 0.188 × 0.104	0.91 × 0.188 × 0.104

Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
θ range for data collection/°	3.199 to 28.277	3.207 to 25.332
Index ranges	$-12 \leq h \leq 12$, $-11 \leq k \leq 11$, $-5 \leq l \leq 5$	$-11 \leq h \leq 11$, $-10 \leq k \leq 10$, $-4 \leq l \leq 4$
Reflections collected	3422	4129
Independent reflections	893 [R_{int} = 0.0463, R_{sigma} = 0.0337]	657 [R_{int} = 0.0313, R_{sigma} = 0.0189]
Data/restraints/parameters	893/2/49	655 / 2 / 49
Goodness-of-fit on F^2	1.087	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0596, wR_2 = 0.1518	R_1 = 0.0404, wR_2 = 0.1010
Final R indexes [all data]	R_1 = 0.0613, wR_2 = 0.1534	R_1 = 0.0408, wR_2 = 0.1019
Largest diff. peak/hole /e $Å^{-3}$	0.667/-0.236	0.601 / -0.218
CCDC number	1587640	1587641

Table S2: Intermolecular interactions within the structure responsible for bending in 4-bromobenzonitrile.

	π···π (*i*1···*i*1) distance (Å)	**N1···Br1 (d) (Å)**	**C5-N1···Br1 (D) (Å)**	**∠C5-N1···Br1 (θ) (°)**	**C1-Br1···N1 (D) (Å)**	**∠C1-Br1···N1 (θ) (°)**	**Closest vdW $H_2 \cdots H_3$ (Å)**	**Closest C2···C3 contact (Å)**
4-BBN-S	4.1352(9)	3.2540(6)	4.3571(8)	166.546(9)	5.1170(1)	167.995(8)	2.9561(9)	4.0578(7)
4-BBN-B	4.1268(20)	3.2510(14)	4.3563(19)	167.636(20)	5.1241(22)	168.479(14)	2.9718(12)	4.0655(15)

***i*1** is the centroid of C1- C6

Table S3: Other shortest non-bonding distances and angles between the molecules**.**

	(D···A) C3-H3···Br1 (Å)	**(∠D-H···A) ∠C3-H3···Br1 (°)**	**(D···A) C2-H2···N1 (Å)**	**(∠D-H···A) ∠C2-H2···N1 (°)**	**C···π (Å)**	**Br···π (Å)**
4-BBN-S	3.7845(6)	125.566(6)	3.7027(6)	151.009(6)	3.7027(7)	3.6989(7)
4-BBN-B	3.7762(13)	125.067(13)	3.7018(13)	151.166 (13)	3.6585(16)	3.7019(15)

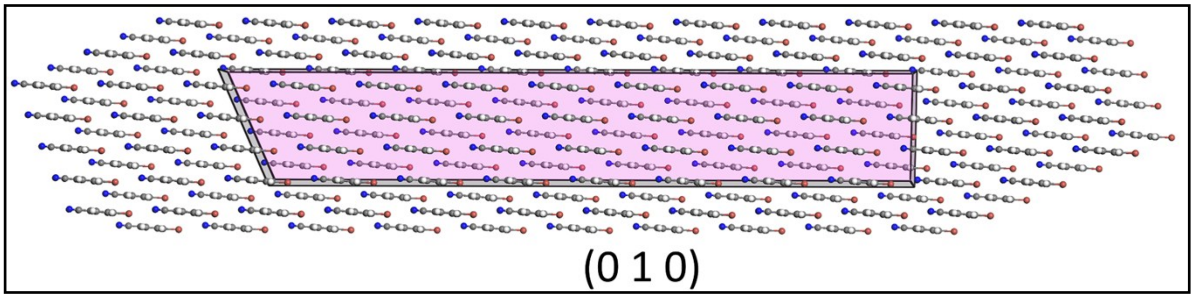


Figure S3: Overlay of crystal habit with the crystal packing along (0 1 0) plane.

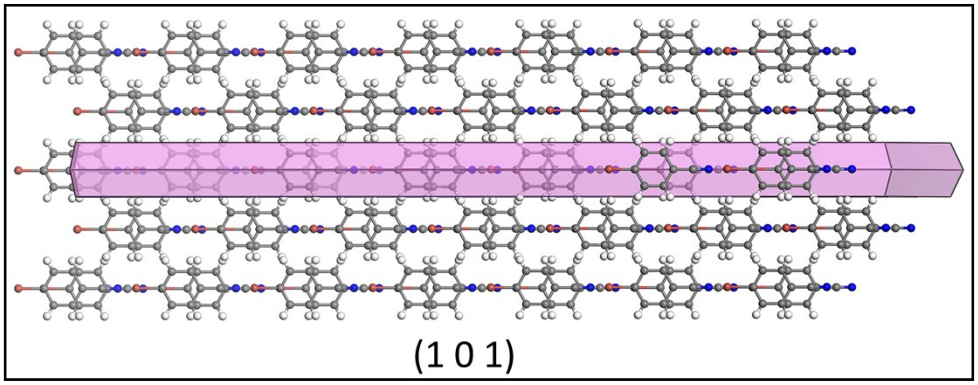


Figure S4: Overlay of crystal habit with the crystal packing along (1 0 1) plane.

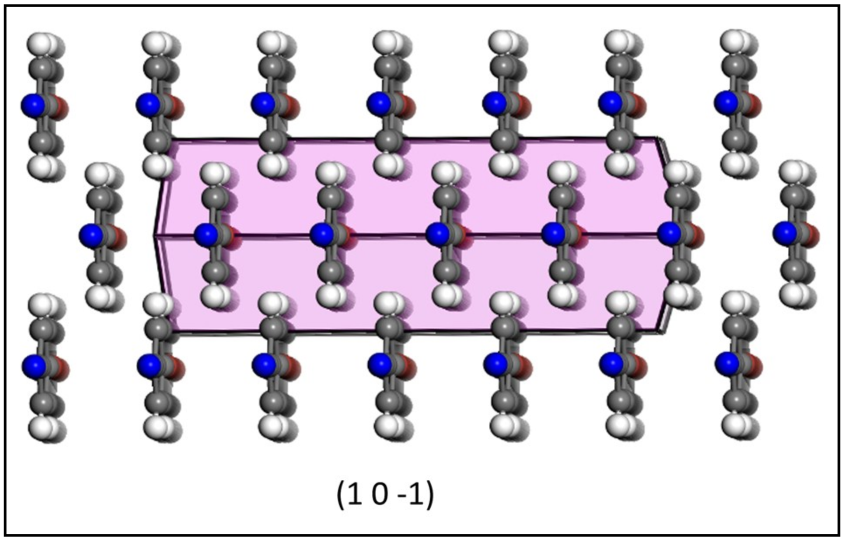


Figure S5: Overlay of crystal habit with the crystal packing along (1 0 -1) plane.

Mechanical bending of the 4-bromobenzonitrile crystal

This mechanical bending of 4-bromobenzonitrile was recorded with the PIXEL camera mounted on a stereo zoom SMZ74 5T trinocular stereoscope using Windows Movie Maker software. This was carried out at room temperature (Movies S1).

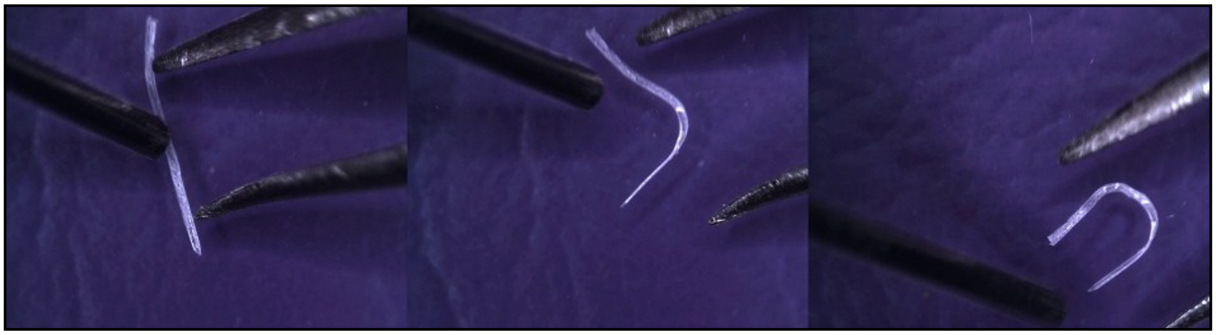


Figure S6: Micrographs showing the mechanical bending of 4-bromobenzonitrile crystal.

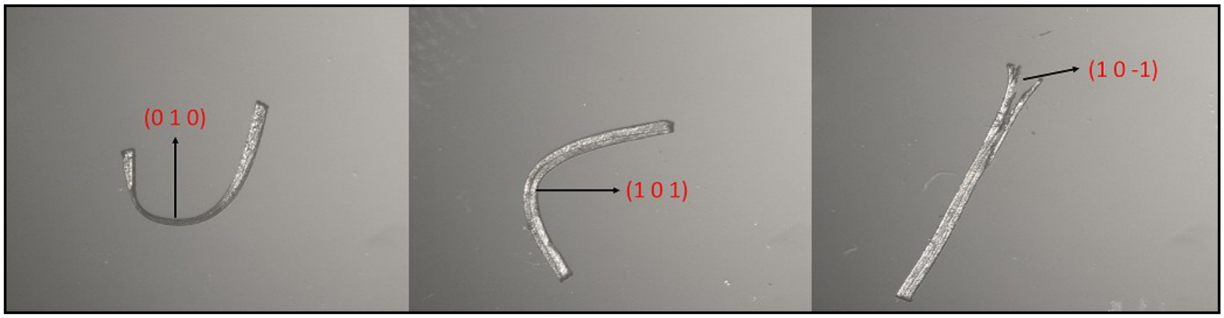


Figure S7: Micrographs of 4-bromobenzonitrile crystal showing the mechanical bending on (0 1 0) and (1 0 1) faces but splitting/breaking on (1 0 -1) face.

Temperature-ramped Differential Scanning Calorimetry (DSC)

Temperature-ramped differential scanning calorimetry of 4-bromobenzonitrile was carried out on TA DSC-Q20 and DSC-Q100 instrument. Crystals were taken on a Tzero aluminium pan and connected to LNG cryostat for low temperature analysis. The low temperature DSC analysis was carried out by cooling from 300 to 100 K and heated back to 300 K at the heating rate of 5 K min^{-1}. Also, the crystal was analysed by heating from room temperature (300 K) to the selected temperature at the ramp rate of 5 K min^{-1}.

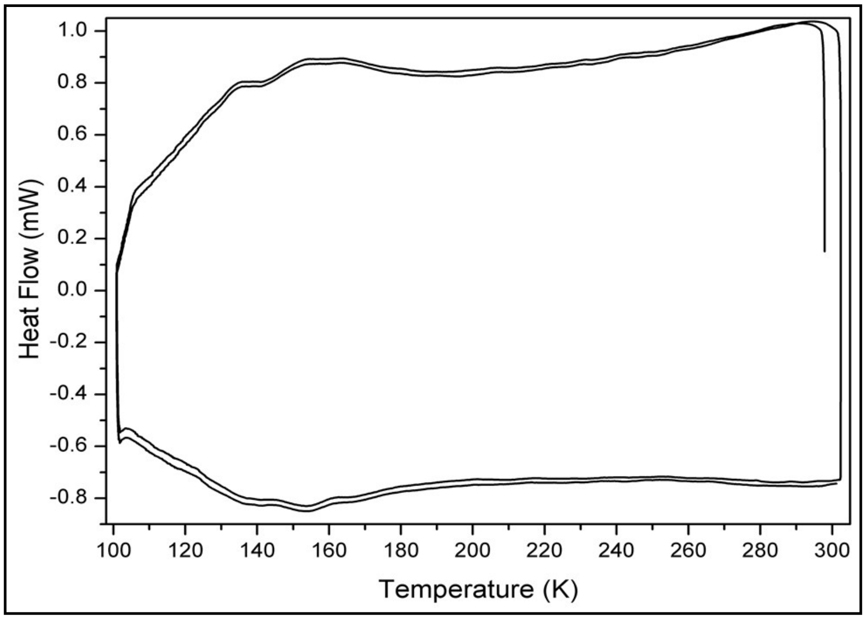


Figure S8: T-DSC curve for 4-bromobenzonitrile in the range of 100-300 K (two cycles).

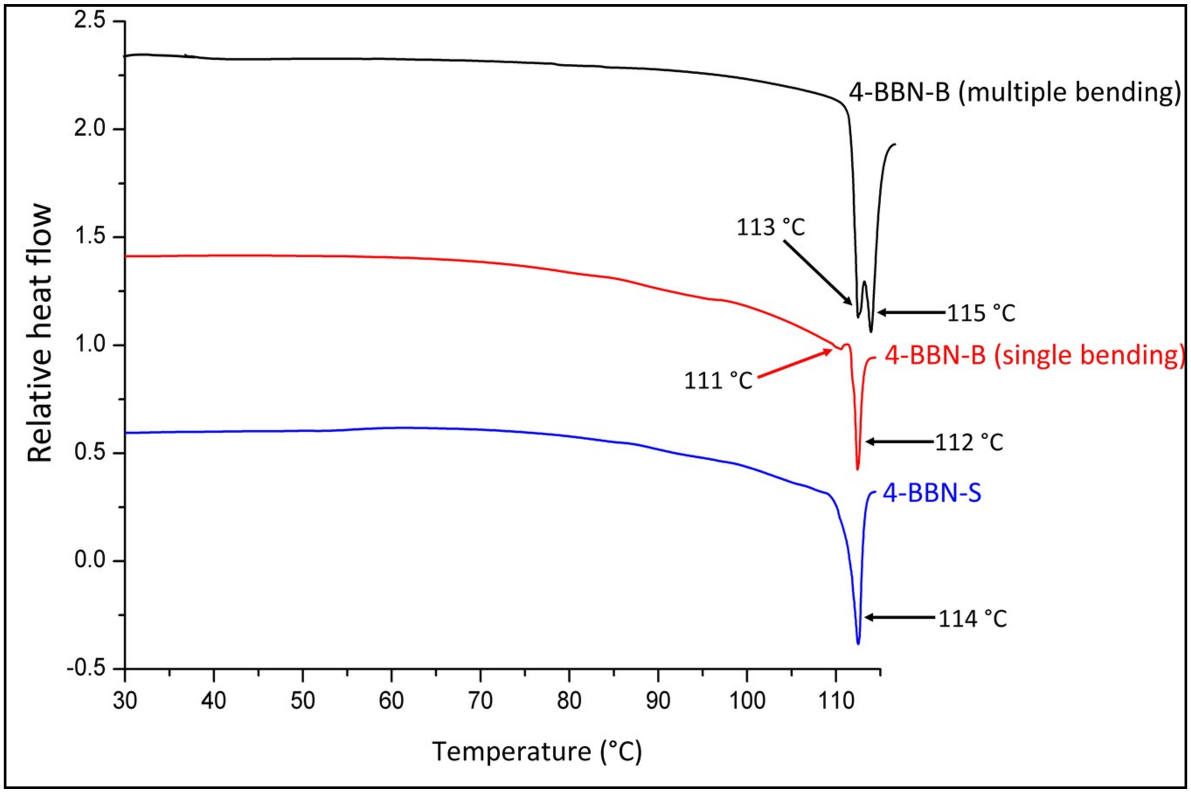


Figure S9: T-DSC thermograms showing the melting points of both straight and bent crystal.

Hot stage Microscopy

Thermomicroscopic behaviour of 4-bromobenzonitrile was observed with hot-stage microscope (Linkam) consisting of a temperature-controlled stage THMS600-PS mounted on a Q-imaging (Q32634) microscope. Crystal of 4-bromobenzonitrile was cooled from room temperature (300 K) to 100 K and heated back to room temperature at a constant heating rate of 5 K min^{-1}. High-speed recordings were obtained with PIXEL camera mounted on a stereo zoom SMZ745T trinocular stereoscope (Movies S2 and S3).

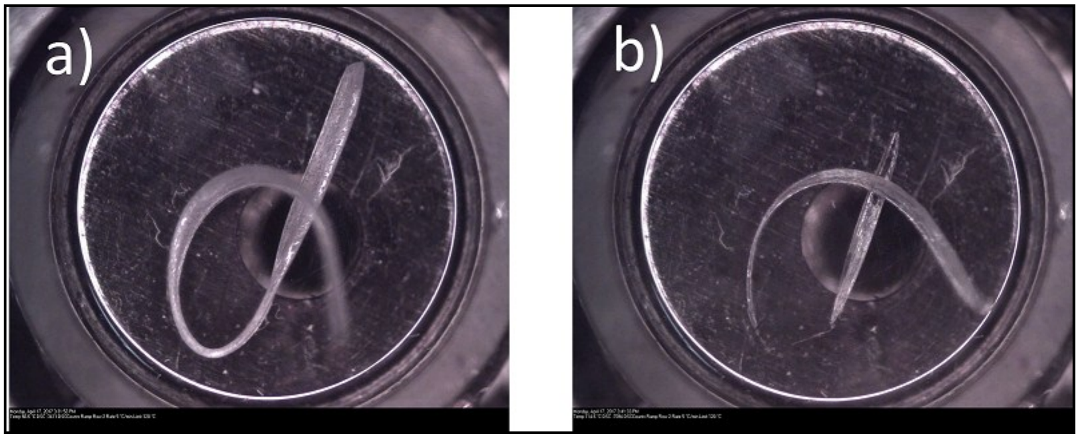


Figure S10: Micrographs showing **a)** bent crystal before melting and **b)** the melting of the bent area of the crystal before other part.

Single crystal structure determination

Single-crystal X-ray diffraction data were collected at 273 K using a Bruker APEX-II DUO CCD area detector diffractometer equipped with an Oxford Cryosystems 700Plus cryostat. A multilayer monochromator with Mo Kα radiation (λ = 0.71073 Å) from an Incoatec IμS micro source was used. Data reduction was carried out by means of a standard procedure using the Bruker software package SAINT.[6] Absorption corrections and correction of other systematic errors were performed using SADABS.[7,8] The structures were solved by direct methods using SHELXS-2016 and refined using SHELXL-2016.[9] X-Seed[10] was used as the graphical interface for the SHELX program suite and the images were rendered with POV-Ray. Hydrogen atoms were placed in calculated positions using riding models.

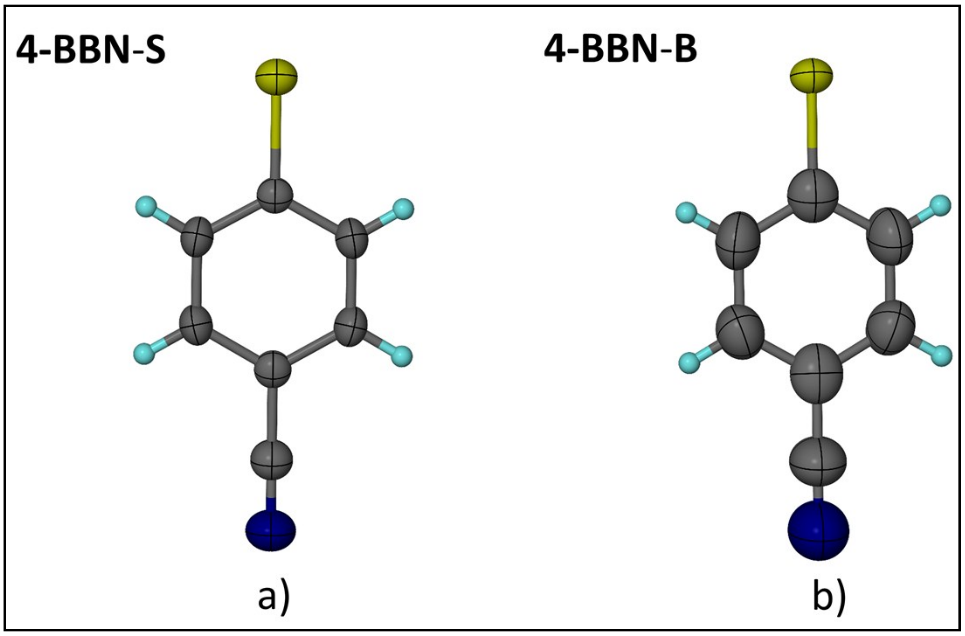


Figure S11: ORTEP representation with 50% probability for a) **4-BBN-S** and b) **4-BBN-B** at 273 K.

Infra-red spectroscopy

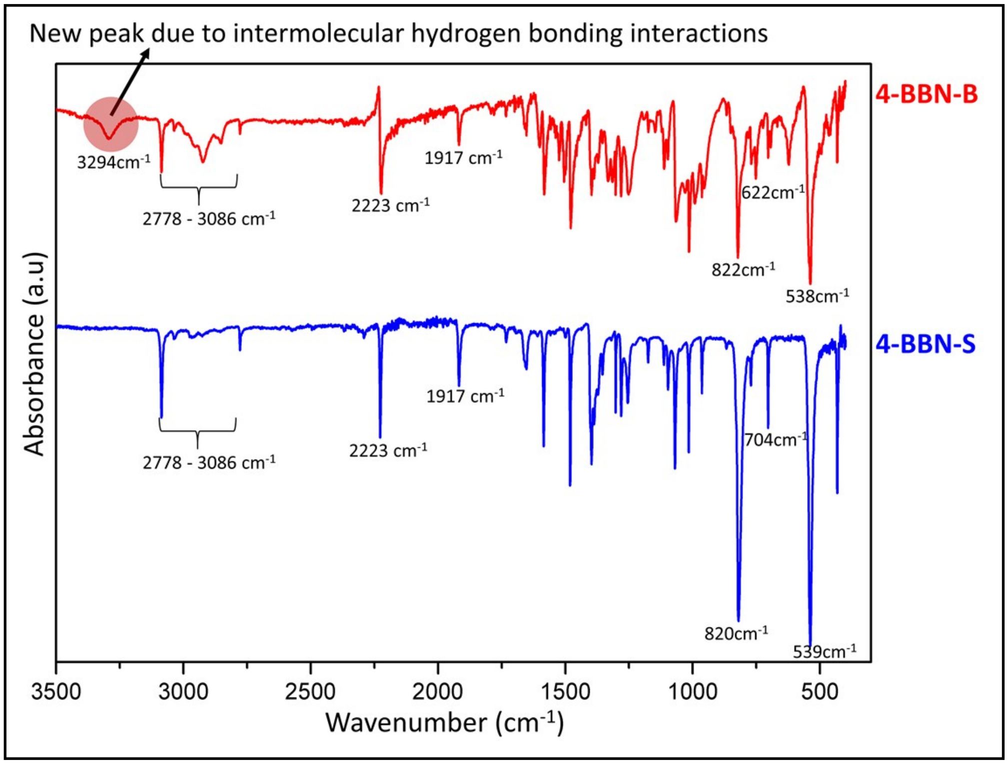


Figure S12: IR spectra of straight and bent crystals of 4-bromobenzonitrile.

References

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