Electronic Supporting Information

Design of Mechanically Flexible Photoresponsive Cyanostilbene Molecular Crystals

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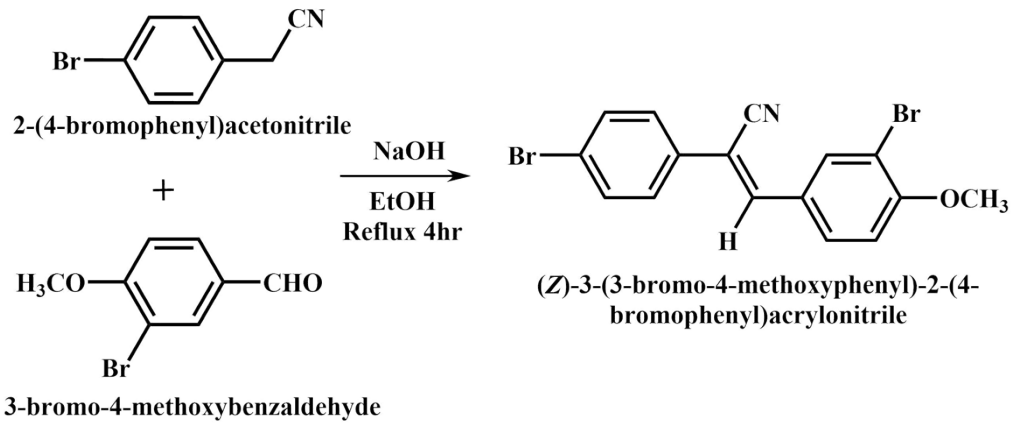
Synthesis Scheme.



Scheme S1. Synthesis route of compound **BN**

The compound **BN** was synthesized following the reported procedure.[1] In a 100 ml round-bottom flask, 4-bromophenylacetonitrile (1 equivalent) was mixed with 15 ml ethanol and 3-bromo-4-methoxybenzaldehyde (1 equivalent). A catalytic amount of NaOH (10 mol %) was added, and the mixture was stirred and refluxed for 6 hours. The product, a white precipitate, was then filtered and dried, achieving an 87% yield.

Recrystallization Table.

Table S1: Results from the recrystallization of Compound **BN** from one solvent or mixture of solvents.

S.No.	Solvents	Compound BN
1.	Ethyl Acetate + n-Hexane (1:1)	Powder
2.	Dichloromethane + Methanol	Powder

	(1:1)	
3.	Ethyl Acetate + Methanol (1:1)	Powder
4.	Ethyl Acetate + n-Hexane (1:1)	Powder
5.	Acetonitrile	Powder
6.	Methanol	Fine Needles
7.	Methanol + Chloroform (1:1)	Fine Needles
8.	Chloroform	Powder

Nuclear Magnetic Resonance (NMR) Analysis.

^{1}H NMR spectra of crystal **BN** were taken in $CDCl_3$ solvent. ^{1}H NMR spectra were collected under standard conditions. Chemical shifts (δ) were reported in parts per million (ppm) and referenced to the residual solvent peak at 7.26 ppm for the $CDCl_3$ solvent peak.

Crystal BN: ^{1}H NMR (500 MHz, $CDCl_3$, TMS) δ 7.99 (dd, J = 14.9, 5.2 Hz, 2H, Ar-H), 7.59 (d, J = 8.7 Hz, 2H, Ar-H), 7.53 (d, J = 8.7 Hz, 2H, Ar-H), 7.40 (s, 1H, –CH=CCN), 7.01 (d, J = 8.6 Hz, 1H, Ar-H), 3.97 (s, 3H, methoxy-H).

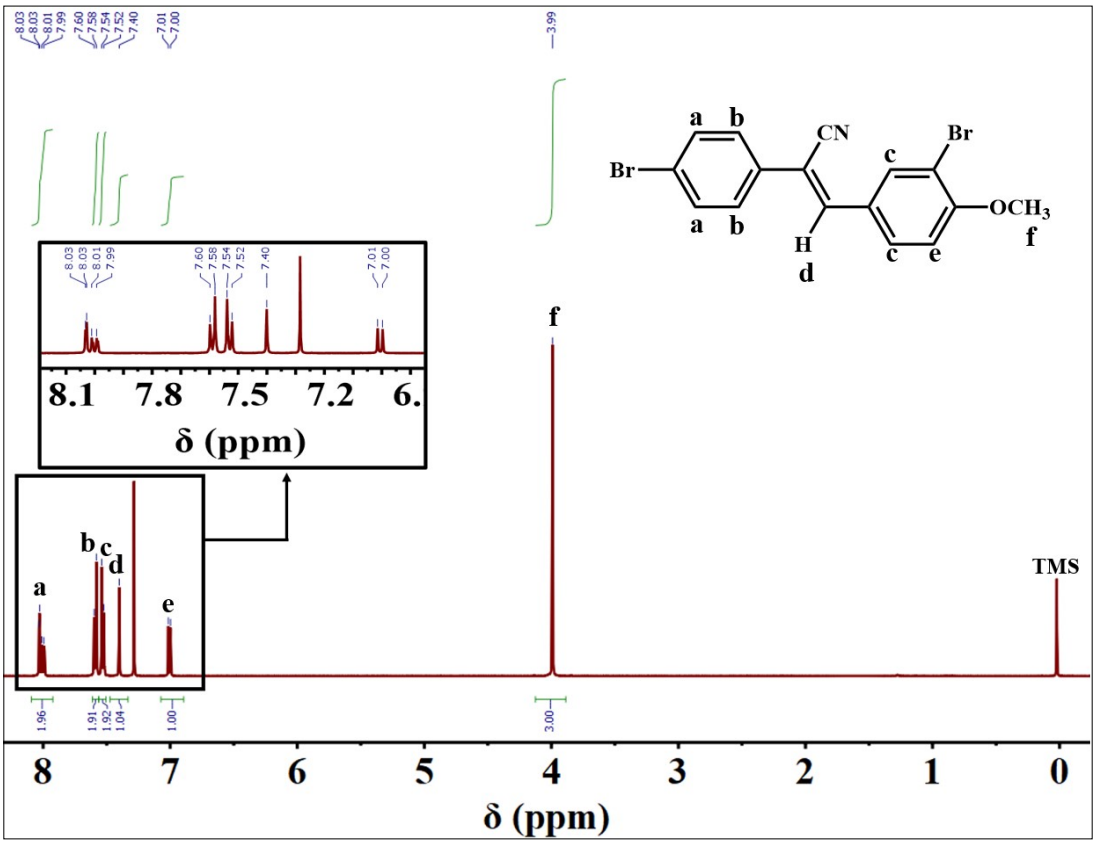


Figure S1. ^{1}H NMR spectrum of crystal **BN** (solvent: $CDCl_3$, peak at 7.26 ppm)

Differential Scanning Calorimetry (DSC) Analysis.

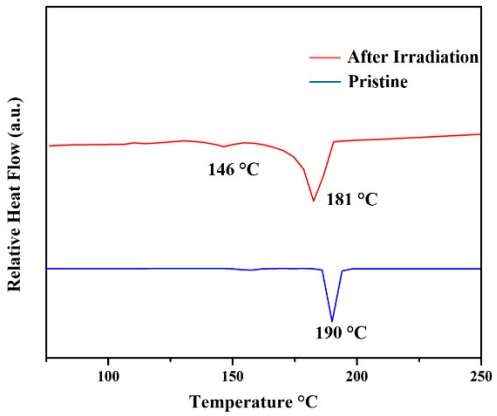


Figure S2. Comparative Differential Scanning Calorimetry (DSC) profile of crystal **BN** before and after irradiation.

Face Indexing Image.

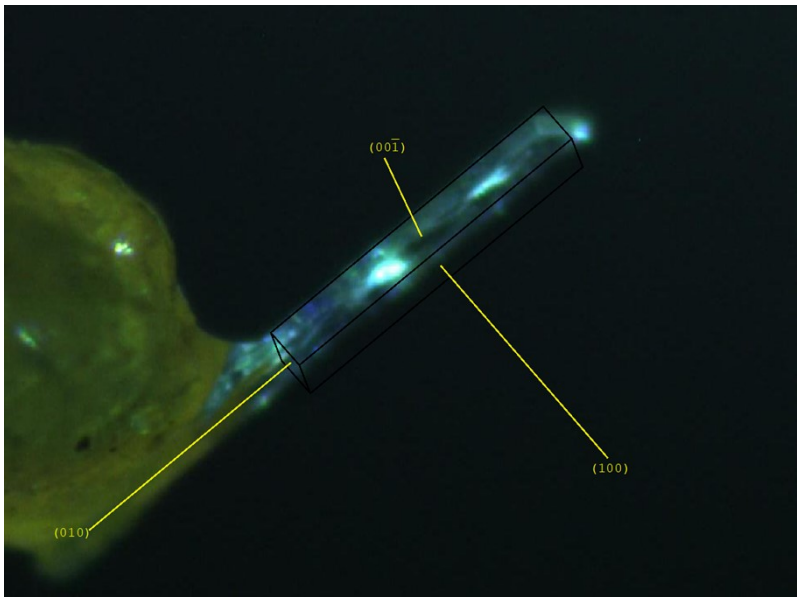


Figure S3. Face indexing image of crystal **BN.**

Crystal Packing Image.

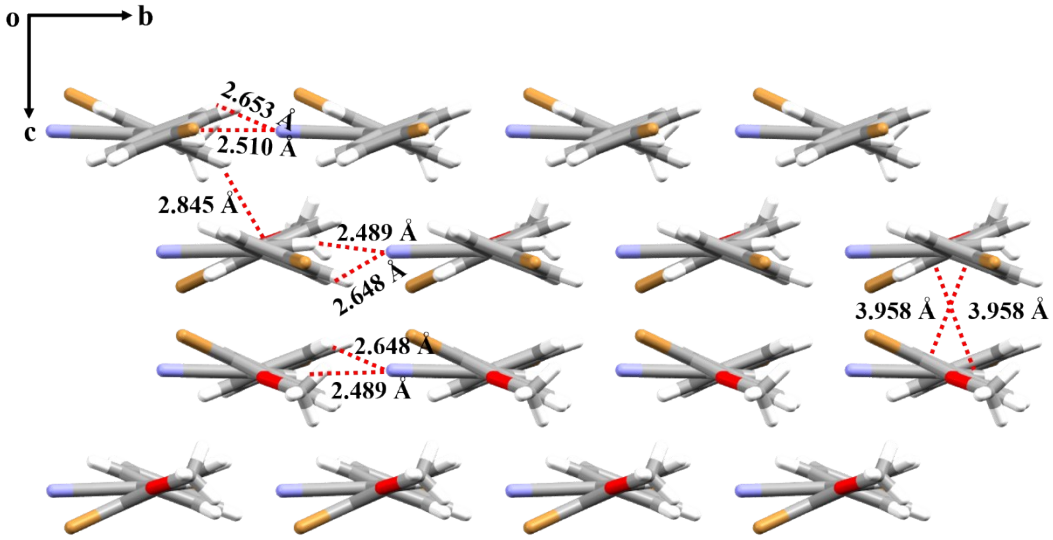


Figure S4. BN crystal packing viewed along *a*-axis.

Energy Framework Calculations.

The energy framework calculations[2,3] relating to intermolecular interactions of crystal **BN** were performed using the software suite Crystal-Explorer based on B3LYP/6-31G(d,p) molecular wavefunctions calculated using the CIF files. For calculations, the hydrogen atoms were normalized to standard neutron diffraction values. The energy frameworks constructed were based on the crystal symmetry and total interaction energy components which included electrostatic, polarization, dispersion, and exchange repulsion components scaled by 1.057, 0.740, 0.871, and 0.618, respectively. The interaction energies below 5 kJ.mol^{-1} are omitted for qclarity and the cylinder thickness is proportional to the intermolecular interaction energies along the parallel vector passing through the cylinder.

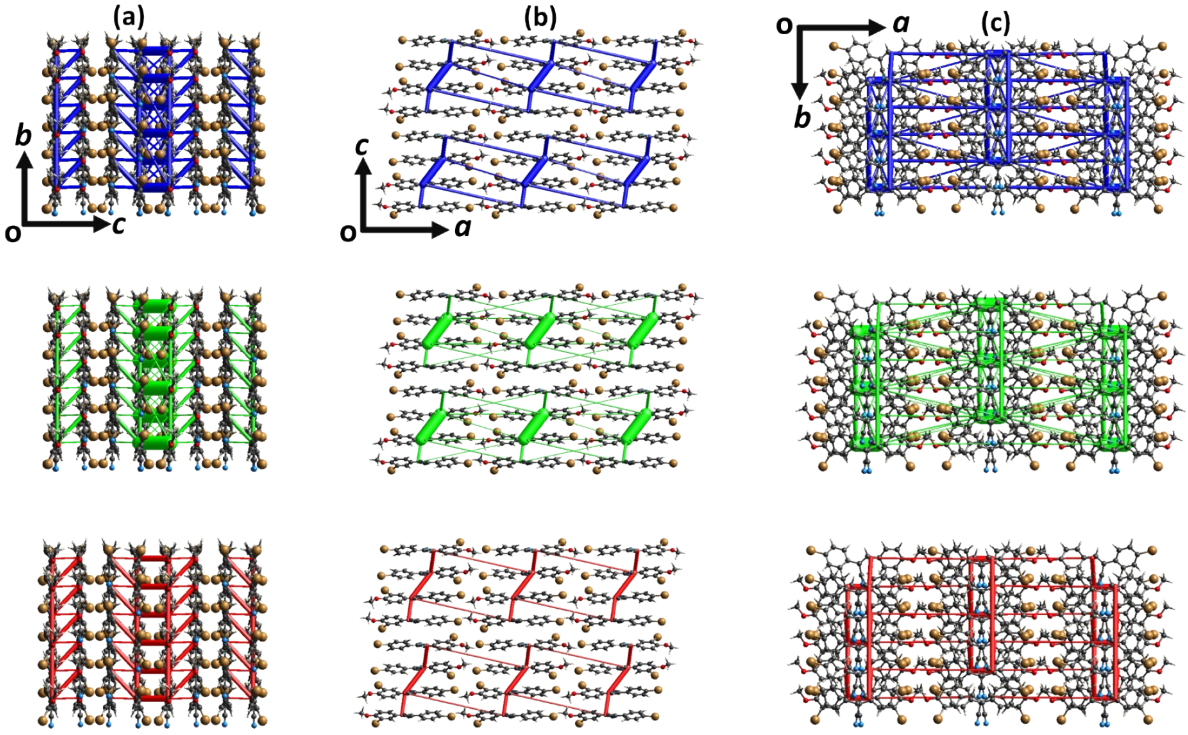
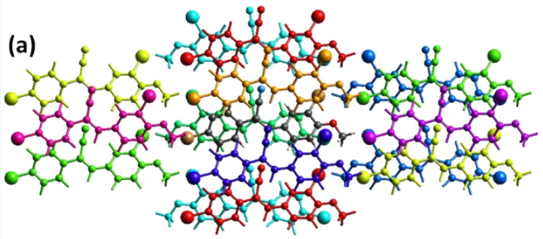


Figure S5. Visualization of energy frameworks showing total interaction energy (top, blue), dispersion (middle, green), and electrostatic (below, red) components crystal **BN**, in the (a) (100), (b) (010) and (c) (001) faces, respectively. The energy threshold is 5 kJ.mol^{-1}.

(a)



(b) Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	2	x, y, z	6.81	B3LYP/DGDZVP	-27.0	-5.8	-25.3	37.8	-31.4
	1	-	5.17	B3LYP/DGDZVP	0.0	0.0	0.0	0.0	0.0
	2	x+1/2, y+1/2, z	15.52	B3LYP/DGDZVP	0.6	-0.7	-6.0	0.0	-5.1
	2	x+1/2, y+1/2, z	15.52	B3LYP/DGDZVP	7.2	-0.7	-10.2	0.0	-1.7
	1	-x, y, -z	3.39	B3LYP/DGDZVP	-35.4	-3.2	-103.4	113.9	-59.4
	2	-x, y, -z	7.61	B3LYP/DGDZVP	-7.9	-1.3	-12.1	10.8	-13.2
	2	-x+1/2, y+1/2, -z	14.49	B3LYP/DGDZVP	-6.9	-0.6	-6.0	0.0	-12.9
	1	-	5.30	B3LYP/DGDZVP	-27.0	-5.8	-25.3	37.8	-31.4
	1	-	16.08	B3LYP/DGDZVP	0.9	-0.7	-6.0	0.0	-4.8
	1	-	15.21	B3LYP/DGDZVP	-10.9	-0.7	-10.2	0.0	-20.9

Scale factors for benchmarked energy models
See Mackenzie et al. IUCrJ (2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Table S2. (a) Molecular structure pairs and (b) the interaction energies (kJ.mol^{-1}) obtained from energy frameworks calculation for crystal **BN**. Scale factors are in the lower table.

Photomechanical Bending Images of BN Crystal.

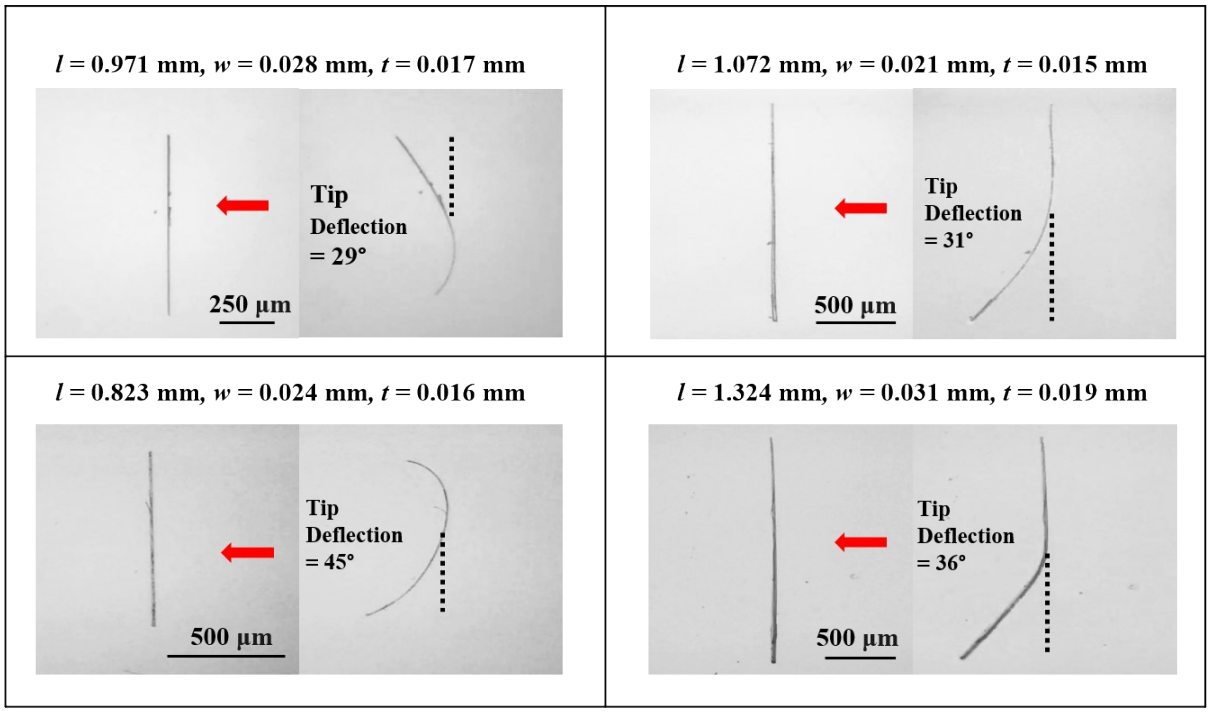


Figure S6. Photomechanical bending images of a set of different dimension crystals of **BN**.

Red arrows denote the direction of the LED source.

Powder X-Ray Diffraction

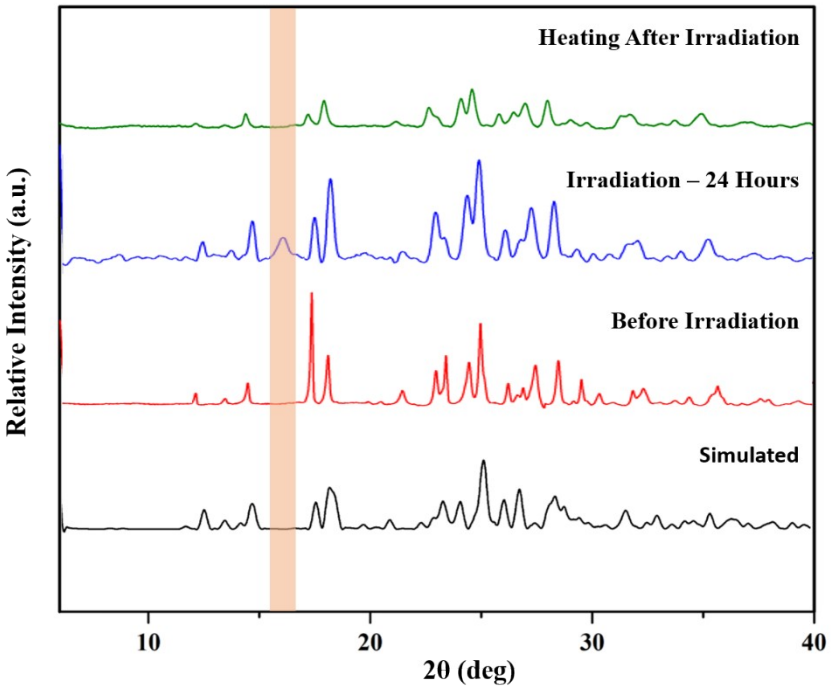


Figure S7. Comparative PXRD profile of crystal **BN** depicting simulated pattern, pristine sample, photoirradiated sample and photoirradiated sample followed by heating.

Crystallographic Information Table.

Table S3: Crystallographic Information Table.

Compound	**Crystal BN**
Formula	$C_{16}H_{11}Br_2NO$
Molecular weight	393.08
T/K	150
Crystal system	monoclinic
Space group	*C*2
a/Å	30.2798(12)
b/Å	6.8134(3)
c/Å	14.1349(6)
α/°	90
β/°	93.921(2)

γ/°	90
Volume/Å^3	2909.3(2)
Z	8
ρ, Mg.cm^{-3}	1.795
μ /mm^{-1}	5.566
Reflections collected	28451
Independent Reflections	6463
R_{int}	0.0584
GOF	1.107
Final R[I>2σ]	0.0485
wR_2	0.1320
CCDC Number	2339475

References.

1. K. Rorig, *J. Am. Chem. Soc.*, 1953, **75**, 5381-5383.
2. M. J. Turner, S. P. Thomas, M. W. Shi, D. Jayatilaka and M. A. Spackman, *Chem. Commun.*, 2015, **51**, 3735-3738.
3. P. R. Spackman, M. J. Turner, J. J. McKinnon, S. K. Wolff, D. J. Grimwood, D. Jayatilaka and M. A. Spackman, *J. Appl. Crystallogr.*, 2021, **54**, 1006-1011.