SUPPORTING INFORMATION

Structure Property Correlation of a Series of Halogenated Schiff Base Crystals and Understanding Molecular Basis Through Nanoindentation

Ragaverthini Chinnasamy,[a] Amutha Arul,[a] Ammar AlMousa,[c] Mangalampalli S. R. N. Kiran,[b] Priyadip Das,[a] Almaz S. Jalilov,[c] Abdul Malik P. Peedikakkal*[c] and Soumyajit Ghosh*[a]

[a]*Department of Chemistry, SRM Institute of Science and Technology, Chennai 603 203, India*

[b]*Nanomechanics Laboratory Department of Physics and Nanotechnology, SRM Institute of Science and Technology, Chennai 603 203, India*

[a]*Department of Chemistry, SRM Institute of Science and Technology, Chennai 603 203, India,* E-mail: soumyajitghosh89@gmail.com

[c]*Department of Chemistry, King Fahd University of Petroleum and Minerals, P.O. Box 5048, Dhahran 31261, Saudi Arabia,* malikchem@gmail.com

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1. Materials and synthesis

Experimental section

Materials. All the compounds Trans-4-methoxy cinnamaldehyde, 2,3-dichloro benzaldehyde, 3,5-di-tertiary-butyl salicylaldehyde, 4-bromoanilne, 4-chloroaniline, 4-fluoro-3-nitro aniline, 3,4-dichloroaniline, 2,5-dichloroanilne were purchased from Sigma-Aldrich. Commercially available solvents were used as received without further purification.

Single Crystal Preparation

The single crystals were grown in a series of solvents such as ethanol, acetone, toluene, methanol, acetonitrile etc., at ambient conditions. Crystals were synthesized by adding one equivalent each of the respective benzaldeydes (Trans-4-methoxy cinnamaldehyde for **1** to **3b**, 2,3 Dichlorobenzaldehyde for **4** and 3,5-di-tertiary-butyl salicylaldehyde for **5**) and halogen substituted aniline in hot ethanol followed by slow evaporation of the solution at ambient conditions. Long, good diffraction quality crystals were obtained after 4-5 days**.**

Powder X-Ray Diffraction (PXRD).

The PXRD patterns were collected on a Rigaku SmartLab with a Cu Kα radiation (1.540 Å). The tube voltage and amperage were set at 40 kV and 50 mA respectively. Each sample was scanned between 5 and 50° 2θ with a step size of 0.02° (Figure S2-S6). The instrument was previously calibrated using a silicon standard.

X-ray Crystallographic Analysis

Intensity data for **1** and **2a** were collected on a Bruker AXS D8 Venture diffractometer using MoKα (λ = 0.71073 Å) radiation generated by Iμs microfocus tube. Data were recorded with a Bruker AXS PHOTON II CPAD detector. The data collections were performed at 298 K using ω-and φ-scans. The data were processed using APEX3 Crystal Structure Analysis Package (Bruker AXS). Data collection: APEX3,[1] cell refinement: SAINT,[2] data reduction:

SAINT,[2] absorption correction: SADABS,[3] structure solution: direct methods (SHELXT-2014)[4] and structure refinement: full-matrix least-squares method on F^2 (SHELXT-2014)[5] using SHELXT as the graphical user interface,[6] molecular graphics: program XP (part of the SHELXT 6.14 program library).[7] The crystal data as well as details of data collection and refinement of **1-5** are summarized in Table S1.

Table S1. Crystallographic Information Table

Compounds	**1**	**2**	**3a**	**3b**	**4**	**5**
Formula	$C_{33}H_{29}Cl_{12}N_7O_2$	$C_{16}H_{14}BrNO$	$C_{16}H_{13}FN_2O_3$	$C_{16}H_{13}FN_2O_3$	$C_{13}H_7Cl_4N$	$C_{20}H_{22}Cl_2NO$
Formula weight	542.47	316.19	311.30	311.30	319.00	363.28
T/K	298(2)	298(2)	296(2) K	296(2) K	296(2) K	296(2) K
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*P*c	*Pna*2$_1$	*P*-1	*Pc*	$P2_12_12_1$	*P*-1
a/Å	31.1422 (2)	6.272(5)	7.7591(4) Å	3.9667(6) Å	4.2341(3) Å	6.1429(11) Å
b/Å	7.1528(4)	7.154(5)	9.7069(6) Å	24.324(4) Å	6.3411(5) Å	10.429(2) Å
c/Å	6.2409(5)	31.32(2)	11.0077(6) Å	29.265(4) Å	48.203(4) Å	16.759(4) Å
α/°	90°	90°	102.169(2)°	90°	90°	104.566(9)°
β/°	90.010(3)°	90°	107.957(2)°	90°	90°	94.636(9)°
γ/°	90°	90°	104.897(2)°	90°	90°	100.047(8)°
Volume/Å ^{3}	1390.19(2)	1405.2(2)	723.24(7)	2823.6(7)	1294.20(17)	1014.5(3)
Z	2	4	2	8	4	2
ρ, Mg.cm^{-3}	1.296	1.495	1.429	1.337	1.637	1.189
μ /mm^{-1}	0.264	2.196	0.106	0.099	0.892	0.326
Reflections collected	12569	14350	21941	10390	9822	33850
Independent Reflections	3796	2006	3614	7419	3144	5022

R_{int}	0.0628	0.0475	0.0575	0.0705	0.0292	0.0488
GOF	0.869	0.895	0.982	1.011	0.840	1.098
Final R[I >2σ]	0.0479	0.0352	0.0525	0.0624	0.0422	0.0634
R_1/ wR_2	0.1314	0.1057	0.1301	0.0750	0.1261	0.1632
CCDC Number.	1905300	1905301	1905303	1905302	1905304	1905305

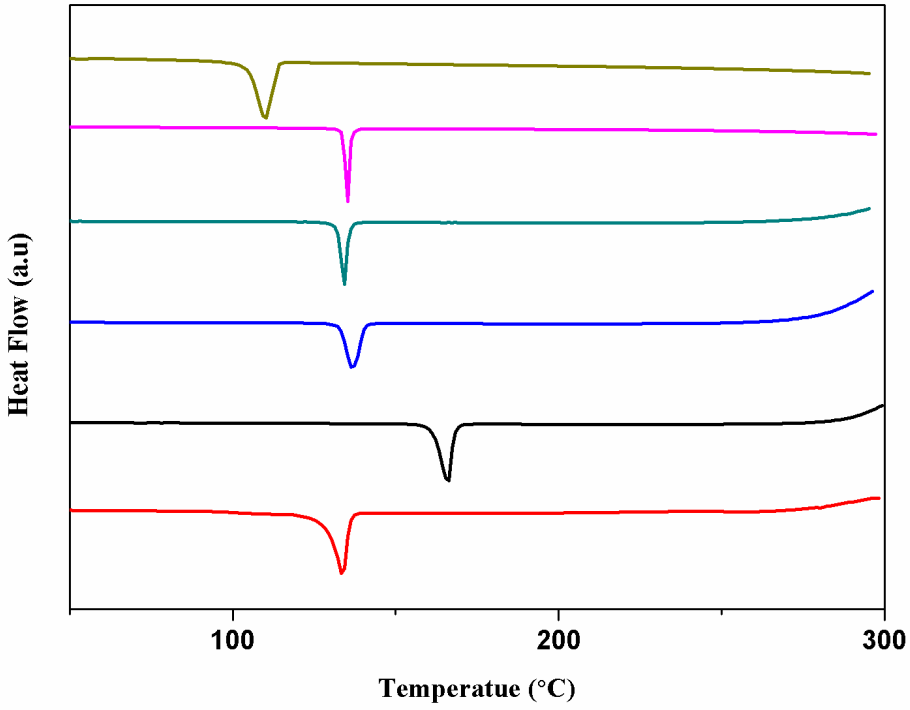
Table S2. Results from the recrystallization of Schiff base from one solvent or mixture of solvents

Compound	**Solvent**	**Observations**
Crystal 1	Ethanol	Block Shaped Crystal
	Methanol	Block Shaped Crystal
	Acetone	Powder
	Acetonitrile	Block Shaped Crystal
	Ethyl Acetate	Powder
	Toluene	Block Shaped Crystal
	DCM	Powder
	Chloroform	Powder
	1,4 Dioxane	Powder
	THF	Powder
	Hexane	Powder
Crystal 2	Ethanol	Block Shaped Crystal
	Methanol	Block Shaped Crystal
	Acetone	Powder
	Acetonitrile	Block Shaped Crystal
	Ethyl Acetate	Powder
	Toluene	Block Shaped Crystal
	DCM	Powder
	Chloroform	Powder
	1,4 Dioxane	Powder
	THF	Powder
	Hexane	Powder
Crystal3a	Ethanol	Plate Shape
	Methanol	Plate Shape
	Acetone	Powder
	Acetonitrile	Plate Shape
	Ethyl Acetate	Powder
	Toluene	Plate Shape
	DCM	Powder
	Chloroform	Powder

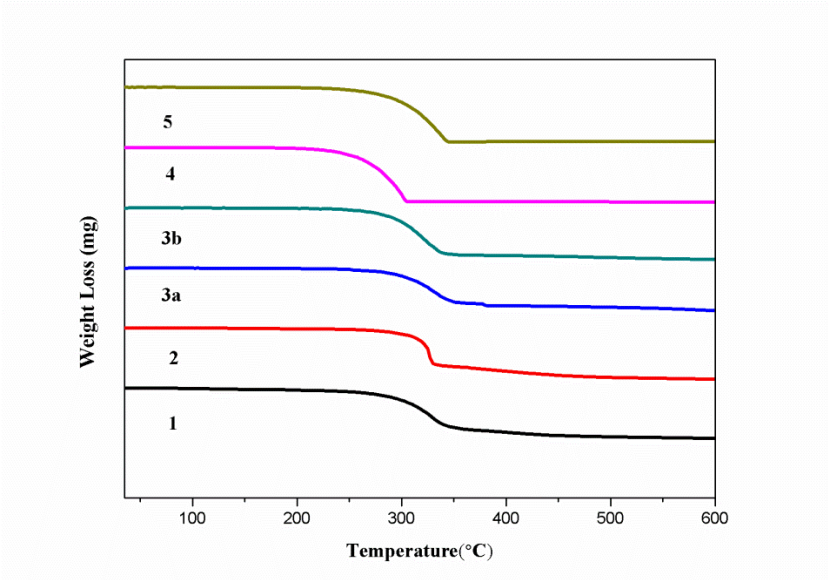
	1,4 Dioxane	Powder
	THF	Powder
	Hexane	Powder
Crystal 3b	Ethanol	Fine needles, block shape
	Methanol	Fine needles, block shape
	Acetone	Powder
	Acetonitrile	Powder
	Ethyl Acetate	Powder
	Toluene	Block Shape
	DCM	Powder
	Chloroform	Powder
Crystal 4	Ethanol	Fine needles
	Methanol	Fine needles
	Acetone	Powder
	Acetonitrile	Plate shape
	Ethyl Acetate	Powder
	Toluene	Fine needles
	DCM	Powder
	Chloroform	Powder
	1,4 Dioxane	Powder
	Hexane	Powder
Crystal 5	Ethanol	Powder
	Methanol	Fine needles
	Acetone	Powder
	Acetonitrile	Powder
	Ethyl Acetate	Powder
	Toluene	Powder
	DCM	Powder
	Chloroform	Powder
	1,4 Dioxane	Powder
	THF	Powder
	Hexane	Powder

Thermal Properties:

A detailed DSC and TGA experiments were carried out of all the above crystals to study their thermal behaviour with respect to its starting materials. Crystal **1** shows a sharp single melting endotherm at 134.23°C and crystal **2** shows at 165.23°C. There are two polymorphs of the same compound **3a** and **3b** where block crystal (**3a**) showing endotherm at 137.23°C whereas needle shaped crystal (**3b**) showing endotherm at 134.23°C. This indicated that the crystal is dimorphic. The needle shaped crystals **4** is showing single melting endotherm at 135.23°C and **5** is showing at 110.23°C. The melting transition temperature of all the crystals were different from either of the individual components confirming the formation of new phase. The thermogram shows the stability of the crystal and proves that there is no weight loss beyond the melting.



(a)



(b)

Figure S1. (a) The endotherm of the DSC corresponds to the melting of the respective phases. (b) TGA corresponds to the decomposition of the respective crystalline phases.

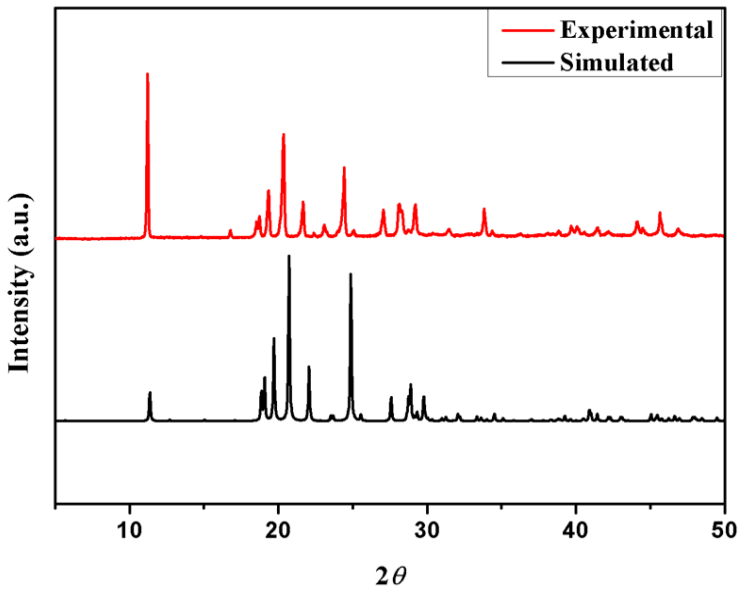


Figure S2. PXRD comparison of simulated pattern and experimental pattern for Crystal **1**.

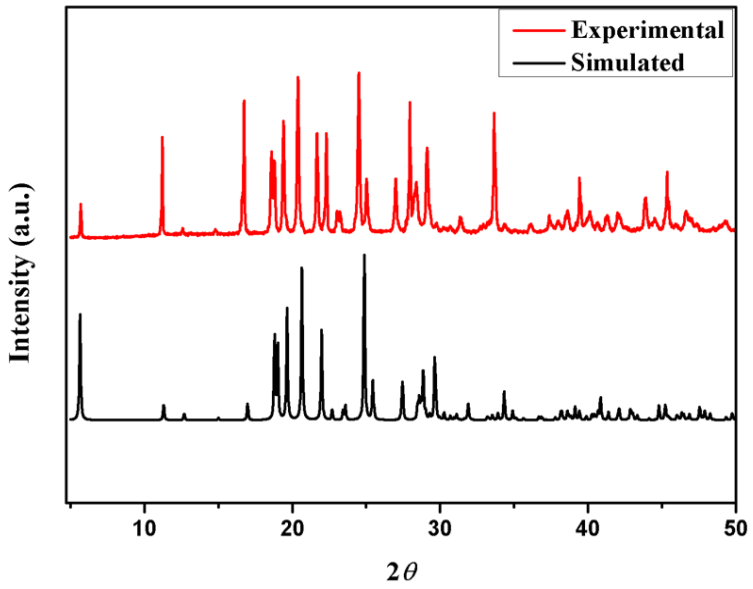


Figure S3. PXRD comparison of simulated pattern and experimental pattern for crystal **2**.

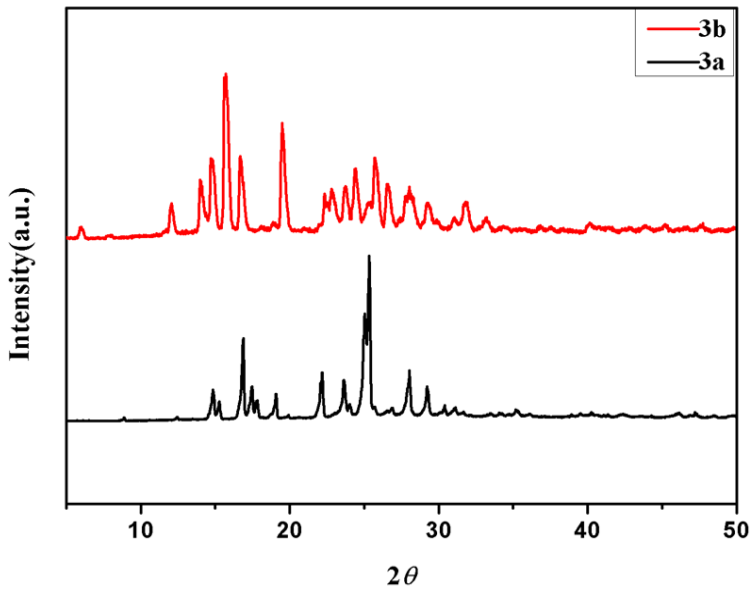


Figure S4. Experimental PXRD comparison of crystals **3a** and **3b**.

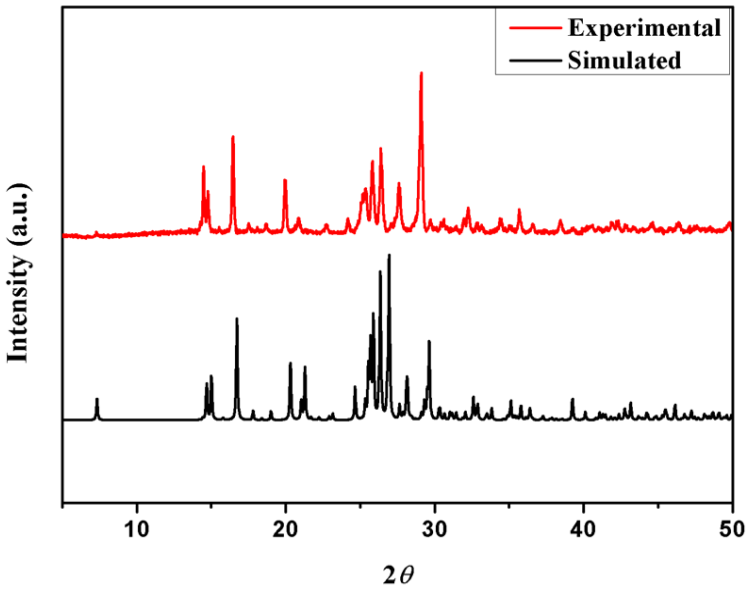


Figure S5. PXRD comparison of simulated pattern and experimental pattern for crystal **4**.

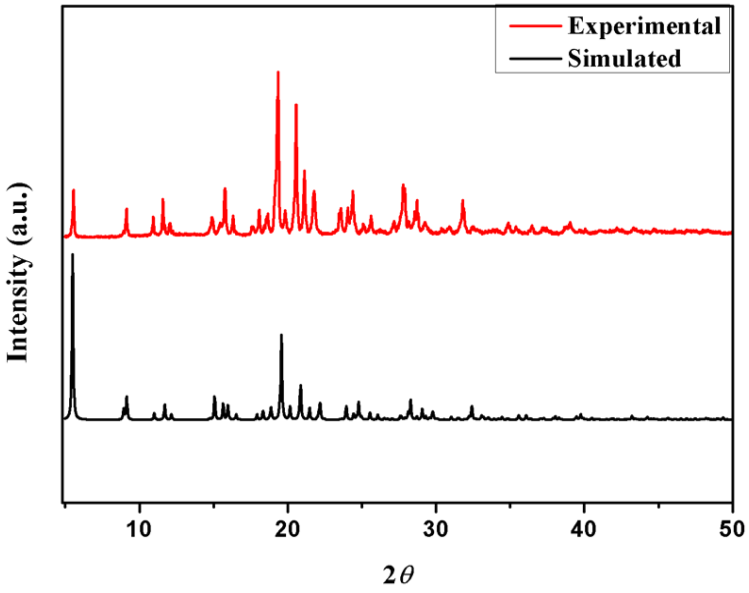


Figure S6. PXRD comparison of simulated pattern and experimental pattern for crystal **5**.

Photoluminescence studies

Room temperature solid-state photoluminescence (PL) measurements were performed on crystalline powder of **4-5** using a HORIBA JobinYvon Nano Log spectrofluorometer using a 450-W Xenon lamp at 350 nm excitation wavelength.

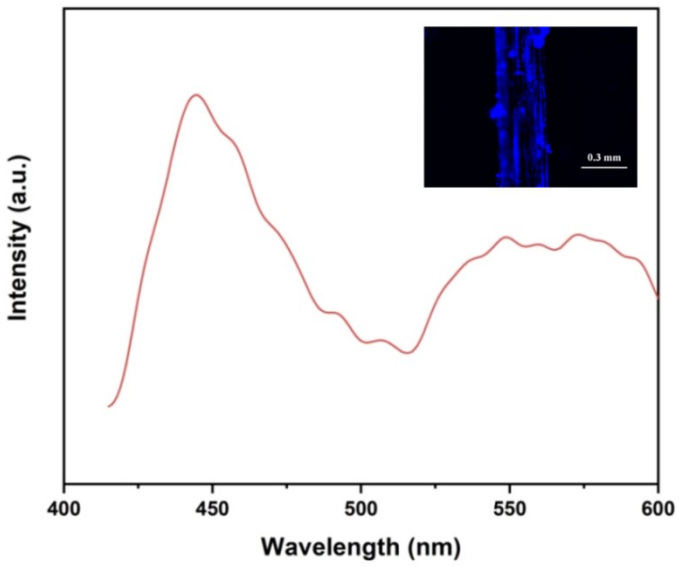


Figure S7. Solid-state luminescent emission spectra of compound **4** with fluorescent crystal image (λ_{ex} = 350 nm) at room temperature (inset). Scale bar is 0.3mm

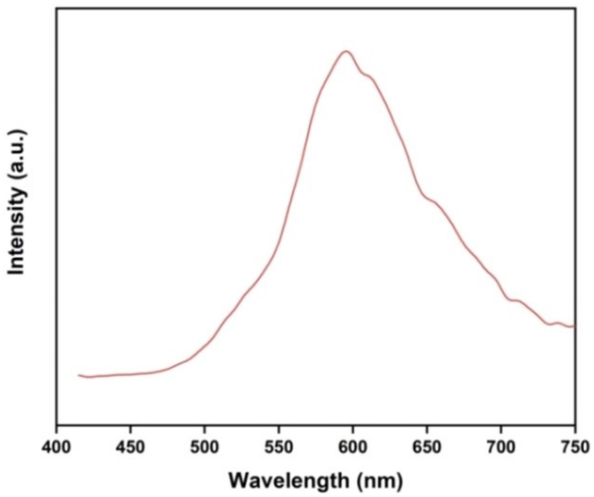


Figure S8. Solid-state luminescent emission spectra of compound **5** (λ_{ex} = 350 nm) at room temperature.

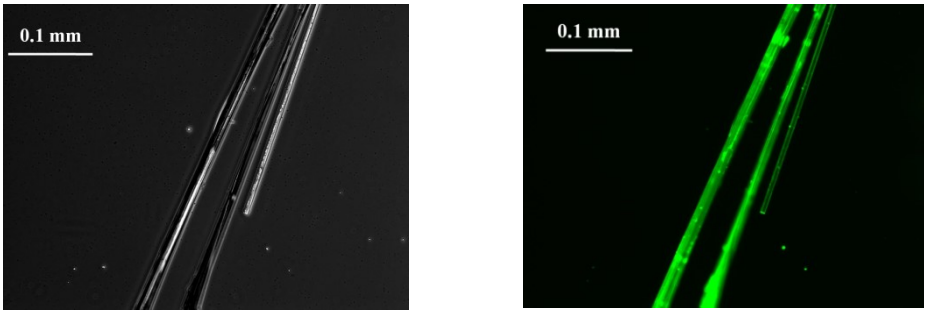


Figure S9. Photographs showing the fluorescence of crystal **3b** irradiation at 410 nm with a scale bar of 0.1mm

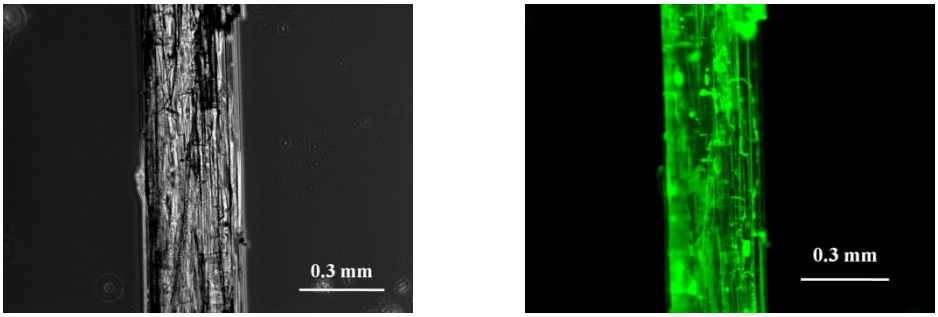


Figure S10. Photographs showing the fluorescence of crystal **4** irradiation at 410 nm with scale bar of 0.3 mm

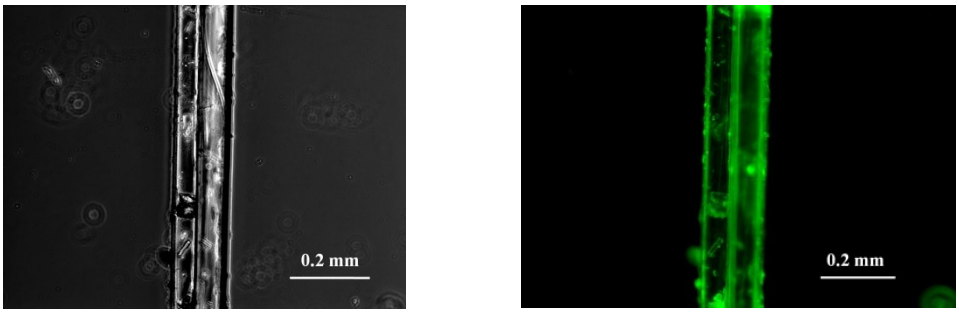
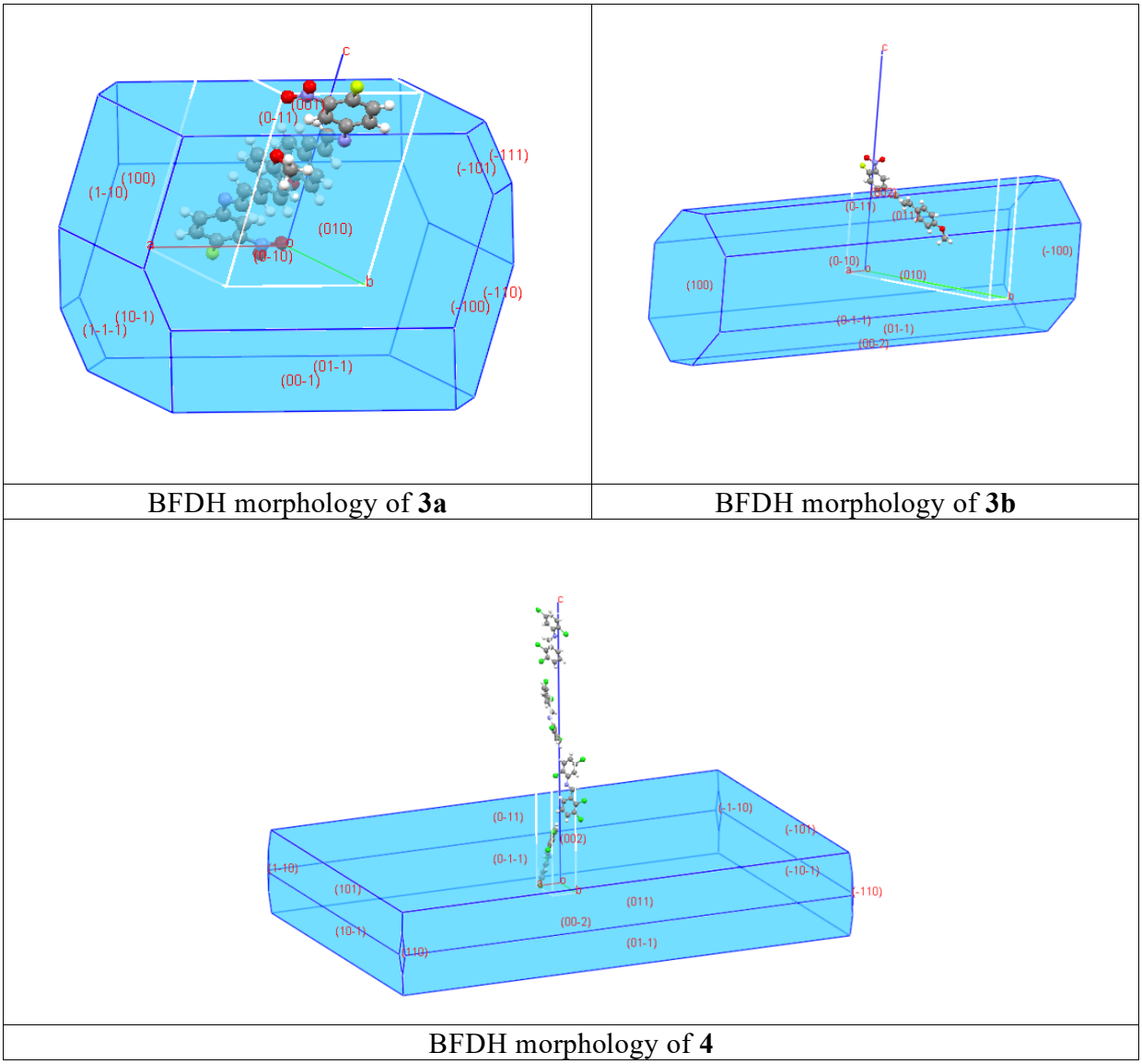


Figure S11. Photographs showing the fluorescence of crystal **5** irradiation at 410 nm with a scale bar of 0.3 mm



BFDH morphology of **3a**	BFDH morphology of **3b**

BFDH morphology of **4**

Figure S12. BFDH morphology of crystals **3a**, **3b** and **4**.

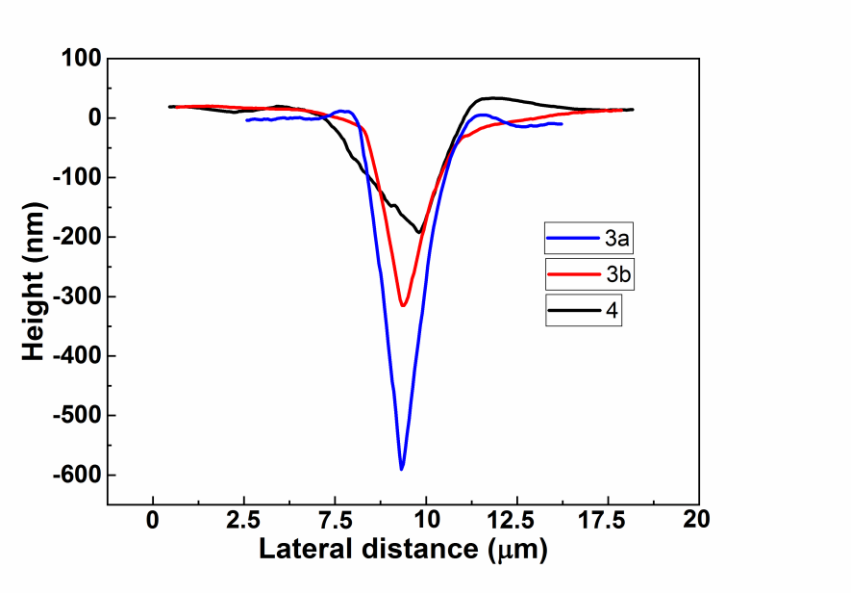
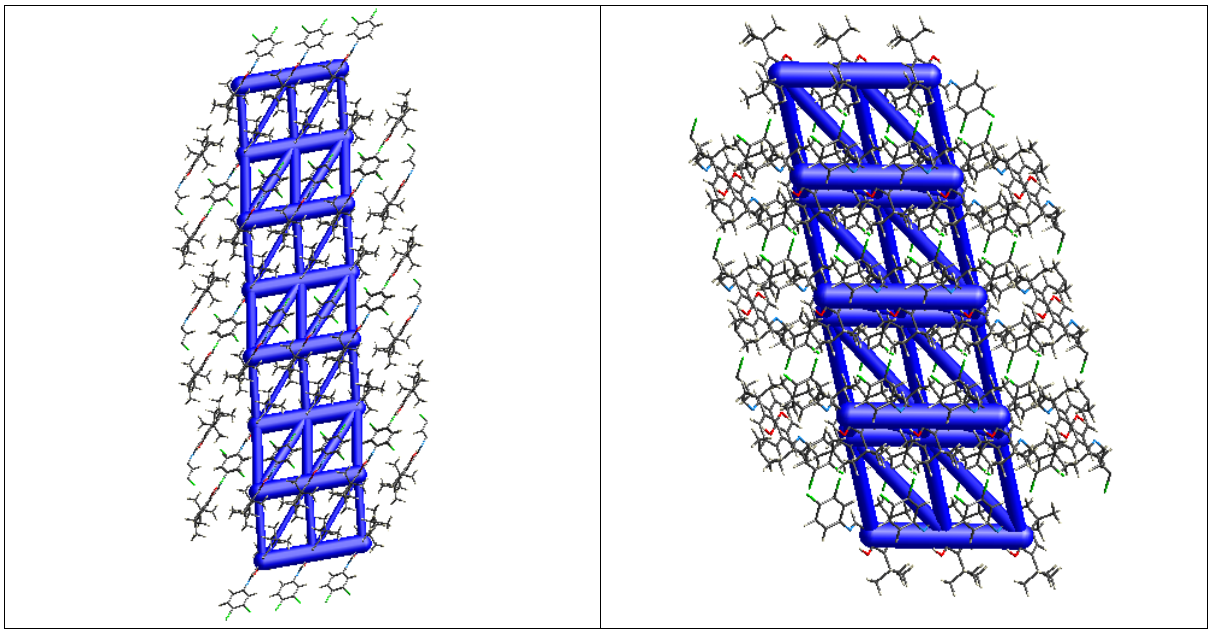


Figure S13. Height profiles of the residual indent images for crystals **3a**, **3b** and **4** immediately after unloading.



Along ***b*** axis	Along ***c*** axis

Figure S14. Total energy of crystal **5** along b and c axis indicates interlocked structure.

References:

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