# Supplementary Information

## Designing Multifunctional Organic Thermochromic Ferroelectric Materials: Remarkable Melt-Cool Large Thermal Hysteresis of Reversible Single Crystal to Single Crystal Transformation

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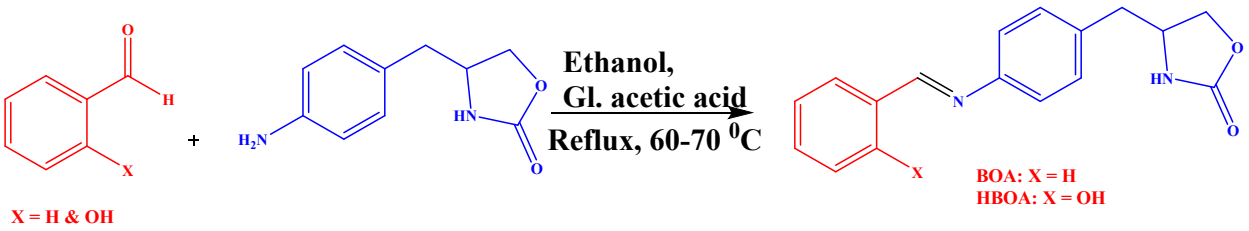


S1: Scheme Synthetic route for BOA and HBOA

**Fourier Transform Infrared Analysis**

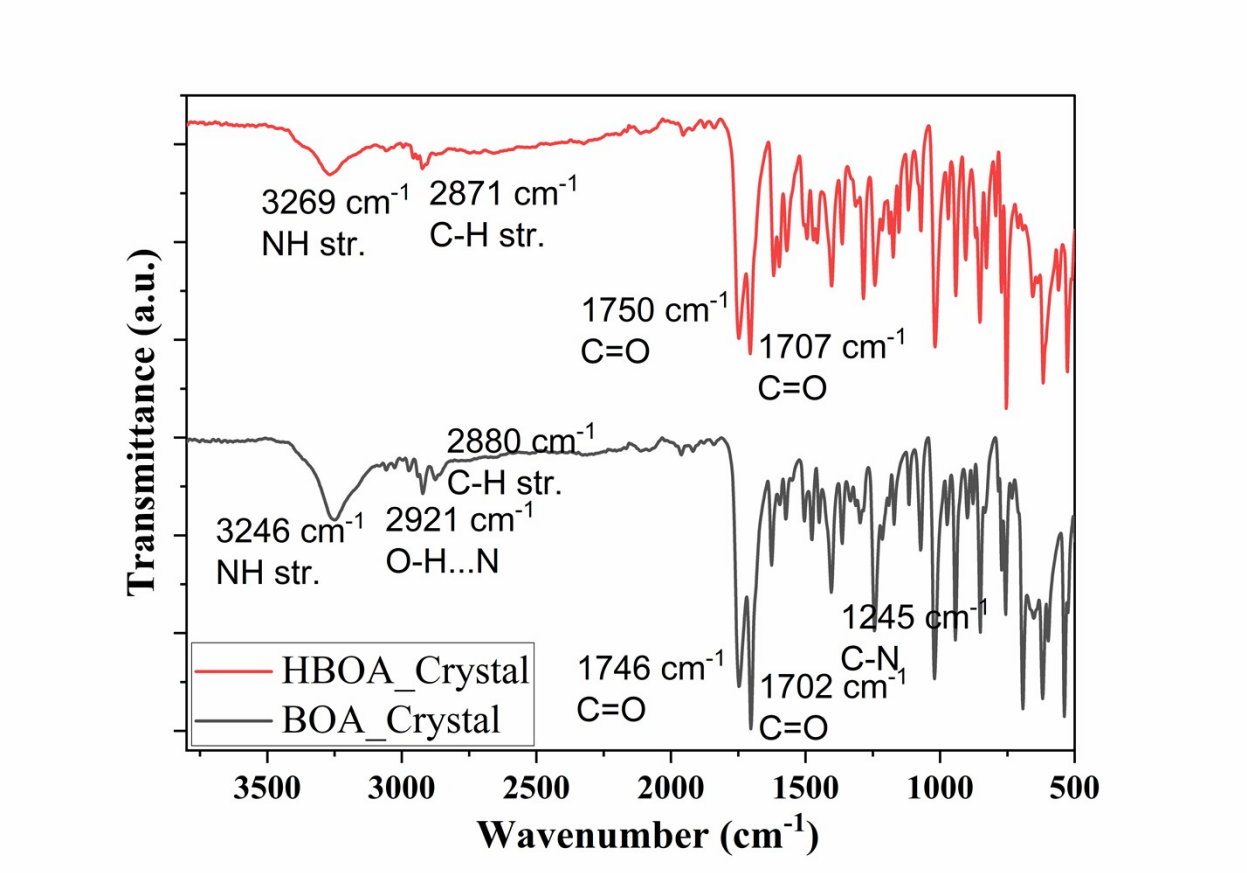


**Figure S2.** The FTIR spectrum of BOA and HBOA show the stretching bands of **-C=O-** appeared at 1746 $cm^{-1}$ and 1750 $cm^{-1}$ respectively. The NH stretching band observed at 3246 $cm^{-1}$and 3269 $cm^{-1}$ for BOA and HBOA respectively. The hydroxyl band (intramolecular hydrogen bond) was observed at 2921 $cm^{-1}$.

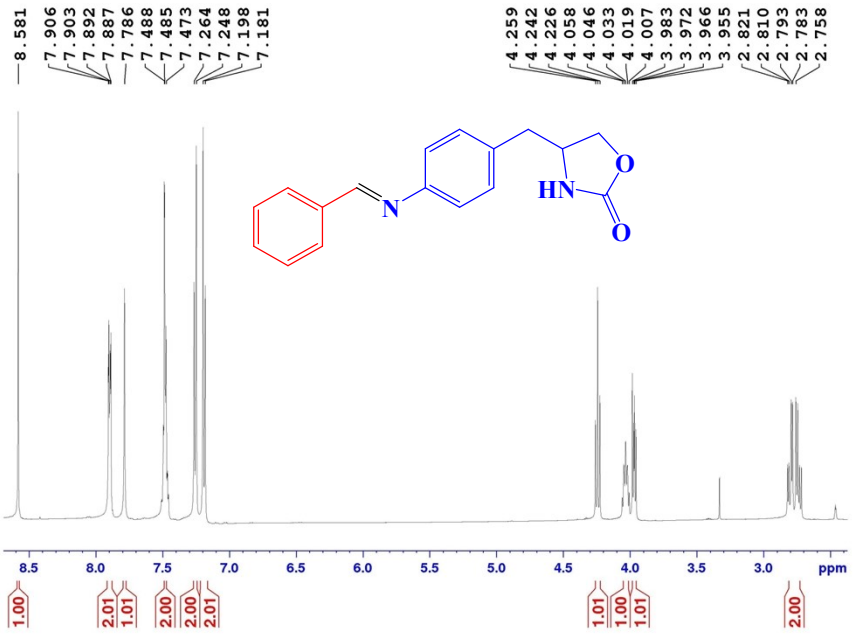


**Figure S3.** $^{1}$H NMR spectrum of BOA in $CDCl_3$.

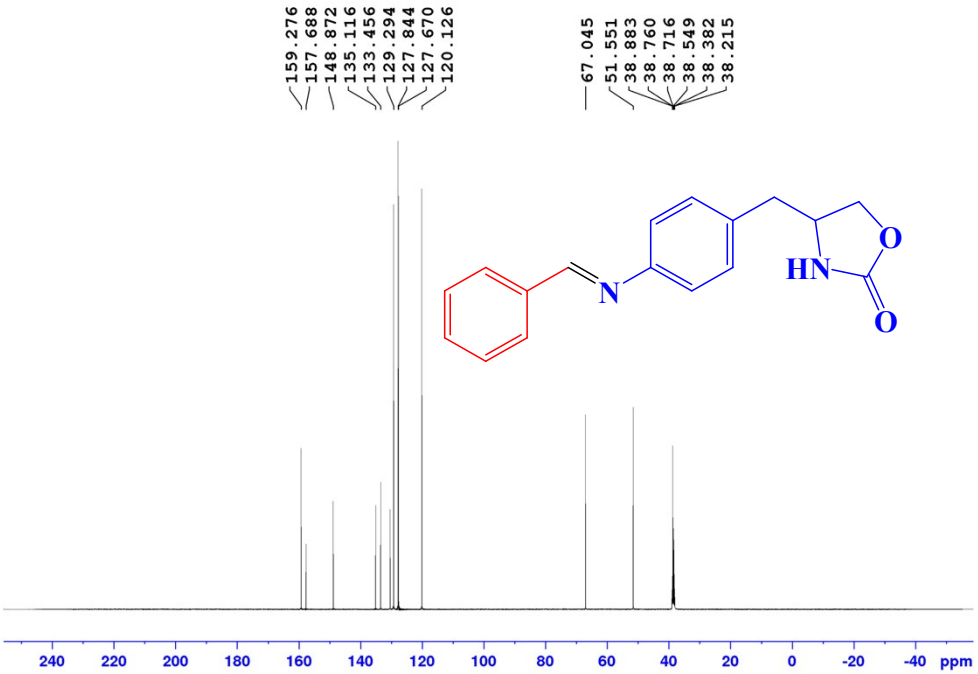


**Figure S4.** $^{13}$C NMR spectrum of BOA in $CDCl_3$.

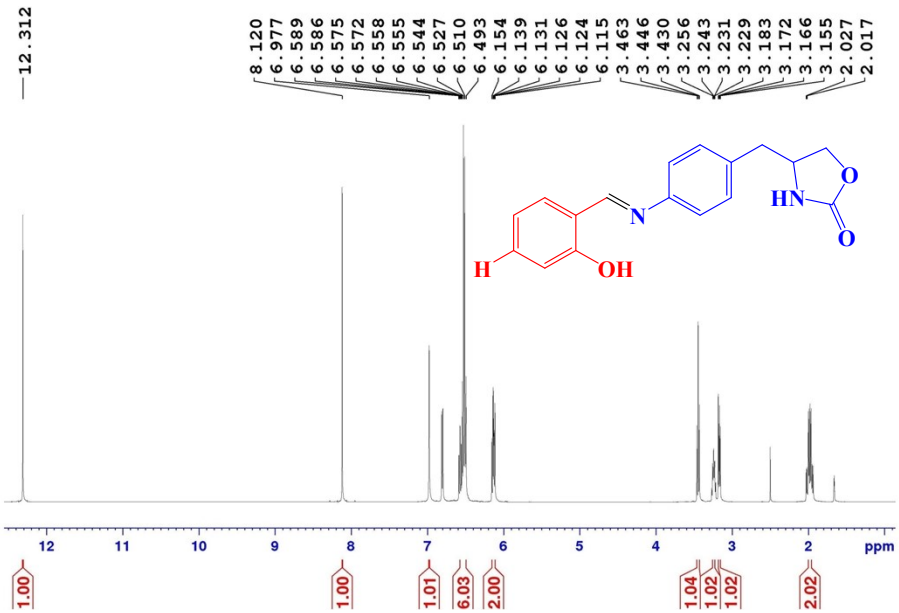


**Figure S5.** $^{1}H$ NMR spectrum of HBOA in $CDCl_3$.

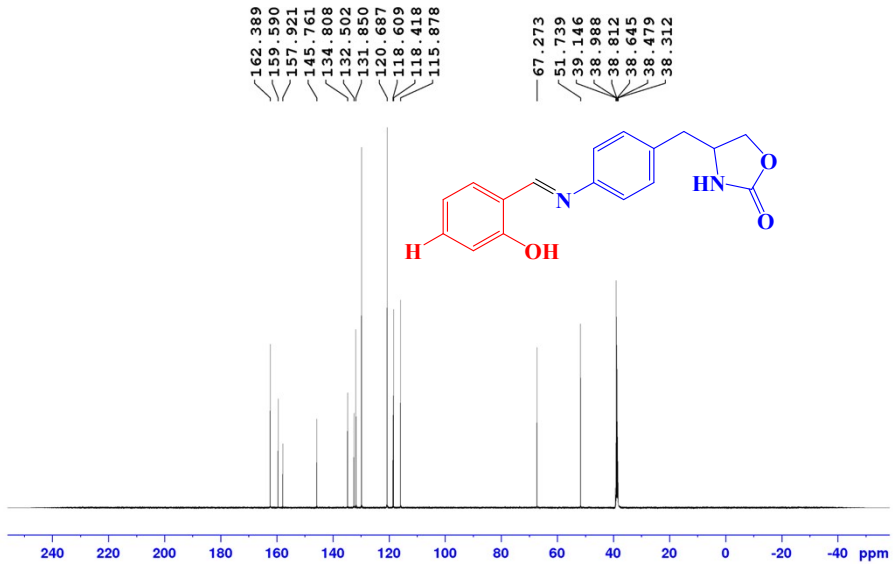


**Figure S6.** $^{13}C$ NMR spectrum of HBOA in $CDCl_3$.

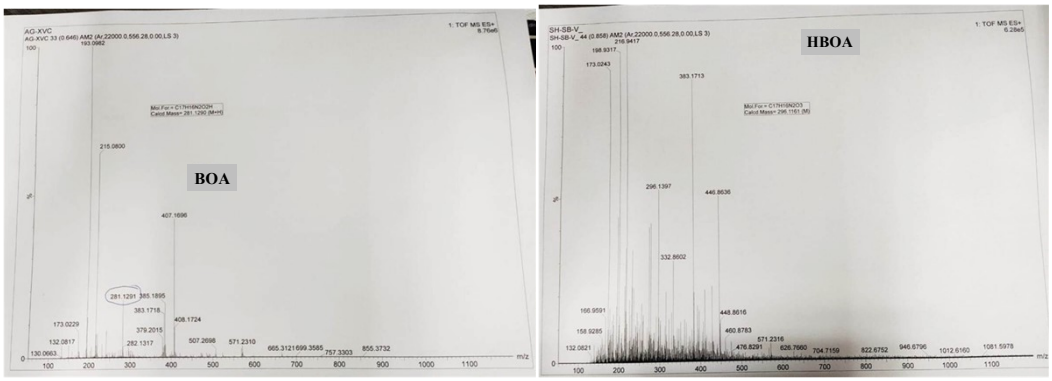


**Figure S7.** Mass spectrum of BOA and HBOA.

**Table S1.** Variable temperature crystal data and structure refinement of **BOA**.

| Compound | **BOA_100K** | **BOA_293K** | **BOA_368K** |
|---|---|---|---|
| CCDC no. | 1983772 | 1983771 | 2026778 |
| Chemical formula | $C_{17}H_{16}N_2O_2$ | $C_{17}H_{16}N_2O_2$ | $C_{17}H_{16}N_2O_2$ |
| Formula weight | 280.3 | 280.3 | 280.3 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1$ | $P2_1$ | $P2_1$ |
| *a* ($A^0$) | 5.9009(1) | 5.9424(3) | 5.930(2) |
| *b* ($A^0$) | 8.4145(2) | 8.5540(4) | 8.588(2) |
| *c* ($A^0$) | 14.2428(3) | 14.3274(7) | 14.312(3) |
| *α* ($^0$) | 90.000 | 90.000 | 90.00(3) |
| *β* ($^0$) | 98.443(2) | 98.358(4) | 98.21(3) |
| *γ* ($^0$) | 90.000 | 90.000 | 90.00(3) |
| *V*($A^{03}$) | 699.54(2) | 720.55(4) | 721.5(3) |
| *Z* | 2 | 2 | 2 |
| *T* (K) | 100.00(2) | 293(2) | 368(2)K |
| $D_{calc}$(g $cm^{-3}$) | 1.33 | 1.29 | 0.64 |
| Abs. coefficient ($mm^{-1}$) | 0.089 | 0.086 | 0.043 |
| *F* (000) | 296.0 | 296.0 | 147.0 |
| *ϑ* Range for data collection ($^\circ$) | 3.5-27.5 | 3.5-27.5 | 1.4-30.6 |
| Limiting indices | -7 ≤ h ≤ 7, -10 ≤ k ≤ 10, -18 ≤ l ≤ 18 | -7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18 | -8 ≤ h ≤ 4, -11 ≤ k ≤ 12, -20 ≤ l ≤ 20 |
| Reflections collected | 10790 | 10688 | 16945 |
| Unique reflections ($R_{int}$) | 3211 (0.033) | 3302 (0.030) | 4391 (0.043) |
| Completeness of *ϑ* | 27.42 (99.77%) | 27.42 (99.77%) | 27.42 (99.77%) |
| Data/restraints/parameters | 3211/1/202 | 10688/1/202 | 4391/1/204 |
| GOF | 1.040 | 1.046 | 0.926 |
| Final R indices [$I>2\sigma(I)$] | $R_1$= 0.037, w$R_2$ = 0.083 | $R_1$= 0.050, w$R_2$ = 0.117 | $R_1$= 0.049, w$R_2$ = 0.105 |

| | | | |
|---|---|---|---|
| *R* indices (all data) | $R_1$= 0.040, w$R_2$ = 0.086 | $R_1$= 0.063, w$R_2$ = 0.128 | $R_1$= 0.152, w$R_2$ = 0.142 |
| $\Delta\rho_{max}$(e. $A^{0\,-3}$) | 0.199 | 0.349 | 0.158 |
| $\Delta\rho_{min}$(e. $A^{0\,-3}$) | -0.207 | -0.162 | -0.133 |
| Flack Parameters | 1.2(6) | 1.1(7) | 0.2(8) |

**Table S2.** Variable temperature crystal data and structure refinement of **HBOA**.

| Compound | **HBOA_100K** | **HBOA_293K** | **HBOA_390K** |
|---|---|---|---|
| CCDC no. | 1972047 | 1972046 | 2305762 |
| Chemical formula | $C_{17}H_{16}N_2O_3$ | $C_{17}H_{16}N_2O_3$ | $C_{17}H_{16}N_2O_3$ |
| Formula weight | 296.3 | 296.3 | 296.3 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1$ | $P2_1$ | $P2_1$ |
| *a* ($A^0$) | 5.7166(1) | 5.7695(2) | 5.7876(7) |
| *b* ($A^0$) | 8.7186(2) | 8.7640(3) | 8.8409(12) |
| *c* ($A^0$) | 14.3362(3) | 14.5821(15) | 14.6760(2) |
| $\alpha$ ($^0$) | 90.000 | 90.000 | 90.000 |
| $\beta$ ($^0$) | 97.672(2) | 98.449(3) | 98.218(3) |
| $\gamma$ ($^0$) | 90.000 | 90.000 | 90.000 |
| *V*($A^{03}$) | 708.13(2) | 729.33(3) | 738.22(4) |
| *Z* | 2 | 2 | 2 |
| *T* (K) | 99.99(10) | 293(2) | 390(2) |
| $D_{calc}$(g $cm^{-3}$) | 1.39 | 1.35 | 1.32 |
| Abs. coefficient ($mm^{-1}$) | 0.097 | 0.094 | 0.092 |
| *F* (000) | 312.0 | 312.0 | 312.0 |
| $\vartheta$ Range for data collection ($^\circ$) | 3.6-27.5 | 2.6-27.5 | 1.4-30.8 |
| Limiting indices | -7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18 | -7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18 | -8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -20 ≤ l ≤ 20 |
| Reflections collected | 10961 | 11140 | 9732 |
| Unique reflections ($R_{int}$) | 3129 (0.029) | 3340 (0.027) | 4383 (0.053) |
| Completeness of $\vartheta$ | 27.42 (99.77%) | 27.42 (99.72%) | 27.42 (99.77%) |
| Data/restraints/parameters | 3129/1/207 | 3340/1/215 | 4383/1/212 |
| GOF | 1.037 | 1.056 | 0.887 |
| Final R indices [$I$>2σ($I$)] | $R_1$= 0.032, w$R_2$ = 0.074 | $R_1$= 0.041, w$R_2$ = 0.088 | $R_1$= 0.045, w$R_2$ = 0.078 |
| *R* indices (all data) | $R_1$= 0.033, w$R_2$ = 0.075 | $R_1$= 0.051, w$R_2$ = 0.098 | $R_1$= 0.174, w$R_2$ = 0.114 |
| $\Delta\rho_{max}$(e. $A^{0\,-3}$) | 0.185 | 0.100 | 0.108 |
| $\Delta\rho_{min}$(e. $A^{0\,-3}$) | -0.172 | -0.127 | -0.100 |
| Flack Parameters | 1.1(4) | -1.1(6) | -3.9(10) |

**Table S3.** Optical activity parameters of BOA

RK-XVI-1

[Data Information]
Creation Date 02-07-2021 11:25

[Measurement Information]
Instrument Name JASCO
Model Name P-2000
Serial No. A109661232
Polarizer Dichrom
Faraday Cell Flint Glass

Accessory PTC-262
Accessory S/N A021561481
Path Length 100 mm

Light Source Na
Monitor wavelength 589 nm
D.I.T. 5 sec
No. of cycle 5
Cycle interval 5 sec
Temp. Monitor Holder
Temp. Corr. Factor 0 at 20 C
Aperture(S) 3.0mm
Aperture(L) Auto
Mode Specific O.R.
Path Length 50 mm
Concentration 1 w/v%
Water content of sample 0 %
Factor 1

[Comment]
Sample name RK-XVI
Comment CHCl3, C = 1.0
User SS
Division OC
Company IISc

| | | No. | PMT Voltage[V] | Mode | Sample No. | Calc. Data | Meas. Data | Temperature(C) | Blank |
|---|---|---|---|---|---|---|---|---|---|
| 1 | * | 1 | 404 | Specific O.R. | RK-XVI-1 | -1.5400 | -0.0077 | 22.00 | -0.6197 |
| 2 | * | 2 | 402 | Specific O.R. | RK-XVI-2 | -2.0000 | -0.0100 | 21.96 | -0.6197 |
| 3 | * | 3 | 402 | Specific O.R. | RK-XVI-3 | -1.7400 | -0.0087 | 21.92 | -0.6197 |
| 4 | * | 4 | 404 | Specific O.R. | RK-XVI-4 | -1.6800 | -0.0084 | 21.90 | -0.6197 |
| 5 | * | 5 | 405 | Specific O.R. | RK-XVI-5 | -1.2800 | -0.0064 | 21.87 | -0.6197 |
| 6 | * | 6 | | | Avg. | -1.6480 | | | |
| 7 | | 7 | | | S.D | 0.2648 | | | |
| 8 | | 8 | | | C.V | 16.0681 | | | |

| | Measurement Date |
|---|---|
| 1 | 02-07-2021 11:24 |
| 2 | 02-07-2021 11:24 |
| 3 | 02-07-2021 11:25 |
| 4 | 02-07-2021 11:25 |
| 5 | 02-07-2021 11:25 |
| 6 | |
| 7 | |
| 8 | |

**Table S4.** Optical activity parameters of HBOA

RK-V-1

[Data Information]
Creation Date 02-07-2021 11:12

[Measurement Information]
Instrument Name JASCO
Model Name P-2000
Serial No. A109661232
Polarizer Dichrom
Faraday Cell Flint Glass

Accessory PTC-262
Accessory S/N A021561481
Path Length 100 mm

Light Source Na
Monitor wavelength 589 nm
D.I.T. 5 sec
No. of cycle 5
Cycle interval 5 sec
Temp. Monitor Holder
Temp. Corr. Factor 0 at 20 C
Aperture(S) 3.0mm
Aperture(L) Auto
Mode Specific O.R.
Path Length 50 mm
Concentration 1 w/v%
Water content of sample 0 %
Factor 1

[Comment]
Sample name RK-V
Comment CHCl3, C = 1.0
User SS
Division OC
Company IISc

| | | No. | PMT Voltage[V] | Mode | Sample No. | Calc. Data | Meas. Data | Temperature(C) | Blank |
|---|---|---|---|---|---|---|---|---|---|
| 1 | * | 1 | 400 | Specific O.R. | RK-V-1 | -9.0000 | -0.0450 | 21.77 | -0.6197 |
| 2 | * | 2 | 401 | Specific O.R. | RK-V-2 | -9.4000 | -0.0470 | 21.71 | -0.6197 |
| 3 | * | 3 | 398 | Specific O.R. | RK-V-3 | -8.8200 | -0.0441 | 21.67 | -0.6197 |
| 4 | * | 4 | 398 | Specific O.R. | RK-V-4 | -9.3800 | -0.0469 | 21.67 | -0.6197 |
| 5 | * | 5 | 399 | Specific O.R. | RK-V-5 | -9.1600 | -0.0458 | 21.70 | -0.6197 |
| 6 | * | 6 | | | Avg. | -9.1520 | | | |
| 7 | | 7 | | | S.D | 0.2484 | | | |
| 8 | | 8 | | | C.V | 2.7145 | | | |

| | Measurement Date |
|---|---|
| 1 | 02-07-2021 11:12 |
| 2 | 02-07-2021 11:12 |
| 3 | 02-07-2021 11:12 |
| 4 | 02-07-2021 11:12 |
| 5 | 02-07-2021 11:12 |
| 6 | |
| 7 | |
| 8 | |

**S8 PFM imaging method:** PFM imaging has been done in a thin film where BOA and HBOA were loaded on a ITO glass substrate. During the testing, the tip scans the sample surface line-by-line while the AC voltage is applied. PFM imaging was performed with a Digital Instruments Dimension PARK NX20 atomic force microscope with platinum-coated tips. PFM images were collected near the cantilever's incontact resonance frequency (0.7 Hz) to enhance the vertical resolution. The imaging signal of 10V peak voltage at (0.7 Hz) was provided by an external function generator. The out-of-plane (vertical PFM) signals were collected. Phase Imaging: Maps the spatial distribution of domains based on phase differences. Bright and dark areas represent opposite polarization directions, respectively. Amplitude Imaging: Reveals domain boundaries as lines or regions of minimal cantilever deflection. The demodulated signal is used to generate a two-dimensional map of the local piezoelectric response, revealing the spatial distribution of piezoelectric response for surface morphology. The result of thin films is very similar like from the observation on bulk single-crystal samples. The contrast patterns reveal the arrangement of surface morphology like staircase within the HBOA material.