# **Supplementary Information**

## Record-high Thermal Stability Achieved in a Novel Single-Component Allorganic Ferroelectric Crystal Exhibiting Polymorphism

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### **Materials and Methods:**

Synthesis: The title compound, 2-(p-tolyl)-1H-phenanthro[9,10-d]imidazole (1), has been synthesized following the procedure (Scheme S1) reported in the literature.<sup>[1]</sup> 1 equivalent each of phenanthrene-9,10-dione and 4-methylbenzaldehyde and 10 equivalents of ammonium acetate (NH<sub>4</sub>OAc) were mixed in glacial acetic acid for refluxing for a period of 4 hours. The reaction progress was monitored via TLC. Upon completion of the reaction, the mixture was poured in icecold water and the product was filtered and purified via column chromatography. Final product formation was confirmed upon characterizations via <sup>1</sup>H (Fig. S1a) and <sup>13</sup>C NMR (Fig. S1b), and HR-ESIMS (Fig. S1c). <sup>1</sup>H NMR (400 MHz, DMSO) δ 13.40 (s, 1H), 8.84 (d, J = 8.3 Hz, 2H), 8.58 (d, J = 7.8 Hz, 2H), 8.22 (d, J = 8.1 Hz, 2H), 7.74 (t, J = 7.4 Hz, 2H), 7.63 (t, J = 7.6 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  = 149.26, 138.84, 129.49, 127.67, 127.54, 127.06, 126.09, 125.14, 123.90, 121.90, 39.52, 20.98. HR-ESIMS (m/z): calcd for C<sub>22</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup> 309.1386, found: C<sub>22</sub>H<sub>16</sub>N<sub>2</sub> [M+H]<sup>+</sup> 309.1407.





2-(p-tolyl)-1H-phenanthro[9,10-d]imidazole (1)

Scheme S1

# a) <sup>1</sup>H NMR



b) <sup>13</sup>C NMR





Figure S1. (a)  $^{1}$ H NMR, (b)  $^{13}$  C NMR and (c) HR-ESIMS for 1.

**Crystallization**: A range of HPLC grade solvents were used for growing crystals of **1** via slow evaporation method at both room temperature (RT,  $22 - 25^{\circ}$ C), high temperature ( $50^{\circ}$ C) and low temperature (LT,  $3 - 6^{\circ}$ C) as listed in **Table S1**. Prismatic crystals grown in acetonitrile and nitromethane were found to be of high-quality as confirmed from single-crystal X-ray diffraction (SCXRD) experiment. In addition, the compound was subjected to the vacuum sublimation crystallization, which produced crystals with block morphology. The hot-stage microscopy (HSM) experiment on **1P** crystals resulted a few crystals with needle morphology along with the majority of the block crystals. The crystal morphologies as captured using an Olympus SC30 polarizing microscope are given in **Figure S2**.

SL No	Solvents	Form	Condition	Morphology/form
1	Acetonitrile	P41	RT & LT	
2	Acetone	<i>P4</i> <sub>1</sub>	RT	
3	Nitromethane	$P4_1$	50°C	Prismatic/1P
4	Chloroform	<i>P4</i> <sub>1</sub>	RT	
5	IPA + CHCl3	<i>P4</i> <sub>1</sub>	RT	
6	DCM + MeOH	<i>P4</i> <sub>1</sub>	RT	
7	None	$P\overline{4}2_1c$	Vacuum sublimation	Block/1N
8	None	$P2_1/n$	Sublimation of <b>1P</b>	Needle/1C

Table S1: Systematic crystallization experiment using slow evaporation method.

b)

a)



1P (Size: 4.0 x 3.0 x 1.5 mm)





1N (Size: 1.1 x 0.6 x 0.2 mm)



**c**)



Figure S2. The crystal morphologies as captured using an Olympus SC30 polarizing microscope.

Single-crystal X-ray Diffraction: The data were collected at 100K, 298K and 373K (Table S2) using a D8 VENTURE diffractometer equipped with IµS microfocus sources ( $MoK_{\alpha}$  and  $CuK_{\alpha}$ ), PHOTON II CPAD detector and cryostream cryogenic system. The monochromatic  $MoK_{\alpha}$  radiation was used for the data collections using phi ( $\phi$ ) and omega ( $\omega$ ) scan strategy. The crystal to detector distance was set to 50 mm. Cell measurement, data collection, integration, and scaling were performed using APEX3 suite<sup>[2]</sup>. The data were processed using SAINT<sup>[3]</sup> and absorption correction was done using SADABS<sup>[4]</sup> program integrated in the APEX3 suite. The structures were solved using

the SHELXT program and refined within the XSHELL graphic interface<sup>[5]</sup>. All atoms including the H-atoms were located in successive difference Fourier syntheses. The non H-atoms were refined with anisotropic thermal parameters. The H-atoms were refined isotropically. ORTEP views of the crystal structures are given in Fig. S3. The crystallographic data and refinement parameters are listed in Table S2. Molecular packing diagrams are shown in Fig S4.

a) 1P



b) 1N







**Figure S3**: ORTEP of a) **1P**, b) **1N** and c) **1C** plotted with 50% ellipsoids. N-atoms are highlighted in cyan color.

Table S2: Crystal	data and refinement	parameters of 1P,	1N and 1C forms
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Crystal forms	1P			1N	1C	
	(Polar)				(Non-polar)	(Centrosymmetric)
Temperature (K)	100K	298K	373K	473K	298K	298K
CCDC No.	1895789	1895791	1895792	1921679	1895794	1921678
Chemical formula			(	$C_{22} H_{16} N_2$		
Formula weight (g)				308.37		
Space group (#)		P4 <sub>1</sub>	(76)		$P\overline{4}2_{1}c(114)$	$P 2_1/n$
<i>a</i> (Å)	14.2215(2)	14.3222(6)	14.3658(4)	14.510(15)	19.2160(4)	18.8380(7)
<b>b</b> (Å)	14.2215(2)	14.3222(6)	14.3658(4)	14.510(15)	19.2160(4)	9.8555(4)
<i>c</i> (Å)	15.6241(2)	15.7591(7)	15.8337(5)	15.944(11)	8.9740(2)	20.0216(7)
β(°)	90	90	90	90	90	115.797(2)
Volume (Å <sup>3</sup> )	3159.99(10)	3232.6(3)	3267.7(2)	3357(7)	3313.69(16)	3346.7(2)
Density (g.cm <sup>-3</sup> )	1.296	1.267	1.254	1.220	1.314	1.224
Z, Z'	8, 2	8, 2	8, 2	8, 2	8, 1	8, 2
Absorption coefficient (mm <sup>-1</sup> )	0.07	0.075	0.09	0.07	0.09	0.072
R(F), Rw(F)	0.0355, 0.0848	0.0406, 0.0982	0.0380, 0.0993	0.1033, 0.3456	0.0343, 0.0889	0.0631, 0.2119
Goodness of fit (S)	1.034	1.046	1.075	0.981	1.026	1.013
Peak (e/Å <sup>3</sup> )	0.15	0.12	0.10	0.49	0.13	0.47
Hole (e/Å <sup>3</sup> )	-0.19	-0.13	-0.12	-0.52	-0.14	-0.16



**Figure S4**. Molecular packing diagrams viewed down the *c*-axis for (**a**) **1P** and (**b**) **1N** and viewed down the *b*-axis for (**c**) **1C**. The N-atoms in cyan color are shown as ellipsoids.

### Energy Framework Analysis<sup>[6]</sup>

#### **Interaction Energies:**

CrystalExplorer17<sup>[6]</sup> was used for the calculations of interaction energies for **1P**, **1N** and **1C** crystal structures. For this, in each case, a cluster of radius 3.8 Å was generated around the central molecule. Total interaction energy (E\_tot) was estimated after taking into account of the electrostatic (E\_ele), polarization (E\_pol), dispersion (E\_dis) and exchange-repulsion (E\_rep) energy contributions. The

calculations were performed based on their crystal geometries using B3LYP<sup>[7]</sup> hybrid functional and 6-311G(d,p) basis sets. The corresponding energies are given in Table S3. The total interaction energies are found to be of -215.3 kJ/mol, -130.8 kJ/mol and -259.6 kJ/mol for **1P**, **1N** and **1C**, respectively.

Table S3:	The interaction	energies (kJ	J mol <sup>-1</sup> ) for (a	a) 1P, (l	<b>b) 1N and</b> (	c) 1C.
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# b) 1N

Ν	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
0	y, -x, z+1/4	14.20	B3LYP/6-311G(d,p)	-0.7	-0.1	-4.6	2.6	-2.8
1	-	12.44	B3LYP/6-311G(d,p)	-1.1	-0.4	-8.8	5.8	-4.5
1	-	5.20	B3LYP/6-311G(d,p)	-73.3	-18.0	-55.2	114.9	-31.6
1		10.62	B3LYP/6-311G(d,p)	-9.5	-1.6	-31.1	26.2	-16.0
0	y, -x, z+1/4	8.81	B3LYP/6-311G(d,p)	-2.6	-0.5	-8.4	2.3	-9.2
0	-x, -y, z+1/2	9.34	B3LYP/6-311G(d,p)	-7.9	-1.4	-24.4	21.1	-12.2
1		5.58	B3LYP/6-311G(d,p)	-8.8	-5.8	-93.1	69.2	-38.5
0	x, y, z	14.32	B3LYP/6-311G(d,p)	-0.2	-0.2	-6.8	3.8	-3.4
1		5.05	B3LYP/6-311G(d,p)	-64.3	-13.6	-60.2	105.9	-32.2
0	y, -x, z+1/4	9.07	B3LYP/6-311G(d,p)	-3.8	-1.1	-17.7	10.0	-12.6
1		12.09	B3LYP/6-311G(d,p)	-0.6	-0.2	-3.9	0.6	-4.1
2	y, -x, z+1/4	9.68	B3LYP/6-311G(d,p)	-4.7	-0.9	-16.0	11.7	-10.6
2	х, у, z	14.32	B3LYP/6-311G(d,p)	-0.3	-0.2	-7.2	4.1	-3.6
2	y, -x, z+1/4	13.32	B3LYP/6-311G(d,p)	-0.3	-0.2	-3.2	0.4	-3.3
2	y, -x, z+1/4	8.75	B3LYP/6-311G(d,p)	-3.4	-0.6	-8.0	2.2	-9.8
2	y, -x, z+1/4	14.17	B3LYP/6-311G(d,p)	0.2	-0.1	-2.9	0.4	-2.4
2	-x, -y, z+1/2	8.94	B3LYP/6-311G(d,p)	-7.1	-1.2	-25.7	18.8	-15.2
2	y, -x, z+1/4	12.66	B3LYP/6-311G(d,p)	0.9	-0.1	-2.7	0.2	-1.7
1		11.55	B3LYP/6-311G(d,p)	-0.1	-0.1	-1.4	0.0	-1.6

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
2	x+1/2, -y+1/2, -z+1/2	10.47	B3LYP/6-311G(d,p)	-6.5	-1.5	-26.4	14.1	-20.3
1	-y, x, -z	11.92	B3LYP/6-311G(d,p)	-2.9	-0.5	-10.9	11.0	-3.3
2	x+1/2, -y+1/2, -z+1/2	12.01	B3LYP/6-311G(d,p)	0.4	-0.4	-10.0	6.5	-3.5
1	-x, -y, z	12.28	B3LYP/6-311G(d,p)	-0.6	-0.2	-8.2	3.1	-5.9
0	y+1/2, x+1/2, z+1/2	12.73	B3LYP/6-311G(d,p)	0.1	-0.1	-4.2	0.6	-3.6
1	x, y, z	8.97	B3LYP/6-311G(d,p)	-4.3	-0.7	-12.0	6.5	-10.5
2	-y+1/2, -x+1/2, z+1/2	5.38	B3LYP/6-311G(d,p)	-42.8	-10.8	-54.4	62.8	-45.2
2	-y, x, -z	7.85	B3LYP/6-311G(d,p)	-11.1	-2.1	-39.9	25.3	-27.8
1	-x, -y, z	10.76	B3LYP/6-311G(d,p)	0.8	-0.4	-6.1	0.6	-5.1
2	-y, x, -z	10.36	B3LYP/6-311G(d,p)	-2.7	-0.3	-12.3	9.7	-5.6

# c) 1C

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	2	8.42	B3LYP/6-311G(d,p)	-11.2	-1.7	-35.0	27.0	-20.9
	1	-	5.24	B3LYP/6-311G(d,p)	-50.3	-12.1	-52.6	76.7	-38.3
	0	x, y, z	9.86	B3LYP/6-311G(d,p)	-5.7	-0.5	-10.9	10.0	-7.1
	1	-	12.68	B3LYP/6-311G(d,p)	-0.5	-0.1	-3.6	0.9	-3.3
	1		9.51	B3LYP/6-311G(d,p)	-6.7	-0.8	-19.8	16.2	-11.1
	1		5.53	B3LYP/6-311G(d,p)	-72.1	-18.4	-46.4	99.4	-37.5
	0	-x, -y, -z	8.96	B3LYP/6-311G(d,p)	-14.3	-2.5	-51.8	34.4	-34.2
	0	-x+1/2, y+1/2, -z+1/2	9.01	B3LYP/6-311G(d,p)	-2.2	-1.4	-26.2	14.7	-15.1
	1	-	11.50	B3LYP/6-311G(d,p)	-6.0	-0.7	-16.8	15.6	-7.9
	1	1	8.40	B3LYP/6-311G(d,p)	-10.8	-1.7	-35.5	26.3	-21.7
	1	-	9.88	B3LYP/6-311G(d,p)	-1.6	-0.6	-10.4	5.7	-6.9
	1		12.36	B3LYP/6-311G(d,p)	-3.7	-0.3	-12.1	12.2	-3.9
	1	-x, -y, -z	8.29	B3LYP/6-311G(d,p)	-5.9	-1.1	-25.6	11.0	-21.6
	2	x+1/2, -y+1/2, z+1/2	11.37	B3LYP/6-311G(d,p)	-3.8	-0.8	-12.1	5.8	-10.9
	2	x, y, z	9.86	B3LYP/6-311G(d,p)	-4.9	-0.5	-10.0	7.1	-8.3
Г	2	-x+1/2, y+1/2, -z+1/2	16.88	B3LYP/6-311G(d,p)	0.3	-0.1	-1.6	0.1	-1.3
	2	x+1/2, -y+1/2, z+1/2	11.54	B3LYP/6-311G(d,p)	-1.8	-0.5	-12.1	5.5	-8.9

### **Energy Frameworks:**

The visual representation of the strength of the energies and the interaction pathways in terms of electrostatic, dispersion and total energy are given in Figs. S5, S6 and S7 for **1P**, **1N**, and **1C** respectively.



**Figure S5**: Energy frameworks for the crystal structure of **1P** showing electrostatic and dispersion energy contributions to the total energy. The energy scale factor is 20, tube size is 85 and the energy threshold is 0 kJ mol<sup>-1</sup>. Formation of helical structure in terms of electrostatic interaction energy of N-H...N hydrogen bonds is zoomed in the bottom inset.



**Figure S6**: Energy frameworks for the crystal structure of **1N** showing electrostatic and dispersion energy contributions to the total energy. The energy scale factor is 20, tube size is 100 and the energy threshold is  $0 \text{ kJ mol}^{-1}$ .



**Figure S7**: Energy frameworks for the crystal structure of **1C (monoclinic)** showing electrostatic and dispersion energy contributions to the total energy. The energy scale factor is 20, tube size is 85 and the energy threshold is 0 kJ mol<sup>-1</sup>.

**Lattice energy calculation based on** *PIXEL*: The lattice energies of the three forms were estimated by using *PIXEL* (version November 2015) program.<sup>8</sup> The molecular electron densities of **1P**, **1N** and **1C** required for the estimation of lattice energy were calculated using *Gaussian09*<sup>[9]</sup> at B3LYP/6-311G\*\* level of theory based on the inputs generated from *PIXEL using the module runpixmt*. The calculations were performed based on their respective crystal geometries. The molecular electron densities were then used in PIXEL program to calculate the four energy terms; Coulomb, polarization, dispersion and repulsion as given in Table S4.

Energies	1P (kJ/mol)	1N (kJ/mol)	1C (kJ/mol)
Coulomb	-83.7	-59.5	-86.3
Polarization	-44.8	-29.7	-43.1
Dispersion	-195.6	-172.7	-172.4
Repulsion	159	98.4	130.9
Total Energy	-166.1	-163.5	-170.9

Table S4: Lattice energies estimated using PIXEL for 1P, 1N and 1C crystals.

**Differential scanning calorimetry (DSC):** Phase transition study on crystals (~2.4 mg) of **1P** and **1N** were carried out using DSC technique with Mettler Toledo DSC3 under  $N_2$  gas atmosphere using scan rate of 5K/min. DSC experiments on powders of the crushed single-crystals resulted same characteristics as those observed on single-crystals. It is to be noted that during heating the amorphous 1P' (phase at the beginning of 2<sup>nd</sup> heating of 1P) is partially converting to crystalline solids at ~440K leading to the broad endothermic melting peak at ~559 K (Fig. 2b, bottom plot). In addition, 1N experiences the similar conversion during the 1<sup>st</sup> cooling (Fig. 2a, top plot) and therefore displaying the similar broad melting peak at ~559K during the 2<sup>nd</sup> heating (Fig. 2b, top plot). The DSC plot with heating up to 550K and cooling is shown in Fig. S8b. The slight elevation in the phase transition temperature could be because this test experiment was performed on a slightly smaller crystal (~2 mg) from a different batch.

**Hot stage microscopy (HSM):** The **1P** and **1N** crystals were subjected to HSM with scan rate of 5K/min under a Nikon polarizing microscope CFI60 infinity equipped with heating stage LTS420. Images as displayed in Fig. S8a were grabbed and the sample temperatures were monitored using Linksys software.

(a)



568K 578K 423K 308K



**Figure S8**: (a) Optical images of **1P** (up) and **1N** (down) crystals captured during the HSM experiment. In both the cases, the crystal images formed upon sublimation on the cover slip at 423K and 308K are captured by de-focusing the microscope from the sample holder slide at the bottom where the solidified material appeared (off focused) as opaque and amorphous. (b) DSC plot recorded on **1P** crystal with heating up to 550K and cooling.

**Powder X-ray diffraction (PXRD):** The data on powder samples (crushed single-crystals) of different forms were collected using D8 VENTURE diffractometer equipped with microfocus  $CuK_{\alpha}$  radiation and PHOTON II CPAD detector. Powder samples were mounted on quartz capillary of about the same size (300µm) as the X-ray beam, in which the sample position was centered. Subsequently, a rotation photograph by scanning  $2\theta$  from 0° to 360° for 2 minutes. The corresponding Debye rings thus obtained were integrated by using "Integrate Debye ring" option as implemented in the APEX3 suite. The raw data in text format were then fed in to *Origin* version 2015<sup>[10]</sup> for plotting the PXRD patterns. Simulated powder patterns as shown in Figure S9 were also plotted using *Origin* version 2015.<sup>[10]</sup> The corresponding data were extracted via Mercury version 3.10.3<sup>[11]</sup> using the respective crystallographic information files (CIF) generated after the final refinement of the crystal structures.



**Figure S9.** PXRD patterns of (a) **1N** (up) *vs* 1P' (down) and (b) **1P** (up) vs 1P' (down) and comparison of experimental PXRD patterns (up) with their corresponding simulated PXRD patterns (down) for (c) **1P** and (d) **1N**, all recorded at RT.

**Thermogravimetric Analysis (TGA):** The thermal stability of **1P** and **1N** were determined by performing TGA on their crystals using Mettler Toledo TGA2 system under  $N_2$  gas (flow rate of 40 ml/min) atmosphere with scan rate of 5 K/min. The amount of samples used for the measurements were 9.47 mg and 9.93 mg for **1P** and **1N**, respectively. The TGA and the corresponding derivative thermogravimetry (DTG) plots for **1P** and **1N** displaying the thermal decomposition temperatures are given in Figure S10. For comparison, the TGA curves were normalized by the mass of each sample.



Figure S10. TGA (curve in solid line) and DTG (curve in dashed line) plots for (a) 1P and (b) 1N.

#### **Dielectric measurements**

A single-crystal of **1P** was cut in to thin parallel plates and both sides coated with silver paste to achieve parallel plate capacitor geometry. The dielectric responses were measured at 20 KHz, 40 KHz and 100 KHz using a multi-frequency LCR meter, HP4275A. The amplitude of the ac field applied was of 0.5 V. The single-crystal sample was heated up to 525 K. The resultant dielectric constants and dielectric losses are given in Figs S11a and S11b, respectively.



**Figure S11.** Temperature dependence of the (a) real ( $\epsilon$ ') and (b) imaginary ( $\epsilon$ '') parts of the electric permittivity of **1P** crystal measured at variable frequencies

#### **Ferroelectric measurements**

The ferroelectric hysteresis loops were measured by using Sawyer-Tower circuit on the single crystal of thickness 0.7 mm and area 1.968 mm<sup>2</sup>. The measurements pertaining to the polarization and fatigue cycles were recorded using hysteresis loop analyser (aixACCT TF Analyser 2000E, Germany). Leakage currents were measured at 600V. The corresponding plot is shown in Figure S12.



Figure S12. The leakage current along with the *P*-*E* hysteresis loop for 1P crystal at 600V and 1Hz.

#### **Spontaneous Polarization Calculations**

The calculations have been performed within the density functional theory (DFT), as implemented in the Vienna *Ab initio* Simulation Package (VASP)<sup>[12]</sup>. The electron-ion interactions are described using the projector augmented wave (PAW) pseudopotential method<sup>[13]</sup>. The exchange-correlation functional has been treated using the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)<sup>[14]</sup>. The structural optimization has been done using only the gamma point for the Brillouin zone integrations due to the large size of the unit cell. The wave function has been expanded using a plane wave basis with cut-off energy of 500 eV. Further, we have incorporated van der Waals (vdw) interactions using Grimme DFT-D3 approach<sup>[15]</sup>. This approach has been selected after studying croconic acid (CA)<sup>[16]</sup> as a test case with different treatments of the vdw interactions such as Grimme's DFT-D2<sup>[17]</sup>, Tkatchenko-Scheffler method<sup>[18]</sup>, Tkatchenko-Scheffler method with iterative Hirshfeld partitioning<sup>[19]</sup>, many-body dispersion energy method<sup>[20]</sup>, and dispersion correction method of Steinmann, and Corminboeuf <sup>[21]</sup>. For these test calculations, we have used 5x7x3 **k**-points mesh for Brillouin zone integrations. In all cases, we have calculated the energy with

a tolerance of  $10^{-5}$  eV and optimized the lattice parameters and atomic positions without any constraint until the absolute value of force on each ion was less than 1 mV/Å. Finally, Berry phase method<sup>[22]</sup> as implemented in VASP program and as used in the case of CA<sup>[16]</sup> has been employed for the calculation of spontaneous polarization (*P*<sub>s</sub>) of **1**. These calculations suggest that DFT-D3 with GGA-PBE provides good agreement for the lattice parameters as well as the *P*<sub>s</sub> with those obtained from experiment (Table S5).<sup>[16]</sup>

**Table S5**: Lattice parameters (a, b and c) and spontaneous polarization  $(P_s)$  for croconic acid calculated at 0 K and compared with the experimental values.

Croconic acid	Theory	Experiment <sup>[14]</sup>
	(DFT-D3 & GGA-PBE)	(SCXRD and <i>P</i> - <i>E</i> loop measurement)
a (Å)	8.750	8.711(1)
<i>b</i> (Å )	5.133	5.169(2)
<i>c</i> (Å )	10.825	10.962(3)
Vol (Å <sup>3</sup> )	486.2	493.6(3)
$P_{\rm s}$ ( $\mu$ C/cm <sup>2</sup> )	18.09	21.00

Accordingly, calculations for the structure optimization of **1** at 0K have been performed starting with the cell parameters and atomic positions obtained from our SCXRD experiment at 100K (Table S2).The optimized lattice parameters at 0 K are given in Table S6. The calculated volume of 3117.9 Å<sup>3</sup> compares well with the experimental volume of 3159.5 Å<sup>3</sup> at 100K, keeping in mind the temperature difference. The calculated intra- and inter-molecular nearest neighbour bond lengths are given in Table S7 and compared with those obtained from the experimental results at 100 K. The experimental values of C-C and C-N bond lengths are well reproduced in our calculations. However, the experimental values of the C-H and N-H bond lengths are found to be smaller compared to the calculated values. Underestimation of X-H bond distances from X-ray diffraction experiment is also realized in the case of CA<sup>[16]</sup>. There are two N-H bond lengths with values of 1.051 Å (molecule A) and 1.044 Å (molecule B). The calculated *sp3* hybridized C-H bonds lie in the range of 1.098 Å – 1.102 Å while the values for the *sp2* hybridized C-H bonds are 1.086 Å and 1.089 Å. The intermolecular N<sub>A</sub>...N<sub>B</sub> and N<sub>B</sub>...N<sub>A</sub> bond distances are 2.807 Å and 2.882 Å, which are in qualitative agreement with the experimental values of 2.850 Å and 2.931 Å, respectively. The calculated cohesive energy is 1.83 eV per molecule with major contributions from van der Waal's interactions. Further, using Berry phase method,<sup>[22]</sup> we calculated  $P_s$ . For the paraelectric phase (centrosymmetric), the position of the H-atoms of the N-H groups of the fully relaxed polar structure has been shifted at the center of the two N-atoms of the neighboring A and B molecules. So that the hydrogen bond networks adopt N<sub>A</sub>...H<sub>A</sub>...N<sub>B</sub>...H<sub>B</sub>...N<sub>A</sub> pattern. There are eight such H atoms in the unit cell. (ii) Subsequently, the  $P_s$  has been calculated at 0 K following the procedure as implemented in VASP<sup>[12]</sup>. The corresponding  $P_s$  compares well with that calculated using the cell parameters and atomic positions obtained from the SCXRD experiment at 100K (Table S6). Further, in order to check the dependency of  $P_s$  on temperature, similarly we calculated  $P_s$  based on the crystal geometries determined via X-ray diffraction at 298 K and 373K (Table S2). Although the value of  $P_s$  slightly increased (~21 %) from that of the fully relaxed structure at 0K, it remained almost unchanged at 298K and 373K (Table S6). Overall, the calculated  $P_s$  values agree well with that of measured from the *P-E* loop experiment at RT.

<b>Table S6</b> : Lattice parameters $(a, b, and c)$ , volu	me (V), spontaneous po	olarization $(P_s)$ and	cohesive
energy for <b>1</b> .			

Methods	Theory	Experiment			
	(DFT-D3 & GGA-PBE)	(SCXRD)			
Parameters	0K	100K	298K	373K	
a = b (Å)	14.172	14.222(1)	14.3222(6)	14.3658(4)	
c (Å)	15.524	15.624(1)	15.7591(7)	15.8337(5)	
$V(\text{\AA}^3)$	3117.93	3160.0(1)	3232.6(3)	3267.7(2)	
$P_{\rm s}$ ( $\mu$ C/cm <sup>2</sup> )	3.25	3.92	3.83	3.85	

**Table S7.** Calculated (0 K) and measured (based on X-ray data at 100 K) intra-molecular nearest neighbour bond lengths in molecules A and B as well as the inter-molecular bond lengths. For numbering scheme of different atoms in molecules A and B, see Fig. S3a.

Covalent and inter-molecular distances	Calculated at	X-ray data at	
	0 K (Å)	100 K (Å)	
N2A (sp <sup>3</sup> hybridised) – H2NA	1.051	0.889 (25)	
C22A (sp <sup>3</sup> hybridised) – H22A	1.098	0.940 (41)	

C22A(sp <sup>3</sup> hybridised) – H22B	1.102	0.980 (40)
C22A(sp <sup>3</sup> hybridised) – H22C	1.099	0.948 (42)
C14A(sp <sup>2</sup> hybridised) – H14A	1.086	0.963 (28)
N1B(sp3 hybridised) – H1NB	1.044	0.938 (27)
C22B(sp3 hybridised) – H22D	1.100	0.955 (36)
C22B(sp3 hybridised) – H22E	1.102	0.999 (36)
C22B(sp3 hybridised) – H22F	1.102	1.023 (39)
C14B(sp2 hybridised) – H14B	1.089	0.995 (27)
N2AN2B	2.807	2.850 (3)
N1BN1A	2.882	2.931 (3)
H2NAN2B	1.758	1.964 (25)
H1NBN1A	1.848	2.002 (27)

**Second Harmonic Generation (SHG) experiment:** SHG activity measurements on homogeneous powdered samples of **1P** and **1N** using Kurtz and Perry method<sup>[24]</sup> have been carried out using a Spectre Physics instrument equipped with an INDI LASER (Nd:Yag Laser 1064 nm) at a repetition rate of 10 Hz and pulse width of 8 ns. Potassium dihydrogenphosphate (KDP) has been used as a standard for comparing the SHG signals (Table S8).

Table S8: Comparison of SHG activities for 1P and 1N with KDP. (Input Energy: 1.2 mJ/pulse).

Sample	Signal (mv)	SHG x KDP
KDP	22	1.00
1P (Polar)	18	0.82
1N (Non-polar)	5	0.23

**Calculations of SHG properties:** The program *CRYSTAL14*<sup>[25]</sup> has been used to perform periodic calculations with B3LYP<sup>[7]</sup> functional and 6-311G(d,p) basis set based on the crystal geometry of **1P**. Grimme's dispersion function (D2)<sup>[15]</sup> has also been taken into account for this calculation. The keywords CPKS (Couple Perturbed Kohn–Sham) along with THIRD (energy derivatives up to the

Structure (Space Group)	Tensor components	β	$\chi^{(2)}$
<b>1P</b> ( <i>P</i> 4 <sub>1</sub> )	xxz = yyz zzz	-6177.45 3929.53	-1.82 1.16
<b>1N</b> ( $P = \overline{4}2_1c$ )	xyz	-1748.85	-0.50

**Table S9**: Estimation of in-crystal first hyperpolarizability ( $\beta$ ) and second-order nonlinear coefficient ( $\chi^{(2)}$ ).

third order) and both ANDERSON and BROYDEN (for mixing of KS matrix derivatives) have been used to perform the in-crystal first hyperpolarizability ( $\beta$ ) and second order nonlinear susceptibility ( $\chi^{(2)}$ ). The procedure as detailed in an earlier study by some of us <sup>[26]</sup> is also followed here. The estimated nonOlinear properties are listed in Table S9.

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