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## ARTICLE

# Self-Assembly Patterns of Steroid-Based *All*-Organic Ferroelectrics: Valuable Insights from the Single-Crystals Derived from Organogel and Solution

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We report herein the first example of a single-crystal grown from a steroid-based organogel matrix. We have delineated the self-assembly process and compared the various non-covalent interactions with that of the single-crystals grown from the solution e.g. **1·Ch** showed a 22 and 14-membered N-H...O H-bonded rings, while **1·Pr** exhibited a 24 and 14-membered rings. In addition, **1·Ch** showed stronger cholesteryl-cholesteryl interactions than **1·Pr**. **1·Ch** exhibited 55% higher polarization.

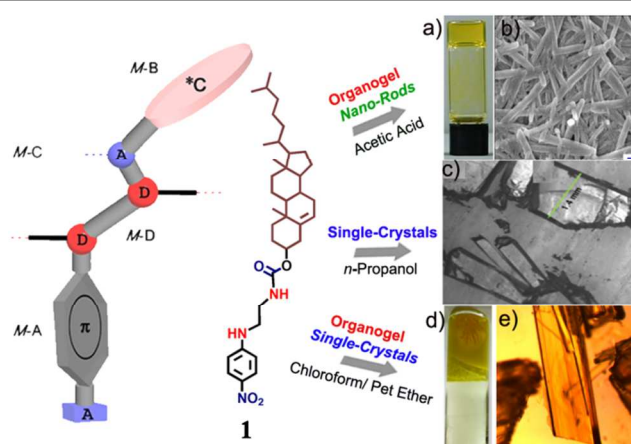
## Introduction

Ferroelectric (FE) materials have shown attractive applications in FE random-access memories (FERAM), FE diodes, etc.<sup>1</sup> FEs are polar materials in which the spontaneous electric polarization can be reversed by inverting the external electric field. It has been realized that all-organic FE materials should provide multi-fold advantages such as synthetic tailorability, tunability of molecular interactions and solution processing in comparison to the inorganic FEs. However, there are only a very few reported all-organic single-component (AOSC) FE materials.<sup>2</sup> The existing AOSC FE materials suffer from low saturation and remnant electric polarization ( $P_s$  and  $P_r$  in  $10^{-9}$  C cm<sup>-2</sup>) and high  $E_C$  in V cm<sup>-1</sup>. Two recent reports, based on croconic acid<sup>2b</sup> and a Schiff base<sup>2c</sup> have shown that exceptional FE properties ( $P_s \sim 20\text{--}60$   $\mu\text{C cm}^{-2}$ ) can also be found in AOSC FEs. On the other hand, organic two-component FE systems<sup>3</sup> and metal-ligand based design<sup>4</sup> have been quite successful. In this regard, application of crystal engineering principles would further benefit designing of new classes of *all*-organic FEs.<sup>5,6</sup>

We recently reported the first modular design strategy coupled with supramolecular<sup>7</sup> self-assembly approach, which leads to ferroelectricity in AOSC crystalline solids as well as in organic nano-architectures at RT.<sup>8</sup> The design for molecule **1**, incorporates four modules: a donor- $\pi$ -acceptor module,  $M_A$ ; a cholesteryl group,  $M_B$ ; H-bonding groups,  $M_C$  and spacer,  $M_D$ .

**1** exhibited remarkable self-assembly properties. It could form stable organogels<sup>9</sup> and could spontaneously gelate acetic acid, carbon tetrachloride and a mixture of various solvents e.g. chloroform:methanol, chloroform:hexane, etc. (see SI, Table 1). Electron microscopy revealed that these gels were formed of well-defined nano-architectures and is dependent on the gelled solvent (Scheme 1a-b). This high propensity to gelate organic solvents created a major challenge to generate good quality

single-crystals. After several attempts with different solvents and their combinations we could accomplish single-crystals by slow evaporation of *n*-propanol (Scheme 1c). These crystals represented as **1·Pr** crystallized in the P1, polar space group and was found to be second harmonic generation (SHG) active and exhibited spontaneous ferroelectric property at room temperature (RT).



Scheme 1: Module-Based design of an *all*-organic ferroelectric **1**; a) Organogel formation in acetic acid and b) SEM image exhibiting the nano-rod like structures; c) Single-crystals grown from *n*-propanol; d) Organogel formation in chloroform:petroleum ether and e) *in situ* formation of single-crystals from the organogel matrix.

With these results in hand, we wanted to modulate the self-assembly characteristics by altering the supramolecular interactions. Our goal was to grow single-crystals of **1** in non-polar solvents, albeit the fact that **1** showed strong propensity to gelate non-polar organic solvents. In this work, we demonstrate the successful growth of single-crystals, **1·Ch** from an

organogel matrix constituted of chloroform and petroleum ether (Scheme 1d-e). To our knowledge this forms the first steroid-based organo-gelator<sup>10</sup> that could be *in situ* crystallized from an organogel matrix.

The single-crystal data of **1·Ch** revealed altered self-assembly pattern, H-bonding interactions, cholesteryl-cholesteryl van der Waals interaction. The modulation of these supramolecular interactions is anticipated to have significant role in tuning the nonlinear optical (NLO)<sup>11</sup> and FE properties of these materials. Furthermore, significant control over the cholesteryl-cholesteryl interactions in the solid state should be important in the design of steroid-based drug molecules.

## Results and discussion

**1·Ch** crystallizes in the triclinic crystal system with polar space group P1, similar to that of **1·Pr**, which comprises of one of the ten polar point groups necessary for ferroelectricity to occur (Table 1). There were four crystallographically independent molecules in the unit cell along with four independent chloroform molecules (see SI for the thermal ellipsoid plot). The cell dimensions in **1·Ch** were slightly elongated and the cell volume was found to be marginally expanded as compared to that of **1·Pr** [ $a = 12.9772(3)$ ,  $b = 14.3714(2)$ ,  $c = 22.6800(6)$ ,  $V = 3779.5(1) \text{ \AA}^3$ ].

**Table 1.** Crystal data of **1**

a) <b>1·Ch</b>		
Empirical formula	$C_{37}H_{56}Cl_3N_3O_4$	
Formula weight	713.20	
Temperature	100(2) K	
Wavelength	0.71073 \AA	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	$a = 13.262(3) \text{ \AA}$	$\alpha = 76.154(8)^\circ$
	$b = 13.508(2) \text{ \AA}$	$\beta = 86.364(9)^\circ$
	$c = 24.549(4) \text{ \AA}$	$\gamma = 63.763(8)^\circ$
Volume	$3825.5(12) \text{ \AA}^3$	
Z	4	
Density (calculated)	$1.238 \text{ Mg/m}^3$	
Absorption coefficient	$0.281 \text{ mm}^{-1}$	
F(000)	1528	
Crystal size	$0.21 \times 0.16 \times 0.10 \text{ mm}^3$	
Theta range for data collection	$1.71$ to $25.40^\circ$	
Reflections collected	50819	
Independent reflections	24785 [R(int) = 0.0503]	
Refinement method	Full-matrix-block least-squares on $F^2$	
Data / restraints / parameters	24785 / 20 / 1717	
Goodness-of-fit on $F^2$	0.975	
Final R indices [I > 2sigma(I)]	R1 = 0.0628, wR2 = 0.1517	
R indices (all data)	R1 = 0.0975, wR2 = 0.1753	
Absolute structure parameter	-0.04(5)	
Largest diff. peak and hole	0.909 and $-0.581 \text{ e.\AA}^{-3}$	
CCDC No. ( <b>1·Ch</b> )	<b>974686</b>	
b) CCDC No. ( <b>1·Pr</b> )	<b>822459</b>	

### Self-assembly characteristics

An infinite bi-layer like assembly of the polar nitrophenyl rings (Head) and the non-polar cholesteryl groups (Tail) in a Head-

Tail-Tail-Head (H-T-T-H) arrangement could be unravelled in **1·Ch** (Figure 1). In this H-T-T-H arrangement, the two cholesteryl T's interact with the peripheral alkyl chains. In the bilayer, the two nitrophenyl rings are stacked off-set to each other and the solvent chloroform molecules are at the periphery of the bilayer and close to the nitrophenyl rings. In the subsequent sections, we would discuss in detail the H-bonding interactions, molecule-solvent interactions,  $\pi$ - $\pi$  stacking and cholesteryl-cholesteryl interactions.

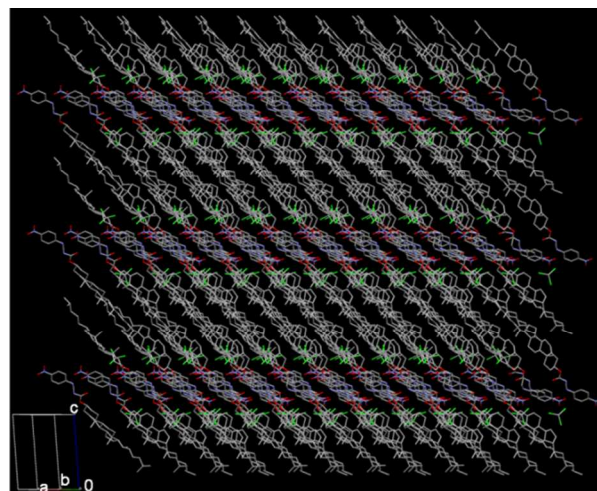


Figure 1: An infinite bi-layer like arrangement of the polar nitrophenyl rings and the non-polar cholesteryl groups in **1·Ch**. H atoms have been removed for clarity. Colour code for atoms: C, Grey; N, Blue; O, Red; Cl, Green.

In **1·Pr**, a similar H-T-T-H bi-layer like assembly was observed with the n-propanol molecules in proximity to the nitrophenyl rings (Figure 2). It is to be noted that similar H-T-T-H arrangement of cholesteryl-based molecules has been observed and characterized in detail in liquid crystals.

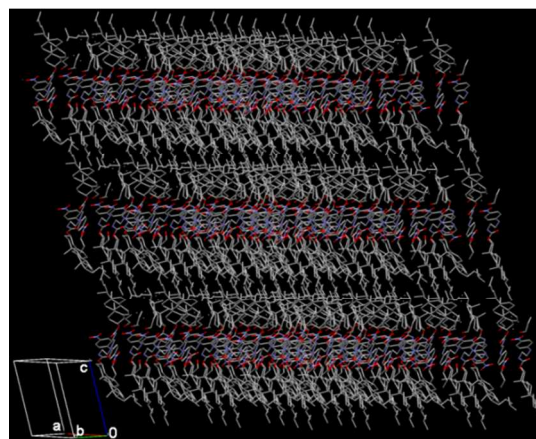


Figure 2: An infinite bi-layer like arrangement of the polar nitrophenyl rings and the non-polar cholesteryl groups in **1·Pr**. H atoms have been removed for clarity. Colour code for atoms: C, Grey; N, Blue; O, Red.

### H-bonding features

In **1-Ch** an infinite H-bonded array was observed formed by the donor NH-groups of the *p*-nitroaniline and the amide moiety and the acceptor O atoms of the nitro-group and the amide moiety. A closer look at the array reveals two-types of well-defined rings (R1 and R2) and a chain that aids to achieve the infinite propagation. The bigger H-bonded ring (R1) is subtended by 22 atoms, while the smaller ring (R2) is subtended by 14 atoms (Figure 3, top panel). In R1, the characteristic H-bonding parameters were found to be: N1---O11 2.959 Å and  $\angle$ N1-H1-O11 of 143° and N7---O3 2.954 Å,  $\angle$ N7-H7-O3 of 135°, while in R2 the H-bonding parameters were found to be: N8---O2 2.87 Å and  $\angle$ N8-H8-O2 of 168° and N2---O10 2.858 Å,  $\angle$ N2-H2-O10 of 162°.

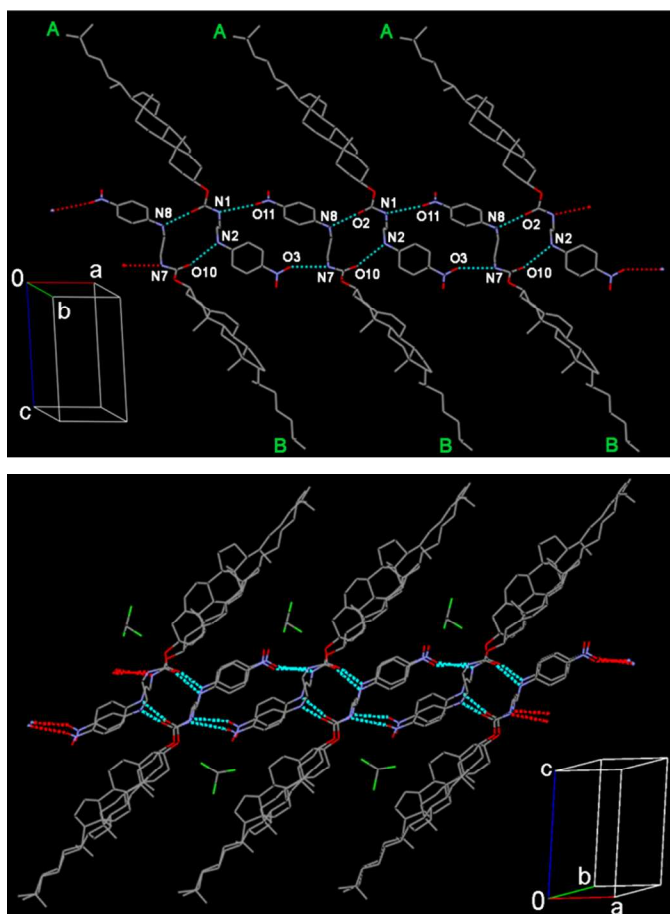


Figure 3: Top: An infinite array of N-H---O H-bonds in **1-Ch** formed by two types of rings R1 (22-membered) and R2 (14-membered) and H-bonded chains along the *a*-axis. Bottom: An infinite array of N-H---O H-bonds along the *a*- and *c*-axis. Note that the solvent chloroform molecules do not participate in forming the infinite rings and the chains in the H-bonded structure.

The solvent chloroform molecules do not participate in the H-bonded ring and chain formation (Figure 3, bottom panel). However, weak C-H---X type of bonding was unravelled between the H atoms of the cholesteryl rings and the Cl atoms,

e.g. H12b---Cl8 2.775 Å,  $\angle$ C12-H12b-Cl8 of 153°; H15a---Cl5 2.847 Å,  $\angle$ C15-H15a-Cl5 of 169°, etc. (See SI).

In contrast to **1-Ch**, the solvent *n*-propanol molecules in **1-Pr** participates in forming the infinite H-bonded array. In this case, R1 is subtended by 24 atoms and the additional two atoms (compared to **1-Ch**) are from the H's of the two propanol molecules. R2 is similar to that of **1-Ch** and is subtended by 14 atoms (Figure 4, top panel). In the ring R2, the notable H-bond distances and angles are: N10c---O49 2.915 Å and  $\angle$ N10c-H10c-O49 of 175° and O49---O1d of 2.915 Å,  $\angle$ O49-H49-O1 of 166°. In R2, the H-bonding parameters were found to be: N7d---O12c 2.893 Å and  $\angle$ N7d-H7d-O12c of 158° and N7c---O12d 2.943 Å and  $\angle$ N7c-H7c-O12d of 168°.

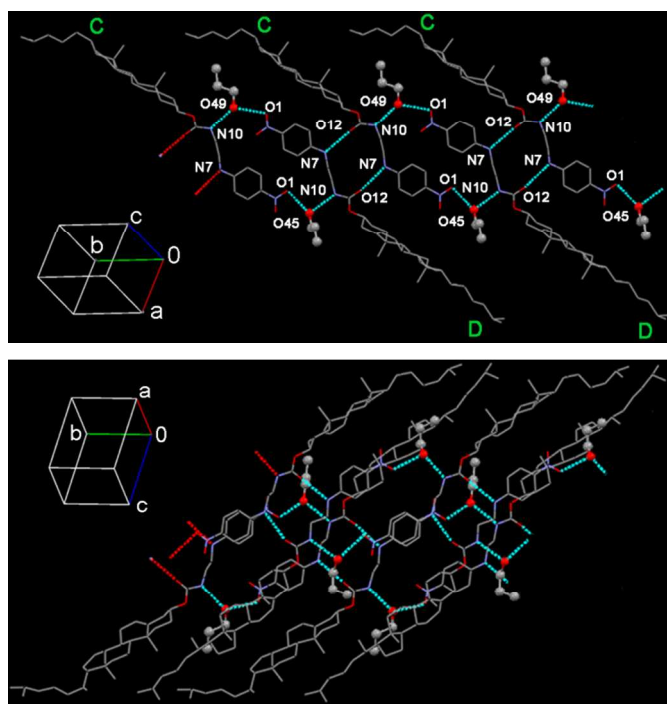


Figure 4: Top: An infinite array of N-H---O and O-H---O H-bonds in **1-Pr** formed by two types of rings R1 (24-membered) and R2 (14-membered) and H-bonded chains along the *b*-axis. Bottom: An infinite array of N-H---O and O-H---O H-bonds along the *a*- and *b*-axis. Note the participation of the solvent propanol molecules (shown in ball and stick) in forming the infinite rings and the chains in the H-bonded structure.

### $\pi$ - $\pi$ stacking interactions

The donor- $\pi$ -acceptor *p*-nitroaniline moiety is stacked in an antiparallel fashion in **1-Ch** and **1-Pr** single-crystals (Figure 5). In the case of **1-Ch** and **1-Pr**, the centroid-centroid distance between the two  $\pi$ -rings were found to be 4.316 Å and 3.851 Å. This shows a weak  $\pi$ - $\pi$  stacking interaction in the organogel matrix. In both of the cases the  $\pi$ -rings were found to be tilted, which provides a net dipole to bulk system as verified from the SHG activity.<sup>8</sup>

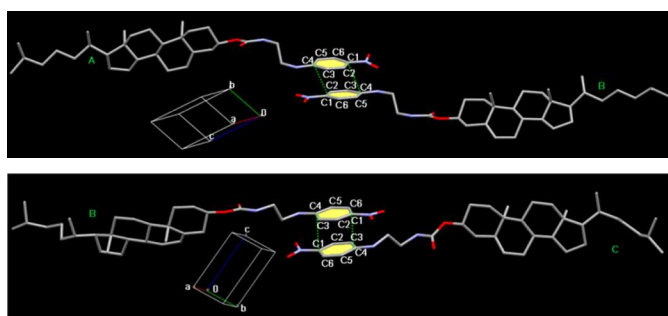


Figure 5: Top:  $\pi$ - $\pi$  stacking interactions in **1.Ch**; Bottom:  $\pi$ - $\pi$  stacking interactions in **1.Pr**.

### Cholesteryl-Cholesteryl van der Waals interaction

The cholesteryl moiety is known to play a significant role towards the design of soft materials like organogels, liquid crystals,<sup>12</sup> well-defined nano-architectures, etc. In addition, understanding and control over their interactions should play a significant role for modulating the efficacy of steroid-based drug molecules. We were interested to delineate the cholesteryl-cholesteryl interactions in **1.Ch** and **1.Pr** and arrive at a synthetic tool-box for engineering soft materials.

In the case of **1.Ch** several short C---C interactions less than 4.0 Å were observed between the cholesteryl moieties. Notable short interactions were found between C61-C24 (3.515 Å), C47-C21 (3.882 Å), C99-C114 (3.997 Å). Such short cholesteryl-cholesteryl interactions have been observed in the single crystals of metal cholesteryl-phosphine complexes.<sup>13</sup> In contrast, the cholesteryl-cholesteryl interactions in **1.Pr** were found to be much weaker, only one short C---C interaction was observed between C19b-C34d (3.507 Å). Therefore, such solvent dependent modulation of cholesteryl-cholesteryl interactions in a small molecule should be useful to tune the material properties associated with soft-materials.

### Ferroelectric Property

Following the standard procedure,<sup>14</sup> which has been recently used to validate the FE properties of croconic acid<sup>2b</sup> we studied the FE properties of crystalline material of **1.Ch** and compared with the previously reported **1.Pr**. We determined the temperature dependent changes in polarization by measuring pyroelectric current during a steady temperature sweep. The pellets were coated with silver paste on both sides and contacts were made using copper wires. The sample was cooled up to 150 K in presence of electric field of 100 V (for details, see the experimental section). It was then heated uniformly upto 310 K at a constant rate and current was measured as a function of temperature using an electrometer. The observed pyroelectric current during heating process was integrated with time to obtain the change in spontaneous polarization (Figure 6). As expected, the polarization gradually decreased with the increase of the temperature. Comparing the results from these two set of experiments, we found that the polarization value for

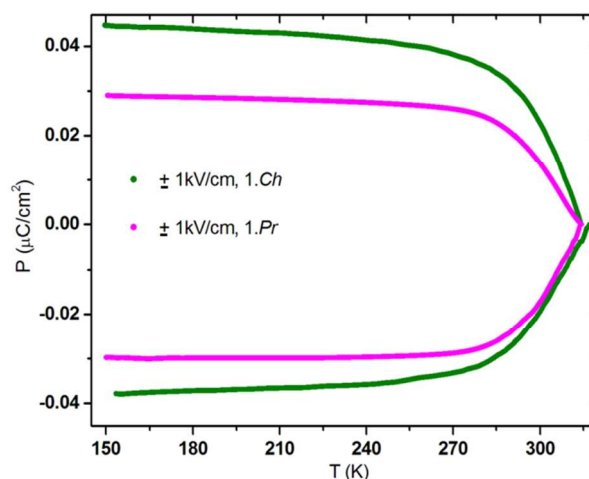


Figure 6: Graphs showing polarization as a function of temperature (T) obtained by pyroelectric current measurement from **1.Ch** and **1.Pr**.

**1.Ch** (0.045  $\mu\text{C}/\text{cm}^2$ ) to be 55% higher compared to polarization in **1.Pr** (0.029  $\mu\text{C}/\text{cm}^2$ ).<sup>14b</sup> This can be attributed to higher asymmetry in molecular packing and also due to the resultant higher dipoles emerging from **1.Ch**. A closer look at Figure 3 (Top and Bottom panels) clearly show that the donor- $\pi$ -acceptor *p*-nitroaniline moiety in **1.Ch** makes a greater tilt angle compared to that in **1.Pr** (Figure 4) and hence the increase in net dipole in **1.Ch**.

### Conclusions

In conclusion, we have provided the first crystallographic snapshots of molecular interactions of a steroid-based all-organic ferroelectric. To the best of our knowledge, this is the first example of a single-crystal (**1.Ch**) grown from a steroid-based organogel matrix. We have delineated the self-assembly process by delving into the H-bonding patterns,  $\pi$ - $\pi$  and cholesteryl-cholesteryl interactions and also the solvent (chloroform) interaction mode with **1**. Furthermore, we compared these non-covalent interactions with that of the single-crystals grown from the *n*-propanol solution e.g. **1.Ch** showed a 22 and 14-membered N-H---O H-bonded rings, while **1.Pr** exhibited a 24 and 14-membered rings formed with the combination of N-H---O and O-H---O H-bonds. In addition, **1.Ch** demonstrated a stronger cholesteryl-cholesteryl interaction compared to that of **1.Pr**. These provides valuable insights for modulating these interactions and tuning the optical, electronic properties of soft-materials. We determined the temperature dependent changes in polarization by measuring pyroelectric current during a steady temperature sweep. **1.Ch** exhibited higher polarization compared to **1.Pr** as a result of higher asymmetry in molecular packing and the emergent net dipole.

## Experimental

### Materials and methods

All chemicals were obtained from Sigma Aldrich or Spectrochem India and were used as received. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator having particle size of 25  $\mu\text{m}$  and was sourced from Sigma Aldrich.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 500 MHz spectrometer in  $\text{DMSO-}d_6$  with TMS as standard. Infra-Red spectra were recorded in KBr pellet using Varian 3100 FT-IR instrument. The morphologies of the xerogels were investigated in a field emission scanning electron microscope (FE-SEM) apparatus (JEOL, JSM-6700F). The samples were platinum coated with thickness of 40 nm by sputtering technique in argon atmosphere and were observed at a voltage of 5 kV.

### Synthetic procedures

The detailed synthetic procedure for **1** has been given in the supplementary material.

In situ growth of single-crystals of **1** from the organogel matrix: 30 mg of **1** was dissolved in 0.5 ml of  $\text{CHCl}_3$  and then petroleum ether (4-times by volume) was added slowly from the top. A turbid layer was formed and the vial was closed and kept at room temperature. The chloroform layer and some part of petroleum ether layer turned in to a gel. After around 6-7 days single-crystals were formed in the organogel matrix.

### Crystallography

The structure for **1** was refined by blocked diagonal refinement procedure as the number of parameters was high, since there were four crystallographically independent molecules in the unit cell along with four independent chloroform molecules. All non-hydrogen atoms were refined anisotropically. All calculations were performed using Wingx package.<sup>15</sup> The amide hydrogens in the structure was located from the difference Fourier synthesis and were refined isotropically with Uiso values 1.2 times of the carrier nitrogen atoms, with fixed distances [0.88(2) Å] wherever needed.

### Ferroelectric Property

The experiments were performed in pellet form. Pellets were obtained by applying 3.0-3.5 ton of pressure under hydraulic pellet press. Pellets were coated with silver paste on both sides and contacts were made using copper wires. Sample was cooled up to 150 K in presence of electric field of 100 V. After removing the applied field, the sample was short to avoid the influence of charge stored during the process of poling and waited for 10 minutes to remove the possibility of any stray charge. Sample was then heated uniformly upto 310 K at a constant rate and current was measured as a function of temperature using Keithle-6514 system electrometer.

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