

Organic and Hybrid Organic-inorganic Two Component Ferroelectric Materials and their Energy Harvesting Applications

विद्या वाचस्पति की
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

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Indian Institute of Science Education and Research, Pune

January 2024

Dedicated to

My Parents, Brother, and Sister



भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान, पुणे

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Certified that the work incorporated in the thesis entitled “***Organic and Hybrid Organic-inorganic Two Component Ferroelectric Materials and their Energy Harvesting Applications***” submitted by **Ms. Supriya Sahoo** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.

Date: 5th January-2024

Place: Pune

Prof. R. Boomi Shankar

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DECLARATION

I declare that, this written submission represents my ideas in my own words and where other's ideas have been included; I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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A handwritten signature in blue ink that reads 'Supriya Sahoo'.

Ms. Supriya Sahoo

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Synopsis

The thesis entitled “**Organic and Hybrid Organic-inorganic Two Component Ferroelectric Materials and their Energy Harvesting Applications**” focused on the synthesis of non-centrosymmetric polar organic and organic-inorganic hybrid ammonium salts supported by mono- and multiatomic anions, analyzing their structure properties, ferroelectric, piezoelectric and dielectric properties and their utilization for mechanical energy harvesting and storage applications in their polymer composite and neat crystallite forms.

Chapter 1: Introduction

The introduction ([Chapter 1](#)) discusses the vital concepts of dielectric materials and their classification into piezoelectric, pyroelectric, and ferroelectric materials. Especially a wide-ranging literature survey on diverse types of ferroelectric materials based on organic and organic-inorganic hybrid noncentrosymmetric polar systems has been described and discussed. In the later part of this chapter, the key examples of the use of piezo and ferroelectric materials in their polymeric composite forms for mechanical energy harvesting applications have been discussed. Finally, an outline of the present thesis is highlighted.

Chapter 2: Piezoelectric Energy Harvesting of a Lead-free Bismuth Halide Perovskite Supported by a Chiral Ammonium Cation

Lead-free hybrid perovskite piezoelectrics have gained enormous attention due to their nontoxic metal content and notable physical properties. In this work, we report a bismuth-bromide-based perovskite-structured material stabilized by chiral ammonium cations. The enantiopure hybrid 1D-network of composition $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ is crystallized in the piezoelectrically active orthorhombic space group $P2_12_12_1$. The piezoelectric measurements on the compacted pellet of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ gave a piezoelectric coefficient (d_{33}) value of 2.6 pC N⁻¹. The dielectric permittivity measurements yielded the real part of the complex dielectric constant (ϵ') value of 6.68 at room temperature and 1 kHz frequency. Furthermore, the piezoelectric energy harvesting applications were performed on the composite films of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ with polylactic acid (PLA) polymer. A considerable output voltage of 10.4 V was obtained for the 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite film. Energy storage application

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was studied by charging a 100 μF capacitor by using the best performing 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ device that reaches its maximum charging point in 60 seconds (Figure 1).

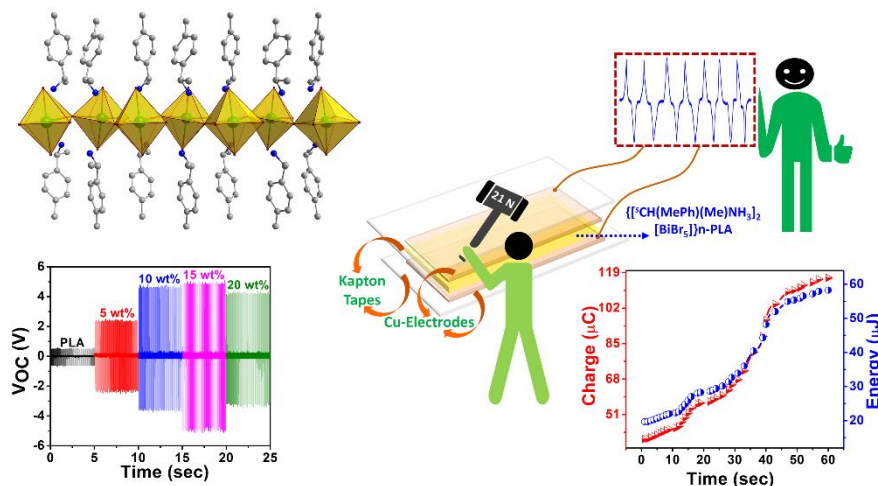


Figure 1: 1D-hydrogen bonded chain structure of polar organic-inorganic hybrid ammonium salt and a representative of piezoelectric energy harvesting on its polymer composite device with the output voltage and stored charge and energy profiles.

Chapter 3: 3D-printed Polymer Composite Devices based on a Ferroelectric Chiral Ammonium Salt for High-performance Piezoelectric Energy Harvesting

Three-dimensional printing (3DP) is an emerging technology to fabricate complex architectures, necessary to realize state-of-the-art flexible and wearable electronic devices. In this regard, top-performing devices containing organic ferro- and piezoelectric compounds are desired to circumvent significant shortcomings of conventional piezoceramics, e.g. toxicity and high-temperature device processability. Herein, we report on a 3D-printed composite of a chiral ferroelectric organic salt $\{[\text{Me}_3\text{CCH}(\text{Me})\text{NH}_3][\text{BF}_4]\}$ (**DMBA•BF₄**) with a biodegradable polycaprolactone (PCL) polymer that serves as a highly efficient piezoelectric nanogenerator (PENG). The ferroelectric property of **DMBA•BF₄** originates from its polar tetragonal space group $P4_2$, verified by P - E loop measurements. The ferroelectric domain characteristics of **DMBA•BF₄** were further probed by piezoresponse force microscopy (PFM), which gave characteristic ‘butterfly’ and hysteresis loops. The PFM amplitude vs. drive voltage measurements gave a relatively high magnitude of the converse piezoelectric coefficient for **DMBA•BF₄**. PCL polymer composites with

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various weight percentages (wt%) of **DMBA•BF₄** were prepared and subjected to piezoelectric energy harvesting tests, which gave a maximum open-circuit voltage of 36.2 V and a power density of 48.1 $\mu\text{W cm}^{-2}$ for the 10 wt% **DMBA•BF₄**-PCL champion device. Furthermore, a gyroid-shaped 3D-printed 10 wt% **DMBA•BF₄**-PCL composite was fabricated to test its practical utility, which gave an excellent output voltage of 41 V and a power density of 56.8 $\mu\text{W cm}^{-2}$. These studies promise the potential of simple organic compounds for building PENG devices using advanced manufacturing technologies. (Figure 2).

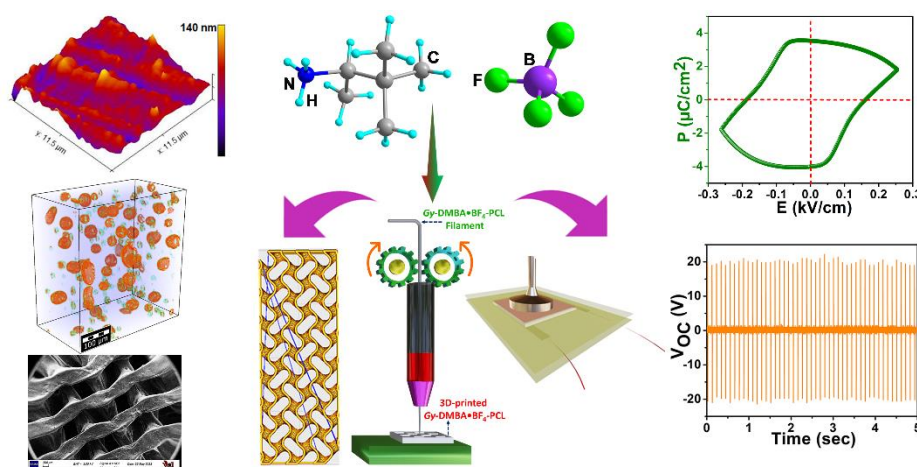


Figure 2: View of molecular structure of **DMBA•BF₄** along with its ferroelectric and domain structure analyses at room temperature. A pictorial representation of 3D printing for the preparation of **Gy-DMBA•BF₄-PCL** composite and its characterizations. The voltage output profile for the 3D-printed **Gy-DMBA•BF₄-PCL** device.

Chapter 4: A Highly Electrostrictive Salt Co-crystal and the Piezoelectric Nanogenerator Application of its 3D Printed Polymer Composite

Ionic co-crystals with hydrogen bonding can form exciting materials with enhanced optical and electronic properties. We present a highly moisture-stable ammonium salt co-crystal $[\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_2][\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_3][\text{PF}_6]$ (**(p-TEA)(p-TEAH)•PF₆**) crystallizing in the polar monoclinic *C*2 space group. The asymmetry in **(p-TEA)(p-TEAH)•PF₆** was induced by its chiral substituents, while the polar order and structural stability were achieved by using the octahedral PF_6^- anion and the consequent formation of salt cocrystal. The ferroelectric properties of **(p-TEA)(p-TEAH)•PF₆** were confirmed through *P-E* loop measurements. The

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piezoresponse force microscopy (PFM) enabled the visualization of its domain structure with characteristic 'butterfly' and hysteresis loops associated with ferro- and piezoelectric properties. Notably, **(p-TEA)(p-TEAH)·PF₆** exhibits a large electrostrictive coefficient (Q_{33}) value of $2.02 \text{ m}^4\text{C}^{-2}$, higher than those found for ceramic-based materials and comparable to that of polyvinylidene difluoride. Furthermore, the composite films of **(p-TEA)(p-TEAH)·PF₆** with polycaprolactone polymer and its gyroid-shaped 3D-printed composite scaled-up device, **3DP-Gy**, were prepared and evaluated for piezoelectric energy harvesting functionality. A high output voltage of 22.8 V and a power density of $118.5 \text{ } \mu\text{W cm}^{-3}$ have been recorded for the **3DP-Gy** device. Remarkably, no loss in voltage outputs was observed for the **(p-TEA)(p-TEAH)·PF₆** devices even after exposure to 99% relative humidity, showcasing their utility under extremely humid conditions (Figure 3).

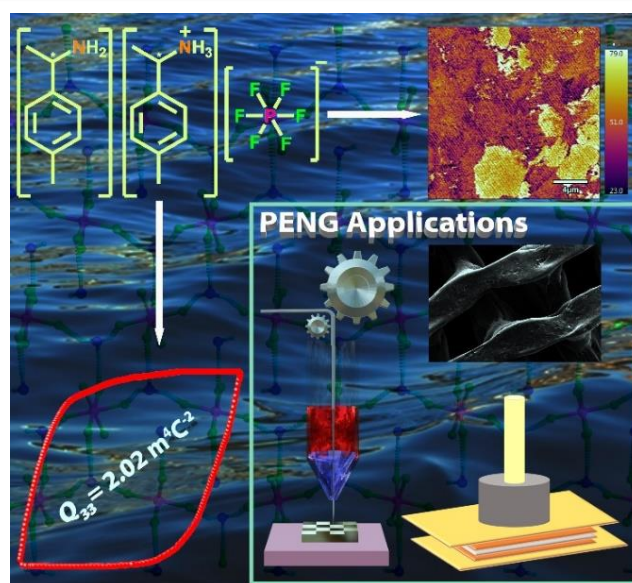


Figure 3: The structure of highly electrostrictive and moisture stable ammonium salt co-crystal **(p-TEA)(p-TEAH)·PF₆** along with P-E hysteresis loop and domain structure at room temperature. A pictorial representation of the preparation of **3DP-Gy** device by utilizing 3D printing for piezoelectric energy harvesting.

Chapter 5: A Chiral B-N Adduct as a New Frontier in Ferroelectrics and Piezoelectric Energy Harvesting

Within the burgeoning field of electronic materials, B-N Lewis acid-base pairs, distinguished by their partial charge distribution across boron and nitrogen centers,

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represent an underexplored class with significant potential. These materials exhibit inherent dipoles and are excellent candidates for ferroelectricity. However, the challenge lies in achieving the optimal combination of hard-soft acid-base pairs to yield B-N adducts with stable dipoles. Herein, we present an enantiomeric pair of B-N adducts [$^{R/S}\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{NH}_2\text{BF}_3$] ($^{R/S}\text{MBA-BF}_3$) crystallizing in the polar monoclinic $P2_1$ space group. The ferroelectric measurements on $^R\text{MBA-BF}_3$ gave a rectangular P - E hysteresis loop with a remnant polarization of $7.65 \mu\text{C cm}^{-2}$, a value that aligns with the polarization derived from the extensive density-functional theory computations. The PFM studies on the drop-casted film of $^R\text{MBA-BF}_3$ further corroborate the existence of ferroelectric domains, displaying characteristic amplitude-bias butterfly and phase-bias hysteresis loops. The piezoelectric nature of the $^R\text{MBA-BF}_3$ was confirmed by its direct piezoelectric coefficient (d_{33}) value of 3.5 pC N^{-1} for its pellet. The piezoelectric energy harvesting applications on the sandwich devices fabricated from the as-made crystals of $^R\text{MBA-BF}_3$ gave an open circuit voltage (V_{PP}) of 6.2 V. This work thus underscores the untapped potential of B-N adducts in the field of piezoelectric energy harvesting (Figure 4).

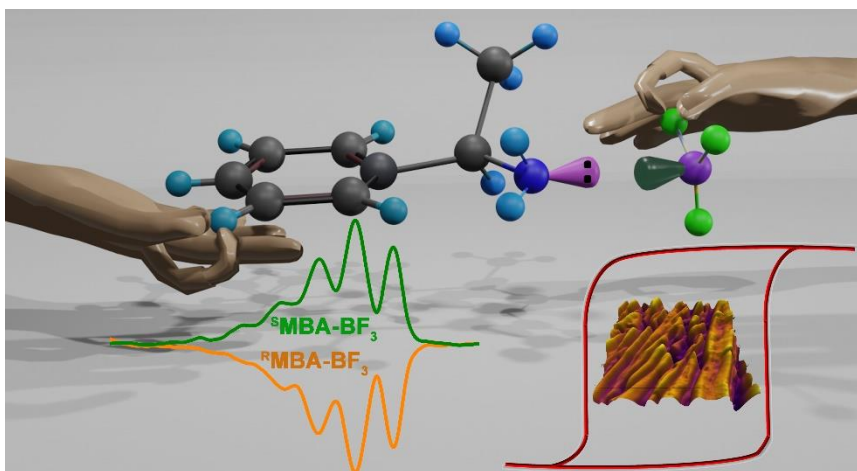


Figure 4: The approach of preparation of the enantiomeric pair of $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$ B-N adducts with their CD spectral analysis. The P - E hysteresis loop for $^R\text{MBA-BF}_3$ along with its topography image.

Abbreviations

Anal.	Analysis
Calcd.	Calculated
CIF	Crystallographic Information File
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
d_{33}	Piezoelectric Coefficient
E_c	Coercive Field
g_{33}	Piezoelectric Voltage Coefficient
ESI	Electron Spray Ionization
FASnI ₃	Formamidinium Tin Iodide
FeRAM	Ferroelectric Random Access Memory
FT-IR	Fourier Transform Infrared Spectroscopy
Hz	Hertz
I_{pp}	Peak-to-peak Short Circuit Current
KDP	Potassium Dihydrogen Phosphate
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization – Time of Flight
MEMS	Micro-electromechanical System
MeOH	Methanol
mg	Milligram
min	Minutes
ml	Milliliter
mm	Millimeter
mmol	Millimoles
M.P.	Melting Point
NaNO ₂	Sodium Nitrite
NEMS	Nano-electromechanical System
NMR	Nuclear Magnetic Resonance
PDMS	Polydimethylsiloxane
PFM	Piezoresponse Force Microscopy
P_r	Remnant Polarization
PLA	Poly(lactic acid)
PCL	Polycaprolactone
P_s	Saturation Polarization
PVDF	Poly(vinylidene difluoride)
PXRD	Powder X-ray Diffraction
RAM	Random Access Memory
RT	Room Temperature
SCXRD	Single Crystal X-ray Diffraction
SEM	Scanning Electron Microscopy
T_c	Curie Temperature
TGA	Thermogravimetric Analysis
TPU	Thermoplastic Polyurethane
V_{OC-PP}	Peak-to-peak Open Circuit Voltage
V_{OC}	Open Circuit Voltage
ZnO	Zinc Oxide
3DP	Three-dimensional Printing

Chapter 2

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Chapter 5

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Contributions Included in the Thesis:

1. Piezoelectric energy harvesting of a bismuth halide perovskite stabilised by chiral ammonium cations
[Supriya Sahoo](#), Nilotpala Deka, Ramamoorthy Boomishankar
CrystEngComm, **2022**, 24, 6172-6177.
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(Manuscript submitted)
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Angew. Chem. Int. Ed., **2024**, e202400366.

Contributions not included in the Thesis:

5. A Ferroelectric Aminophosphonium Cyanoferrate with a Large Electrostrictive Coefficient as a Piezoelectric Nanogenerator
Thangavel Vijayakanth, [Supriya Sahoo](#), Premkumar Anil Kothavade, Vijay Bhan Sharma, Dinesh Kabra, Jan K. Zaręba, Kadiravan Shanmuganathan, Ramamoorthy Boomishankar
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6. A Flexible Energy Harvester from an Organic Ferroelectric Ammonium Salt
Rishabh Gupta, [Supriya Sahoo](#), Swati Deswal, Premkumar Anil Kothavade, Prashant Dixit, Jan K. Zaręba, Kadiravan Shanmuganathan, Ramamoorthy Boomishankar
Chem. Asian J., **2021**, 16, 4122–4129.
7. Ferroelectricity and Piezoelectric Energy Harvesting of Hybrid A_2BX_4 -Type Halogenocuprates Stabilized by Phosphonium Cations

Publications

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8. Ferroelectricity in an All-organic Amine-Boronic Acid Co-crystal
[Supriya Sahoo](#), Nilotpall Deka, Jan K. Zaręba, Ramamoorthy Boomishankar
(*Manuscript under preparation*)
9. Advancements in Organic and Organic-inorganic Hybrid Derived Piezoelectric Energy Harvesters
[Supriya Sahoo](#), Nilotpall Deka, Ramamoorthy Boomishankar
(*Manuscript under preparation*)
10. A Ferroelectric Organic-Inorganic Hybrid Ammonium Halogenobismuthate(III) for Piezoelectric Energy Harvesting
Namonarayan Meena, [Supriya Sahoo](#), Nilotpall Deka, Jan K. Zaręba, Ramamoorthy Boomishankar
(*Manuscript submitted*)
11. A Ferroelectric Aminophosphonium Cyanocobaltate for Ferro- and Piezoelectric Studies
Thangavel Vijayakanth, [Supriya Sahoo](#), Premkumar Anil Kothavade, Jan K. Zaręba, Kadhiraavan Shanmuganathan, Ramamoorthy Boomishankar
(*Manuscript under preparation*)
12. Piezoelectric Energy Harvesting of a 2D-hybrid A_2BX_4 -type Ferroelectric Perovskite Stabilized by Ammonium Cations
Nilotpall Deka, [Supriya Sahoo](#), Jan K. Zaręba, Ramamoorthy Boomishankar
(*Manuscript under preparation*)
13. Ferroelectricity and Piezoelectric Energy Harvesting of an A_2MX_9 -type Organic-inorganic Hybrid
Namonarayan Meena, [Supriya Sahoo](#), Nilotpall Deka, Jan K. Zaręba, Ramamoorthy Boomishankar
(*Manuscript under preparation*)

Chapter 1



Introduction

1.1 Introduction to ferro- and piezoelectric materials for mechanical energy harvesting applications

Materials chemistry is an essential subject in the field of applied sciences and includes compounds ranging from inorganic, organic and organic-inorganic hybrid materials.¹⁻⁵ Materials with properties like ferroelectricity, piezoelectricity, and pyroelectricity are of great interest due to their broad applications in optoelectronic devices, memory devices, photovoltaics and mechanical to electrical energy conversion that are widely termed as nanogenerators.⁶⁻¹⁰ Preparing materials of this origin is directly related to the structural aspects of the molecule. Ferroelectric materials are a subclass of dielectric materials where polarization is developed in the molecule due to the application of an external electric field.¹¹⁻¹³ Additionally, spontaneous polarization can be reversed in ferroelectric materials by applying an external electric field in the reverse direction.¹³ The first reported ferroelectric materials are sodium potassium tartrate tetrahydrate (Rochelle salt, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) and potassium dihydrogen phosphate (KDP, KH_2PO_4).¹⁴⁻¹⁶ The polarization in these two molecules was attributed to the presence of H-bonding interactions in them. Subsequently, a number of inorganic ceramic oxide materials with predominant ionic interactions have been reported and shown to possess excellent ferroelectric polarization attributes.¹⁷⁻¹⁹ However, these inorganic ceramic materials, despite their superior ferroelectric characteristics, have certain disadvantages associated with them, particularly, due to the presence of heavy toxic metal contents in them.²⁰ Hence, research on alternative materials to ceramic oxides with environmental friendly attributes with reliable ferroelectric properties gained prominence. One of the important strategies in this effort involves the development of small molecule-based systems derived from organic compounds and organic-inorganic hybrids as they can be tailored to exhibit advantages like low-temperature processibility, easy synthesis, high thermal stability, lightweight, high Curie temperature, high remnant polarization, flexibility, etc.²¹⁻²⁴ Apart from these, they have also been explored for various applications involving ferroelectric random access memory, ultrasound imaging, capacitors, actuators, transistors, sensors, and photovoltaics.^{12, 25-29} Recently, these materials have been investigated for their thermoelectric and piezoelectric energy harvesting applications promising their utility in next-generation electronics.^{7, 30-32}

The production of sustainable and renewable energy resources includes harvesting of wind, wave, biomass, thermal, and mechanical energies in an efficient manner.³³⁻³⁷ Amongst these approaches of energy harvesting, the ones involving mechanical energy can be somewhat easier by subjecting them to human body activities such as applying pressure, bending, folding and stretching motions.³⁸⁻⁴⁰ Materials with properties like ferroelectricity, piezoelectricity, pyroelectricity, and triboelectricity are very advantageous because they convert mechanical energy into electrical energy by using the external stimuli effect of electric field, mechanical force, heat and friction, respectively.⁴¹⁻⁴³ In 2006, the very first piezoelectric nanogenerator (PENG) was discovered by Wang and co-workers, containing zinc oxide nanowires.⁴⁴ This extraordinary discovery spurred the development of many similar kinds of materials, such as perovskite-type inorganic ceramic oxides and polymeric materials such as polyvinylidene difluoride (PVDF), which were utilized and examined for PENG applications.⁴⁵⁻⁴⁷ Nevertheless, the use of traditional ceramic materials in wearable electronics is still limited, because of their disadvantages owing to their brittleness, high-temperature processibility, poling requirements, toxic metal contents, environmental unfriendliness, etc.²⁰ Similarly, the PVDF-based materials require additional processes such as melt quenching, high-temperature annealing, mechanical stretching, the addition of external binders, ultra-high cooling, and high-voltage poling procedures, etc.^{48, 49} Therefore, it is desirable to prepare noncentrosymmetric polar all-organic and organic-inorganic ferroelectric materials with no heavy metal contents and their composites with non-piezoelectric commercial polymers for PENG applications.

In view of this, the present thesis aims in the development of small-molecule-based organic and organic-inorganic hybrid ferro- and piezoelectric materials and their PENG applications in the native form or as their polymer composites. The introductory chapter gives a general idea about the background of dielectric materials and their subclasses, such as piezo-, pyro-, and ferroelectric materials. It focusses on some key examples of earlier reported piezo and ferroelectric materials comprising organic and organic-inorganic hybrid compounds and literature relating to the essential examples of mechanical energy harvesters in the form of composites of ferro- and piezoelectric materials.

1.2 Dielectric Materials

The electrical insulators that fail to conduct electric currents are named dielectric materials. These materials prohibit the electric current flow, unlike the conducting materials. External stimuli such as an electric field can align the opposite charges (positive and negative charges) towards or in opposite directions of the applied electric field in such materials, and the induced amount of positive and negative charges on either side of the plates is the same from the macroscopic point of view. Four polarisation mechanisms, which are described below, account for the polarization in a dielectric material.^{50, 51}

1. **Electronic Polarization:** All materials, upon being subjected to an electric field, experience this polarisation mechanism. The atom's nucleus and the center of its electron cloud move from their equilibrium positions in response to an electric field, creating a small dipole with a minute amount of polarization.

2. **Ionic Polarization:** This phenomenon is the most common in ionic compounds, where the ions are arranged in a symmetrical crystal lattice. In contrast to electronic polarization, when an electric field is applied, the positive and negative ions begin to move in opposite directions, causing a displacement that is considerably more significant.

3. **Dipole (or Orientation) Polarization:** Materials with a permanent dipole moment experience this polarization. An average net dipole moment is generated in such molecules as a result of their rotation in the direction of the applied field when exposed to an electric field.

4. **Space Charge (or Interfacial) Polarization:** In the interfaces of polycrystalline solids, this polarization primarily results from periphery charges, which result from impurities or uneven geometry. This additional type of polarization results from the highly mobile nature of these charges, which tend to migrate when subjected to an electric field.

Dielectric materials are generally classified into two classes: a) linear and b) nonlinear dielectric materials. In the case of linear dielectrics, the dielectric polarization is directly

associated with the applied electric field, showing a linear dependence. Whereas, the nonlinear dielectrics can retain their electric polarization even in the absence of an applied electric field and can, therefore, be utilized in various electronics involving transducers, transformers, actuators, and resonators.⁵²

The nonlinear dielectric property of any molecule is mainly related to the molecule's physical properties involving symmetry elements and crystal symmetry of the system. This context directly relates to the “Neumann’s principle”, which states the relationship of such structural aspects of the molecule with the symmetry elements present in the crystal lattice.¹⁵ Any system in three dimensions is comprised of 32 crystallographic point groups and 14 Bravais lattices belonging to 7 crystal lattice systems. Out of these 32 point groups, 11 of them possess a center of inversion (called centrosymmetric, and the remaining 21 do not possess an inversion center (called non-centrosymmetric)).²² The nonlinear dielectric materials where polarization is induced by mechanical stress (piezoelectric materials) find their place in 20 of the 21 non-centrosymmetric point groups (except the point group 432). Among these 20, only 10 possess a unique polar axis and are considered a subgroup of piezoelectric materials exhibiting pyroelectricity (thermal changes induce polarization in the system) and ferroelectricity (polarization reversal is attained by applied electric field). The statement “All ferroelectrics are piezo- as well as pyroelectric” is true, but the reverse is not. Hence, the nonlinear dielectric materials are classified into three main subgroups such as a) piezoelectric, b) pyroelectric, and c) ferroelectric materials (Figures 1.1 and 1.2).⁵²

1.2.1 Subgroups of dielectrics (piezo-, pyro- and ferroelectrics)

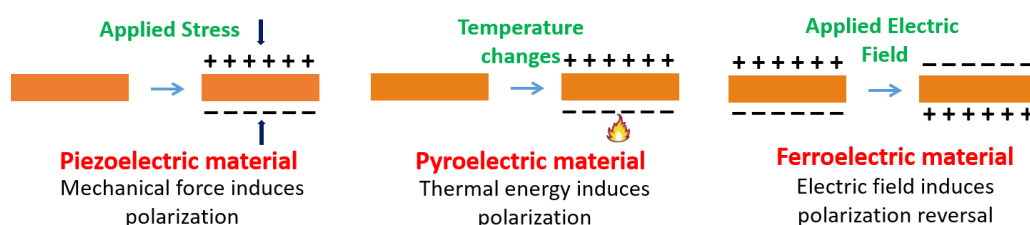


Figure 1.1: Types of Non-linear Dielectric Materials.

Piezoelectric materials, when subjected to applied stress or mechanical force, generate electrical polarization. The first ever piezoelectric single crystal Rochelle salt was developed 100 years ago by Pierre and Jacques Curie. The piezoelectric effect in a material results from the linear relationship between mechanical stress (or force) and applied electric field.⁵²

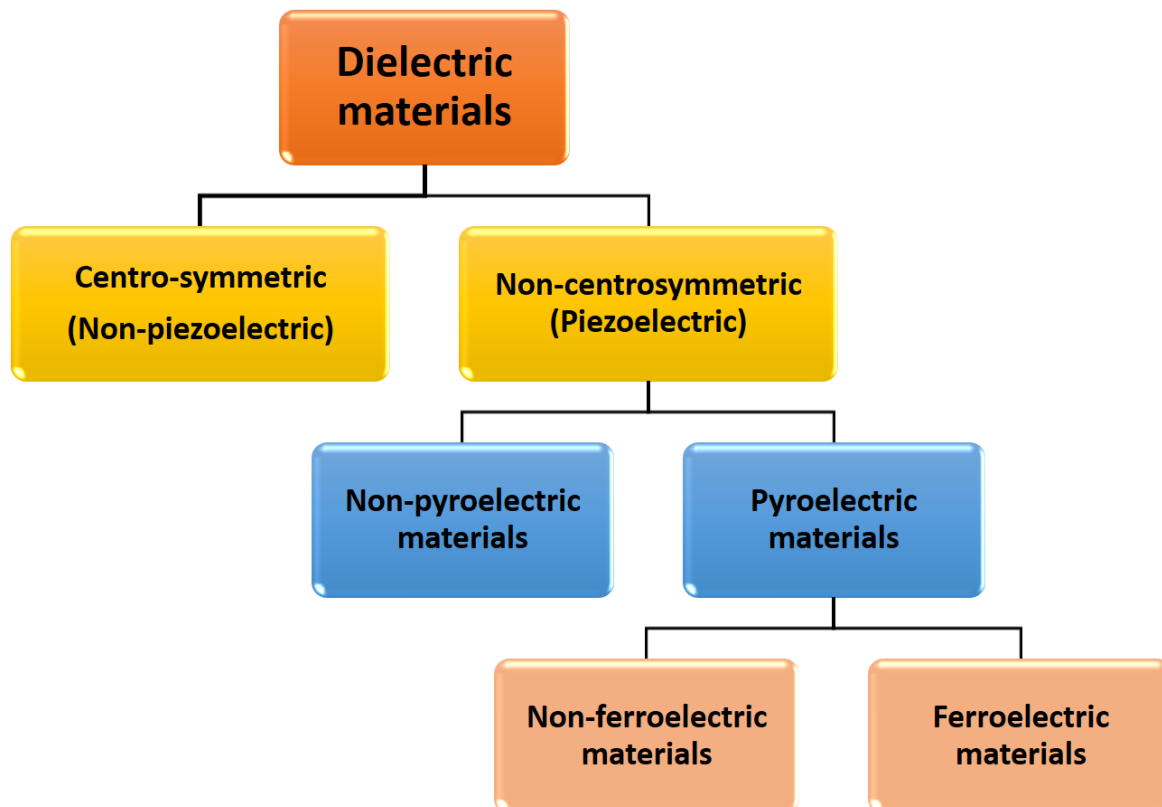


Figure 1.2: Classifications of dielectric materials.

The piezoelectric effect is generally classified into two types such as a) direct piezoelectric effect and b) converse piezoelectric effect. The piezoelectric charge constant coefficient is defined as the change in polarization per applied mechanical stress (direct piezoelectric effect) or strain developed in any nonlinear material per unit of an applied electric field (converse piezoelectric effect). Such materials can be categorized by piezoelectric coefficients such as d_{31} , d_{32} , and d_{33} , respectively.^{52, 53} The double subscripts describe the direction of different quantities, such as applied force and the generation of electrical charges on the piezoelectric material. The first

subscript denotes the electric polarization, while the second describes the applied electric field. The magnitude of different piezoelectric coefficients are expressed with the units pC N^{-1} (direct piezoelectric effect) and pm N^{-1} (converse piezoelectric effect). The “Berlincourt” method, which is associated with a dynamic mechanical force setup made up of a commercial piezo-meter, is used to measure the direct piezoelectric charges developed in a material. Such materials are utilized in many real-life applications involving piezoelectric sensors, actuators, transformers, and energy harvesters, etc.⁵³

Materials with polar point groups (1, 2, m, mm2, 3, 3m, 4, 4mm, 6, 6mm) generating electrical polarization under different thermal conditions (heating or cooling), are known as pyroelectric materials. The polarization mechanism involves the change in atomic spatial position, producing a transient voltage across the crystal lattice. Every piezoelectric material exhibits pyroelectricity and thus finds its corresponding application in gas sensing devices, infrared sensors, pyroelectric sensors, thermistors, pyrometers, detectors, pyroelectric energy harvesters, etc.^{51, 54}

The distinct class of dielectric substances, in which the reorientation of spontaneous electrical polarization is possible by the application of an external electric field, are known as ferroelectric materials. The crystalline materials adopting one of the 10 polar point groups (C_1 , C_2 , C_{1h} , C_{2v} , C_3 , C_{3v} , C_4 , C_{4v} , C_6 , and C_{6v}) exhibit ferroelectricity and are known to be a subgroup of piezo- and pyroelectric materials. These materials can switch their polarization direction as a result of the application of an electric field in the reverse direction, giving rise to a typical P - E hysteresis loop. As depicted in [Figure 1.3](#), at point O, the positive and negative domains are dispersed equally, generating a net polarization of zero magnitude. Further, incrementing the applied electric field in a positive direction result in the alignment of the dipoles in the direction of the applied electric field, giving rise to saturation polarization (P_s). The application of a reverse electric field at zero points (I) results in the remnant polarization (P_r) because some of the dipoles are still aligned in one direction, giving rise to a nonzero net dipole moment. The application of some additional electric field in the reverse direction, called as coercive field (E_c), results in zero remnant polarization. The extension of the electric field strength in the opposite direction results in the alignment of all the switchable

negative domains in the negative polarity of the electric field (FE) and thus completes the hysteresis loop for any polar acentric material that exhibits ferroelectricity.⁶

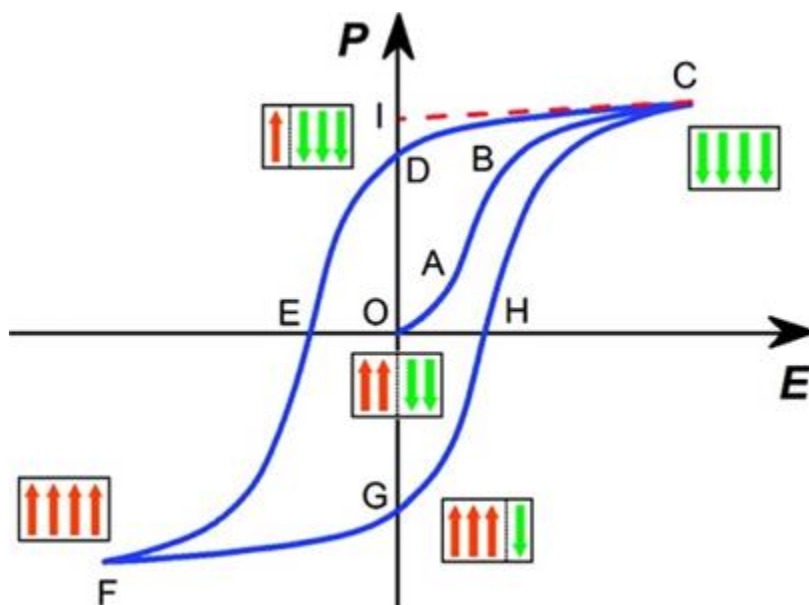


Figure 1.3: The relationship between polarization (P) and electric field (E) hysteresis loop. Adapted with permission from ref. 6. Copyright © 2012 American Chemical Society.

In ferroelectric materials, the increase in temperature gradients can disturb polar arrangements within the material. Above a specific temperature known as Curie temperature (T_c), the nonlinear dielectric (ferroelectric) becomes linear dielectric (paraelectric) material. Such structural changes in a ferroelectric material depend on several factors, such as Gibbs free energy, temperature, pressure, etc., and are mainly classified into two types: first-order and second-order transition. A polar arrangement disturbance within a material leads to structural phase transitions in the molecule from high symmetry, high-temperature paraelectric phase to lower symmetry ordered arrangement, low-temperature ferroelectric phase.⁵⁵ Such phase changes in a dielectric material can result in changes in crystal symmetry, electrical and thermal properties. Characterization techniques such as thermal analysis, single crystal, and powder X-ray analyses, P - E hysteresis loop, temperature and frequency-dependent

dielectric constant measurements, second harmonic generation, etc. can be performed to detect these phase changes.⁵⁵

1.3 Classification of ferroelectric materials

The initial research on ferroelectric materials was mainly focused on hydrogen bonded assemblies like Rochelle salt (sodium potassium tartrate tetrahydrate, $\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) potassium dihydrogen phosphate (KH_2PO_4 , KDP) and Triglycine sulfate ($[(\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4]$, TGS).^{7, 14, 56} These salts have some disadvantages due to their instability, poor mechanical strength, low ferroelectric polarization and very low Curie temperatures (T_c). This led to the development of many inorganic ceramic oxides of generic formula ABX_3 (where, A = a monovalent cation, B = a divalent transition metal ion, and X = oxygen anion), which were very advantageous in terms of their excellent ferroelectric properties and high structural stability over a wide temperature range. Perovskite materials like barium titanate (BaTiO_3), potassium niobate (KNbO_3), lithium, lead titanate (PbTiO_3), niobate (LiNbO_3), lead zirconate titanate (PbZrTiO_3) exhibit excellent ferroelectric properties with stability advantages such as high Curie temperature, air stability, water insolubility etc.⁵⁷⁻⁵⁹ Because of these advantages, oxide-based inorganic ceramic materials find commercial applications as non-volatile memory devices, photovoltaic devices, capacitors, storage devices, field-effect transistors, piezoelectric sensors, magnetic field detectors, and recently in the field of mechanical energy harvesters.^{25, 60} However, ceramic materials have some disadvantages because of their critical synthesis at high temperatures, brittle nature, polling requirements and toxic metal contents and thus are not environment-compatible to be used in wearable electronics. Polymeric materials with all organic contents have also been explored for their ferro- and piezoelectric properties. Studies on polyvinylidene difluoride (PVDF) and its copolymers revealed remarkable ferro- and piezoelectric attributes.⁴⁷ But even these polymeric materials require high coercive fields to activate the β phase.⁴⁵

Thus, one of the ways to tackle the challenges posed by inorganic ceramic oxides and polymeric ferroelectric materials could be the development of low molecular weight all-organic and organic-inorganic hybrid materials. These are easy to synthesize and could be tuned to exhibit excellent physical properties like flexibility, thermal stability,

lightweight, high ferroelectric polarization, low coercive field, high Curie temperature, etc. Recently, several groups have embarked on the synthesis of examples of organic and organic-inorganic hybrid-based ferro- and piezoelectric materials, which show excellent energy harvesting properties when embedded in a polymer matrix (composites).^{61, 62}

Ferroelectric materials can be classified into three types depending on their atomic and molecular content such as inorganic, organic, and organic-inorganic hybrid materials, respectively. The different kinds of ferroelectric materials, along with their subclassifications, are discussed in the subsequent sections.

1.4 Inorganic ferroelectric materials

The first inorganic ferroelectric ceramic materials like BaTiO₃, LiNbO₃ and (Pb(Zr, Ti)O₃) are examples of non-hydrogen bonded ferroelectric materials.⁶ These materials were polar due to the relative displacement of ions from their atomic positions rather than the presence of polar ions in their crystal structure. Ceramic materials have high ferroelectric polarization values and high Curie temperatures in a wide range of temperatures. However, the environmental concerns that arise due to the toxic metal ion contents in ceramic materials impede their use in wearable electronics. Sodium nitrite (NaNO₂), is another example of ferroelectric material, in which the reorientation of dipolar NO₂⁻ ions results in ferroelectric polarization.⁶³ KDP (KH₂PO₄), which showed the spontaneous polarization of 4.8 μC cm⁻² at very low Curie temperature (T_c = 123 K), is another example of hydrogen-bonded inorganic ferroelectric material.¹⁴ Hence, the search for alternate ferroelectric materials for high technological applications has intensified over the past two decades.

1.5 Organic ferroelectric materials

Organic ferroelectric materials, due to their advantages like facile synthesis, lightweight, mechanical flexibility, non-toxic elements, etc., are gaining tremendous attention.^{16, 64} These materials are getting their applications in electro-optic and molecular organic electronics due to their flexible nature. The organic ferroelectrics are subdivided into two categories, namely single-component and organic binary salts.

The current section mainly focuses on single-component organic, organic binary salt, and charge-transfer materials derived ferroelectrics.

1.5.1 Single-component organic ferroelectric materials (SCOFM)

A. L. Solomon discovered the first single-component, low-molecular-mass ferroelectric substance, thiourea, in 1956.⁶⁵ Thiourea exhibits multifunctional behavior (pyroelectric, ferroelectric, and piezoelectric) below ambient temperature. It exhibits outstanding ferroelectric polarization at low Curie temperature ($T_c \sim 120$ K) ($P_s \sim 3.2 \mu\text{C cm}^{-2}$). Further, a number of SCOFM were described based on TEMPO, (2,2,6,6-tetramethyl-1-piperidinyloxy), DNP (diacetylene-1,6-bis(2,4-dinitrophenoxy)-2,4-hexadiyne), TCAA (trichloro acetamide), Benzil, CDA (cyclohexane-1,1-diacetic acid), etc.^{16, 64, 66-69} Despite this, there are not many studies on single-component organic ferroelectric materials with high spontaneous polarization and Curie temperatures in the literature.

The above-room temperature ferroelectric behavior of croconic acid (4,5-dihydroxy-4-cyclopentene-1,2,3-trione, $\text{H}_2\text{C}_5\text{O}_5$) molecular crystals was described by Tokura and coworkers in 2010.^{66, 69} It has been demonstrated that the derivatives of other families of cyclic oxocarbon acid systems crystallize in centrosymmetric space groups.^{66, 70, 71} Each pentagonal ring of carbon atoms in croconic acid was joined by oxygen and hydroxyl groups, which play a role in the cooperative proton tautomerism mechanism (Figure 1.4a). The ferroelectricity in croconic acid is produced via proton migration over a polarizable π -conjugated link. The measured spontaneous polarization for the 2D hydrogen-bonded polar sheet was found to be $21 \mu\text{C cm}^{-2}$. The most intriguing finding in croconic acid is that it exhibits no phase changes (Curie temperature) up to 400 K, which makes it different from the reported ferroelectric materials.^{66, 69}

The enhanced ferroelectric polarization ($P_s \sim 30 \mu\text{C cm}^{-2}$) based on a single crystal of croconic acid has recently been demonstrated by the same research team (Figure 1.4b).⁶⁹ Despite outperforming other single-component organic ferroelectric materials in terms of ferroelectric performance, it is unstable and corrosive even at ambient temperatures, limiting its applicability in organic electronics applications. Croconic acid thin films are predicted to produce a reduced or zero effective remnant polarization for

its randomly oriented crystallites due to the uniaxial ferroelectric polarization character of croconic acid (with only two opposed polarization orientations along the polar c -axis).

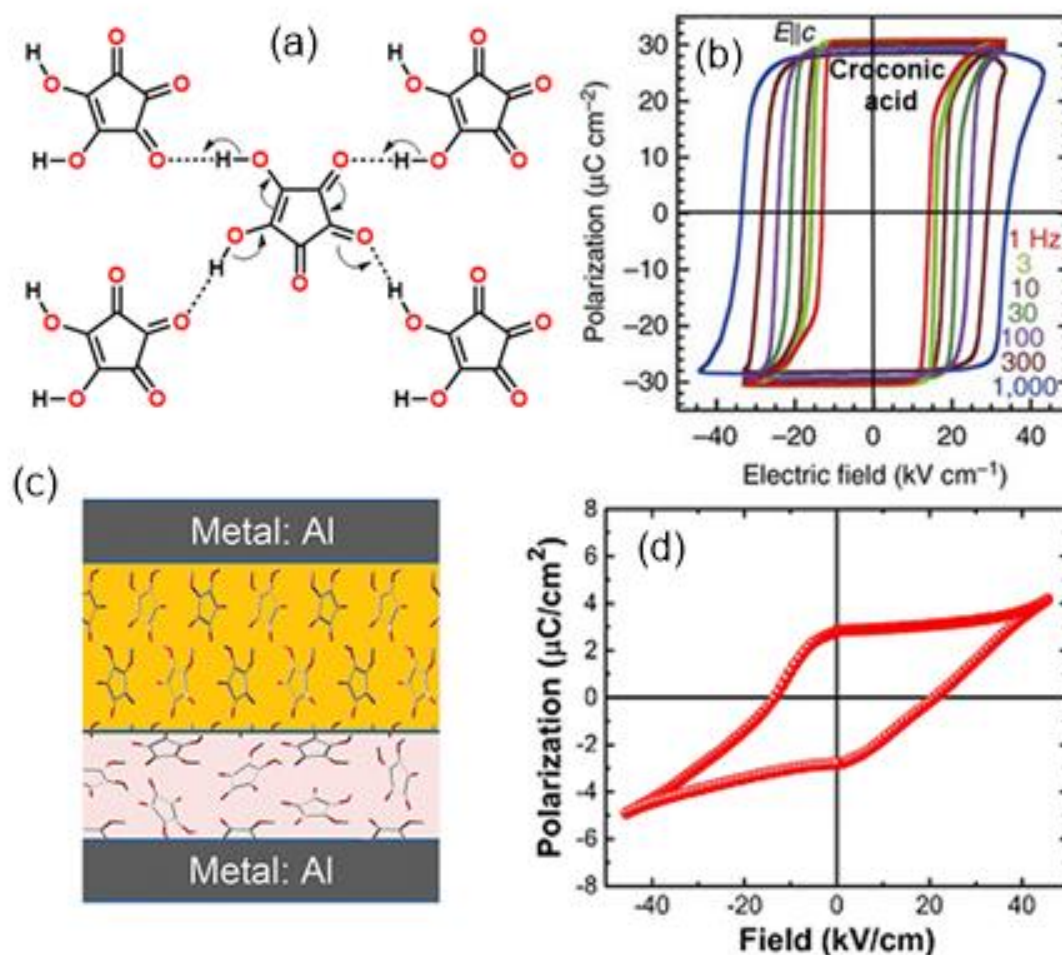


Figure 1.4: (a) Proton tautomerism in croconic acid. (b) P - E hysteresis loop obtained for a croconic acid single crystal. (c) The schematic view of the uniaxial croconic acid devices ($500 < d < 2100$ nm) with Al electrodes depicting a double-layer system with different crystalline orientations. (d) The polarization-voltage hysteresis loop of the device based on the thin film of croconic acid (with thickness ~ 2 nm) after applying a bias of 20 V. Adapted with permission from ref. 69. Copyright © 2017 The Author(s) of Publication and ref. 72. Copyright © 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

In this endeavor, C. Cong and coworkers proved that ferroelectricity can exist in croconic acid films that have been thermally evaporated and formed on various substrates, demonstrating the possibility of such a film serving as a memory device.⁷² As seen in cross-sectional scanning electron microscopy (SEM) pictures of the film, the as-grown thick films (>500 nm) acquire the desirable crystallographic orientation (Figure 1.4c), which is essential for polarization. Additionally, when measuring the devices using PFM, polarization-voltage (P - V), and current density-voltage (J - V) techniques in the air (i.e., with some relative humidity), as compared to measurements made in a vacuum, a higher polarization was obtained. This finding reveals that the stable ferroelectric polarization is apparently caused by the space charges, which are created by moisture and the charge injection/trapping near the electrodes. According to the thickness of the film, the devices made of croconic acid films have polarization values between 3 and 30 $\mu\text{C cm}^{-2}$ and coercive fields between 13 and 30 kV cm^{-1} , which are equivalent to the values obtained for its single crystals (Figure 1.4d). The devices that have been obtained can also function at low operational voltages (5 V).⁷²

1.5.2 Acid-base adducts as organic ferroelectric materials

The domains of chemical, physical, and materials science are all impacted by the multifunctional nature of organic ferro- and piezoelectric materials. Organic piezoelectric materials are desirable for printable, flexible, and sensor-electronic systems because of their light weight, mechanical flexibility, affordability, environmental friendliness, and low manufacturing temperature. The use of organic piezo- and ferroelectric materials based on small molecules in mechanical energy harvesting applications is highlighted in this sub-section. Trimethylamine borane (TMAB), a commercially available acid-base adduct, has recently been used to show its applicability in piezoelectric energy harvesting (Figure 1.5a).⁷³ Alteration of the nonpolar nature of the five-carbon containing branched hydrocarbon neopentane by swapping out the central C–C bond with a N–B bond results in a charge separation giving rise to a ferroelectric system. The single crystal X-ray diffraction investigation of TMAB revealed its space group to be polar rhombohedral $R3m$ (Figure 1.5b). The packing diagram of TMAB reveals the head-to-tail interactions present between the

Me_3N and BH_3 groups along their polar axes with a B-N bond distance of 1.6174(58) Å (Figure 1.5c).

By applying mechanical pressure and temperature oscillations, this Lewis acid-base adduct exhibits piezo- and pyroelectric sensing potential. The flexible TMAB device, after poling, displayed an open-circuit voltage and short-circuit current of 10.85 V and 0.42 A, respectively, upon application of mechanical stress by finger tapping (Figure 1.5d-1.5e).⁷³ This is the first occasion where a straightforward flexible substrate made of amine-borane exhibits multi-modal energy-harvesting abilities. Future investigations of many organic piezoelectric material-based devices could be inspired by this innovative design method.

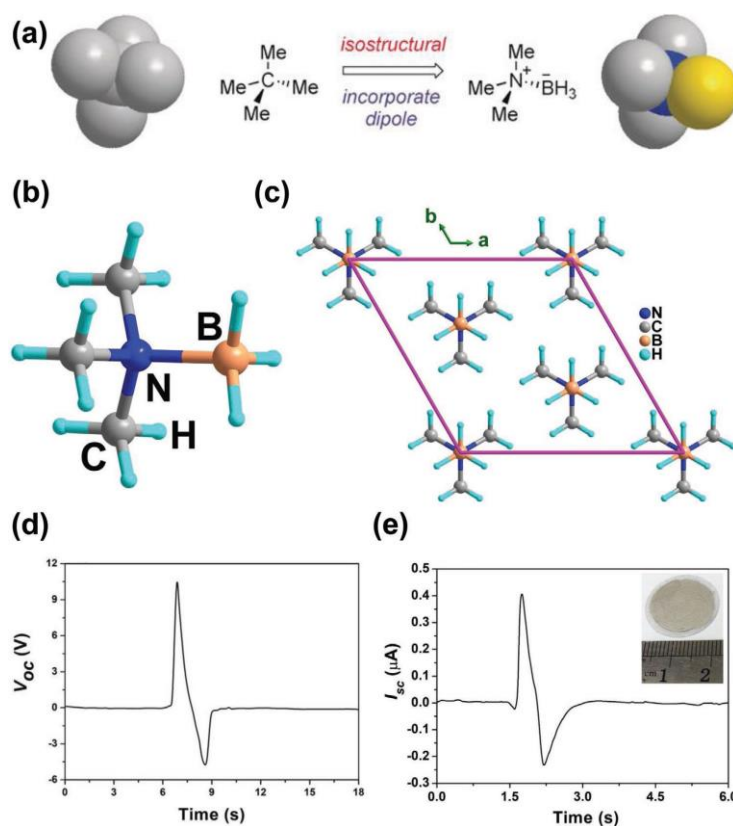


Figure 1.5: (a) The design principle of TMAB. (b) Molecular structure and (c) packing diagram of TMAB along the crystallographic "c" axis. (d) Piezoelectric energy harvesting Output voltage (e) The output current of TMAB device. Adapted with permission from ref. 73. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.5.3 Binary organic ferroelectric materials

There have been a number of investigations on the piezoelectric and ferroelectric capabilities of organic binary salts. The recent intriguing reports involving the binary organic ferroelectric salts are highlighted here.

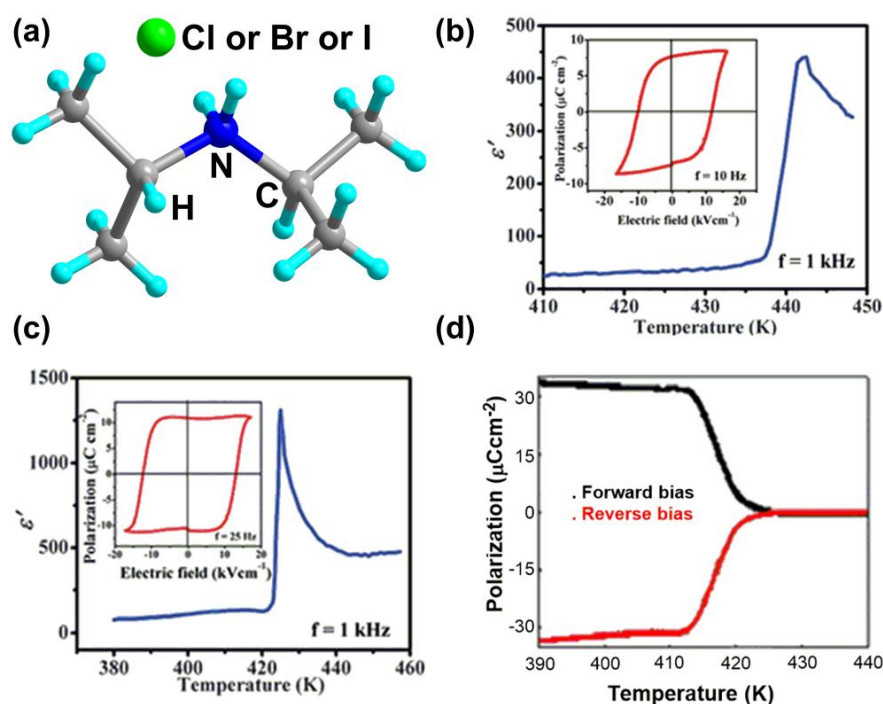


Figure 1.6: (a) The molecular structure of the halide salts of DIPA cation. Temperature-dependence of the dielectric constant for (b) DIPAC and (c) DIPAB crystals along the *b*-axis. Insets: The *P*-*E* hysteresis loops of DIPAC and DIPAB, respectively. (d) The temperature-dependent pyroelectric measurement of DIPAI. Adapted with permission from ref. 22. Copyright © 2016 The Royal Society of Chemistry and ref. 76. Copyright © 2017 AIP Publishing.

Simple molecular crystals of diisopropyl ammonium halides (DIPAH, where H = Cl, Br, I) have recently been the subject of a thorough exploration of new molecular ferroelectric materials.⁷⁴⁻⁷⁶ All three of these derivatives, diisopropyl ammonium chloride (DIPAC), diisopropyl ammonium bromide (DIPAB), and diisopropyl ammonium iodide (DIPAI), exhibit the ordered and disordered structure of ammonium cations in the corresponding low-temperature and high-temperature phases, which

governs their ferroelectric behavior. Ferroelectric polarization of all DIPAC, DIPAB, and DIPAI show a rising trend, with P_s values of 8.9, 23, and 33 $\mu\text{C cm}^{-2}$, respectively (Figure 1.6). From the observed trends in the ferroelectric polarizations of DIPAC, DIPAB, and DIPAI, it is evident that the atomic sizes of the anions in the DIPA salts influences the magnitude of the dipole moments in them. These outcomes are equivalent to those obtained with numerous conventional inorganic ceramic oxides and ferroelectric polymers.^{6, 16}

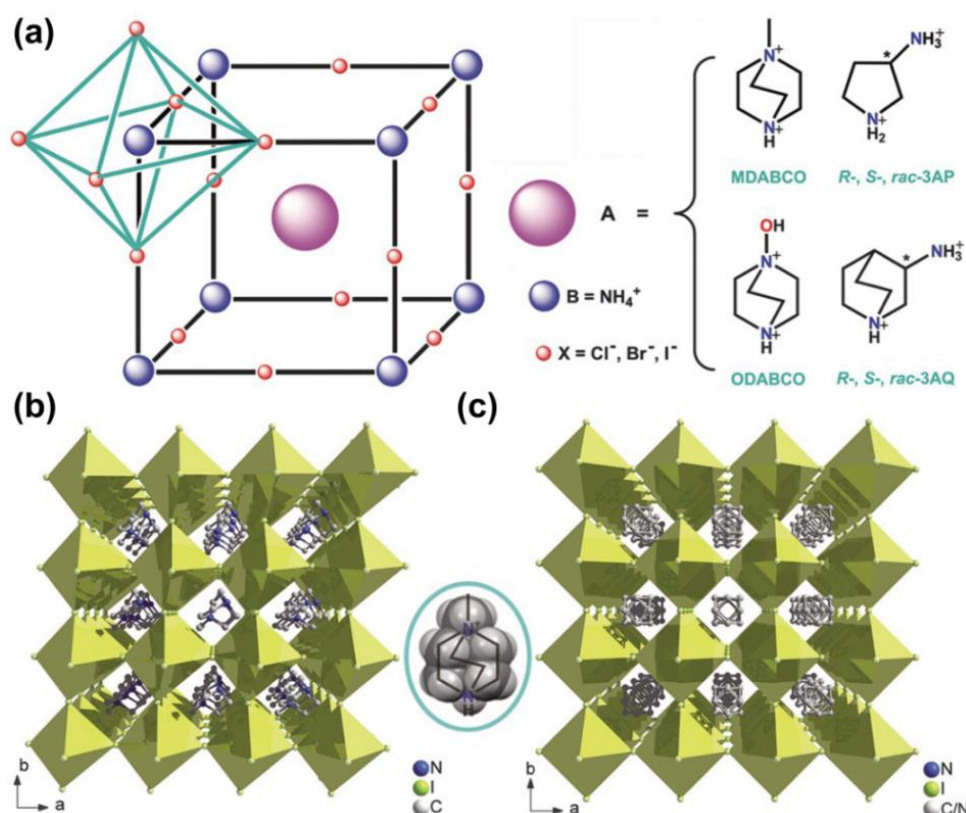


Figure 1.7: (a) The chemical structures of 3D-metal free ferroelectric perovskite. (b) and (c) crystal packing diagrams of MDABCO-NH₄I₃ in the ferroelectric (293 K) and paraelectric phase (463 K). Adapted with permission from ref. 77. Copyright © 2018 The American Association for the Advancement of Science.

Metal-free three-dimensional perovskite structured organic ferroelectric materials have lately (in 2018) been reported by Xiong and co-workers (Figure 1.7). For example, the MDABCO (N-methyl-N'-diazabicyclo[2.2.2]octonium)-ammonium triiodide salt is a representative member of these organic metal-free perovskites with

the generic formula ABX_3 (A = organic divalent cation, B = organic monovalent cation, and X = halide anions).⁷⁷ The organic ammonium cations are positioned in the center of the cavities, and the 3D-perovskite structures were created by corner-sharing of $(NH_4)X_6$ (X = Cl, Br, or I) octahedra that encompass the overall framework. The ionic and hydrogen-bonded interactions maintain the forces of attraction between the host and guest frameworks. The X-ray single crystal study of MDABCO- NH_4I_3 revealed that it crystallized in the space groups of trigonal $R\bar{3}$ and cubic $P432$, respectively, at ferroelectric (293 K) and paraelectric (463 K) phases. The MDABCO- $(NH_4)I_3$ single crystals exhibit outstanding ferroelectric and piezoelectric polarization. Further evidence for the observed ferroelectric polarization comes from pyroelectric current measurements, which yielded a P_s value of $22 \mu C cm^{-2}$ along the crystallographic [111] plane. These findings demonstrate the potential of these compounds as an alternate material choice for applications involving flexible electronic devices and are comparable to those of inorganic ceramic perovskite materials.

1.6 Organic-inorganic hybrid ferroelectric materials

Perovskite compositions of the type ABX_3 (X = O) have been studied at several research frontiers, particularly in light-emitting diodes and solar cells. By varying the organic cations and anions, such as azides (N_3^-), cyanides (CN^-), halides (Cl^- , Br^- , and I^-), dicyanamides ($N(CN)_2^-$), borohydrides (BH_4^-), and formates ($HCOO^-$) additional functionalities and structural flexibility were gained by these materials.^{78, 79} The utilized cations and anions aid in the construction of numerous hybrid frameworks, including 1D, 2D, and 3D assemblies. This section gives some notable instances of organic-inorganic hybrid materials that exhibit strong ferroelectric characteristics.

1.6.1 Halogenometallate ferroelectric materials

Perovskite halogenometallates are well known for their use as light-harvesting layers in solar cells, but recent studies have focused on some of their ferroelectric properties as well.⁸⁰

A novel two-dimensional multi-layered ferroelectric perovskite framework $[(C_4H_9NH_3)_2(CH_3NH_3)_2][PbBr_{10}]$ was recently published by Luo and co-workers (Figure 1.8). At $T_c = 315$ K, this material undergoes a phase change from ferroelectric to

paraelectric state.⁸¹ Further evidence supporting the existence of ferroelectricity comes from P - E hysteresis loop measurements, which show a P_s value of $2.9 \mu\text{C cm}^{-2}$ and a coercive field of 16 kV cm^{-1} . This 2D perovskite's crystal wafer was used to create stable photodetectors on a single functional layer with a very low dark current, high response rate, and significant on/off current ratio. These findings indicate its potential in various applications, including high-performance optoelectronic devices, multiferroics, and photoferroelectric characteristics.

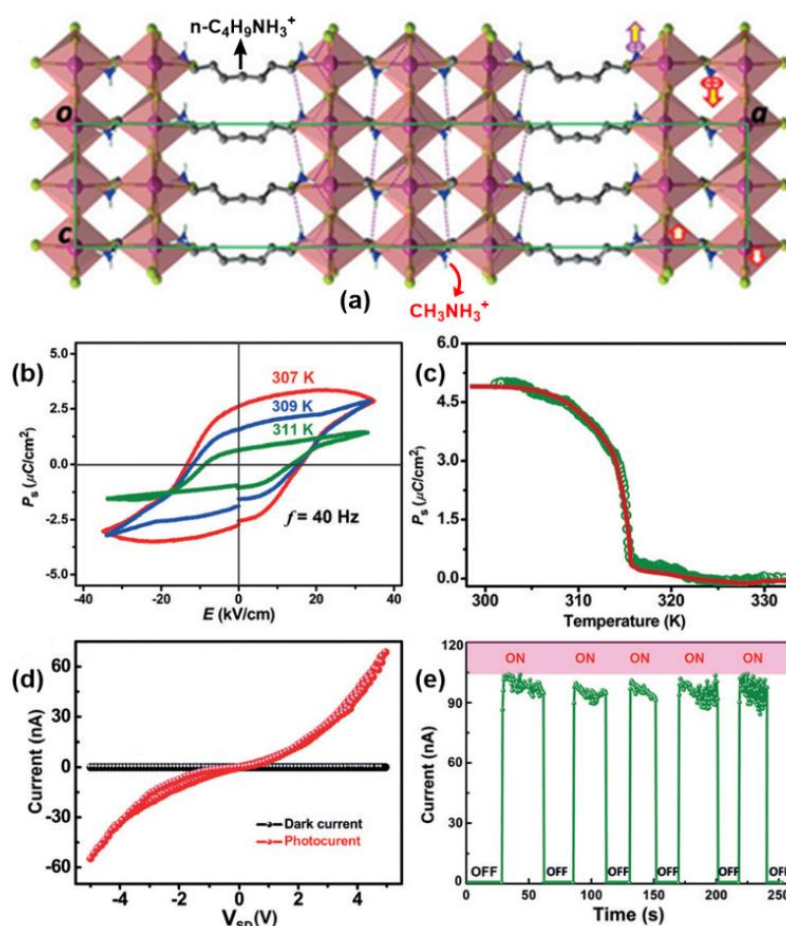


Figure 1.8: (a) Packing structure of $[(\text{C}_4\text{H}_9\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2][\text{PbBr}_{10}]$ along b -axis at 293 K, (b) Its ferroelectric hysteresis loops at various temperatures. (c) The temperature dependence of its spontaneous polarization obtained by the pyroelectric measurements. (d) The on/off ratio of photocurrent to dark current ($\lambda=420 \text{ nm}$). (e) The recyclable switching operation of photocurrent response, showing no obvious reduction in long-time illumination. Adapted with permission from ref. 81. Copyright © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Finding an alternative source for lead-free perovskite frameworks, however, remains a difficult task. A recent study shows the compound (N-methylpyrrolidinium)₃Sb₂Br₉ exhibits high P_s and P_r values of 7.6 $\mu\text{C cm}^{-2}$ and 7.3 $\mu\text{C cm}^{-2}$, respectively.⁸² The deformed SbBr₆ octahedra in this perovskite-like compound was the cause of its discrete nature. Additionally, the band-gap value of 2.76 eV indicates the semiconducting behavior of the compound.

Xiong and co-workers reported the above room-temperature ferroelectricity for the semiconducting (2-(ammoniomethyl)pyridinium)SbI₅ hybrid perovskite. The Curie temperature (T_c) of this material was found to be 360 K.⁸³ In the ferroelectric phase, there is a significant spontaneous polarization ($P_s \sim 4 \mu\text{C cm}^{-2}$) as well as a weak coercive field ($E_c \sim 9 \text{ kV cm}^{-2}$). Additionally, it has a narrow bandgap of 2.03 eV and a powerful absorption ability that is much smaller than those of lead-halide perovskite ferroelectrics (2.7 eV) and bifunctional iron oxide (2.7 eV) (2.7-3.65 eV). These features suggest that it could be used in high-performance ferroelectric optoelectronic and photovoltaic systems.

By replacing Me_4N^+ with a $\text{Me}_3\text{NCH}_2\text{Cl}^+$, Xiong and co-workers have obtained a novel 1D ABX_3 type perovskite (TMCM) MnCl_3 (TMCM: trimethylchloromethylammonium) (Figure 1.9).⁸⁴ The observed piezoelectric coefficient (d_{33}) value of 185 pC N^{-1} for this compound is comparable to many well-known piezoceramics like BTO (190 pC N^{-1}). (TMCM) MnCl_3 has a spontaneous polarization value of 4 $\mu\text{C cm}^{-2}$ with a high T_c of 406 K, enabled by the order-disorder transition of the cations from the ferroelectric to the paraelectric phase. They have also synthesized (TMCM) CdCl_3 , with a much higher piezoelectric coefficient of 220 pC N^{-1} .⁸⁵ In a similar manner, the piezoelectric characteristics of (TMBM) MnBr_3 (TMBM: trimethylbromomethylammonium)⁸⁶ and (TMCM) CdBr_3 ⁸⁷ were carefully studied. (TMBM) MnBr_3 demonstrated a high T_c of 415 K and a sizable piezoelectric coefficient of 112 pC N^{-1} , whereas (TMCM) CdBr_3 displayed a lower T_c of 346 K but a noteworthy d_{33} of 139 pC N^{-1} . These attributes demonstrate the potential of small-molecule-derived systems for biomedical sensor applications, micro-electromechanical systems (MEMS), and flexible devices.

Although the piezoelectric capabilities in the aforementioned instances were extremely inspiring, they still could not compete with the most expensive PZT ceramics. In order to get a larger piezoelectric coefficient, Xiong and co-workers used a molecular design approach to find the solid solution $(\text{TMFM})_x(\text{TMCM})_{1-x}\text{CdCl}_3$ ($0 \leq x \leq 1$), which revealed the existence of a piezoelectric coefficient of 1540 pC N^{-1} at $x = 0.26$ composition.⁸⁵ The extremely high d_{33} value, which is nearly two times that of commercially available PZT piezoceramics, was primarily because of the morphotropic phase boundary between the monoclinic and hexagonal phases at the specified composition. This ground-breaking finding paved the way for molecular perovskites towards next-generation piezoelectric medical devices.

1.6.2 Metallocyanate ferroelectric materials

One of the most important groups of organic-inorganic hybrid materials, metallocyanates are discovered to have intriguing magnetic, electric, and optical properties.^{80, 88-90} The compounds $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Co}(\text{CN})_6]$, and $\text{K}_3[\text{Cr}(\text{CN})_6]$ are a few well-known examples of cyanide ion connected metal coordination complexes (metallocyanates or cyanometallates). They exhibit the general compositions, ABX_3 and $\text{A}_2[\text{BM}(\text{X})_6]$, where A is the monovalent organic cation, B is the monovalent alkali cation, M is the transition metal ion, and X is CN. These hybrid compounds can form single and double perovskite structures.

The binding between B-CN in this heterometallic perovskite structure is weak and ionic, while the bond between M-CN is stronger and covalent. The structure featuring B site atoms and CN functions as a host framework, while the A-site cations (ammonium or phosphonium cation) can operate as a guest molecule. The topology of the overall structure of these assemblies ranges from higher dimensional (3D) to lower dimensional (0D), which is often determined by the interactions of the host and guest frameworks and the size of the guest ions. The majority of these hybrid frameworks were found to exhibit multiple dielectric phase transitions that were augmented by the order-disorder nature of the ions, and mostly crystallized in centrosymmetric space groups at room temperature.^{79, 80} Results relating to metallocyanates-based nonlinear dielectric materials are uncommon in the literature.

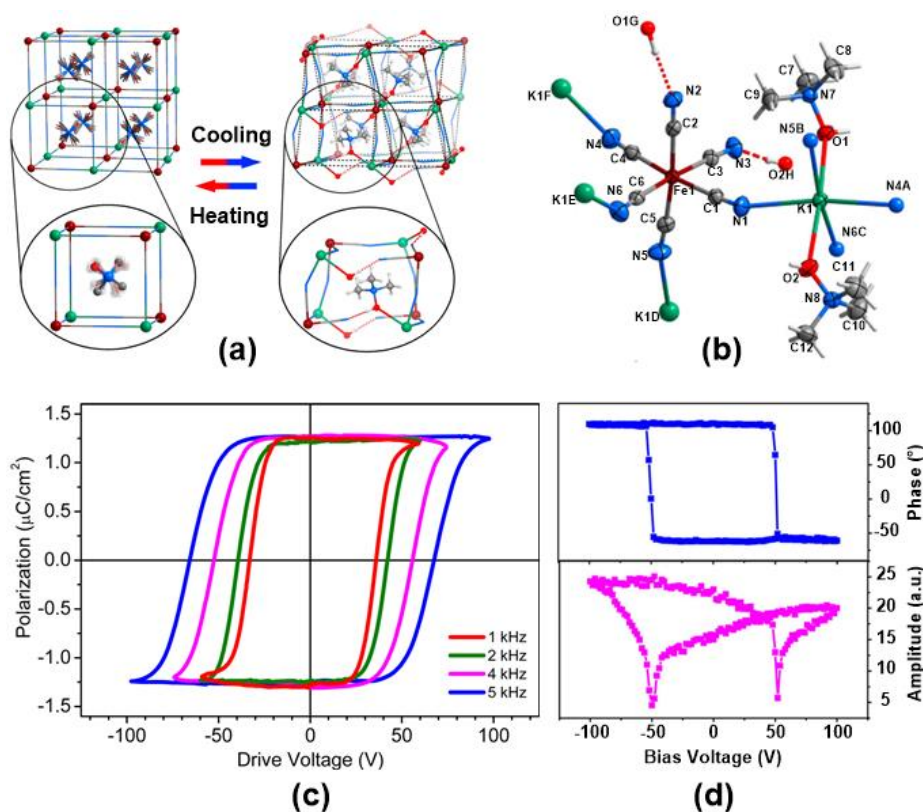


Figure 1.10: (a) Temperature-dependent bond switching in $[(CH_3)_3NOH]_2[KFe(CN)_6]$ due to the disordered and ordered nature of $[(CH_3)_3NOH]^+$ cation at HTP and LTP, respectively. (b) The asymmetric unit of $[(CH_3)_3NOH]_2[KFe(CN)_6]$ in the LTP and (c) its 298 K P-E hysteresis loops. (d) The phase and amplitude hysteresis loops obtained during by PFM measurements on the thin film of $[(CH_3)_3NOH]_2[KFe(CN)_6]$. Adapted with permission from ref. 91. Copyright © 2017 American Chemical Society.

Xiong and co-workers recently demonstrated the ferroelectric to paraelectric phase transition in $[(CH_3)_3NOH]_2[KFe(CN)_6]$ (TMC-1) salt for the first time (Figure 1.10).⁹¹ Equivalent amounts of trimethylamine N-oxide hydrochloride and $K_3[Fe(CN)_6]$ were mixed at room temperature to create the cyanometallate TMC-1. TMC-1 exhibits the monoclinic Cc (polar at low temperature) and cubic $Fm\bar{3}m$ (non-polar at high temperature) space groups at 298 K and 408 K, respectively, determined by the X-ray single crystal analysis. Four of the six cyanide ions, primarily bonded to the Fe^{3+} ions are bridged to the alkali K^+ ions through the N-atoms of the cyanide ligands. Remarkably, the transition from the high temperature phase to the low temperature

phase causes the hydroxy group of the $(\text{CH}_3)_3\text{NOH}^+$ cation to change from an uncoordinated state to a coordinated state, leading to an efficient cation ordering responsible for the polarization. This is the first instance where coordinate bond rearrangements has been shown as a cause of order-disorder mechanism in organic-inorganic hybrids.

1.7 Applications of ferroelectric materials

Ferroelectric materials have been utilized for several commercial applications since their invention (Figure 1.11). The switchable polarization under an external electric field is the characteristic that is most frequently exploited, and it serves as the foundation for its application in ferroelectric random-access memory (FeRAM), micro- and nanoelectromechanical systems (MEMS and NEMS), field-effect transistors (FeFET), photovoltaics, energy conversion and storage devices, electro-optical systems, and energy harvesters for mechanical energy harvesting applications. ⁹²⁻⁹⁶

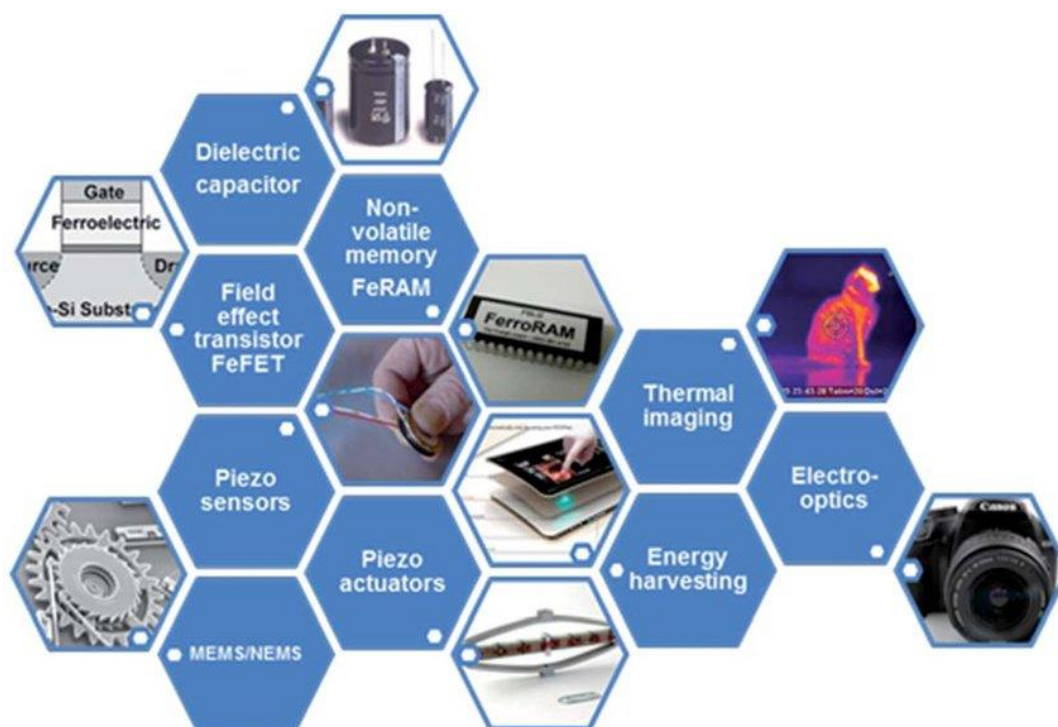


Figure 1.11: (a) Diverse applications of non-linear dielectrics (piezo, pyro, and ferroelectric materials). Adapted with permission from ref. 96. Copyright © 2013 The Royal Society Chemistry.

Numerous other industrial uses originating from the piezoelectric properties of the ferroelectric materials have been found, such as piezo sensors, piezo actuators, transducers, television remote controls, microphones, fire alarms, igniters, and micro-robotics. Moreover, the ABX₃-type piezo- and ferroelectric perovskite materials with remarkable light-harvesting capabilities are used for photovoltaics, incorporating solar cell devices with extremely high-power conversion efficiencies.⁹⁷⁻⁹⁹ These materials perform better than other materials in optoelectronic applications due to their high charge mobility, strong optical absorption, photoconductivity, and tunable bandgap characteristics, which are all straightforward to achieve through solution synthesis.¹⁰⁰⁻¹⁰²

Notably, flexible electronic materials made of piezo- and ferroelectric materials, as well as a variety of polymers, have recently been marketed in order to capture the electromechanical reaction from natural energy sources. This section largely emphasizes the usage of piezo- and ferroelectric materials for mechanical to electrical energy conversion applications.

1.8 Application of piezo- and ferroelectric materials in mechanical energy harvesting

Global energy consumption has increased recently as a result of population growth and industrialization. Because of this, producing electricity using fossil fuels alone has several drawbacks, such as a resource shortage, contamination of the environment, and global warming. Renewable energy sources have drawn a lot of interest from the scientific community to reduce the consumption of fossil fuels. Natural energy sources that are typically accessible, such as solar, wind, hydro, and geothermal, are greatly influenced by location and thus have limitations.¹⁰³⁻¹⁰⁶

In this context, mechanical energy harvesters (popularly termed as nanogenerators), capable of transforming mechanical energy into electrical outputs, have made their place as an alternative method for energy production. These sources of energy are completely present and abounding in the surroundings, including background noise, vibration, light airflow, and different bodily functions like breathing, walking, finger bending, arm swinging, and so on. A nanogenerator device can effectively harness the electromechanical responses provided through various mechanical energy

sources and make them available for various applications requiring sustainable power sources and sensors, as shown in Figure 1.12.¹⁰⁷

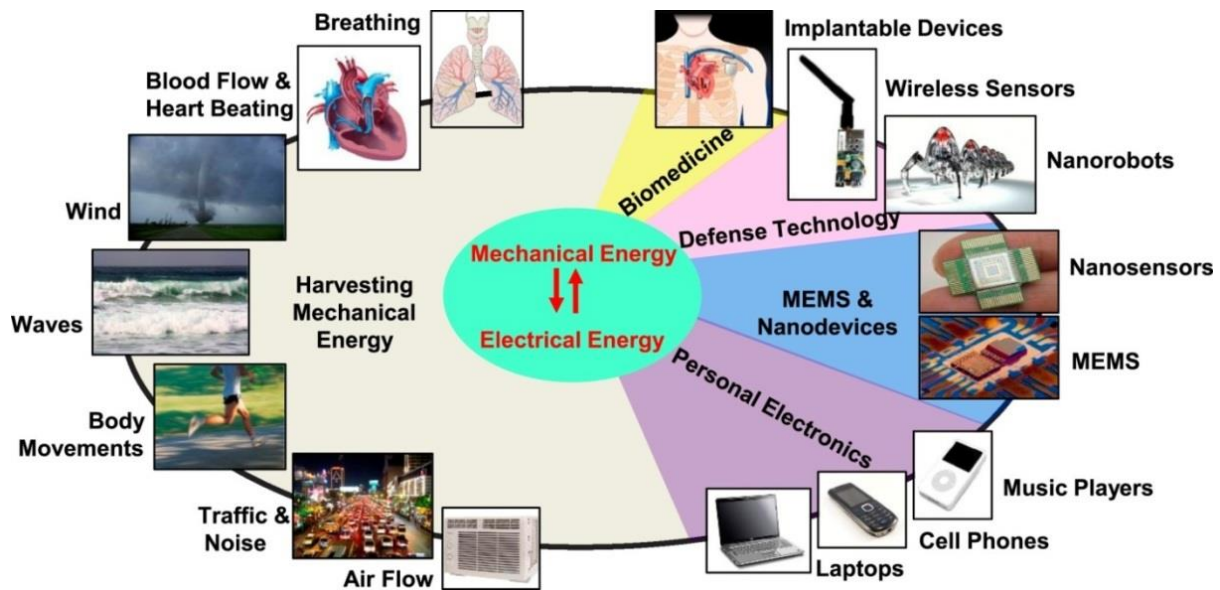


Figure 1.12: Viewpoints of various energy sources for harvesting mechanical energy and converting into electrical energy (left) and their potential utility for future electronic devices (right). Adapted with permission from ref. 107. Copyright © 2016 Elsevier Ltd.

Wang and co-workers introduced the concept of piezoelectric nanogenerators (PENGs) in 2006, which coincided with the discovery of piezoelectricity in ZnO nanowires (Figure 1.13).⁴⁴ An array of nanowires consisting of zinc oxide fibers were shown to exhibit the conversion of mechanical energy at the nanoscale into electrical energy upon the deflection from a conductive atomic force microscope tip operating in the contact mode. The piezoelectric properties of the zinc oxide generated the strain field and charge separation across the nanowires as an outcome of its bending. On an active area of $10 \times 10 \mu\text{m}^2$, with an applied frequency of 1 MHz, an output of 8 mV and an output power of 0.5 pW were attained.

These nanoscale ZnO energy harvesters produce output voltages that are far too low to be used in any commercial application. This is because of its low d_{33} (12 pC/N^{-1}) value, which affects the nanogenerator performance. In order to improve the device's overall output performance, it is important to have piezo- and ferroelectric materials with an effective permanent dipole moment and high spontaneous polarization. This

is because the piezoelectric coefficient is directly proportional to the material's remnant polarization ($d_{33} \propto \epsilon P_r$).

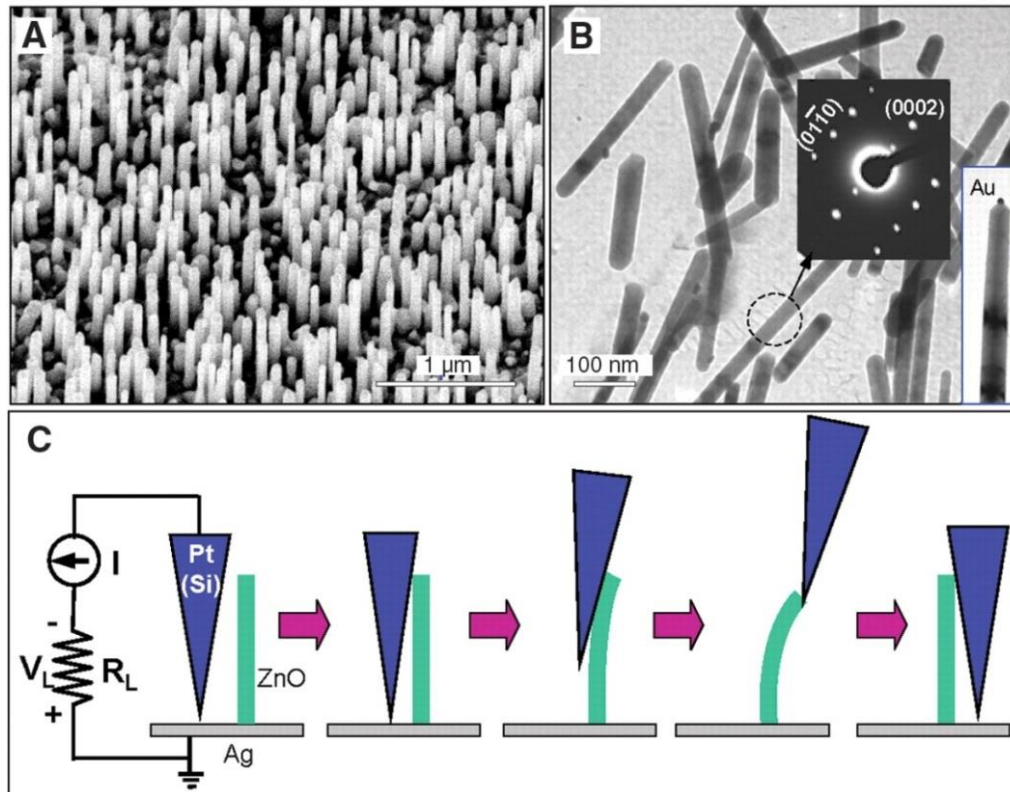


Figure 1.13: (a) and (b) Scanning electron and Transmission electron microscopic images of ZnO nanowires. (c) Experimental arrangement and procedures for deforming the ZnO nanowires with conductive AFM tip to harvest the electromechanical response. Adapted with permission from ref. 44. Copyright © 2006 American Association for the Advancement of Science.

Several piezo- and ferroelectric materials made of inorganic ceramic metal oxides (barium titanate, sodium niobate, lead titanate, lead zirconate titanate, and lithium niobate) have been utilized for piezoelectric energy harvesting applications. These materials were inspired by the earlier discovery of ZnO nanowire nanogenerator (Figure 1.14). However, the use of conventional inorganic ceramic oxides in wearable electronics suffer from the high-temperature manufacturing techniques, extensive processing times, laborious poling procedures, the inclusion of heavy density elements, and poisonous metal content, all of which pose serious environmental risks.¹⁰⁸

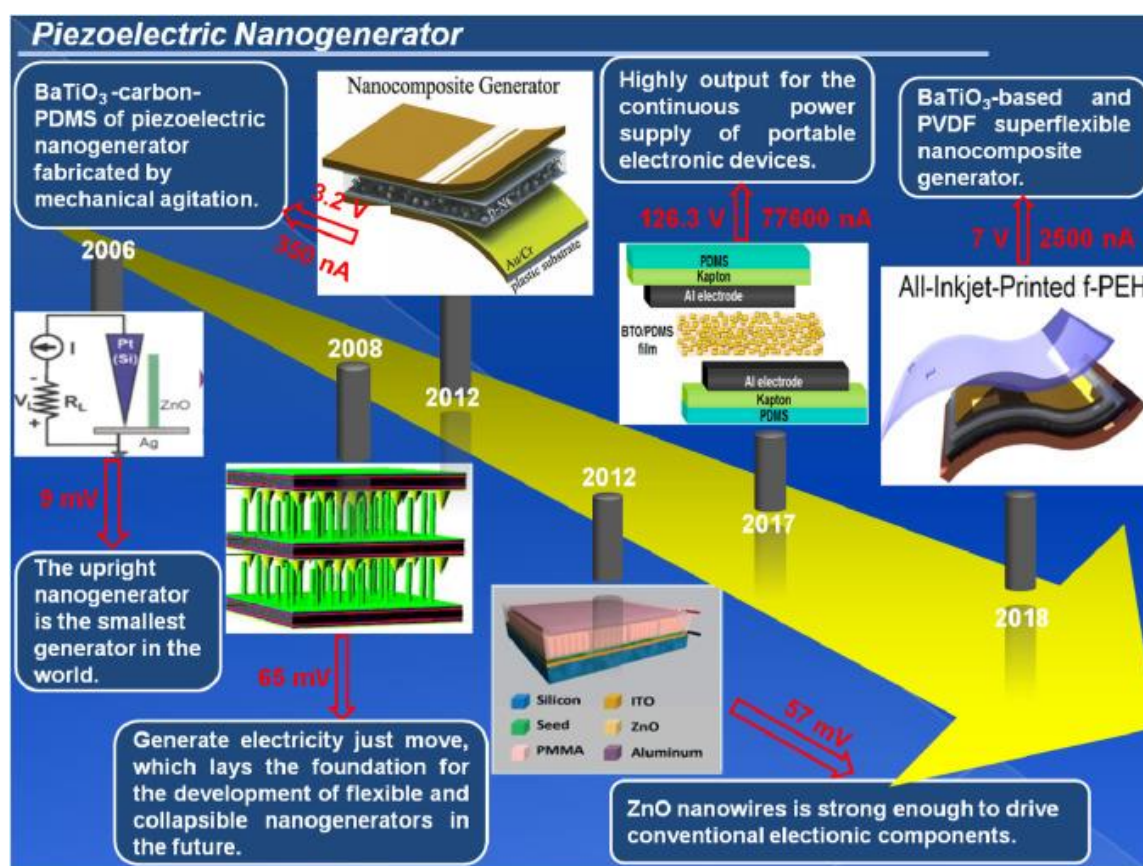


Figure 1.14: Developments in the piezoelectric energy harvesters since the discovery of ZnO nanowires in 2006. Adapted with permission from ref. 108. Copyright © 2018 Elsevier Ltd.

To overcome the shortcomings of ceramic materials, it is desirable to prepare heavy metal-free materials for piezoelectric energy harvesting applications. In this direction, organic polymer composite materials made of polyvinylidene fluoride (PVDF), as well as its copolymers have been discovered and were used as mechanical energy harvesters. Nevertheless, it is quite difficult to ensure the ferro- and piezoelectrically active β phase of PVDF in such devices as PVDF contains four different phases in its semi-crystalline structure.^{48, 49, 109}

The family of organic-inorganic hybrid and all-organic piezo- and ferroelectric materials serve as an alternative for ceramic- and polymer-based materials because of their facial synthesis, lightweight, simple fabrication techniques, low cost and mechanical flexibility. Recent research on these materials focus on the formation of the polymeric composites of these materials, which are further used as piezoelectric energy

harvesters.^{12, 110} Kim and co-workers in 2016, used polydimethylsiloxane (PDMS) polymer composite films of methylammonium lead iodide (MAPbI₃) as piezoelectric energy harvester (Figure 1.15a and b).

The non-poled devices of these composites gave an open circuit voltage of 1 V and a current density of 50 nA cm⁻².¹¹¹ An enhanced output voltage 2.7 V and current density of 140 nA cm⁻² were recorded when the MAPbI₃-PDMS composite devices when subjected to a very high electric field of 80 kV cm⁻¹ in the poling process. However, the low output performance of these devices limits their utility for any commercial applications.

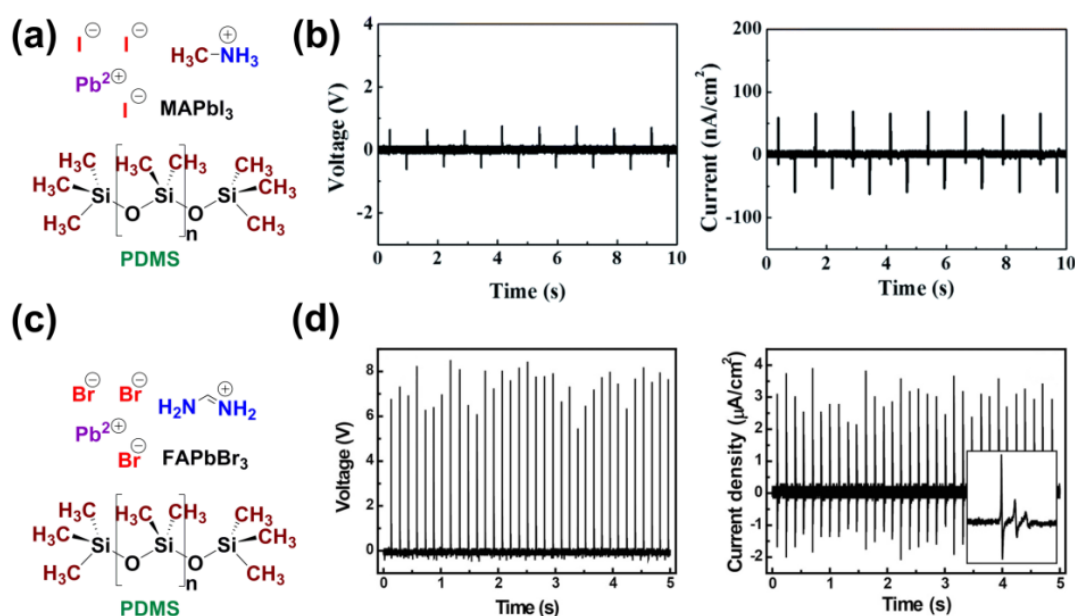


Figure 1.15: (a) and (c) Schematic view of the chemical structures of MAPbI₃-PDMS and FAPbBr₃-PDMS. (b) and (d) Piezoelectric energy harvesting output of MAPbI₃-PDMS and FAPbBr₃-PDMS composite devices. Adapted with permission from ref. 20. Copyright © 2016 The Royal Society of Chemistry and ref. 111. Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Subsequently, formamidinium lead bromide (FAPbBr₃) with PDMS polymer composite was designed and was shown to exhibit the maximum open circuit output voltage of 8.5 V and current density of 3.8 μA cm⁻², respectively (Figure 1.15c and d).²⁰ Further, a 47 nF capacitor was charged using a four-diode full-wave bridge rectifier circuit, and the stored charge was then utilized for lighting light-emitting diodes (LEDs).

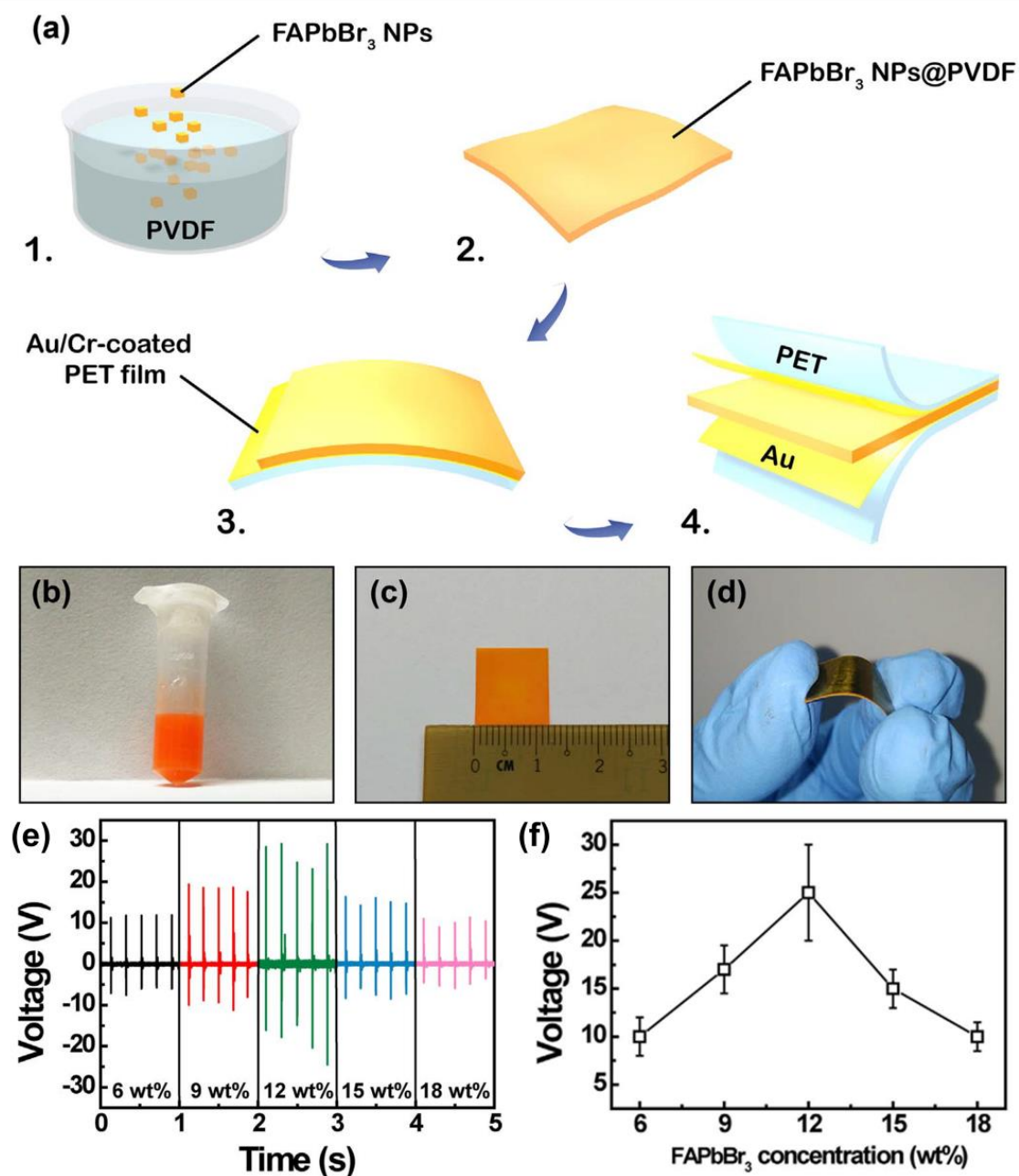


Figure 1.16: (a) The procedure for preparing composite films of FAPbBr₃ NPs @PVDF. (b), (c) and (d) Photograph of a mixed solution, selective area (1.2 x 1.4 cm²) and a flexible composite device of FAPbBr₃ NPs @PVDF nanogenerator. (e) and (d) Output performance of FAPbBr₃ NPs @PVDF nanogenerator. Adapted with permission from ref. 112. Copyright © 2017 Elsevier Ltd.

Later on, Zheng and coworkers reported another piezoelectric composite energy harvester based on formamidinium lead bromide (FAPbBr₃) nanoparticles (NPs) embedded on polyvinylidene difluoride (PVDF) polymer matrix (Figure 1.16).¹¹² The

composite films were prepared by the dissolution of FAPbBr_3 NPs into the PVDF solution by solution casting method. These films were peeled off from the glass substrate after the thermal annealing, and uniform distribution of FAPbBr_3 NPs in the polymer composite films was observed. The device architecture was completed by sandwiching these films between gold (Au) and chromium (Cr) coated polyethylene terephthalate (PET) substrates that act as the top and bottom electrodes of the device. These flexible and poled devices resulted in a high enhancement in the energy harvesting performance with the maximum output voltage and current density of 30 V and $6.2 \mu\text{A cm}^{-2}$, respectively, for an optimized ratio of 12 wt % FAPbBr_3 NPs @PVDF composite devices (Figure 1.16e and f). The enhancement in nanogenerator performance in these devices can be attributed to the use of piezoelectric PVDF polymer and the homogeneous distribution of FAPbBr_3 nanoparticles in the polymer composite films.

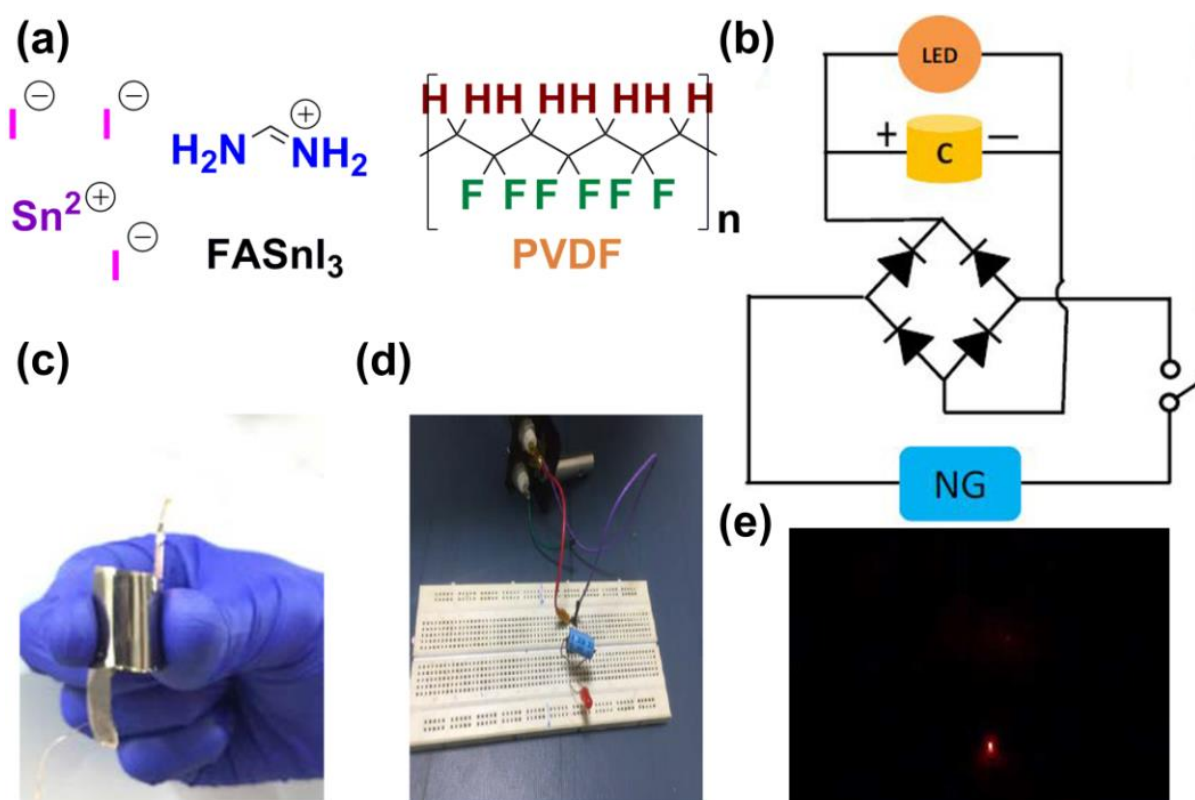


Figure 1.17: (a) Chemical structure of FASnI_3 -PVDF. (b) Schematic circuit diagram for capacitor charging experiment. (c) A view of the flexible composite film of FASnI_3 -PVDF. (d) Capacitor charging and LED driving set up and (e) glowing LED. Adapted with permission from ref. 113. Copyright © 2019, American Chemical Society.

An excellent output voltage of 23 V and power density of 35.05 mW cm^{-2} has been shown by a lead-free formamidinium tin iodide (FASnI_3) embedded PVDF polymeric hybrid composite nanogenerator for its (0.5:0.5) wt% of FASnI_3 :PVDF composite device (Figure 1.17).¹¹³ The practical applications of these devices are investigated by charging a capacitor and lighting up of the LEDs. Other examples of piezoelectric energy harvesters include encapsulated ZnO nanowires into a parylene C polymer matrix,¹¹⁴ Electrospun Nanofiber Mat of MAPbI_3 -PVDF,¹¹⁵ MAPbI_3 -PVDF,^{116, 117} MASnI_3 -PVDF,¹¹⁸ etc., which were fabricated and shown to exhibit low to moderate piezoelectric energy harvesting output performance. Despite their excellent output performances, several of these composite materials suffer from air and moisture instability issues due to the presence of reactive metal-halide bonds and lack environmental-friendliness due to the presence of heavy toxic metal ions.¹¹⁹

A solution to the above-mentioned concerns can be the preparation of organic-inorganic hybrid structures by the combination of 3d metal ions with pseudo-halogenometallate counter-anions and also the preparation of all-organic ferroelectric materials. Subsequently, the polymer composites of these all-organic and organic-inorganic hybrids can be prepared to fabricate their nanogenerator devices.

Our group has been exploring such 3d metal ion-based halogenometallates, which are less toxic and are easy to synthesize compared to those of ceramic-based materials. Recently, we reported two phosphonium-based halogenometallate of type A_2MX_4 . The single crystal X-ray diffraction analysis revealed that the hybrid Cu(II) containing materials $[\text{Ph}_3\text{PMe}]_2[\text{CuCl}_4]$ and $[\text{Ph}_3\text{PMe}]_2[\text{CuBr}_4]$ crystallize in orthorhombic *Fdd2* and monoclinic *Cc* space groups, respectively.¹²⁰ The lead-free Cu(II) halides $[\text{Ph}_3\text{MeP}]_2[\text{CuCl}_4]$ and $[\text{Ph}_3\text{MeP}]_2[\text{CuBr}_4]$ behaved as room-temperature ferroelectric materials with remnant polarizations of 17.16 and $26.02 \text{ } \mu\text{C cm}^{-2}$, respectively. The direct piezoelectric response (d_{33}) of both salts $[\text{Ph}_3\text{MeP}]_2[\text{CuCl}_4]$ and $[\text{Ph}_3\text{MeP}]_2[\text{CuBr}_4]$ at an operating frequency of 110 Hz and with an applied mechanical stress of 0.25 N were measured to be 1.73 pC N^{-1} and 1.80 pC N^{-1} respectively. The piezoelectric properties of $[\text{Ph}_3\text{MeP}]_2[\text{CuCl}_4]$ was also exploited in its thermoplastic polyurethane (TPU) composites (Figure 1.18). In addition to the excellent ferroelectric characteristics, $[\text{Ph}_3\text{MeP}]_2[\text{CuCl}_4]$ was able to give a notable peak-to-peak voltage

output of 25 V and power density of $14.1 \mu\text{W cm}^{-2}$ for the 15 wt% TPU composite film, which was further utilized for charging a $100 \mu\text{F}$ capacitor within 30 seconds. The best-performing device was also checked for cyclic stability up to 10000 cycles with the device showing no drop in voltage up to 10000 cycles.

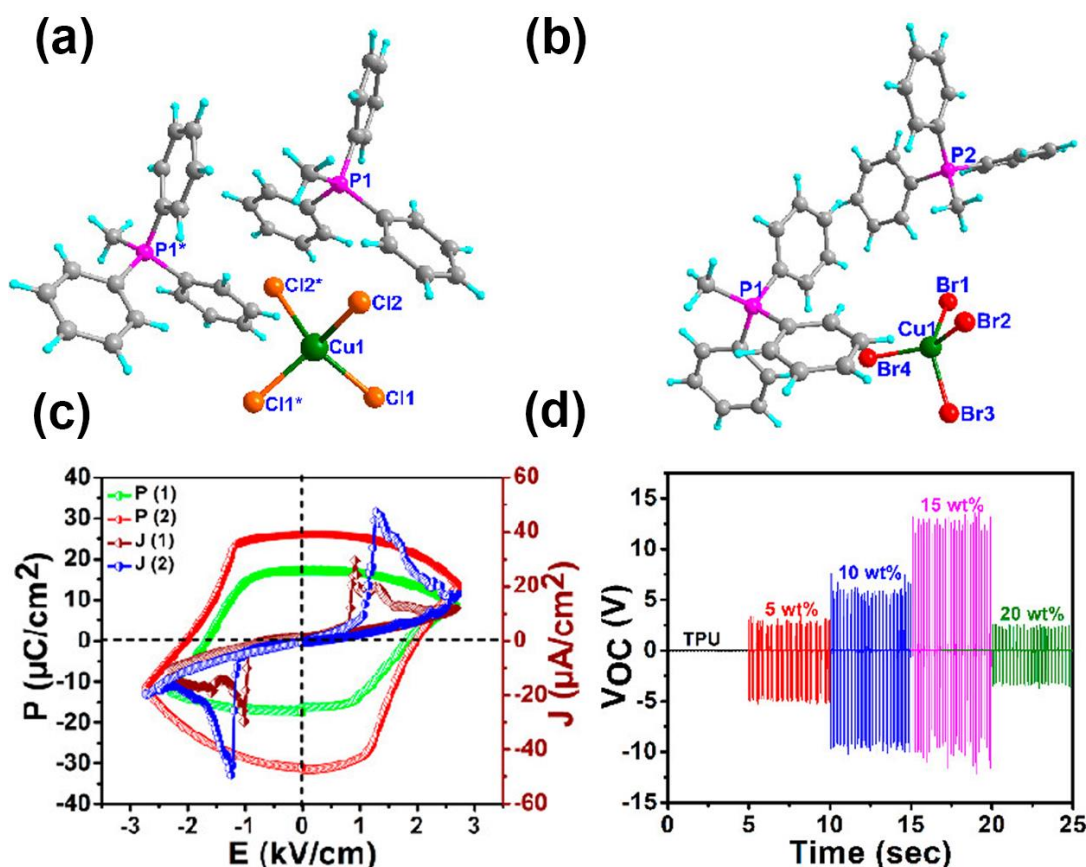


Figure 1.18: Molecular structures of (a) $[\text{Ph}_3\text{MeP}]_2[\text{CuCl}_4]$ and (b) $[\text{Ph}_3\text{MeP}]_2[\text{CuBr}_4]$. (c) Ferroelectric P - E hysteresis loops of $[\text{Ph}_3\text{MeP}]_2[\text{CuCl}_4]$ and $[\text{Ph}_3\text{MeP}]_2[\text{CuBr}_4]$. (d) Piezoelectric open circuit voltages of $[\text{Ph}_3\text{MeP}]_2[\text{CuCl}_4]$ -TPU composite devices. Adapted with permission from ref. 120. Copyright © 2021 American Chemical Society.

In 2022, Boomishankar and co-workers reported a ferro- and piezoelectrically efficient hybrid perovskite $[\text{Ph}_3\text{MeP}]_3[\text{Bi}_2\text{Br}_9]$ (MTPBB).¹²¹ MTPBB resulted in a ferroelectric hysteresis loop with a remnant polarization value of $2.1 \mu\text{C cm}^{-2}$. From the piezoresponse force microscopy (PFM) experiments, the piezoelectric strain coefficient (d_{33}) for an MTPBB single crystal and thin film sample were extracted along

with the characteristic phase-bias hysteresis and amplitude-bias butterfly loops. The bismuth-based perovskite was then embedded in polydimethylsiloxane (PDMS) matrix at various concentrations (5, 10, 15, 20, and 25 wt%), and the prepared devices were tested for piezoelectric energy harvesting with the application of 40 N force at 24 Hz frequency. The 20 wt% MTPBB-PDMS device was observed to be the champion device in the series with maximum peak-to-peak open-circuit voltage and power density of 22.9 V and $7 \mu\text{W cm}^{-2}$, respectively (Figure 1.19). Also, the 20 wt% MTPBB-PDMS composite was checked for direct piezoelectric response measurements and was shown to give a d_{33} value of 4.24 at an applied load of 0.25 N and a frequency of 110 Hz. Furthermore, the champion device was also utilized to charge various capacitors (2.2, 4.7, and 10 μF) using the four-diode full wave bridge rectifier circuit.

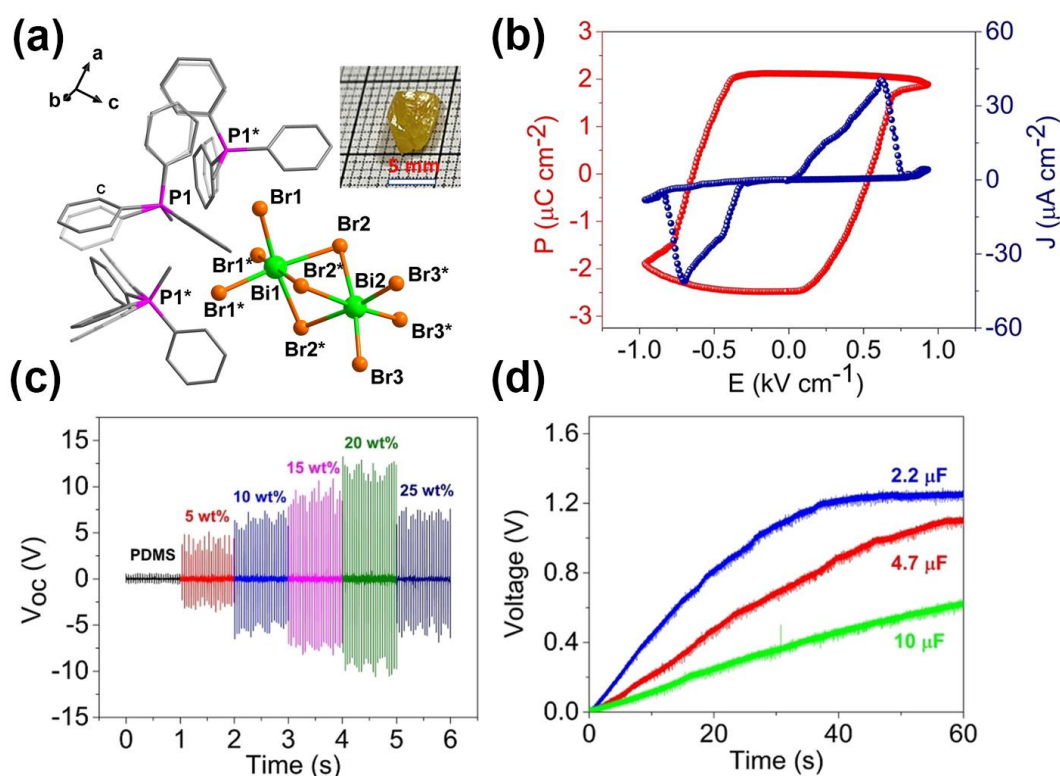


Figure 1.19: (a) Chemical structure of MTPBB. (b) Ferroelectric P-E hysteresis loop of MTPBB at room temperature. (c) Piezoelectric open circuit voltages of MTPBB-PDMS composite devices. (d) Capacitor charging curves obtained by utilizing the 20 wt% MTPBB-PDMS composite device. Adapted with permission from ref. 121. Copyright © 2022 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

In one of the recently published works, the very first ferroelectric hybrid pseudo-halogenometallate complex of a 3d metal ion containing a discrete A_4MX_6 type phosphonium-based hybrid $[Ph_3MeP]_4[Ni(NCS)_6]$ was reported by Boomishankar and co-workers.¹²² The polar nature of the compound was evidenced by the observation of a high remnant polarization (P_r) of $18.71 \mu C cm^{-2}$, at room temperature. Furthermore, thermoplastic polyurethane (TPU) composite films of $[Ph_3MeP]_4[Ni(NCS)_6]$ were prepared and employed for mechanical energy harvesting applications at 17 N force with an operating frequency of 8 Hz. The 15 wt% $[Ph_3MeP]_4[Ni(NCS)_6]$ /TPU composite device exhibited a maximum output voltage and power density of 19.29 V and $2.51 mW cm^{-3}$, respectively (Figure 1.20). The practical utility of the composite device was again verified by capacitor charging experiments.

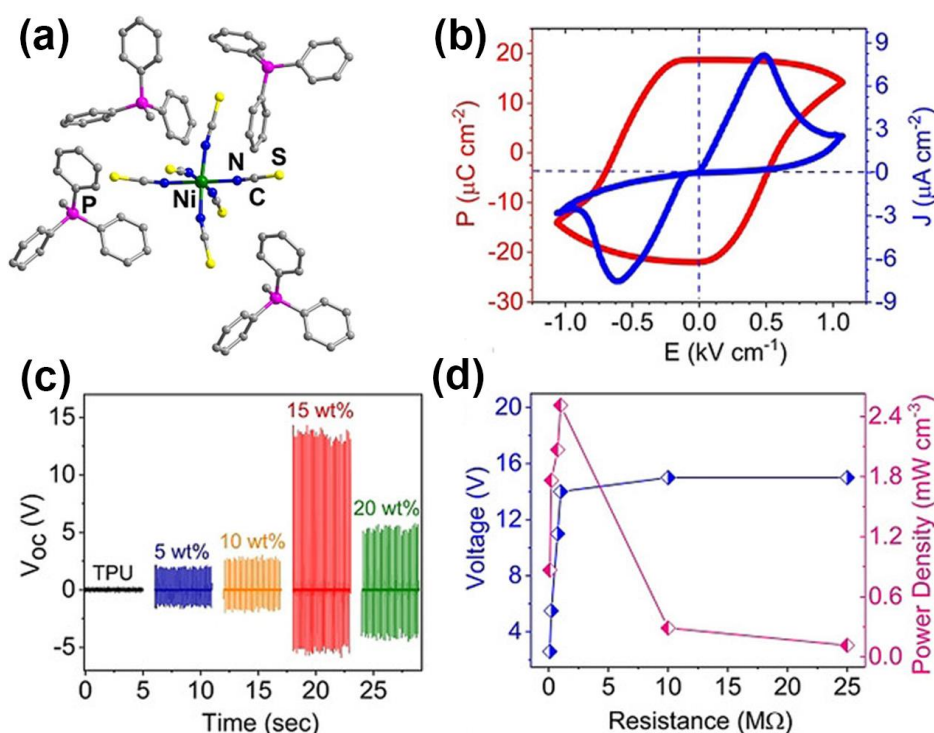


Figure 1.20: (a) Crystal structure of structure of $[Ph_3MeP]_4[Ni(NCS)_6]$. (b) Ferroelectric P - E hysteresis loop of $[Ph_3MeP]_4[Ni(NCS)_6]$ at room temperature. (c) Piezoelectric open circuit voltages of $[Ph_3MeP]_4[Ni(NCS)_6]$ /TPU composite devices. (d) The voltage drop and power density data of 15 wt% $[Ph_3MeP]_4[Ni(NCS)_6]$ /TPU film under various load resistances. Adapted with permission from ref. 122. Copyright © 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Later on, Boomishankar and co-workers explored ferroelectricity in cyanometallates using the amino-phosphonium cation. Though hybrid cyanometallates containing ammonium cations has received a lot of attention in the past, the analogous phosphonium cyanometallates were not been reported for such PENG applications. The salt $[\text{Ph}_2(\text{iPrNH})_2\text{P}]_3[\text{Fe}(\text{CN})_6]$ is the first ferroelectric A_3BX_6 type cyanometallate hybrid, which showed a sizable saturation polarization (P_s) value of $\sim 3.7 \mu\text{C cm}^{-2}$, at room temperature along with strong piezoelectric voltage (g_{33}) and electrostrictive (Q_{33}) coefficient values of $\sim 63.27 \times 10^{-3} \text{ V m N}^{-1}$ and $\sim 1.86 \text{ m}^4 \text{ C}^{-2}$, respectively.¹²³ Further, thermoplastic polyurethane (TPU) polymer composite films with various wt% of $[\text{Ph}_2(\text{iPrNH})_2\text{P}]_3[\text{Fe}(\text{CN})_6]$ were prepared and utilized as piezoelectric energy harvesters. Notably, the 15 wt % $[\text{Ph}_2(\text{iPrNH})_2\text{P}]_3[\text{Fe}(\text{CN})_6]$ -TPU device produced a maximum output voltage of 13.57 V with an estimated power density of $60.35 \mu\text{W cm}^{-2}$ (Figure 1.21).

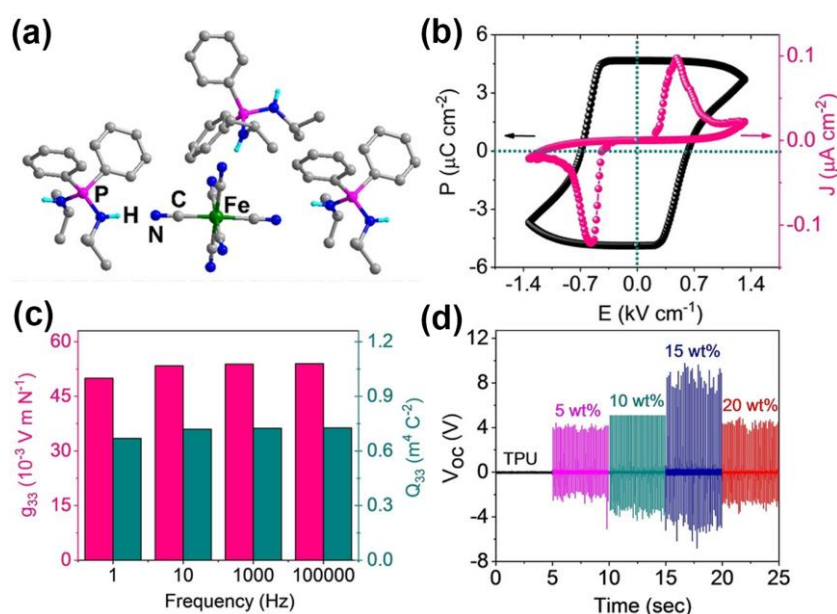


Figure 1.21: (a) Molecular structure of $[\text{Ph}_2(\text{iPrNH})_2\text{P}]_3[\text{Fe}(\text{CN})_6]$. (b) P-E hysteresis loop for $[\text{Ph}_2(\text{iPrNH})_2\text{P}]_3[\text{Fe}(\text{CN})_6]$ at room temperature. (c) The frequency dependence of computed piezoelectric voltage and electrostriction coefficients of $[\text{Ph}_2(\text{iPrNH})_2\text{P}]_3[\text{Fe}(\text{CN})_6]$. (d) Piezoelectric open circuit voltages of $[\text{Ph}_2(\text{iPrNH})_2\text{P}]_3[\text{Fe}(\text{CN})_6]$ /TPU composite devices. Adapted with permission from ref. 123. Copyright © 2022 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

These excellent outcomes from hybrid ferro- and piezoelectric materials suggest their potential utility in future wearable electronics, where environmental friendliness is a critical factor. Nevertheless, the preparation and utilization of such nontoxic simple hybrid salts need more research in terms of scaling up, miniaturization, device fabrication, etc.

1.9 3D printing for piezoelectric energy harvesting

Until now several two-dimensional (2D) thin-film PVDF-based piezoelectric energy harvesting devices have been reported. The thin-film structures possess significant local residual stress, which disturbs the movement of dipoles and charge separation and hence lessens the cumulative piezoelectric coefficient. Additive manufacturing, also known as three-dimensional printing (3DP), is a growing technology that involves the printing of physical objects in a layer-by-layer fashion.¹²⁴⁻¹²⁶ 3DP has gained attention since its discovery for engineering complex architectures that are otherwise difficult to prepare by conventional manufacturing. 3DP has gradually achieved its place owing to its customizable device preparation by simple techniques and is discovering its way into pharmaceutical industries, electronics, robotics, sensing, etc.¹²⁵ Compared to 2D planar structures, the 3D printed designs possess certain advantages such as uniform distribution of holes and arrays, reduction of material modulus due to their porous nature, while enhancing the piezoelectric outputs, and most importantly, customizable device fabrication techniques.

3D printing, as an evolving additive manufacturing technology, has its own advantages of low cost and high efficiency for the flexible design of complex structures. Amongst the developed 3DP techniques, such as stereolithography (SLA),¹²⁷ fused deposition modeling (FDM),^{128, 129} and selective laser sintering (SLS),¹³⁰ FDM is the most common 3DP technique due to its advantages of easy operation, high efficiency, environmental benignity, and low cost. Recently, Zhang and coworkers investigated improvement in the piezoelectric output voltage of 3D printed PVDF as compared to that of the neat PVDF-based device.¹³¹ They proposed a one-step 3DP strategy for the preparation of self-poled complex-shaped piezoelectric devices of β -PVDF for energy harvesting applications and paved the way towards the exploration of many unexplored piezoelectric polymers that can find their applications in wearable

electronics. Zhang and coworkers manufactured a PVDF piezoelectric device with a 3D hemispherical protrusion array (HPA) structure (thickness = 3.4 mm) using the FDM 3DP technique. The 3D-printed HPA structure was seen to create significantly more vertical strain than that generated by the flat PVDF under the same load. A higher piezoelectric signal is produced by a greater compressive strain. Conversely, a greater compressive strain produces a greater piezoelectric signal. As a result, the HPA-PVDF PVDF piezoelectric device exhibited higher output voltage and current. The V_{oc} and I_{sc} of HPA-PVDF are 4.2 V and 71 nA, respectively, which were 4.7 and 3.4 times higher than those of the flat 2D PVDF device (Figure 1.22).

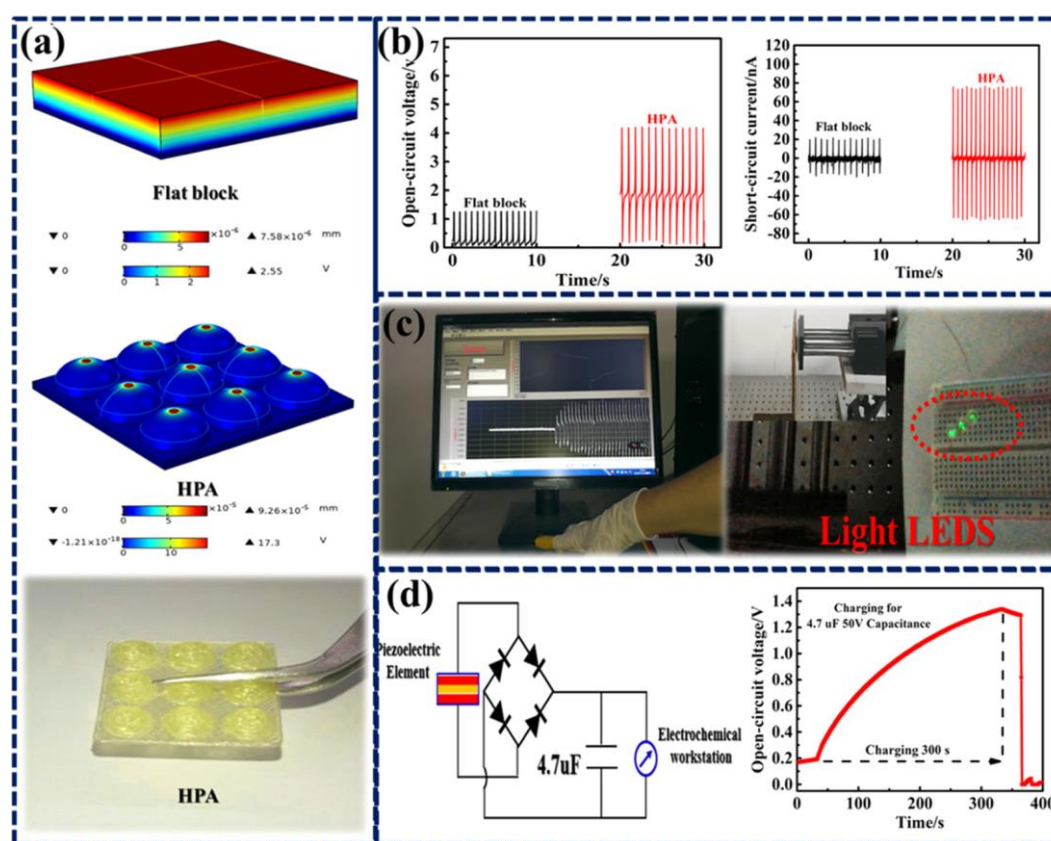


Figure 1.22: (a) Simulation of the strain distribution of HPA and flat block structure PVDF, and the photograph of the HPA-PVDF device, (b) the piezoelectric output of HPA-PVDF and flat block PVDF, (c) the photographs showing the response under slight force and lighting the light-emitting diodes (LEDs), and (d) circuit diagram of bridge rectifier setup and the charging curve for accumulating the charge in 300 s by using the HPA-PVDF device. Adapted with permission from ref. 131. Copyright © 2021 American Chemical Society.

However, PVDF-based devices require external additives to enhance the content of piezoelectrically active β -phase and annealing or high-voltage poling processes to align the dipoles due to their very high coercive fields. Whereas the preparation of composites with ceramic materials is challenging due to their high weight and toxic metal contents and the requirement of high-temperature fabrication techniques. Therefore, it is desirable to investigate ferro- and piezoelectrics of small-molecule derived organic and organic-inorganic hybrids as 3D-printable piezoelectric nanogenerator devices. Since these materials can be dissolved in common solvents and are compatible with several polymers, they can be customized into different complex shapes using the common FDM technique.

2. Scope of the present thesis

This thesis presents the syntheses of organic and hybrid organic-inorganic ferroelectric and piezoelectric materials based on acentric polar or chiral ammonium cations for mechanical energy harvesting applications. [Chapter 2](#) will describe the synthesis of a chiral ammonium-based bismuth halide perovskite, which shows excellent piezoelectric properties. [Chapter 3](#) will discuss the synthesis of an all-organic ammonium-based tetrafluoroborate salt, which displays excellent piezo and ferroelectric polarization. Further, for piezoelectric energy harvesting applications, flexible composite devices for this salt were prepared with non-piezoelectric polycaprolactone (PCL) polymer. For the first time, additive manufacturing (3D printing) technology has been used to prepare composite devices based on any all-organic or organic-inorganic hybrid material, where the scaling-up capabilities of the ammonium salt are vividly discussed with excellent energy harvesting outputs. [Chapter 4](#) will discuss the utility of a highly electrostrictive ammonium salt co-crystal for piezoelectric energy harvesting. The composite devices of the co-crystal with biodegradable polymer PCL showed sizable piezoelectric output performance. Again, 3D printing enabled the complex architected device forming capabilities of the material, with enhanced output performance. [Chapter 5](#) will discuss the synthesis of chiral organic boron-nitrogen (B-N) adducts for piezo and ferroelectric studies. These B-N adducts exhibited excellent ferroelectric properties along with remarkable mechanical energy harvesting performance on the as made crystals.

Thus, the present thesis aims:

- To synthesize the low symmetric organic-inorganic hybrid and all-organic ammonium salts supported by bismuth halide-based and organic anions.
- To study the non-centrosymmetric nature of organic and hybrid organic-inorganic salts containing piezoelectric and ferroelectric properties.
- To utilize them for potential piezoelectric energy harvesting applications in their polymer composite forms.

In this regard, a new synthetic design to obtain lower symmetric molecular ferroelectric materials with their enhanced ferroelectric and composite device performance was briefly addressed. These outcomes demonstrate the effectiveness of organic and organic-inorganic hybrid ferroelectric materials for piezoelectric energy harvesting applications and promise their potential utility in future wearable electronics.

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End of Chapter 1

Chapter 2



**Piezoelectric Energy Harvesting of
a Lead-free Bismuth Halide
Perovskite Supported by a Chiral
Ammonium Cation**

2.1 Introduction

Mechanical energy is one of the abundant and renewable sources of energy, which can be readily harvested and stored as electrical power.¹⁻³ Among several types of renewable electricity generators, the ones operating under the piezoelectric effect have a suitable mechanism for sustainably seizing the ambient mechanical energy and altering it into electrical energy.^{1, 4, 5} Moreover, the piezoelectric harvesters are exclusively based on the intrinsic polarization of the material and do not require a separate power source. Traditionally, materials exhibiting piezoelectric properties have found applications in various electronic devices, such as actuators, transducers and sensors.^{4, 6} Particularly, piezoelectric energy harvesters (popularly termed as piezoelectric nanogenerators) act as elegant and simple devices to power miniature electronics via external impact forces. Many nanogenerator devices have been prepared using ceramic materials like barium titanate, lithium niobate, lead titanate, lead zirconate titanate (PZT), zinc oxide, etc.⁷⁻¹² Piezoelectric materials like PZT, made from poly-crystalline ceramics, are multipurpose and can easily fit into specific purposes depending upon their morphologies. However, these ceramic materials have certain drawbacks due to their toxic metal ion contents, less flexibility and the requirement of a high-voltage polling process.^{4, 13-17} One of the easiest ways to tackle these limitations is by designing organic and organic-inorganic hybrid materials with suitable ferro- and piezoelectric properties.¹⁸⁻²³

Perovskite-structured hybrid compounds are an attractive class of compounds and can exhibit various compositions such as AMX_4 , $A_3M_2X_9$, A_2MX_5 , $A_2M_5X_{12}$, etc.²¹ These materials are extensively probed for their structural flexibility, high-temperature processibility, reconcilable optical characteristics, and lately for piezoelectric energy harvesting properties.^{8, 18, 24, 25} A number of two-component systems such as $FASnI_3$, $MASnI_3$, $MAPbI_3$, $(BA)_2PbCl_4$ have been explored for their efficient piezoelectric energy harvesting properties.²⁶⁻²⁹ However, the toxicity of $Pb(II)$ ions and the hydrolytic instability of the $Sn(IV)$ halides impedes their widespread utility in wearable electronics. In contrast, $Bi(III)$ derived hybrid perovskites have demonstrated excellent properties akin to those of $Pb(II)$ systems but with far less toxicity.^{30, 31}

Recently, we have reported a phosphonium stabilized Bi-complex $[\text{Ph}_3\text{P}(\text{CH}_3)]_3[\text{Bi}_2\text{Br}_9]$, which shows excellent ferro- and piezoelectric properties and is utilized as an efficient piezoelectric nanogenerator.³² Inspired by its performance, we turned our attention toward different types of bismuth-halide moieties containing various chiral and achiral organic cations. Herein, we report a "lead-free" chiral hybrid 1D-perovskite material $\{[\text{S}^*\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$, containing an infinite chain of $\{[\text{BiBr}_5]^{2-}\}_n$ motif supported by an enantiopure $[\text{S}^*\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]^+$ cation. This material crystallizes in the orthorhombic $P2_12_12_1$ space group, which is suitable for piezoelectric studies. The polymer composites with various (5, 10, 15, and 20) weight percentages (wt%) of $\{[\text{S}^*\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ were prepared with polylactic acid (PLA) and were used for mechanical energy harvesting applications. A maximum output open-circuit voltage of 10.4 V and a power density of $5.26 \mu\text{Wcm}^{-2}$ has been measured for the 15 wt% $\{[\text{S}^*\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA polymer composite film. In addition, the 15 wt% $\{[\text{S}^*\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device has been used for charging a 100 μF capacitor storing the highest voltage of 1.16 V in 60 seconds.

2.2 Experimental section

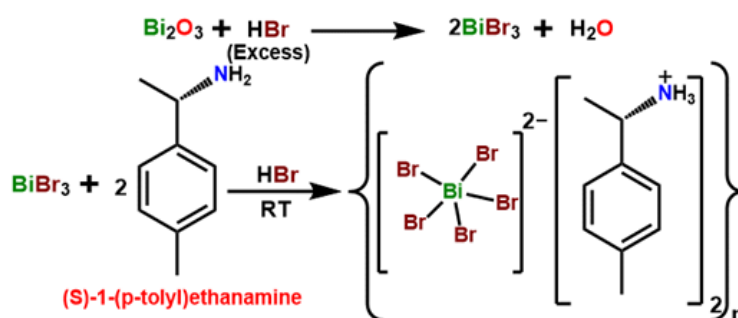
2.2.1 General remarks

(S)-1-(p-Tolyl)ethanamine was purchased from BLD pharm and was used without further purification. Hydrobromic acid and bismuth (III) oxide were purchased from Avra Chemicals. Polylactic acid (PLA) was purchased from Sigma Chemicals and was used as received. The thermogravimetric analyses (TGA) were performed using the PerkinElmer STA-6000 analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. Melting point analyses were done using a Buchi M-560 melting point apparatus and were uncorrected. The powder X-ray diffraction (PXRD) data were measured in the 2θ range of 5 to 50° on a Bruker-D8 Advance X-ray diffractometer. The field-emission scanning electron microscopy (FE-SEM) analysis of all the piezoelectric composite films was performed using the Zeiss ultra plus FE-SEM instrument with a minimum spatial resolution of $1 \mu\text{m}$. The UV-Visible spectrum of $\{[\text{S}^*\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was measured in an optical glass cuvette at room temperature using a Shimadzu UV-3600 spectrophotometer with a visible region range

of 400–800 nm. The optical band gap was calculated from absorption spectra using the procedure described in the literature.³³ A Vario-EL cube elemental analyzer was used for elemental analysis.

2.2.2 Synthesis

Bi₂O₃ [0.5 mmol, 0.233 g] was added to an excess of HBr and was left for mechanical stirring at room temperature. To the resulting solution containing BiBr₃, (S)-1-(p-Tolyl)ethanamine [1 mmol, 0.135 g] (1:1 with respect to Bi₂O₃) was added, resulting in a yellowish precipitate (Scheme 2.1). Further, the yellow residue was dissolved in methanol and was left for slow evaporation at room temperature. After three to four days, yellow needle-like single crystals of {[^sCH(MePh)(Me)NH₃]₂[BiBr₅]}_n were observed, then dried and utilized for further study. Yield: 88 %. Melting point: 240 to 245 °C. Anal. Calcd. For C₁₈H₂₈BiBr₅N₂: C 24.54; H 3.20; N 3.18. Found: C 24.55; H 3.21; N 3.17.



Scheme 2.1. Synthesis of {[^sCH(MePh)(Me)NH₃]₂[BiBr₅]}_n.

2.2.3 Crystallography

The single-crystal X-ray diffraction (SCXRD) data were obtained from Bruker Smart Apex Duo diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The crystal structures were solved using Apex 3 program, and the refinements were done by full-matrix least-squares against F² using SHELXL-2014/7 built in the Apex 3 program.³⁴ The crystallographic refinement data for {[^sCH(MePh)(Me)NH₃]₂[BiBr₅]}_n at different temperatures are listed in (Table 2.1). All the nonhydrogen atoms were refined

anisotropically. Hydrogen atoms were constrained to geometric positions to their parent atoms using a riding model.³⁵ The structural images were prepared by using DIAMOND-3.1 software.

Table 2.1: Details of crystallographic data collection and structure refinements for $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$.

Crystallographic details	$\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$	$\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$
Chemical formula	C ₁₈ H ₂₈ Br ₅ N ₂ Bi	C ₁₈ H ₂₈ Br ₅ N ₂ Bi
Formula weight (g/mol)	880.95	880.95
Temperature	100(2)K	298(2)K
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
a (Å); α (°)	7.903(2); 90	8.016(3); 90
b (Å); β (°)	14.943(4); 90	15.184(7); 90
c (Å); γ (°)	21.449(6); 90	21.635(9); 90
V (Å ³); Z	2533.0(12); 4	2633.4(19); 4
ρ (calc.) g cm ⁻³	2.310	2.222
μ(Mo K _α) mm ⁻¹	14.854	14.288
2θ _{max} (°)	50.04	54.04
R(int)	0.2107	0.1010
Completeness to θ	99.8	99.7
Data / param.	4478/242	4648/241
GOF	1.102	1.123
R1 [F > 4σ(F)]	0.0773	0.0448
wR2 (all data)	0.0933	0.0764
max. peak/hole (e.Å ⁻³)	1.481/-1.522	1.483/-1.306

2.2.4 General procedure for the preparation of polymer composite films and devices

Poly(lactic acid) (PLA) had been used to make $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA polymer composite films. To a chloroform solution of PLA (0.55 g), an appropriate quantity of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ (corresponding to 5, 10, 15, and 20 wt% contents) was added (Table 2.2). The resulting mixture was subjected to mechanical stirring for 30 minutes followed by vortex mixing for 15 minutes to obtain a homogeneous mixture. The solution mixture was then drop-cast onto a glass slide and was kept at room temperature until a dry film was obtained. The free-standing films were then peeled off from the glass surface. These films were embedded with adhesive copper tapes on both sides and were electroded with copper wires. The devices were then covered completely with Kapton tape to protect them from the surface charges. A separate device with a similar architecture was prepared with neat PLA for a performance comparison.

Table 2.2: Details about the preparation of various weight percentage (wt %) $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composites.

Composite (wt%)	$\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ (in mg)	$\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ + PLA (in mg)
5 wt%	28.94	578.94
10 wt%	61.11	611.11
15 wt%	97.05	647.05
20 wt%	137.50	687.50

2.2.5 Dielectric and piezoelectric Measurements

The dielectric measurements were done on the disc-shaped powder pressed pellet of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ (with a diameter of 8 mm and 1.2 mm thickness) electroded with copper adhesive tapes. The experiments were performed using the Solartron Analytical Impedance Analyzer 1260 coupled with a Dielectric Interface 1296A operating with Janis 129610A cryostat sample holder and a Lakeshore 336 model temperature controller.

The piezoelectric tests were performed on a custom-built impact instrument. A Tektronix 4034 Digital Phosphor Oscilloscope operating at an input impedance of 1 M Ω was used to measure the output voltages and currents. The thickness and the active area of the devices under test were ~ 2 mm and 360 mm², respectively.

The direct piezoelectric response of compacted $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ and $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composites was measured with a piezometer system (model PM300) using the "Berlincourt" method.

2.3 Results and discussion

2.3.1 Syntheses, characterization and crystal structures

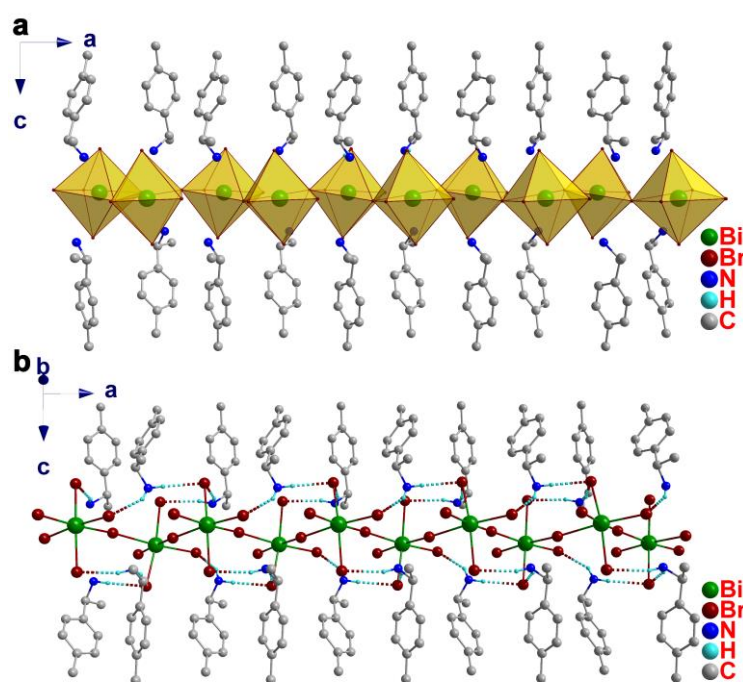


Figure 2.1: (a) 1-D chain structure of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ at 100 K and (b) The hydrogen-bonding interactions in $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ mediated by $\text{N-H}\cdots\text{Br}$ interactions.

The chiral perovskite-structured material $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was prepared by adding S-tolylamine to an HBr solution of Bi_2O_3 . The yellow-colored

precipitate $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was then crystallized from methanol. The single-crystal X-ray diffraction shows that $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ crystallizes in the nonpolar noncentrosymmetric orthorhombic $P2_12_12_1$ space group at both 100 and 298 K (Table 2.1). The asymmetric unit of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ consists of one BiBr_5^{2-} unit and two ammonium cations (Figure 2A.1a, Appendix 2). A closer look at the molecule revealed an infinite 1D array of octahedral BiBr_6 units that are associated via one μ_2 -bridged Br^- ion. The two chiral ammonium cations are placed above and below the 1D-chain structure that propagates parallel to the crystallographic a -axis (Figure 2.1a). The Bi cation is located in a distorted octahedral geometry in which the bridging Bi-Br bonds (2.970(77) Å) are longer than the terminal Bi-Br bonds (2.788(65) Å). Furthermore, the protons attached to the ammonium cations were found to be involved in N-H $\cdots$ Br interactions with the bromide ions of the BiBr_5^{2-} moiety (Figures 2.1b, 2A.2 and Table 2A.1, Appendix 2). Each BiBr_6 unit was surrounded by three ammonium cations through N-H $\cdots$ Br interactions along the growing 1D-chain of the anionic network (Figure 2A.2a, Appendix 2).

The bulk purity of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was identified by powder X-ray diffraction (PXRD) analysis, which matched well with the simulated pattern from its single-crystal X-ray data collected at 298 K (Figure 2A.3, Appendix 2). The thermogravimetric (TGA) and differential thermal analysis (DTA) data showed the stability of the molecule up to 320 °C (Figure 2A.4, Appendix 2). Furthermore, the differential scanning calorimetry (DSC) analysis confirmed no phase change in the molecule up to its melting point (245 °C).

2.3.2 Dielectric and piezoelectric studies

The point group symmetry of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ is D_2 , which is one of the 20-point groups suitable for piezoelectric studies. The direct piezoelectric measurements on a compacted pellet of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ exhibit a piezoelectric coefficient (d_{33}) value of 2.6 pC/N. It is to be noted that the $P2_12_12_1$ symmetry (space group 19, class 222) permits only the shear piezoelectric strain constants (d_{14} , d_{25} , d_{36}) and no longitudinal piezoelectric coefficients (d_{11} , d_{22} , d_{33}). Nevertheless, a random d_{33} can be observed upon pelleting/compositing of the crystals. This could be due to the presence of a positive directionality obtained from

the overall vector sum of all randomly directed dipoles in the compacted sample.³⁶ Furthermore, the piezoelectric voltage coefficient (g_{33}) value of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ has been calculated using the formula $g_{33} = d_{33}/\epsilon_{33}$. The highest g_{33} value for $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was obtained to be $42.68 \times 10^{-3} \text{ V m N}^{-1}$ ($\epsilon_{33} = 6.88$ at 1 kHz). The capacitance of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was calculated to be 2.49 pF, using the formula $C = C_0\epsilon_r$, where $C_0 = \epsilon_0 A/d$ ($\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$, $A = 50.26 \text{ mm}^2$, $\epsilon_r = 6.68$ at 1 kHz and $d = 1.18 \text{ mm}$).

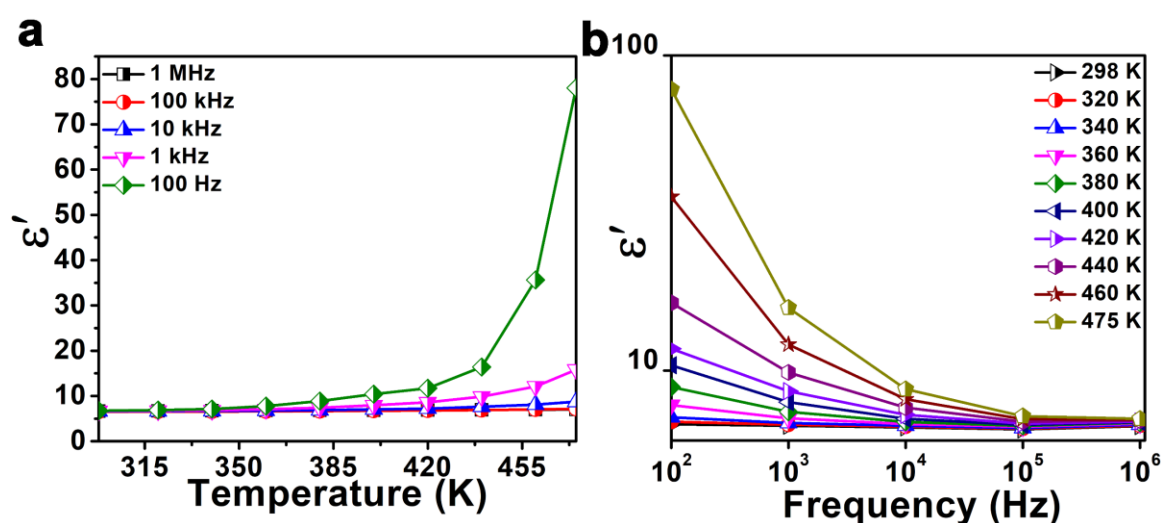


Figure 2.2: (a) The temperature and (b) frequency dependence of ϵ' of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$.

To check the bulk polarization property of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$, temperature and frequency dependant dielectric permittivity measurements were performed on its powder-pressed pellet (Figure 2.2a). The real part of the complex dielectric permittivity (ϵ') measured in the temperature range of 300 to 475 K displayed no obvious heat anomalies (Figure 2.2a). A sharp rise in the ϵ' at higher temperatures ($> 420 \text{ K}$), can be attributed to its ionic structure and the mobility of ions (Figure 2.2b). At higher temperatures, the ionic systems generate more polarizable dipoles and exhibit increased ionic conductivity. From the frequency dependant measurements, a sizable ϵ' value of 6.68 was observed at 298 K and at 1 kHz frequency. Furthermore,

the compound exhibits relatively low dielectric loss values, as evidenced from its $\tan \delta$ vs. T plot (Figure 2A.5a, Appendix 2). Similar trends were observed for the frequency-dependent ϵ' and $\tan \delta$ profiles as well (Figure 2.2b and 2A.5b, Appendix 2).

Since bismuth-containing perovskite structured materials are known to exhibit semiconducting characteristics, we examined the optical properties of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ (Figure 2A.6, Appendix 2). The compound exhibits a strong absorption with band onset at 402 nm. The extracted bandgap from the Tauc plot is found to be 2.60 eV. This is comparable to many organic-inorganic lead-based ferroelectric semiconductors and is substantially lower than many reported ceramic materials.^{29, 37-40}

2.3.3 Fabrication and characterizations of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite devices

Encouraged by the earlier reports on the fabrication of nanogenerator devices employing perovskite materials, $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was investigated for piezoelectric energy harvesting applications.^{23, 41-43} For this purpose, polymer composite films containing 5, 10, 15, and 20 wt% of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ were prepared with polylactic acid (PLA), which itself is a weakly-active piezo-polymer (Figure 2.3a). The prepared $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA films were found to be flexible for various kinds of bending and folding motions (Figure 2.3b). The structural stability of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ embedded in the PLA films was confirmed by powder X-ray diffraction (PXRD) analysis. The PXRD analysis on the composite films revealed that the crystalline nature of the compound was intact inside the PLA matrix (Figure 2.3c). Also, the characteristic peaks of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ were found to grow in intensity as the loading of the crystallites increased. The presence of all the characteristic hkl peaks of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ was found in all the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite films as well, showing the intact nature of the crystallites in the composites (Figure 2A.7, Appendix 2). Furthermore, the morphology and crystallinity of the piezoelectric crystallites in the polymer matrix were visualized by FE-SEM analyses (Figures 2.3d and 2A.8, Appendix 2). The

architecture for the nanogenerator devices was completed by placing adhesive copper tapes as the upper and bottom electrodes. Finally, the devices were encapsulated with Kapton tape, which provides both electrical insulation and flexibility to the devices.

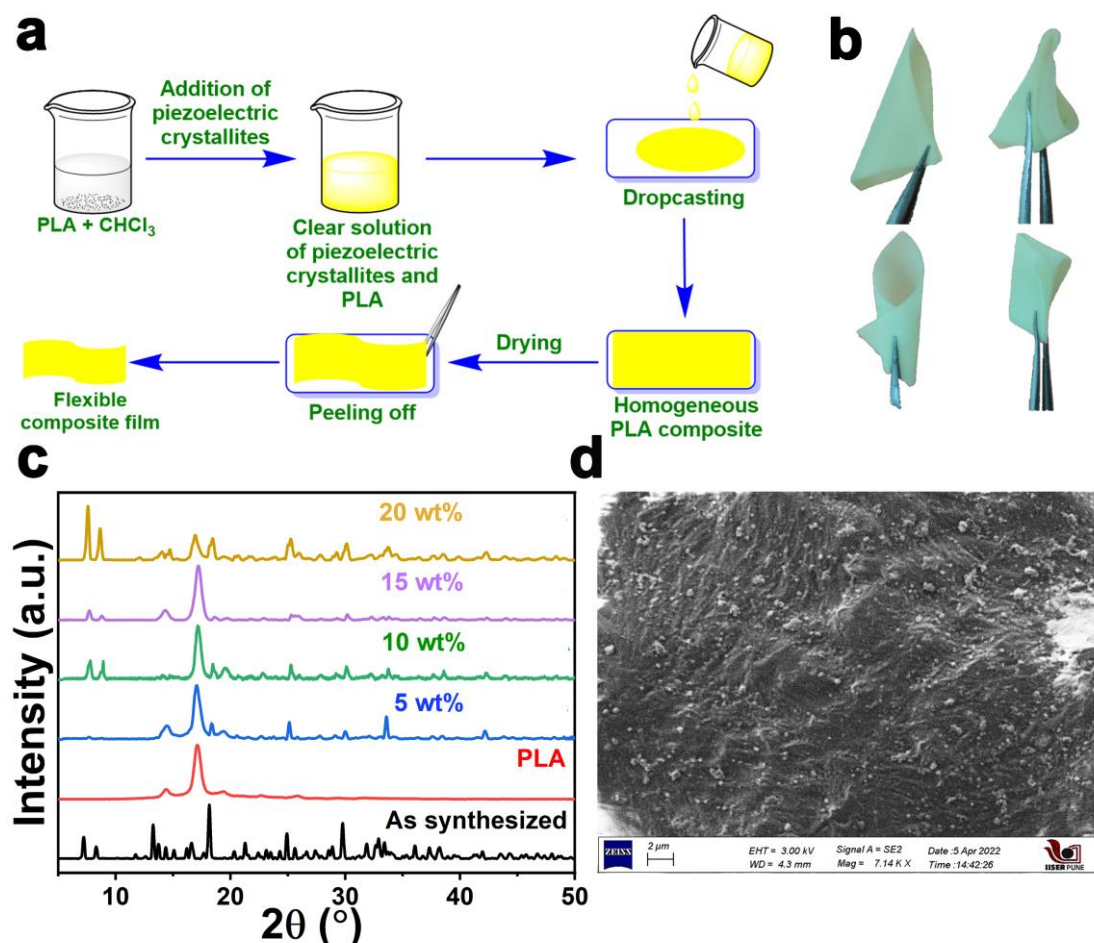


Figure 2.3: (a) Schematic diagram showing the preparation of $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ Composite films. (b) Photographs of a representative $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ film showing its flexibility towards folding, bending, rolling and two-fold bending operations (from left to right). (c) Stacked PXRD profiles of $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ films along with those of neat PLA and as-synthesized $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$. (d) Visualization of piezoelectric crystallites through FE-SEM analysis of 15 wt% $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ composite.

The piezoelectric output performance for the composite devices was measured using a custom-built impact setup. All the measurements were done at a constant application of 21 N impact force and at an operating frequency of 10 Hz. Output peak-to-peak voltages (V_{PP}) of 5.12, 8.70, 10.40, and 7.92 V were observed for 5, 10, 15, and 20 wt% composite devices, respectively (Figure 2.4a and 2A.9, Appendix 2). The neat PLA device gave an open circuit voltage of 1.54 V due to its weak-piezoelectric nature (Figure 2.4a).^{44, 45} The V_{PP} followed a periodic increasing trend with an increase in the crystallite loading in the PLA matrix up to 15 wt% and decreases upon increasing the loading to 20 wt% of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$. The increasing output performance with an increase in crystallite loading (up to 15 wt% of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$) can be attributed to the presence of interfacial polarization (generation of Maxwell-Wagner-Sillars polarization⁴⁶ resulting in a change in dielectric constants) of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ with the polymer matrix. However, the observed decreased output performance of the 20 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device indicates the amalgamation of interfaces on increasing particle loading in the polymer matrix. To confirm this, the frequency dependant dielectric constant values of all the composite films and neat PLA were measured (Figures 2A.10, Appendix 2). An increase in ϵ' value with the increase in loading of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ in PLA was observed up to its 15 wt% composites. However, a reduction in the dielectric constant values was observed in the ϵ' vs. f profile for the 20 wt% film, which indicates the amalgamation of the interfaces causing a reduction in the dipole moment of the system. Also, the direct piezoelectric measurements performed on the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite films showed a similar trend in the piezoelectric coefficient values. The obtained d_{33} values for the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA (5, 10, 15, and 20 wt%) devices were found to be 1.3, 1.5, 2.2, and 1.9 pC/N, respectively, at an operating frequency of 110 Hz and with applied mechanical stress of 0.25 N (Figure 2A.11, Appendix 2). The neat PLA film under the same conditions gave a d_{33} value of only 0.07 pC/N showing its weak piezoelectric nature compared to $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ (Figure 2A.11, Appendix 2).

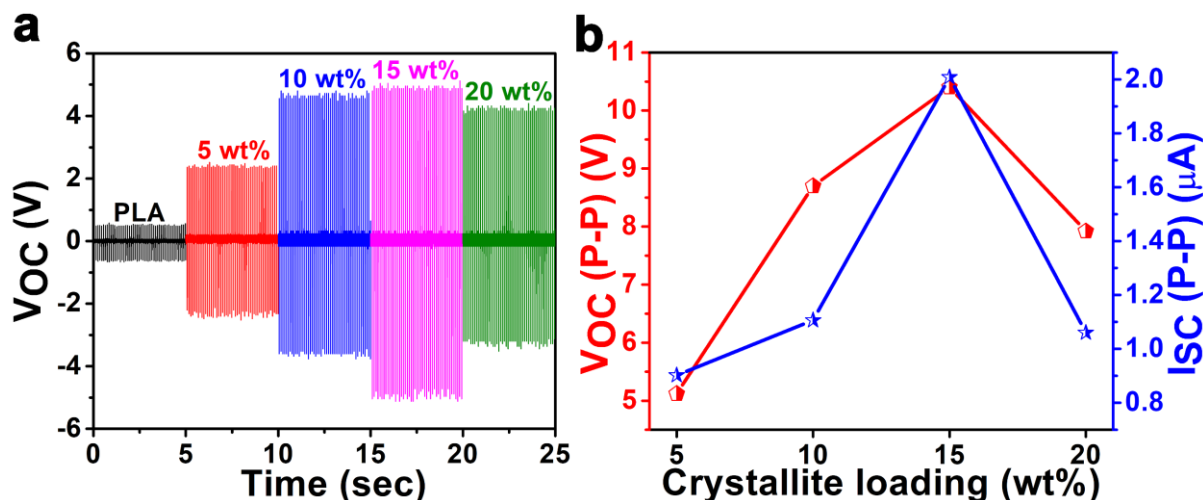


Figure 2.4: (a) Measured V_{PP} profile for neat PLA and all the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite devices. (b) Comparative V_{PP} and I_{PP} values of all $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite devices.

Apart from their notable output voltages, the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA films also show sizable short circuit currents (I_{PP}) upon connecting these devices to a 4.7 M Ω resistor. The I_{PP} values were observed to be 0.9, 1.1, 2.2, and 1.6 μ A for the 5, 10, 15, and 20 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite devices, respectively (Figures 2A.12-2A.13, Appendix 2). The maximum recorded V_{PP} and I_{PP} were found to be 10.4 V and 2.2 μ A, respectively, for the 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device (Figure 2.4b and Table 2A.2, Appendix 2). The current density (CD) and power density (PD) values were subsequently calculated by using the formula V/RA and VI/A (A = area of the device used for measurement) respectively. The maximum CD and PD of 0.5 μ A/cm² and 5.26 μ W/cm², respectively, were observed for the 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device during these studies at the 4.7 M Ω resistance (Figure 2.5a and Table 2A.2, Appendix 2). The obtained output performances of 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA is comparable with

several of the reported composites of organic-inorganic hybrid materials (Table 2A.3, Appendix 2).⁴⁷⁻⁵⁶

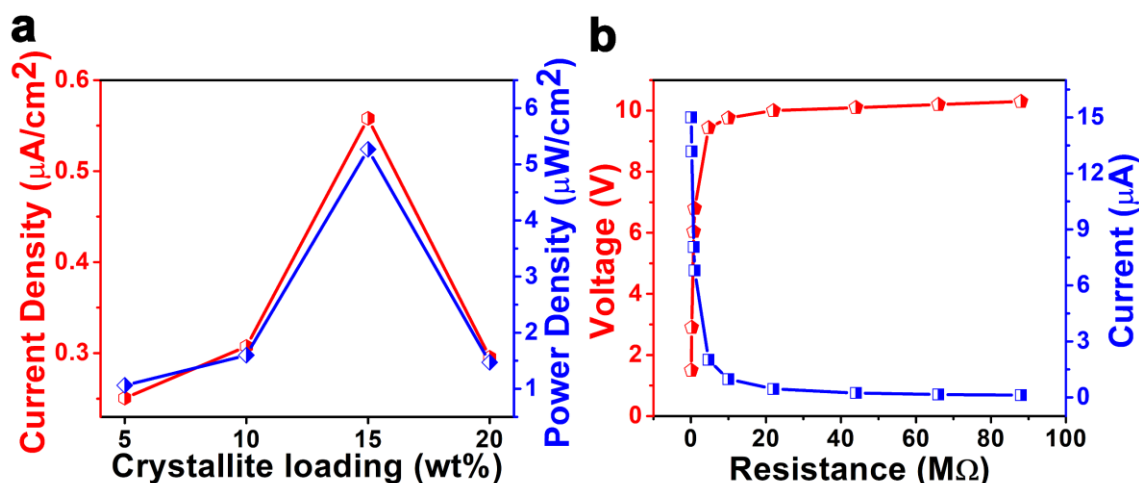


Figure 2.5: (a) Current density (CD) and power density (PD) of the $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ composite devices (b) The comparative voltage-drop and calculated current data for the 15 wt % $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ composite device under various load resistances.

To demonstrate the practical utility of the $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ composite device, the output voltages of these devices were measured under various load resistances ranging from 100 k Ω to 88 M Ω . All these devices showed an increasing trend in the V_{PP} values and a decreasing trend in the I_{PP} values, as the load resistance increased. Again, a maximum voltage of 10.3 V and a current of 0.2 μA were obtained at the maximum load resistance of 88 M Ω . The trends observed in these measurements are in good agreement with those reported in the literature (Figures 2.5b and 2A.14, Appendix 2).⁵⁷ The cycling experiments were also performed on the 15 wt% $\{[{}^5\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ composite device to test the long-time stability of the device. These studies revealed no significant drop in V_{PP} for up to 10000 cycles (Figure 2A.15, Appendix 2).

To demonstrate the energy storage capabilities of the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA device, the best performing 15 wt% device was utilized for charging a 100 μF capacitor (Figure 2.6a). A four-diode full-wave bridge rectifier circuit was employed to convert the AC potentials to the DC voltages. A maximum of 1.16 V was stored in the capacitor that reaches the saturation point in 60 seconds (Figure 2A.16, Appendix 2). The corresponding energy and charge stored in the capacitor were calculated to be 58.25 μJ and 116.5 μC , respectively (Figure 2.6b).

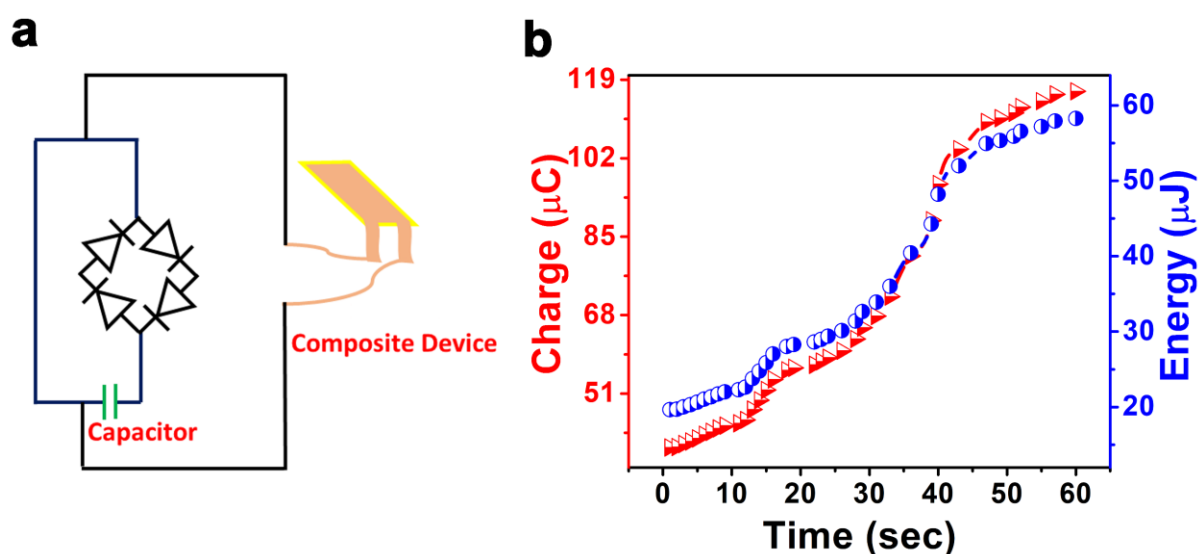


Figure 2.6: (a) Four diode rectifier circuit (b) Charge and energy stored in a 100 μF capacitor by utilizing the 15 wt % $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device.

2.4 Conclusion

To summarize, we have synthesized a bismuth-bromide perovskite-structured material containing a μ_2 -bridged $\{[\text{BiBr}_5]^{2-}\}_n$ anionic 1D-framework charge-neutralized by chiral tolylethanammonium cations. The two-component system crystallizes in the piezoelectrically active orthorhombic $P2_12_12_1$ space group and exhibits dielectric and piezoelectric properties. Further, the piezoelectric energy harvesting measurements were done on the polymer composite device of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ in PLA. The maximum peak-to-peak voltage of 10.4 V and the maximum peak-to-peak

current of 2.2 μA was observed for the 15 wt% $\{[\text{S}^+\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device. The corresponding current density and power density values of 0.5 $\mu\text{A}/\text{cm}^2$ and 5.26 $\mu\text{W}/\text{cm}^2$ were obtained at an optimal load resistance of 4.7 M Ω . In addition to this, the capacitor charging ability of the 15 wt% composite device was examined by charging a 100 μF capacitor. A maximum of 1.16 V voltage was stored along with the reasonably good values for the stored charges and energies in the capacitor. These findings inspire the generation of lead-free hybrids supported by chiral organic cations not only to yield perovskite-structured materials with less toxic metal contents but also in realizing structures with non-linear dielectric properties.

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End of Chapter 2

Chapter 3



**3D-printed Polymer Composite
Devices based on a Ferroelectric
Chiral Ammonium Salt for High-
performance Piezoelectric Energy
Harvesting**

3.1 Introduction

Perhaps composite materials simultaneously exhibiting ferroelectric, dielectric, and piezoelectric properties are one of the most renowned multifunctional materials for their applications in memory devices, sensors, transducers, wearable electronics, medical devices, robots, and energy storage materials.¹⁻⁴ Ferroelectric materials with embedded piezoelectric characteristics facilitate the interconversion between electric voltage and mechanical stimuli and are employed as mechanical energy harvesters, popularly known as piezoelectric nanogenerators (PENGs).^{1, 5-9} PENGs are perceived to possess numerous applications in modern high-tech electronics and devices that function in the harvesting, storage, and dissipation of electrical energy.¹⁰ In recent years, many PENGs derived from conventional ferro- and piezoelectric ceramics such as lead zirconate titanate, lithium niobate, zinc oxide, barium titanate and polymers such as polyvinylidene fluoride (PVDF) have been explored, and commercially applied.¹¹⁻¹⁷ The PENGs based on these materials are typically commissioned in their neat form or as composites with flexible materials such as polymers.

Additive manufacturing, also known as three-dimensional printing (3DP), is the emerging technology to print physical objects layer-by-layer and provides efficiency to the scale-up processes for device miniaturizations.¹⁸⁻²¹ This technique has gained prominence due to its simple, customizable preparation and is finding its way into the pharmaceutical, electronic and robotic industries.¹⁹ Three important techniques, namely, fused deposition modelling (FDM),^{22, 23} stereolithography (SLA),²⁴ and selective laser sintering (SLS)²⁵ are well-explored for 3DP applications. Amongst these, the FDM is the most common in 3DP technology due to easy operation, environmental benignity, high efficiency, and low cost.²⁶⁻²⁸ The use of the 3DP technique for PENG applications is highly desired as it offers efficient force-to-electricity conversion compared to traditional 2D thin-film-based devices. Moreover, the 3D printing prompts the uniform distribution of the compressive stress during PENG measurements and facilitates the directional arrangement of dipole moments leading to improved output performance. 3D-printed architectures of ceramic and oxide materials are somewhat known in the recent literature. However, using these

materials brings certain disadvantages for application in miniature and wearable electronics because of the challenges associated with their device formulations. The most pressing challenge is the poor mechanical stiffness, even at low strain values, apart from toxic metal contents.²⁹ Recently, Zhang and co-workers have demonstrated the enhancement of piezoelectric output voltage of a 3D printed PVDF device compared to that of a device composed of neat PVDF film.³⁰ This may be attributed to the reduction in the material modulus prompted by the porous nature of the casted material. However, PVDF-based devices require external additives or high-voltage poling to exhibit the desired effects.^{10, 31}

Thus, it is advantageous to investigate small-molecule-derived ferro- and piezoelectrics and their composites as 3D-printable PENG devices. Because these materials are soluble in common solvents and are compatible with several polymer matrices, they can be printed into customized shapes using the FDM technique. Organic materials and their polymer composites are highly advantageous in terms of their flexibility, toughness and mechanical properties. Scientific community has previously reported efficient energy harvesting outputs derived from all-organic-based composite devices. For instance, composites like DPDP·PF₆/PDMS, DPDP·BF₄/TPU, [Bn(4-BrBn)NMe₂]·BF₄, Boc-FF_PCL, 3NA@PCL, etc.³²⁻³⁶ have shown sizable PENG outputs but were only tested in the form of their 2D thin-films. However, studies on such materials using additive manufacturing technique could offer attractive solutions for obtaining complex scalable architectures for energy applications. Also, it is desirable to prepare organic ferroelectrics with high output characteristics to achieve 3DP PENG devices.

Herein, we report a simple organoammonium salt {[Me₃CCH(Me)NH₃][BF₄]} (**DMBA·BF₄**), containing 3,3-dimethyl-2-butylammonium (DMBA) cation with a chiral carbon center and tetrafluoroborate anion. Compound **DMBA·BF₄** crystallizes in the tetragonal *P*4₂ space group at both 120 and 298 K suitable for ferroelectric properties. The ferroelectric behavior of **DMBA·BF₄** was confirmed by polarization (*P*) versus electric field (*E*) hysteresis loop measurement, which gave a saturation polarization (*P_s*) of 1.82 μC cm⁻² at 298 K. The PFM analysis showed excellent ferroelectric domain structures and characteristic amplitude and phase responses at a single point of the

crystalline thin film. Further, various composite devices (5, 10, 15 and 20 wt%) of **DMBA•BF₄** were prepared in combination with the biodegradable polycaprolactone (PCL) polymer and employed as PENGs. The optimal 10 wt% **DMBA•BF₄**-PCL gave a maximum open-circuit peak-to-peak voltage (V_{OC-PP}) of 36.2 V with the corresponding power density of 48.1 $\mu\text{W cm}^{-2}$. Subsequently, gyroid (Gy) shaped 3D-printed ensembles were prepared for the 10 wt% **DMBA•BF₄**-PCL composite with an enhanced output voltage of 41 V and power density of 56.8 $\mu\text{W cm}^{-2}$. These results present the potential of 3D-printed all-organic PENG devices for efficient energy harvesting applications and open up new avenues for them in future wearable electronics.

3.2 Experimental section

3.2.1 General remarks

S-3,3-dimethyl-2-butylamine was purchased from Sigma Aldrich and was used without further purification. Tetrafluoroboric acid was purchased from Avra Chemicals. Polycaprolactone (PCL) was purchased from Sigma Aldrich and was used as received. The thermogravimetric analyses were performed using the PerkinElmer STA-6000 analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a TA Q20 differential scanning calorimeter with heating and cooling rates of 10 °C/min under the nitrogen atmosphere. NMR spectra were recorded on a Bruker 400 MHz spectrometer (¹H NMR, 400.13 MHz; ¹³C{¹H} NMR, 100.62 MHz) in CDCl₃ solvent. Melting point analyses were done using a Buchi M-560 melting point apparatus and were uncorrected. The FT-IR spectrum was performed using a Perkin-Elmer spectrometer with samples prepared as KBr pellets in the ranges between 400 and 4000 cm⁻¹. The variable temperature powder X-ray diffraction (VT-PXRD) data were measured in the 2-theta range of 5 to 50 ° on a Bruker-D8 Advance X-ray diffractometer. The field-emission scanning electron microscopy (FE-SEM) analysis of all the composite films (all different wt%) was performed using the Zeiss ultra plus FE-SEM instrument with a minimum spatial resolution of 1 μm . The 3D X-Ray microtomography analyses were performed using a Carl Zeiss Versa 510 microscope with an applied X-ray energy of 80 kV. The Raman spectral analysis of compound **DMBA•BF₄**, neat PCL and the

polymer composite films (**DMBA•BF₄**-PCL) were recorded by using a Horiba Jobin Yvon Raman spectrometer with a 50X objective lens. The compound **DMBA•BF₄** and **DMBA•BF₄**-PCL composite devices were exposed to different humid conditions using ESPC SH-222 Bench-Top Type Temperature and Humidity Chamber. The static mechanical testing (stress-strain behavior) of pure PCL and the polymeric composite films was performed on an Instron 5943 model Universal Testing Machine (UTM) using rectangular film strips (0.2 mm thickness, 5 mm width, and 30 mm overall length) at 50 mm/min strain rate and 1 kN load cell.

3.2.2 Synthesis

To a stirred solution of HBF₄ (1 g, 2.80 mmol) in methanol (10 mL), (S)-3,3-dimethyl-2-butyl amine (0.312 g, 1.40 mmol) in methanol (10 mL) was added slowly over a period of 30 minutes. The reaction mixture was subsequently stirred for 1 hour at room temperature. The obtained clear solution was filtered through a thick pad of celite and kept for crystallization at room temperature. White crystals of **DMBA•BF₄** were obtained after 7 days. A quick comparison of the optical rotation values indicates that the chirality of compound **DMBA•BF₄** is probably changed from that of the precursor (S)-3,3-dimethyl-2-butylamine in their bulk methanolic solution. However, we are unable to confirm the chirality of the compound as it was inactive for circular dichroism (CD) measurements. Yield: 89 %. Melting point: 510-518 K. ¹H NMR (400 MHz, CDCl₃) δ 3.20 (q, *J* = 6.8 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 3H), 1.02 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) 58.07 (s), 33.05 (s), 25.36 (s), 14.03 (s). FT-IR data in KBr pellet (cm⁻¹): 3245, 2962, 1613, 1516, 1390, and 1008. Anal. Calcd. for C₆H₁₆BF₄N: C 38.18; H 8.53; N 7.41. Found: C 38.17; H 8.54; N 7.43.

3.2.3 Crystallography

The single-crystal X-ray diffraction data for **DMBA•BF₄** at 120 K and 298 K were obtained on a Bruker Smart Apex Duo diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystal structures were solved using the direct method and then refined by full-matrix least-squares against F² using SHELXL-2014/7 built in the Apex 3 program.³⁷ The crystallographic refinement data for **DMBA•BF₄** at different temperatures are listed in Table 3.1. All the nonhydrogen atoms were refined anisotropically. Hydrogen atoms were constructed in geometric positions to their

parent atoms.³⁸ The structure was refined as the two-component racemic twin. The fluorine atoms of the BF₄ anions in the 298 K data were disordered. Atom positions of the disordered fragments were refined for similar distances and U-restraints using the SIMU/SAME/SADI routine of the SHELX. The structural illustrations were prepared by using DIAMOND-3.1 software.

Table 3.1: Details of crystallographic data collection and structure refinements for DMBA•BF₄.

Crystallographic details	120 K	298 K
Chemical formula	C ₆ H ₁₆ BF ₄ N	C ₆ H ₁₆ BF ₄ N
Formula weight (g/mol)	189.01	189.01
Temperature	120(2)K	298(2)K
Crystal system	Tetragonal	Tetragonal
Space group	<i>P</i> 4 ₂	<i>P</i> 4 ₂
a (Å); α (°)	15.808(3); 90	15.93(3); 90
b (Å); β (°)	15.808(3); 90	15.93(3); 90
c (Å); γ (°)	7.9627(18); 90	8.241(16); 90
V (Å ³); Z	1989.9(10); 8	2090(9); 8
ρ (calc.) g cm ⁻³	1.262	1.201
μ (Mo K _α) mm ⁻¹	0.125	0.119
2θ _{max} (°)	50.484	45.024
R(int)	0.0922	0.1843
Completeness to θ	100	99.9
Data / param.	4973/174	2748/300
GOF	1.550	1.023
R1 [F > 4σ(F)]	0.0995	0.0850
wR2 (all data)	0.2673	0.2837
max. peak/hole (e.Å ⁻³)	0.954/-0.645	0.296/-0.190
Flack parameters	0.0(4)	-0.3(10)

3.2.4 Hirshfeld surface analysis

The Hirshfeld surface analysis was mapped with d_{norm} and 2D fingerprint plots using Crystal Explorer 3.1 program. For this study, the single-crystal X-ray crystallographic information file (CIF) was utilized to visualize all the different types of interactions present on the Hirshfeld surface. These interactions were obtained as 3D color mapping images such as normalized contact distance (d_{norm}), shape index, and curvedness. The diverse surface color mappings of **DMBA•BF₄** were generated on the Hirshfeld surface by different color coding based on intense (red), medium (blue), and weak (white) interactions. The 2D fingerprint plot is in fact a histogram which can be constructed by compiling all the distances of given atoms that are nearest to the interior (d_i) and exterior (d_e) of the generated Hirshfeld surface. The different contours (blue and grey color) that are present in the 2D fingerprint plot explain the various types of molecular interactions.

3.2.5 Nonlinear optical measurements

Nonlinear optical measurements was performed by using a direct output from a Coherent Astrella Ti:Sapphire regenerative amplifier providing femtosecond laser pulses (800 nm, 75 fs) at a 1 kHz repetition rate. The output was used unfocused. Laser fluence at samples was equal to 0.28 mJ/cm².

In order to perform a Kurtz-Perry powder test, the single crystals of **DMBA•BF₄** and KDP were crushed with a spatula and sieved through an Aldrich mini-sieve set, collecting a microcrystal size fraction of 125–177 μm . Next, size-graded samples were fixed in-between microscope glass slides to form tightly packed, uniform layers, sealed, and mounted to the horizontally aligned sample holder. No refractive index matching oil was used. Under the same excitation conditions, the SHG signal was collected for **DMBA•BF₄** and KDP for 6000 ms and 500 ms, respectively.

The employed measurement setup operates in the reflection mode. Specifically, the laser beam delivered from the regenerative amplifier, passed through a 5 mm aperture, was directed onto the sample at 45° to its surface. Emission collecting optics consisted of a Ø25.0 mm plano-convex lens of focal length 25.4 mm mounted to the 400 μm 0.22 NA glass optical fiber and was placed along the normal to the sample surface. The distance between the collection lens and the sample was equal to 30

mm. The spectra of SHG responses were recorded by an Ocean Optics Flame T fiber-coupled CCD spectrograph with a 200 μm entrance slit. Scattered pumping radiation was suppressed with the use of a Thorlabs 750 nm short pass dielectric filter (FESH0750).

In the case of temperature-resolved measurement, the same geometry of the experimental setup was employed. The temperature control of the sample was realized ($dT/dt = 5 \text{ K/min}$) using a Linkam LTS420 Heating/Freezing Stage. Temperature stability was equal to 0.1 K.

3.2.6 Ferroelectric, dielectric and piezoelectric Measurements

The P - E hysteresis loop measurements on **DMBA•BF₄** were performed on its compact disc sample with approximately 8 mm diameter and 1.2 mm thickness electroded with Cu adhesive tapes. The ferroelectric polarization vs. electric field (P - E) measurements were performed on the aixACCT TF-2000E model hysteresis loop analyzer. The leakage currents were dynamically recorded during the hysteresis loop measurements.

The dielectric permittivity measurement was performed on the powder pressed pellet of **DMBA•BF₄**. The measurements were performed using the Solartron Analytical Impedance Analyzer model 1260 coupled with a Dielectric Interface 1296A operating with Janis 129610A cryostat sample holder and a Lakeshore 336 model temperature controller.

The piezoelectric nature of **DMBA•BF₄** was again confirmed from the d_{33} measurements using the Berlincourt Piezotest meter model PM300 on the compacted disc of **DMBA•BF₄** with approximately 8 mm diameter and 1.2 mm thickness.

3.2.7 Dipole moment calculations

The polarization exhibited by these two materials was further confirmed from the preliminary theoretical dipole moment ONIOM calculations performed by using the Gaussian 09 program. For this calculation, the anionic parts were taken as the high layer, and the cationic parts were regarded as the lower layer. These dipole moment (ONIOM) calculations were performed using the Density Functional Theory (DFT) method.³⁹

3.2.8 Piezoresponse force microscopy studies

The ferroelectric domain structure of **DMBA•BF₄** thin film and its micro crystals were done using a commercial AFM system [MFP 3D, Asylum Research in the contact mode (vector mode)]. The vertical and lateral domain orientations were probed by using the Pt/Ir coated tip [SCM-PIT-V2 by Bruker] with spring constant of 2.8 N/m and tip radius of 25 nm and imaging were done by using Pt-coated silicon probe. To enhance the signal, resonant enhanced PFM mode was used with a frequency of 285 KHz and AC amplitude of 2 V. The switching ability of the domains on thin films was checked by the application of external DC bias of ± 40 and ± 60 V using the PFM tip in contact mode. The thin films of the compound were prepared by drop casting 40 mg of the compound **DMBA•BF₄** in 1 mL Methanol and drop cast it on the substrate followed by annealing at room temperature for 30 minutes.

3.2.9 General procedure for the preparation of polymer composite films and devices

The composite films of **DMBA•BF₄** were prepared by dissolving 5, 10, 15 and 20 wt% of the ferroelectric crystallites into nonpiezoelectric biodegradable polycaprolactone (PCL) in dimethylformamide (DMF) solution. Homogeneous solutions were prepared by keeping the solutions for mechanical stirring at 50 °C for 15 min, followed by vortex mixing for 15 min. The homogeneous solutions were poured onto a glass slide and kept undisturbed in an oven at 50 °C for 3 h. The dried free-standing composite films comprising 5, 10, 15, and 20 wt% of **DMBA•BF₄** in PCL were subsequently peeled off from the glass slide. To perform the energy harvesting applications on **DMBA•BF₄**-PCL composite films, the device structures were made by placing adhesive copper contacts on either side of the film and soldering Cu-wires (0.3 mm) to the contact strips. The device architectures were completed by covering them with Kapton tapes, which protect the devices from the impact force and minimize the static charge developed during the piezoelectric measurement.

3.2.10 General procedure for the preparation of **DMBA•BF₄**-PCL filaments

All **DMBA•BF₄**-PCL composite filaments were prepared by solution mixing followed by melt extrusion. **DMBA•BF₄**-PCL composite films that were prepared as per the

protocol mentioned above were shredded and then melt compounded in a Haake Mini CTW twin-screw extruder at 110 °C for 3 min. Subsequently filament having a diameter of 2.75 ± 0.2 mm was extruded from the die of the extruder by optimizing the screw and take up roller speed.

3.2.11 Procedure for the preparation of 3D printed polymer composite devices

Prior to 3D printing, the prepared **DMBA•BF₄**-PCL composite filaments were dried in a vacuum oven at ambient temperature for 24 h. Ultimaker 3 FDM type 3D printer was used to print 3D shapes with different infill patterns (zig-zag, grid, gyroid and triangular). The optimal printing conditions for **Gy-DMBA•BF₄**-PCL composite are given below.

Table 3.2: Details of crystallographic data collection and structure refinements for DMBA•BF₄.

Process Parameters	Values
Bed	Glass plate
Nozzle size (mm)	0.4
Nozzle temperature (°C)	120
Bed temperature (°C)	30
Infill degree (%)	50
Layer height (mm)	0.1
Flow (%)	100
Print speed (mm/s)	30

3.2.12 Piezoelectric energy harvesting and storage measurements

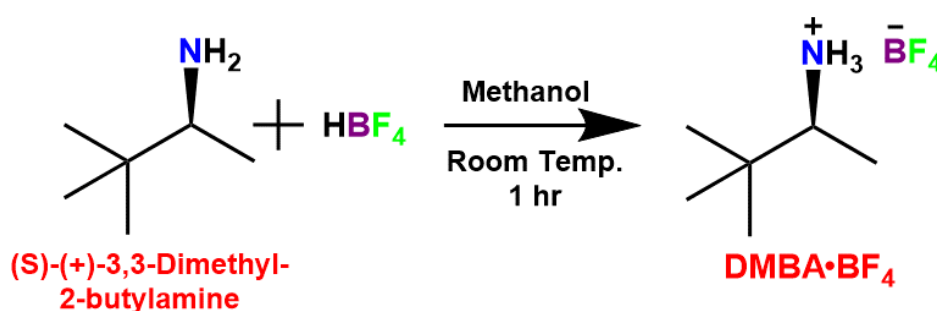
The mechanical energy harvesting experiments were conducted on a custom-built periodic impact instrument operating at an impact force of 21 N and frequency of 10 Hz (Picture S1). The output voltages and currents were measured using a Tektronix 2024 Mixed Signal Oscilloscope operating at an input impedance of 1 MΩ. The

thickness and the active area of the devices (**DMBA**•**BF₄**-PCL) under test were ~1 mm and 360 mm², respectively. The thickness and area of the 3D-printed **Gy-DMBA**•**BF₄**-PCL devices were ~2 mm and 600 mm² respectively. The energy storage attributes of the 10 wt% **DMBA**•**BF₄**-PCL and **Gy-DMBA**•**BF₄**-PCL devices during impact measurements were tested with a 100 μF capacitor by connecting the devices and the capacitor with a full wave-bridge four-diode circuit.

3.3 Results and Discussion

3.3.1 Syntheses, characterization and crystal structures

The chiral ammonium salt **DMBA**•**BF₄** was prepared by adding tetrafluoroboric acid into a methanol solution of (S)-3,3-dimethyl-2-butylamine (Scheme 3.1 and Figures 3A.1-3A.2). Rod-shaped colorless crystals of **DMBA**•**BF₄** were obtained from the reaction mixture after seven days. The single-crystal X-ray diffraction (SCXRD) analysis revealed that at 120 K, **DMBA**•**BF₄** crystallizes in the tetragonal *P*4₂ space group. The asymmetric unit of **DMBA**•**BF₄** contained two DMBA cations and two BF₄[−] anions (Figure 3.1a). The packing diagram of **DMBA**•**BF₄** shows the presence of an H-bonded tetrameric assembly consisting of four DMBA cations and four BF₄[−] anions. In the tetramer structure, each DMBA cation is H-bonded to two BF₄[−] anions and in return, the BF₄[−] anion is bonded to two ammonium cations (Figure 3.1b). These tetramers are seen to stack one below the other via the N-H⋯F interactions and form a helical 1D network (Figures 3.1b and 3A.4 and Table 3A.1).



Scheme 3.1. Synthesis of **DMBA**•**BF₄**.

The single crystal X-ray diffraction (SCXRD) data of **DMBA•BF₄** at 298 K was solved in the same tetragonal $P4_2$ space group (Figure 3.1c). Although, the obtained structure shows similar structural features as that of its 120 K data, the fluorine atoms in both the BF₄⁻ anions are disordered with each of them being located in two independent sites. Nevertheless, the H-bonded tetrameric assembly is retained in **DMBA•BF₄** at 298 K as well (Figure 3A.5 and Table 3A.2, Appendix 3). A detailed Hirshfeld surface analysis of **DMBA•BF₄** was carried out for its structure at 120 and 298 K. Among several interactions present in the molecule the H...F/F...H interactions were found to contribute significantly to the inter-molecular interactions contributing 45.8 % of the total interactions at 298 K (Figures 3.1d, 3A.6-3A.11, Appendix 3).

The thermogravimetric analysis (TGA) of **DMBA•BF₄** shows the high stability of the compound until 550 K (Figure 3A.12, Appendix 3). The differential scanning calorimetry (DSC) experiment was performed in the temperature range of 200-450 K to map any structural phase transitions in **DMBA•BF₄**. From the DSC profiles, two phase transitions at 239/230 K (low-temperature phase (LTP) to intermediate-temperature phase (ITP)) and 326/320 K (intermediate-temperature phase (ITP) to high-temperature phase (HTP)) were noticed in the heating/cooling runs (Figure 3.2a). The enthalpy changes were found to be 3.90/4.45 Jg⁻¹ and 14.30/7.34 Jg⁻¹ respectively at 239/230 K and 326/320 K in the heating/cooling runs. The corresponding entropy changes were estimated to be 0.0163/0.0193 Jg⁻¹K⁻¹ and 0.0438/0.0229 Jg⁻¹K⁻¹. The first phase transition at 239/230 K corresponds to the ferroelectric-ferroelectric phase transition (*vide infra*) as observed from the SCXRD data of **DMBA•BF₄** at 298 K (in the same space group of $P4_2$). Notably, the disorder of the BF₄⁻ anions and some perturbations of the cations could have caused the heat anomaly in the DSC profile. The HTP structure of **DMBA•BF₄** could not be obtained as the crystals of **DMBA•BF₄** turned opaque above 320 K. Hence, to track the HTP of **DMBA•BF₄**, temperature-dependent powder X-ray diffraction (PXRD) measurements were carried out. The room temperature PXRD profile of **DMBA•BF₄** shows a good correlation with that of the simulated patterns from the 298 K SCXRD data. Changes in the PXRD profiles were noticed from 328 K onwards and the stabilization of the new phase was noticed at 338 K (Figure 3A.13, Appendix 3). Indexing the 338 K PXRD profile yields the unit

cell parameters for the HTP of **DMBA•BF₄** in the chiral tetragonal space group $P4_22_12$ (Table 3A.3, Appendix 3). This suggests a polar to non-polar structural transformation of **DMBA•BF₄** in the HTP.

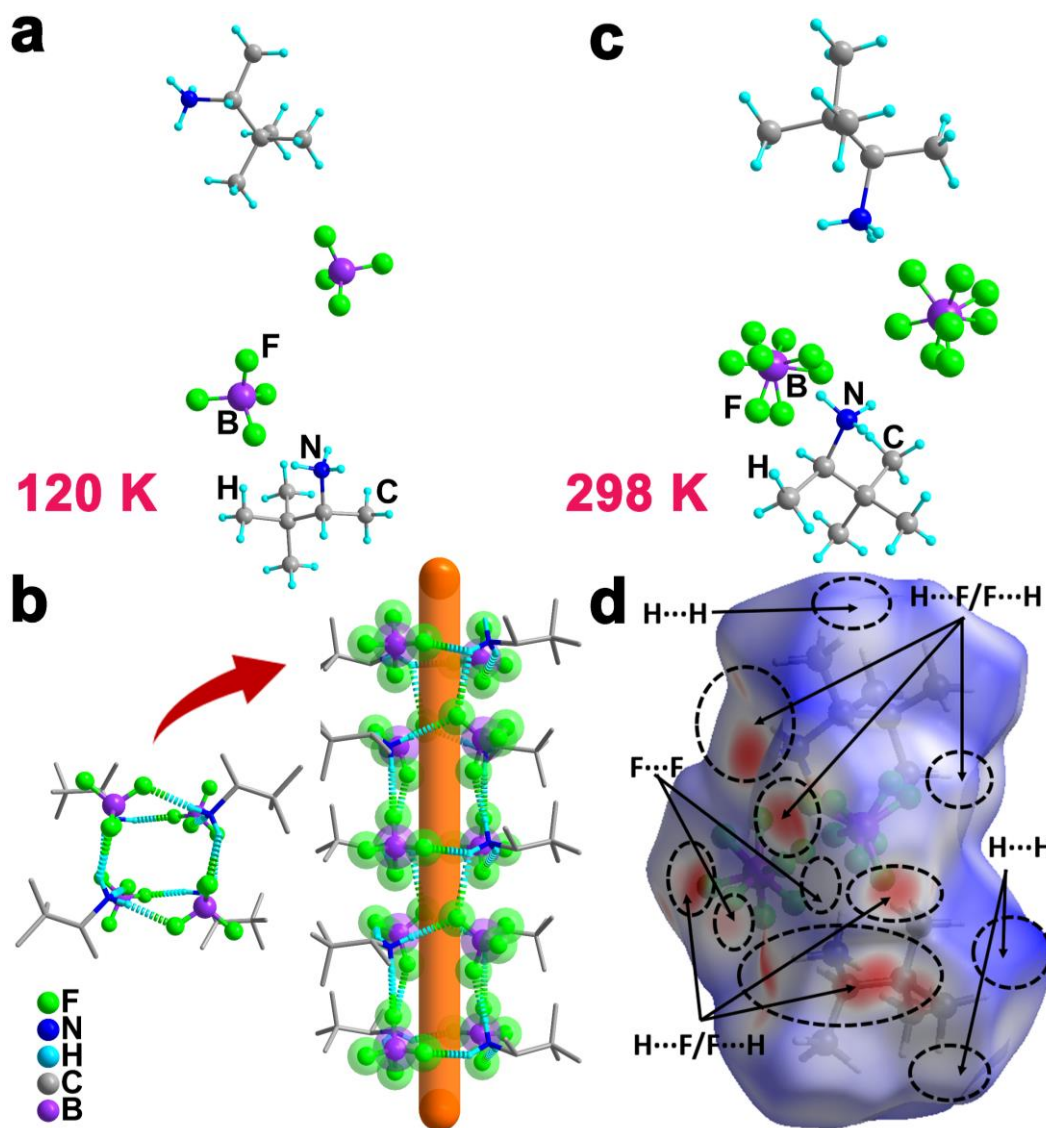


Figure 3.1: (a) Molecular structure of **DMBA•BF₄** at 120 K. (b) Hydrogen bonding interactions in **DMBA•BF₄** mediated by N-H...F interactions at 120 K showing a primary tetrameric motif (left), which assembles into a helical H-bonded 1D-structure (right) (c) Molecular structure of **DMBA•BF₄** at 298 K. (d) Projection of d_{norm} -mapped Hirshfeld surface of **DMBA•BF₄** at 298 K.

Furthermore, the PXRD analysis of **DMBA•BF₄** after a period of five months showed no degradation in the peak profiles, confirming its long-term stability (Figure 3A.14a, Appendix 3). Since ammonium salts are known to suffer from moisture instability, the stability of **DMBA•BF₄** was checked by performing PXRD measurements after exposing the powder sample of **DMBA•BF₄** to different relative humid conditions (RH = 25% to RH = 99%) at 298 K. As observed from the PXRD analyses, compound **DMBA•BF₄** retains its crystallinity up to RH = 75% (Figure 3A.14b, Appendix 3). However, signs of the loss in crystallinity were evident upon exposing **DMBA•BF₄** to 99% RH condition.

3.3.2 SHG, dielectric, ferroelectric and piezoelectric studies

The non-centrosymmetric nature of **DMBA•BF₄** is further supported by the second harmonic generation (SHG) measurements at room temperature, using the measurement of a Kurtz-Perry type.⁴⁰ The powder sample of **DMBA•BF₄** upon irradiation with 800 nm, 1 kHz laser pulses with a width of ca. 75 fs produces the SHG (400 nm) signal with the relative efficiency of 0.01 with respect to the standard potassium dihydrogen phosphate (KDP) sample of the same particle size (Figure 3.2b). The temperature-resolved SHG experiment ($dT/dt = 5 \text{ K min}^{-1}$) in the range from 140 to 400 K shows that room temperature ITP crystal phase features approximately 9-fold higher relative SHG intensity than neighboring LT (low temperature) and HT (high temperature) phases (Figures 3.2b inset and 3A.15, Appendix 3).

To further understand the structural transformations of **DMBA•BF₄**, the dielectric permittivity measurements were recorded on its powder-pressed pellet in a frequency range of 1 kHz to 1 MHz (Figure 3A.16, Appendix 3). The temperature-dependent real-part of dielectric permittivity (ϵ') at a frequency of 100 kHz showed two heat anomalies for **DMBA•BF₄**: a broad transition peaking around 250 K and a step-like transition onset above 350 K. These two anomalies are consistent with the phase changes observed from the DSC and X-ray diffraction data (Figure 3.2c and 3A.17, Appendix 3). A maximum ϵ' value of 14.8 was recorded at 277 K at 100 kHz frequency associated with the LTP-ITP transition. Moreover, the temperature dependence of dielectric loss factors ($\tan \delta$) profile of **DMBA•BF₄** matches with the ϵ' vs. T plot, consistent with the observed phase changes in the system. The permittivity values of **DMBA•BF₄** are well-

supported by the reasonably high dipole moment values obtained from the ONIOM calculations on their crystal structures (Table 3A.4, Appendix 3).

Compound **DMBA•BF₄** exhibits a point group symmetry of C_4 , which is one of the ten polar point groups that allow for ferroelectricity. The polarization (P) vs. electric field (E) measurements on a powder-pressed pellet of **DMBA•BF₄** gave a rectangular P - E hysteresis loop. A polarization value of $1.82 \mu\text{C cm}^{-2}$ was obtained at the maximum electric field of 0.25 kV cm^{-1} at 298 K and 0.01 Hz (Figure 3.2d). The obtained current density vs. electric field (J - E) curve shows very low leakage current densities and exhibits two opposite peaks at the coercive field (E_c) of 0.15 kV cm^{-1} , which is typical for ferroelectric materials (Figure 2.2d). The existence of ferroelectricity in the LTP of **DMBA•BF₄** was again confirmed by performing the P - E loop measurements at 218 K (Figure 3A.18, Appendix 3).

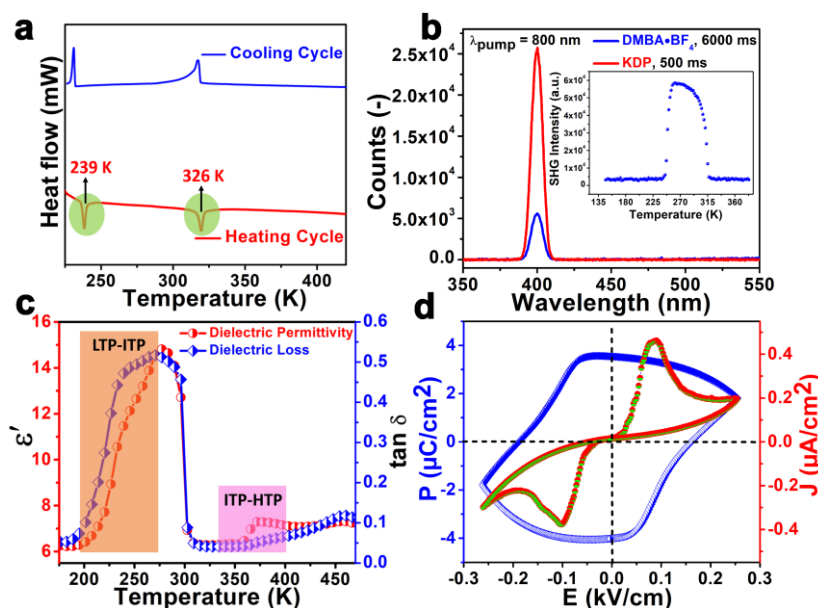


Figure 3.2: (a) The DSC trace of **DMBA•BF₄** in the heating and cooling runs (10°C/min). (b) The spectra of SHG response of **DMBA•BF₄** and the reference KDP. The inset shows the integral SHG intensity of **DMBA•BF₄** plotted as a function of temperature. (c) The temperature dependence of ϵ' and $\tan \delta$ data for **DMBA•BF₄**. (d) The P - E hysteresis loop measurements and leakage current densities of **DMBA•BF₄**.

Furthermore, the microscopic polarization state of the crystals of **DMBA•BF₄** was examined by the vector-mode piezoresponse force microscopy (PFM) technique. Figures 3a-d show the observed ferroelectric amplitude and phase domain structures overlaid on the corresponding topography (Figure 3.3e). The PFM data show stripes of alternating upward and downward ferroelectric polarization patterns. Significant displacements in opposite directions as observed from the amplitude images indicate a pronounced piezoresponse in **DMBA•BF₄**. From the amplitude images, it is evident that the out-of-plane (V-PFM) piezoresponse is more pronounced than the in-plane (L-PFM) response; however, they are in good correspondence to each other. From the phase responses, large domains with opposite polarity can be visualized. From the phase responses noted from the out-of-plane and in-plane images, the existence of multi-axial polarization can be observed.⁴¹ Similar responses have been observed in the vertical (V-PFM) and lateral (L-PFM) measurements on a drop-casted film of **DMBA•BF₄** as well (Figure 3A.20, Appendix 3). Additionally, the PFM spectroscopy measurements were performed at a single point on the thin film of **DMBA•BF₄** by applying a constant bias voltage of ± 60 V at the tip. This resulted in a phase-bias rectangular hysteresis loop and butterfly-shaped amplitude-bias loop characterizing the ferro- and piezoelectric nature of the material (Figure 3.3f).⁴²

We also obtained a PFM resonance curve at 2 V on the crystal surface of **DMBA•BF₄**, which shows an excellent piezoelectric response compared to the standard DIPAB sample (Figure 3.3g). Furthermore, pointwise amplitude vs. drive voltage measurements was performed on the ferroelectric domains across both **DMBA•BF₄** and the standard sample of DIPAB (Figure 3.3h). A linear rise in the amplitude data firmly confirms the intrinsic piezoelectric nature of these samples. The slopes of these fitted straight lines yield the comparative measure of the piezoelectric coefficient of **DMBA•BF₄** to that of DIPAB. From Figure 3f it is evident that the magnitude of the relative piezoelectric coefficient of **DMBA•BF₄** is more than twice that of DIPAB.^{43, 44}

The direct piezoelectric response (d_{33}) of **DMBA•BF₄** was obtained using the “BerlinCourt” method on its compacted pellet. The bulk d_{33} coefficient of **DMBA•BF₄** was measured to be 3.7 pC N^{-1} at an operating frequency of 110 Hz and with applied mechanical stress of 0.25 N. The corresponding piezoelectric voltage ($g_{33} = d_{33}/\epsilon_{33}$)

and the transduction ($d_{33} \times g_{33}$) coefficients were calculated to be $10.60 \times 10^{-3} \text{ V m N}^{-1}$ and $39.24 \times 10^{-15} \text{ m}^3 \text{ J}^{-1}$, respectively, suggesting the feasibility of **DMBA•BF₄** for efficient mechanical to electrical energy conversion.

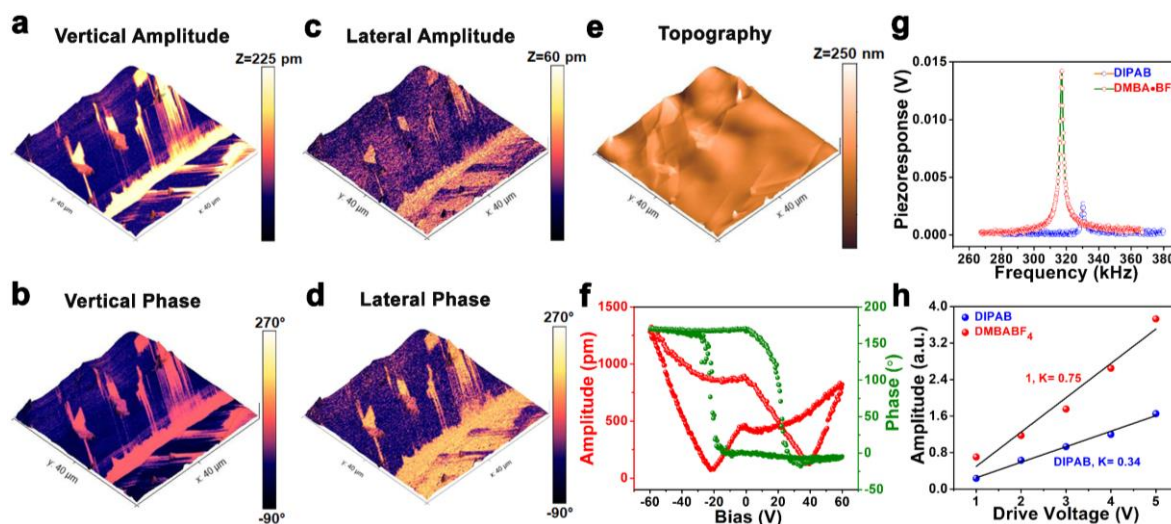


Figure 3.3: The vector PFM data of microcrystals of **DMBA•BF₄** showing (a) 3D-vertical amplitude, (b) 3D-vertical phase, (c) 3D-lateral amplitude, (d) 3D-lateral phase images overlaid on the corresponding topography and (e) the blank 3D-topography image. (f) The amplitude-bias butterfly and phase-bias hysteresis loops of **DMBA•BF₄** at a single point. (g) Comparative PFM resonance curves of **DMBA•BF₄** and DIPAB at 2 V. (h) The amplitude vs. drive voltage measurement on the surfaces of **DMBA•BF₄** and DIPAB.

3.3.3 Fabrication and characterizations of **DMBA•BF₄**-PCL composite films

The utility of **DMBA•BF₄** for PENG applications was further probed on its polymer composite films that endow the crystallites of **DMBA•BF₄** with high mechanical flexibility. Various weight percent (5, 10, 15 & 20 wt%) composite films of **DMBA•BF₄** were prepared with polycaprolactone (PCL) polymer by adding appropriate quantities of **DMBA•BF₄** into a DMF solution of PCL (Figure 3A.22, Appendix 3). The folding, bending, stretching, and rolling operations performed on the **DMBA•BF₄**-PCL films

demonstrate the excellent flexibility of these composite materials (Figure 3.4a). Concomitantly, a film of neat PCL was also prepared for comparative studies.

The field-emission scanning electron microscopy (FE-SEM) analysis shows a uniform distribution of the crystalline ferroelectric particles in the 5 and 10 wt% **DMBA•BF₄**-PCL composite films, while the aggregation of the particles was observed for the 15- and 20-wt% composite films (Figure 3.4b and 3A.23-3A.26, Appendix 3). The X-ray 3D-microtomography images were recorded for all the composite films, which gave a clearer visualization of the embedded particles in the composites (Figures 3.4c and 3A.27-3A.29, Appendix 3).

Both the FE-SEM and 3D-microtomography images suggest the presence of voids in the particle distribution in all the composites.⁴⁵ The PXRD profiles of all the **DMBA•BF₄**-PCL composites reveal the crystalline nature of the embedded particles and the phase purity of **DMBA•BF₄** in the heterostructure (Figure 3A.30, Appendix 3). Furthermore, the intact nature of the crystallites of **DMBA•BF₄** inside the PCL matrix has been verified by Raman spectral analysis (Figure 3A.31, Appendix 3). For neat PCL, the Raman active modes were observed for C-C (1037, 1064, and 1109 cm⁻¹), CH₂ (1418 and 1441 cm⁻¹) and C=O (1723 cm⁻¹) groups.⁴⁶ The compound **DMBA•BF₄** showed Raman active vibrational modes corresponding to the C-H (2816, 2912, 2976 cm⁻¹), C-C (900 cm⁻¹), C-N (767 cm⁻¹), N-H (2875 cm⁻¹) and B-F (538 and 700 cm⁻¹) functionalities. Notably, the characteristic peaks due to both **DMBA•BF₄** and PCL were seen to be present in all the **DMBA•BF₄**-PCL composite films validating the retention of crystallinity of the compound inside the polymer matrix.

To check the mechanical strength and modulus of all the **DMBA•BF₄**-PCL composites, their stress-strain behavior was determined using a Universal Testing Machine. All the composite films were stretchable up to 50 % strain (Figure 3A.32, Appendix 3). Noticeably, the stress values for 5 and 10 wt% composites at 50 % strain were found to be uncompromised (12.52 and 9.29 MPa) relative to neat PCL (12.11 MPa) suggesting the efficient structural and interfacial interaction between the polymer and the ferroelectric particles. Reduced stress values of 6.15 and 5.14 MPa for the 15 and 20 wt% composites at 50% strain can be attributed to the agglomeration of **DMBA•BF₄** in PCL matrix, as suggested by the FE-SEM and X-ray 3D-microtomography analyses.

3.3.4 Mechanical energy harvesting application and the outputs $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite devices

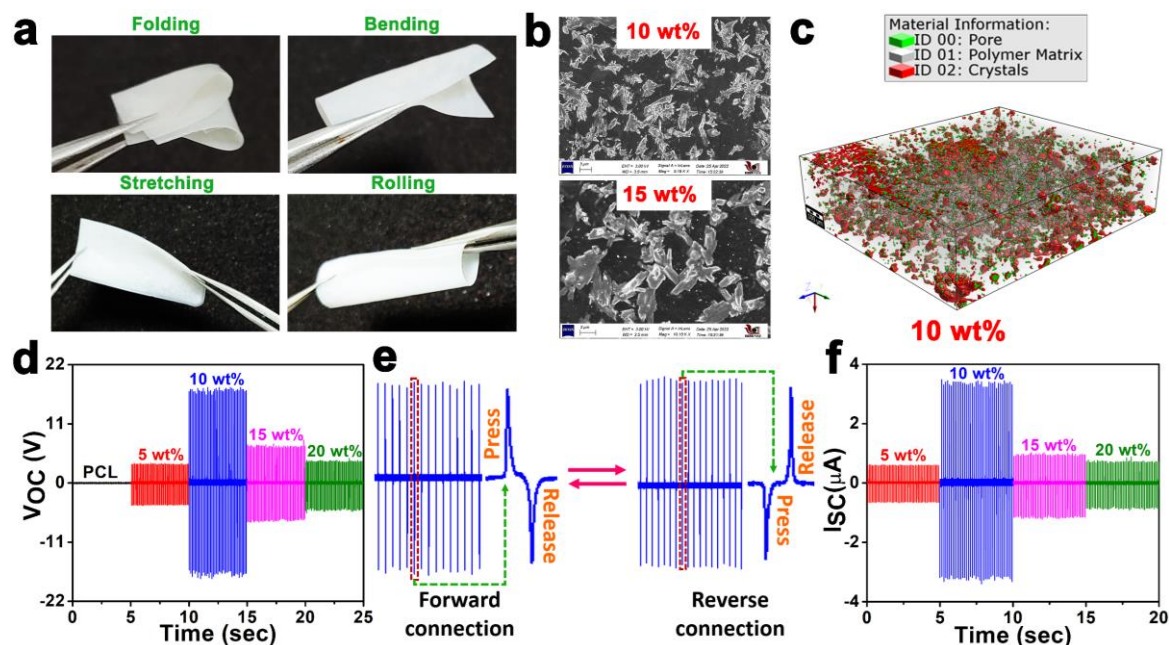


Figure 3.4: (a) Pictures of a representative $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite film showing its flexibility towards folding, bending, stretching, and rolling operations. (b) FE-SEM images of the 10 and 15 wt% $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite films. (c) X-ray 3D-microtomography image of 10 wt% $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite film showing the distribution of ferroelectric crystallites inside the polymer matrix. (d) Open-circuit peak-to-peak output voltages ($V_{\text{OC-PP}}$) of $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite devices. The shifted time-axis provided here is a guide to the eye. (e) The reversibility of the output signals obtained upon providing forward and reverse connection to the oscilloscope. (f) The calculated output current (I_{PP}) profiles of $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite devices.

For the PENG measurements, the composites were suitably electroded and protected with Kapton tapes. All the measurements involving $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite devices were performed at an optimized external load of $\sim 21 \text{ N}$ and an operating frequency of 10 Hz (Figure 3A.34, Appendix 3). The measured peak-to-peak open-circuit voltages ($V_{\text{OC-PP}}$) for the 5, 10, 15, and 20 wt% $\text{DMBA} \cdot \text{BF}_4\text{-PCL}$ composite

devices are 7.9, 36.2, 15.3, and 10.6 V, respectively (Figures 3.4d and 3A.35, Appendix 3). The device made up of a neat PCL device gave a V_{OC-PP} of only 0.34 V, confirming that the voltages obtained from the composites originate from the piezoelectric nature of **DMBA•BF₄**. As seen in Figure 3.4d, the V_{OC-PP} increases until the 10 wt% of **DMBA•BF₄** in the PCL composites and abruptly decreases for the 15 and 20 wt% **DMBA•BF₄**-PCL composites. This decrease in voltage output can be related to the agglomeration of the crystallites of **DMBA•BF₄** in the polymer matrix at higher concentrations as evident from FE-SEM images (15 and 20 wt% composites). Also, the measured frequency-dependent dielectric permittivities on all the composite films show an initial increasing trend in the ϵ' values and exhibit the maximum values for the 10 wt% **DMBA•BF₄**-PCL material (Figure 3A.36, Appendix 3). A reduction in ϵ' values for the higher wt% (15 and 20 wt%) composites clearly indicates the reduction in the effective dipoles in the system. The agglomeration of the particles is known to produce weak insulation of composites (Maxwell-Wagner-Sillars polarization) and lower the dielectric constants due to electrical breakdown.

Furthermore, the polarity-switching test, by reversing the connections to the electrodes, was performed on the best-performing 10 wt% **DMBA•BF₄**-PCL device ($V_{OC-PP} = 36.2$ V). The observation of the signal of equal magnitude and opposite directions for the press and release operations confirms the true piezoelectric nature of the composite device (Figures 3.4e and 3A.37, Appendix 3). Subsequently, the peak-to-peak currents (I_{PP}) were calculated by attaching a 4.7 M Ω resistor and measuring the voltages across the circuit. The obtained I_{PP} values were observed to be 1.3, 6.9, 2.2, and 1.8 μ A for the 5, 10, 15, and 20 wt% **DMBA•BF₄**-PCL, respectively (Figures 3.4f and 3A.38-3A.39, Appendix 3).

3.3.5 Construction of 3D printed Gy-DMBA•BF₄-PCL composite films

Spurred by the high V_{OC-PP} value of the 10 wt% **DMBA•BF₄**-PCL device, we explored the fabrication of a 3D-printed large-scale device for this composition. To minimize the compound and polymer required for large-area devices, hollow 3D-printed patterns were probed for this application. Thus, we first prepared four different 3D-printed slabs of neat PCL polymer (1.5 x 4 cm²) in the grid, zig-zag, triangular and gyroid geometries, which showed the % porosities of 51.3, 56.7, 56.9 and 59.8 %, respectively.

respectively (Figure 3A.40, Appendix 3). Finally, the gyroid-shaped pattern was chosen for obtaining the 3D-printed PENG devices due to its higher porosity and increased exposure area. Before the FDM printing, the 10 wt% **DMBA•BF₄**-PCL composite filaments were prepared from the as-made composite film using a melt extruder (Figure 3.5a). Subsequently, the composite filament was fed to the 3D printer and patterned as gyroid-shaped slabs (Figure 3.5b).

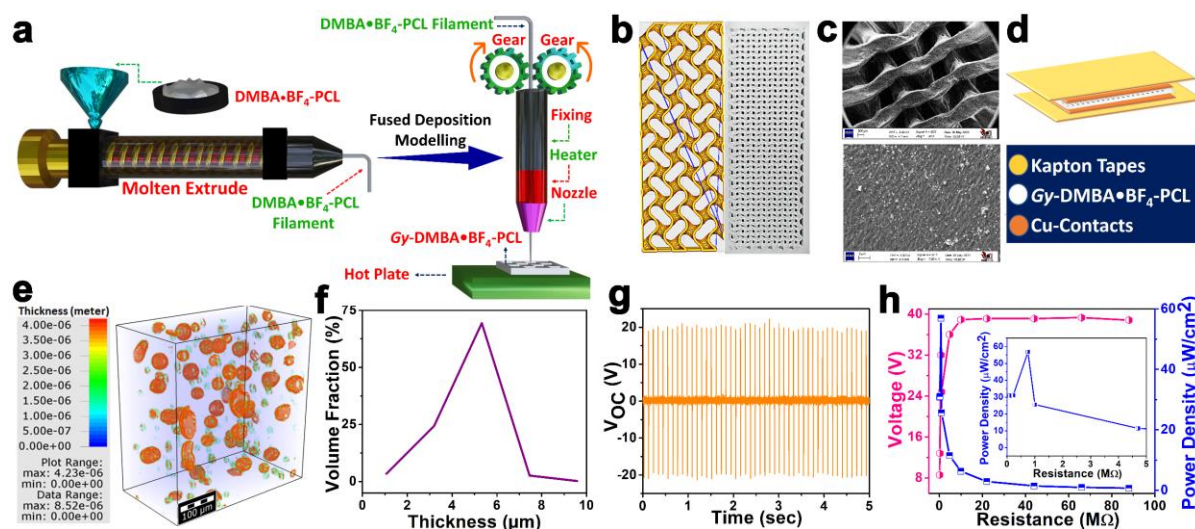


Figure 3.5: (a) Schematic showing the melt extrusion process to obtain the composite filament and the FDM printing of **DMBA•BF₄**-PCL composite slab. (b) Image of a computerized gyroid design and the photograph of a 3D printed **Gy-DMBA•BF₄**-PCL slab (c) FE-SEM images of the 3D printed **Gy-DMBA•BF₄**-PCL composite device showing its pore structure (top) and the distribution of the crystallites in it (bottom). (d) Schematic of a **Gy-DMBA•BF₄**-PCL Device assembly. (e) X-ray 3D-microtomography images of the 3D-printed **Gy-DMBA•BF₄**-PCL composite showing the particle distribution in the 3D-printed gyroid slab (scale: 100 μm). (f) The thickness profile of the crystallites of **DMBA•BF₄** in the **Gy-DMBA•BF₄**-PCL composite obtained from X-ray 3D-microtomography analysis. (g) Measured open-circuit V_{OC-PP} , and (h) Voltage (V) and power density (PD) values of the **Gy-DMBA•BF₄**-PCL composite device under different load resistances. The inset shows magnified view of the PD profile in the low resistance region showing the maximum value at 760 kΩ.

The microstructure analysis of the 10 wt% gyroid **DMBA•BF₄-PCL** (**Gy-DMBA•BF₄-PCL**) shows a clearly formed gyroid pore and uniform distribution of the crystallites of **DMBA•BF₄** in the polymer matrix at the walls of the gyroid slabs as evident from its FE-SEM (Figures 3.5c). The 3D-microtomography analysis reveals the thickness of the crystallites in **Gy-DMBA•BF₄-PCL** in the range of 1-10 microns with an average thickness of around 5 microns (Figures 3.5e-3.5f and 3A.41, Appendix 3).

3.3.6 Mechanical energy harvesting applications of **Gy-DMBA•BF₄-PCL** composite device

The **Gy-DMBA•BF₄-PCL** device (Figure 3.5d) was then utilized for piezoelectric energy harvesting under similar operating conditions of ≈ 21 N and 10 Hz. These measurements gave a V_{OC-PP} of 41 V signifying that the output voltages were uncompromised during the scale-up process (Figures 5g, 3A.42a and 3A.43, Appendix 3). A marginal increase in voltage output (4.8 V) for **Gy-DMBA•BF₄-PCL** as compared to that of the thin-film based 10 wt% **DMBA•BF₄-PCL** device could be attributed to better dipole alignment provided by the shear force of the 3D printing process, reduced clamping effect and increased device surface area (3.6 to 6 cm²). The I_{PP} of the **Gy-DMBA•BF₄-PCL** device was measured to be 7.6 μ A at a load resistance of 4.7 M Ω , which is slightly higher than that of the 10 wt% **DMBA•BF₄-PCL** device (6.9 μ A) (Figures 3.5h inset and 3A.42b, Appendix 3).

Furthermore, to evaluate the utility of the **Gy-DMBA•BF₄-PCL** for practical applications, its output voltages were measured under different load resistances ranging from 100 k Ω to 88 M Ω (Figure 3A.44, Appendix 3). For comparison, a parallel set of experiments were performed for all the composite film-based devices as well (Figure 3A.45, Appendix 3). Notably, the voltage increases with the increase in load resistances approaching a value close to V_{OC-PP} and saturates for higher load resistances for all these devices. The corresponding power density (PD) values at each load resistances were calculated using the formula VI/A (where V , I and A are the peak voltage, peak current at 760 k Ω and area of the device respectively). The maximum power density (PD) value of 56.8 μ W cm⁻² was observed for the **Gy-DMBA•BF₄-PCL** device at a peak resistance of 760 k Ω (Figure 3.5h). This value is

slightly higher than that of the thin-film based 10 wt% **DMBA•BF₄-PCL** device ($48.1 \mu\text{W cm}^{-2}$) (Figure 3A.46, Appendix 3). The observed PD values for both these devices are among the highest reported for any nanogenerator device containing all-organic components (Table 3A.5, Appendix 3).⁴⁷⁻⁶⁴ The durability test performed on the best-performing 10 wt% **Gy-DMBA•BF₄-PCL** and **DMBA•BF₄-PCL** devices for 10000 cycles showed no degradation in the output voltages confirming the mechanical robustness of the embedded material in them (Figure 3A.47-3A.48, Appendix 3).

The PENG measurements performed on both the 10 wt% **DMBA•BF₄-PCL** and **Gy-DMBA•BF₄-PCL** devices showed significant durability even after a period of 5 months at ambient conditions (Figures 3A.49, Appendix 3). Remarkably, both these devices, 10 wt% **DMBA•BF₄-PCL** and **Gy-DMBA•BF₄-PCL**, showed no performance degradation after exposing them to different relative humidity conditions ranging from 25 to 99 % corroborating their utility under practical conditions (Figure 3A.50, Appendix 3). The retention in voltage output even at 99% RH can be attributed to the device architecture involving the encapsulation of the ferroelectric crystallites in the polymer matrix and its further protection by using Kapton tapes.

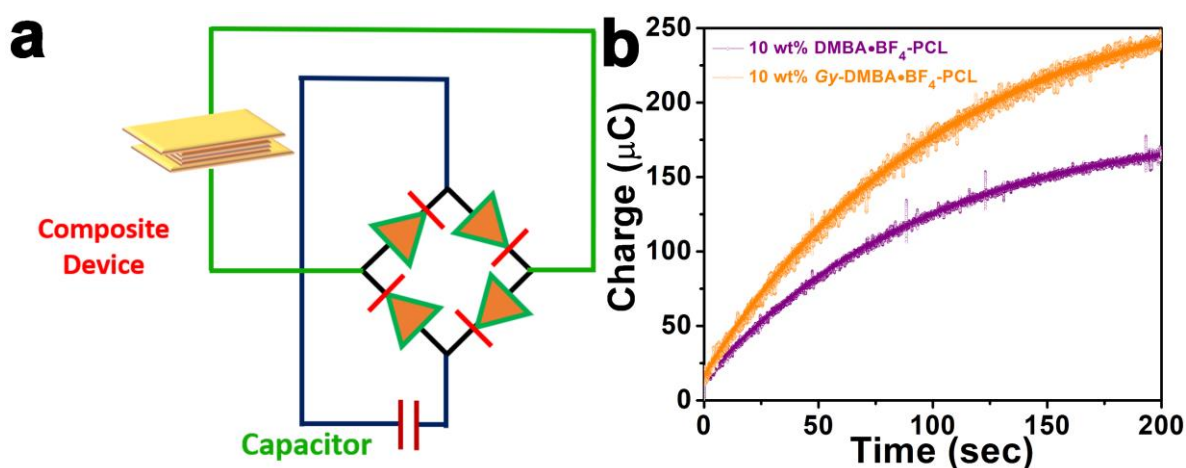


Figure 3.6: (a) Circuit diagram of the full-wave four-diode bridge rectifier circuit employed for energy storage. (b) The plot of the stored charge (Q) in the $100 \mu\text{F}$ capacitor obtained from 10 wt% **DMBA•BF₄-PCL** and **Gy-DMBA•BF₄-PCL** devices.

Capacitor charging experiments were performed to evaluate the energy storage capabilities of both **Gy-DMBA•BF₄-PCL** and 10 wt% **DMBA•BF₄-PCL** devices by using a 100 μF capacitor. For this purpose, a four-diode bridge rectifier circuit was connected to these devices to convert the generated AC voltages during the impact measurements into DC potentials (Figure 3.6a). Both these devices store sizable charges (calculated from the voltages stored shown in Figure 3A.51, Appendix 3) with the **Gy-DMBA•BF₄-PCL** storing a higher value of 241.7 μC , while the 10 wt% **DMBA•BF₄-PCL** stores 164.9 μC (Figure 3.6b). The corresponding energies stored in the capacitor were also seen to follow a similar trend with the maximum stored energies of 121.6 and 83.2 μJ , respectively, for the **Gy-DMBA•BF₄-PCL** and 10 wt% **DMBA•BF₄-PCL** devices (Figures 3A.52, Appendix 3). The increase in the charge accumulated in the capacitor using the **Gy-DMBA•BF₄-PCL** device is a testament to the efficient energy harvesting and storage capabilities of the large-scale 3D printed device.

3.4 Conclusion

Design and discovery of high-fidelity mechanical energy harvesting devices necessitate fine-tuning of piezoelectric material performance at both molecular and macroscopic levels. In this work, the chiral molecule containing DMBA cation was employed to code for the polar order and resulting phenomena of its tetrafluoroborate salt. While the supramolecular material **DMBA•BF₄** is intrinsically efficient at piezoelectric energy harvesting, as shown for 10 wt% composite devices with PCL polymer (output voltage of 36.2 V and power density of 48.1 $\mu\text{W cm}^{-2}$) its performance could be preserved by the fabrication of gyroid-shaped microstructures through 3D printing. Indeed, miniaturized gyroid-shaped 10 wt% **DMBA•BF₄-PCL** composite slabs feature an exceptionally high output voltage of 41 V translating to a power density of 56.8 $\mu\text{W cm}^{-2}$, thus setting up a new benchmark for energy harvesting performance in the class of all-organic nanogenerator devices. Remarkably, the output performance of the material was found to be uncompromised after the scale-up process.

This advancement has been enabled by obtaining a new chiral organic ammonium salt **DMBA•BF₄** crystallizing in the non-centrosymmetric tetragonal $P4_2$ space group with rich inter-molecular H-bonding interactions that strengthen its long-range polar

order. The SHG measurements confirm the acentric setting of **DMBA•BF₄** across all phases. Indeed, **DMBA•BF₄** exhibit two phase transitions, namely of ferroelectric-ferroelectric and ferroelectric-piezoelectric type, as determined from XRD, DSC, dielectric and *P-E* loop measurements. The ferro- and piezoelectric domain characteristics and polarization switching behavior of **DMBA•BF₄** were further established by PFM measurements. Also, the piezoelectric nature of **DMBA•BF₄** was further established by *d*₃₃ measurement on its compacted pellet. All in all, from an environmental perspective, combining a biodegradable polymer such as PCL with a high-polarization salt such as **DMBA•BF₄** makes these **DMBA•BF₄**-PCL composite devices less toxic and less expensive for future use in wearable electronics. Currently, we are working towards such processes in employing these and similar materials for next-generation electronics.

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End of Chapter 3

Chapter 4



A Highly Electrostrictive Salt Co-crystal and the Piezoelectric Nanogenerator Application of its 3D Printed Polymer Composite

4.1 Introduction

Co-crystallization of two or more compounds offers a facile route for the generation of distinctive supramolecular assemblies with a range of applications as innovative materials.¹ Co-crystal engineering is well-known for the creation of new organic materials with extraordinary properties that enable comprehensive studies on their structure-property relationships.^{1, 2} In this regard, non-covalent interactions such as hydrogen bonds, halogen bonds, $\pi\cdots\pi$ stacking and ion-dipole interactions play a pivotal role in the design of organic co-crystals.³⁻⁵ These interactions provide significant stability and directional preference, leading to enhanced physiochemical properties desired for functional organic materials.⁶ Materials possessing ferroelectric, dielectric, and piezoelectric properties are extensively explored as memory devices, sensors, transducers, wearable electronics, medical devices, robots, and energy storage materials.⁷⁻¹⁶ Among these, ferroelectric materials possessing piezoelectric characteristics are particularly useful for their ability to convert mechanical stimuli into electrical voltage, making them suitable for use in piezoelectric nanogenerators (PENGs).¹⁷⁻²⁰ PENGs have become increasingly important in modern high-tech electronics, particularly for energy harvesting, storage, and dissipation.²¹⁻²⁵ However, the electrostrictive coefficient (Q_{33}), the measure of PENG output for any piezoelectric material is low for traditional ceramic materials ($0.034\text{--}0.096\text{ m}^4\text{C}^{-2}$) in comparison with organic piezoelectrics such as polyvinylidene difluoride ($1.3\text{ m}^4\text{C}^{-2}$).^{26, 27} Hence, single and two-component organic compounds are attractive candidates for obtaining piezoelectrics with high electromechanical properties.²⁸⁻³⁰ However, two-component ionic ferroelectrics based on common ammonium cations suffer from the problems of moisture instability due to their hygroscopic characteristics. Hence, we postulated that ferro- and piezoelectric materials with improved stability and polarization attributes could be achieved for ionic co-crystals containing organic salts and neutral compounds via the synergistic combination of ionic and non-covalent interactions.

Herein, we report a ferroelectric ionic co-crystal $[\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_2][\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_3][\text{PF}_6]$ ((*p*-TEA)(*p*-TEAH)·PF₆), obtained from the combination of an ammonium salt and a neutral amine. The

structural asymmetry in this co-crystal is imposed by homochiral *S*-*p*-tolylethylamino substituents, while the labile octahedral PF_6^- anion greatly contributes to the electric field-reversible polar property necessary for the ferroelectric phenomenon. Compound **(*p*-TEA)(*p*-TEAH)·PF₆** is insoluble in water and exhibits remarkable moisture stability even at 99% relative humidity (RH) conditions. Ferroelectric *P*-*E* hysteresis loop measurements on **(*p*-TEA)(*p*-TEAH)·PF₆** gave a saturation polarization (P_s) of 0.95 $\mu\text{C cm}^{-2}$ at 298 K, while its direct piezoelectric (d_{33}) coefficient was found to be 4 pC N⁻¹. Remarkably, these values yielded a high electrostriction coefficient (Q_{33}) value of 2.02 m⁴ C⁻², which is higher than those of the piezoceramics and close to that of polyvinylidene difluoride (PVDF). Subsequently, the PENG applications of **(*p*-TEA)(*p*-TEAH)·PF₆** have been established on its various weight percentage (wt%) composites with biodegradable polycaprolactone (PCL) polymer. The optimal 10 wt% **(*p*-TEA)(*p*-TEAH)·PF₆**-PCL composite device showed a maximum peak-to-peak open-circuit voltage ($V_{\text{OC-PP}}$) of 13.1 V and power density of 104.2 $\mu\text{W cm}^{-3}$, respectively. Spurred by its high moisture stability and sizable PENG output characteristics, we prepared the scaled-up device for the 10 wt% **(*p*-TEA)(*p*-TEAH)·PF₆**-PCL composite using the 3D-printing technique. Notably, the performance of the gyroid-shaped 3D-printed PENG device was found to be nearly doubled with a $V_{\text{OC-PP}}$ of 22.8 V and the power density rising up to 118.5 $\mu\text{W cm}^{-3}$. 3D-printed PENG devices based on organic composite materials are in the early stages of research and materials selection for such processes require thorough optimization to establish the synergy between the organic compound and polymer matrix.³¹ These results emphasize that the co-crystallization of two-component charge-separated systems with neutral organic compounds is an effective strategy for obtaining highly stable organic ferroelectrics for next-generation energy harvesting devices.

4.2 Experimental section

4.2.1 General remarks

(*S*)-1-(*p*-Tolyl)ethanamine, Hexafluorophosphoric acid (HPF₆), and Polycaprolactone (PCL) were purchased from Sigma Aldrich and directly used in the reactions. A dry nitrogen atmosphere was employed for both the thermogravimetric analyses performed on the PerkinElmer STA-6000 analyzer with a heating rate of 10 °C/min,

and in the differential scanning calorimetry (DSC) measurements conducted using a TA Q20 differential scanning calorimeter with heating and cooling rates of 10 °C/min. Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker 400 MHz spectrometer (^1H NMR, 400.13 MHz; $^{13}\text{C}\{^1\text{H}\}$ NMR, 100.62 MHz) in CDCl_3 solvent. Melting point analyses were conducted on a Buchi M-560 melting point apparatus and were not corrected. The Perkin-Elmer spectrometer was used to perform the FT-IR spectrum with samples prepared as KBr pellets within the 400-4000 cm^{-1} range. The Bruker-D8 Advance X-ray diffractometer was used for the powder X-ray diffraction (PXRD) data collection within the 2θ range of 5 to 50°. Zeiss ultra plus FE-SEM instrument was used for the field-emission scanning electron microscopy (FE-SEM) analysis of all composite films (at different weight percentages) with a minimum spatial resolution of 1 μm .

The X-ray photoelectron spectroscopy (XPS) analysis for compound **(p-TEA)(p-TEAH)·PF₆** was conducted by utilizing a Thermo Fisher Scientific instrument, UK ModelK alpha+ spectrometer using mono-chromatic Al K α anode (1486.6 eV) as X-ray source operating at 72 W power. Vacuum pressures of 1.2×10^{-8} mbar and 2×10^{-9} mbar were maintained in the sample loading and analyzer chambers, respectively. Data acquisition utilized micro-focused X-ray sources with a spot size of 400 μm . The high-resolution survey scan was performed with a 200 eV pass energy, while individual core-level spectra were captured using a 50 eV pass energy. Charge compensation, maintained through ultra-low energy co-axial electron and Ar^+ ion beams, remained active during spectral acquisition. The C1s standard value at 284.6 eV was used for final binding energy calibration to determine binding energies of various elements in the sample. The spectrometer base pressure was kept typically better than 5×10^{-9} mbar and 1×10^{-7} mbar during data collection with the flood gun active. With an instrument resolution of ± 0.1 eV, raw data were processed using Avantage software, applying smart background subtraction for peak fitting.

4.2.2 Synthesis

To a flask containing (S)-p-tolylethanamine (0.3 g, 2.21 mmol), excess HPF₆ (3.2 g, 22.1 mmol) was added slowly under constant stirring over a period of 10 minutes at room temperature. A white precipitate was formed, which was then dissolved again by

adding methanol to obtain a clear solution. The solution was then filtered through a thick pad of celite and kept for crystallization at room temperature. White crystals of **1** were obtained after 7 days. Yield: 85 %. Anal. Calcd. for $C_{18}H_{27}F_6N_2P$: C 51.92; H 6.54; N 6.73. Found: C 51.02; H 6.23; N 6.70. Melting point: 490-500 K. 1H NMR (400 MHz, MeOD) δ 7.30 (dd, $J = 41.7, 8.0$ Hz, 4H), 4.43 (q, $J = 6.8$ Hz, 1H), 2.35 (s, 3H), 1.62 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, MeOD) δ 138.67 (s), 135.50 (s), 129.35 (s), 126.26 (s), 50.67 (s), 19.73 (s), 19.30 (s). FT-IR data in KBr pellet (cm^{-1}): 3100, 1600, 1521, 1230, and 1016.

4.2.3 Crystallography

The molecular structure of compound $(p\text{-TEA})(p\text{-TEAH})\cdot PF_6$ at 100 and 298 K was solved from its single-crystal X-ray diffraction data collected on a Bruker Smart Apex Duo diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073\text{\AA}$). The crystal structures were solved using the direct method, and refined by full-matrix least-squares against F^2 , employing the SHELXL-2014/7 program integrated into the Apex 3 software. All the nonhydrogen atoms were refined anisotropically. The crystallographic refinement data for $(p\text{-TEA})(p\text{-TEAH})\cdot PF_6$ at different temperatures are listed in Table 4.1. Hydrogen atoms were constrained in geometric positions to their parent atoms. The structure was refined as the two-component racemic twin. Two fluorine atoms of the PF_6^- ion in the asymmetric unit were positionally disordered over two sites and located in special positions with half-occupancies each. The TEAH and TEA moieties in $(p\text{-TEA})(p\text{-TEAH})\cdot PF_6$ cannot be distinguished crystallographically; hence, their protons are refined with partial occupancies to provide an accurate charge balance. Thus, H1A has a full occupancy (1.0) while H1B and H1C atom are refined with 0.75 occupancies each. The structural illustrations were generated using the DIAMOND-3.1 software.

Table 4.1: Details of crystallographic data collection and structure refinements for $(p\text{-TEA})(p\text{-TEAH})\cdot PF_6$.

Crystallographic details	$(p\text{-TEA})(p\text{-TEAH})\cdot PF_6$ (100 K)	$(p\text{-TEA})(p\text{-TEAH})\cdot PF_6$ (298 K)
Chemical formula	$C_{18}H_{27}F_6N_2P$	$C_{18}H_{27}F_6N_2P$
Formula weight (g/mol)	416.38	417.39
Temperature	100(2)K	298(2)K

Crystal system	Monoclinic	Monoclinic
Space group	C2	C2
a (Å); α (°)	10.027(2); 90	10.131(2); 90
b (Å); β (°)	6.391(2); 104.41(3)	6.573(2); 103.48(3)
c (Å); γ (°)	16.343(3); 90	16.490(3); 90
V (Å ³); Z	1014.3(4); 2	1067.9(5); 2
ρ (calc.) g cm ⁻³	1.363	1.295
μ (Mo K α) mm ⁻¹	0.194	0.184
2 $\theta_{\max}$ (°)	50.002	50.948
R(int)	0.0844	0.0963
Completeness to θ	99.9	99.9
Data / param.	1775/145	1893/145
GOF	1.043	1.022
R1 [F > 4 σ (F)]	0.0440	0.0492
wR2 (all data)	0.1138	0.1223
max. peak/hole (e.Å ⁻³)	0.320/-0.475	0.169/-0.262
Flack parameters	0.1(3)	0.2(3)

4.2.4 Hirshfeld surface analysis

The Hirshfeld surface analysis of **(p-TEA)(p-TEAH)·PF₆** was conducted using the Crystal Explorer 3.1 program. The single-crystal X-ray crystallographic information file (CIF) was utilized to visualize the various types of interactions present on the Hirshfeld surface, including normalized contact distance (d_{norm}), shape index, and curvedness. The resulting 3D color mapping images showed the diverse surface color mappings of compound **(p-TEA)(p-TEAH)·PF₆**, with intense interactions represented by red, medium interactions by blue, and weak interactions by white. The 2D fingerprint plot, essentially a histogram, was generated by compiling the distances between given atoms closest to the interior (d_i) and exterior (d_e) of the Hirshfeld surface. The different

contours in the 2D fingerprint plot were represented by blue and grey colors, providing insight into the various types of molecular interactions.

4.2.5 Nonlinear optical measurements

The Kurtz-Perry powder tests were done by using a Coherent Astrella Ti: Sapphire regenerative amplifier (RA) to generate femtosecond laser pulses at a repetition rate of 1 kHz. These laser pulses were passed through a wavelength-tuneable Topaz Prime Vis-NIR optical parametric amplifier (OPA) to obtain the desired wavelength of 800 nm. The laser beams were unfocused and had a 0.20 mJ cm^{-2} fluence at 800 nm. The SHG relative efficiency of **(p-TEA)(p-TEAH)·PF₆** was estimated using the Kurtz-Perry powder method, where potassium dihydrogen phosphate (KDP) was used as the SHG reference. Microcrystals of **(p-TEA)(p-TEAH)·PF₆** and KDP were ground and sieved through an Aldrich mini-sieve set to obtain a microcrystal size fraction of 250–177 μm . The laser beam was directed at the samples at 45° , and the diffused SHG spectra were recorded by an Ocean Optics Flame T spectrograph after suppressing the scattered pumping radiation with a 750 nm short-pass dielectric filter.

4.2.6 Ferroelectric, dielectric and piezoelectric measurements

To investigate the ferroelectric behaviour of **(p-TEA)(p-TEAH)·PF₆**, *P-E* hysteresis loop measurements were conducted on a compact disc sample of approximately 8 mm diameter and 1.2 mm thickness, which was electroded with Cu adhesive tapes. These measurements were performed using the aixACCT TF-2000E model hysteresis loop analyzer. The experiments were conducted by applying the dynamic leakage current compensation (DLCC) mode to reduce the contributions from non-hysteretic components of the loop. The ferroelectric fatigue measurements were performed for 10^6 cycles under the same DLCC conditions. The ferroelectric fatigue measurements were performed at a frequency of 100 Hz and an applied voltage of 100 V, respectively.

The dielectric permittivity of **(p-TEA)(p-TEAH)·PF₆** was measured on its powder pressed pellet sample. The measurements were conducted using the Solartron Analytical Impedance Analyzer model 1260, coupled with a Dielectric Interface 1296A. The sample was placed in a Janis 129610A cryostat sample holder, and the temperature was controlled using a Lakeshore 336 model temperature controller.

The piezoelectric (d_{33}) coefficient of **(p-TEA)(p-TEAH)·PF₆** was obtained from the Berlincourt Piezotest meter model PM300. The measurements were performed on a compacted disc sample of approximately 8 mm diameter and 1.2 mm thickness.

4.2.7 Piezoresponse force microscopy studies

The PFM measurements were conducted using the Asylum Research MFP-3D atomic force microscopy (AFM) system for a drop-casted thin film of **(p-TEA)(p-TEAH)·PF₆** on silicon surface. A contact mode AFM experiment was carried out, utilizing RMN-12PT300B cantilever probes with a spring constant of 1.12 N m⁻¹ and a tip diameter of less than 8 nm to measure the piezoresponse of the crystal films. Vertical-PFM experiments were employed to acquire PFM data, with the bottom electrode being grounded while an AC voltage was applied to the conductive AFM tip. PFM images were collected at resonance frequency of 300 +/- 20 kHz with a varied applied bias of 60 and 80 V. The measurements were performed using dual AC resonance tracking (DART) mode PFM. The switching ability of the domains of the single crystal located on the thin film was recorded by the application of external DC bias of ±50 using the PFM tip in contact mode.

4.2.8 General procedure for the preparation of polymer composite films and devices

To prepare the composite films of **(p-TEA)(p-TEAH)·PF₆**, varying amounts (5, 10, 15, and 20 wt%) of the ferroelectric crystallites were dispersed in nonpiezoelectric biodegradable polycaprolactone (PCL) in chloroform (CHCl₃) solution. The solutions were mechanically stirred at 50 °C for 15 min and vortex mixed for 15 min to obtain homogeneous solutions. These solutions were then poured onto a glass slide and allowed to dry undisturbed at room temperature for 8 h. The resulting free-standing composite films were peeled off from the glass slide and copper with conductive adhesive tapes were attached to both sides for electrical contacts. The devices were then covered with Kapton tapes to complete the architecture. Additionally, a neat PCL polymer film encapsulated with Kapton tape was also prepared and tested under similar experimental conditions for comparison.

4.2.9 General procedure for the preparation of (p-TEA)(p-TEAH)·PF₆-PCL filaments

The (p-TEA)(p-TEAH)·PF₆-PCL composite filaments were produced through a two-step process involving solution mixing and melt extrusion. Firstly, (p-TEA)(p-TEAH)·PF₆-PCL composite films were prepared following the protocol mentioned earlier and then shredded. These shredded films were further melt compounded in a Haake Mini CTW twin-screw extruder for 3 minutes at 110 °C. The screw and take-up roller speeds were optimized to extrude filaments of 2.85 ± 0.15 mm diameter from the extruder die.

4.2.10 Procedure for the preparation of 3D printed polymer composite devices

The (p-TEA)(p-TEAH)·PF₆-PCL composite filaments, prepared as described earlier, were dried in a vacuum oven at ambient temperature for 24 hours before 3D printing. A Ultimaker 3 FDM type 3D printer was utilized to produce 3D structures with gyroid pattern. For the **3DP-Gy** composite, the printing parameters were optimized to achieve the best results, and are listed below.

Table 4.2: The optimal printing conditions for 3DP-Gy composite.

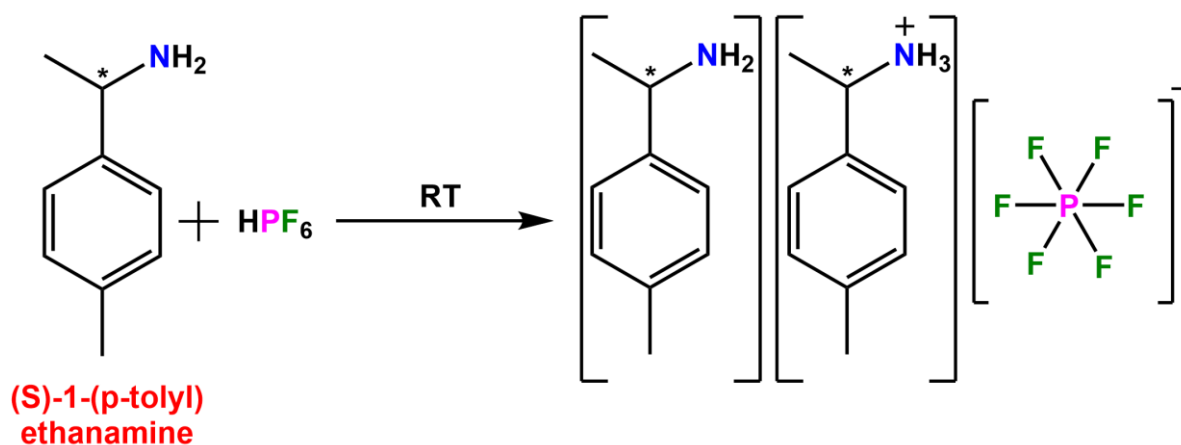
Process Parameters	Values
Bed	Glass plate
Nozzle size (mm)	0.4
Nozzle temperature (°C)	120
Bed temperature (°C)	30
Infill degree (%)	50
Layer height (mm)	0.1
Flow (%)	100
Print speed (mm/s)	30

4.2.11 Piezoelectric energy harvesting and storage measurements

A custom-built periodic impact instrument was used to conduct the mechanical energy harvesting experiments, operating at tunable frequencies (2-10 Hz) and an impact force of 21 N. The Tektronix 2024 Mixed Signal Oscilloscope was used to measure the output voltages and currents, with an input impedance of 1 MΩ. The devices under test had a thickness of approximately 0.5 mm and an active area of 360 mm², while the 3D-printed **3DP-Gy** devices had a thickness of about 0.9 mm and an area of 600 mm². To test the energy storage attributes of the devices during impact measurements, different capacitors with varying capacitance values were used. For the capacitor charging experiments, the devices and capacitor were connected using a full wave-bridge four-diode circuit. The flash-lighting of a green-LED (Power rating = 60 mW) was achieved by connecting the LED in series to the capacitor.

4.3 Results and Discussion

4.3.1 Synthesis, characterizations, crystal structures, and SHG studies



Scheme 4.1. Schematic showing the synthesis of **(p-TEA)(p-TEAH)·PF₆**.

The co-crystal $[\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_2][\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_3^+][\text{PF}_6^-]$ (**(p-TEA)(p-TEAH)·PF₆**) was synthesized by the treatment of (S)-1-(p-Tolyl)ethanamine (**p-TEA**) with hexafluorophosphoric acid (**HPF₆**) (Scheme 4.1). The molecular structure of **p-**

TEA)(*p*-TEAH)·PF₆ was solved in the monoclinic C2 space group at both 100 and 298 K (Figures 4.1a-4.1b, 4A.3-4A.4, Appendix 4). The asymmetric unit of **(*p*-TEA)(*p*-TEAH)·PF₆** at both these temperatures was found to contain one *p*-TEA unit and one-half of a disordered PF₆⁻ anion. The molecular structure contains two *p*-TEA motifs and one PF₆⁻ anion, in which formally one *p*-TEA is cationic and the other one is neutral. Two fluorine atoms of the PF₆⁻ ion in the asymmetric unit were positionally disordered over two sites and located in special positions with half-occupancies each. Thus, the charge due to the PF₆⁻ anion is neutralized by one organic unit (referred to as *p*-TEAH) and the other neutral *p*-TEA motif provides additional H-bonding to the PF₆⁻ anion. It is to be noted that the *p*-TEAH and *p*-TEA moieties cannot be distinguished crystallographically and hence, their protons are refined with partial occupancies to provide the accurate charge balance. The packing diagram of **(*p*-TEA)(*p*-TEAH)·PF₆** reveals the presence of rich H-bonding interactions in which this molecule participates. A close view of the structure reveals that each PF₆⁻ ion is surrounded by four *p*-TEA/ *p*-TEAH groups, while each *p*-TEAH cation is connected with three PF₆⁻ ions. The cumulative effect of these interactions leads to the formation of a 2D-sheet-like network along the *ab*-plane. It consists of a series of alternate macrocycles represented by graph set $R_8^8(24)$ and $R_4^4(12)$ rings (Figures 4.1c, 4A.5 and Table 4A.1, Appendix 4).³² The view of the extended structure including the disorders indicates different types of macrocycles with graph set $R_4^4(12)$ and $R_4^4(12)$ configurations (Figure 4A.6, Appendix 4). The interactions present in compound **(*p*-TEA)(*p*-TEAH)·PF₆** were further quantified using Hirshfeld surface analysis of its data collected at 100 K (Figures 4.1d, 4A.7-4A.9, and Tables 4A.2-4A.3, Appendix 4). The analysis revealed multiple types of intermolecular interactions in which the H...F interactions contribute 24.3 % to the total intermolecular interactions (Table 4A.3, Appendix 4).

The structural composition of **(*p*-TEA)(*p*-TEAH)·PF₆** was further examined by using X-ray photoelectron spectroscopy (XPS). The XPS composition analysis showed the existence of the elements C, N, P, and F. The deconvoluted peaks of C(1s) with binding energies at 284.48 and 285.78 eV, correspond to the respective C-C/C-H and C-N bonds (Figure 4A.10a, Appendix 4).³³ The N(1s) spectra consist of two peaks with

binding energies of 401.08 and 401.88 eV corresponding to N-H groups in NH₂ and NH₃⁺ functionalities, respectively (Figure 4A.10b, Appendix 4).³⁴ Additionally, other binding energy peaks at 685.38 and 133.88 eV were observed in the respective F(1s) and P(2p) spectra (Figure 4A.10c-4A.10d, Appendix 4).³⁵

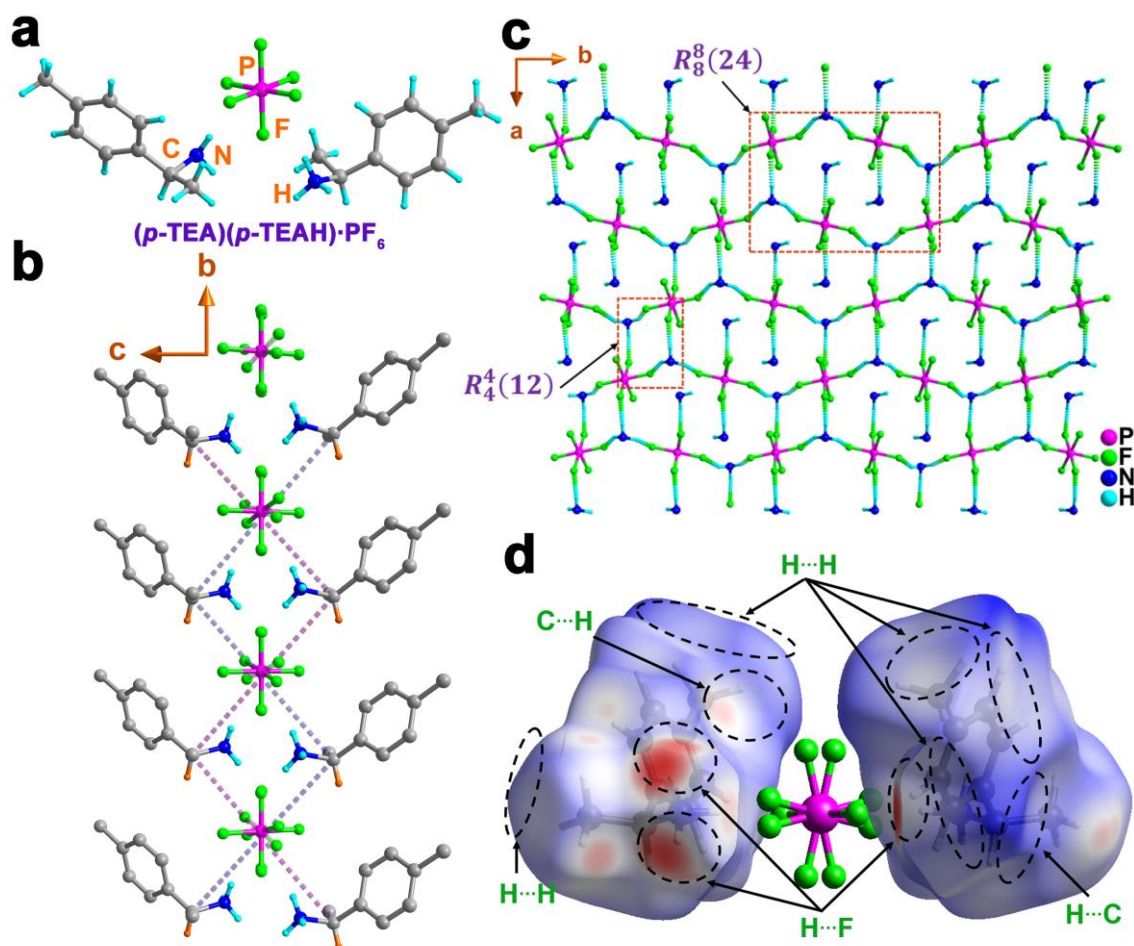


Figure 4.1: (a) The molecular structure of **(p-TEA)(p-TEAH)·PF₆** at 100 K (the disordered F-atoms are omitted for clarity). (b) The view of the zig-zag packing of **(p-TEA)(p-TEAH)·PF₆** along a-axis (including the disordered F-atoms). (c) The view of two-dimensional hydrogen bonding N-H...F interactions in **(p-TEA)(p-TEAH)·PF₆** along the ab-plane. (d) The d_{norm} mapped Hirshfeld surface analysis of **(p-TEA)(p-TEAH)·PF₆** (including the disordered F-atoms) from its crystal structure at 100 K showing the various interactions present in it.

The acentric structure of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ at room temperature was further confirmed by second harmonic generation (SHG) measurement, using a Kurtz-Perry type setup. The size-graded powder of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ was irradiated with an 800 nm, 1 kHz laser with a pulse width of 75 fs. The compound $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ was observed to emit a SHG with a relative efficiency of 0.1 with respect to the standard potassium dihydrogen phosphate (KDP) sample (Figure 4.2a).

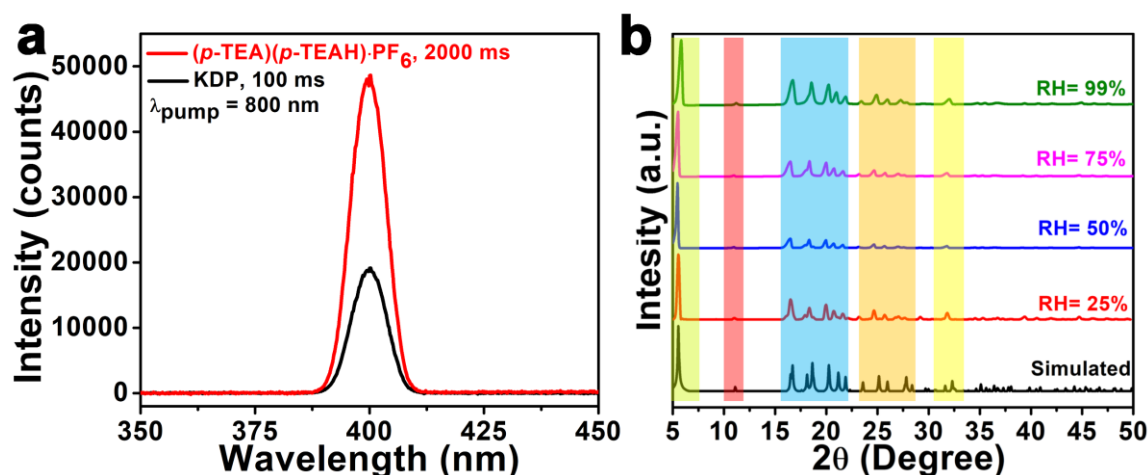


Figure 4.2: (a) The SHG profile of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ and its comparison with standard KDP, obtained upon irradiation with 800 nm femtosecond laser pulses. (b) PXRD profiles of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ upon exposure to various humidity conditions showing its high stability.

The phase purity of compound $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ was confirmed from its powder X-ray diffraction (PXRD) profile. The experimental PXRD peaks matched well with the simulated pattern obtained from the single-crystal diffraction data of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ (Figure 4A.11, Appendix 4), providing evidence of a phase identity. The instability of ammonium salts in the presence of moisture is a common issue in two-component ferroelectrics.³⁶ Hence, to check the moisture stability of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$, it was exposed to different RH conditions ranging from 25 to 99% and its PXRD profiles were compared with that of the pristine sample (Figure 4.2b). Also, the Raman spectral analyses were performed for $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ after exposing it to different conditions of varied humidity and the presence of characteristic Raman

active modes associated with C-H ($2952, 3024, 3064\text{ cm}^{-1}$), C-C (809 cm^{-1}), C-N (1373 cm^{-1}), and N-H (2920 cm^{-1}) were observed with no significant changes in their peak profiles (Figure 4A.12, Appendix 4). Remarkably, compound **(p-TEA)(p-TEAH)·PF₆** is insoluble in water and shows crystalline stability even at 99% RH conditions. This can be attributed to the ionic co-crystalline nature of this material, which involves the hydrophobic PF₆⁻ unit.

The thermal stability of **(p-TEA)(p-TEAH)·PF₆** was confirmed by thermogravimetric (TGA) analysis, which shows no weight loss up to its decomposition temperature of 550 K (Figure 4A.13, Appendix 4). Additionally, differential scanning calorimetry (DSC) measurements showed that the compound does not undergo any phase transition with temperature until its melting point at 490 K. These findings proved that compound **(p-TEA)(p-TEAH)·PF₆** is both thermal and moisture-stable under ambient conditions for an extended period and is capable of retaining its crystallinity even at high relative humidity conditions promising its utility for various applications.

4.3.2 Ferroelectric, dielectric and piezoelectric studies

Compound **(p-TEA)(p-TEAH)·PF₆** possesses the point group symmetry C_2 , which belongs to one of the ten polar point groups compatible with ferroelectric properties. Polarization vs. electric field (P - E) hysteresis loop measurements were conducted on the powder-pressed pellets of **(p-TEA)(p-TEAH)·PF₆** using a Sawyer-Tower circuit setup at room temperature to investigate its ferroelectric response. A typical rectangular-shaped P - E loop was observed for **(p-TEA)(p-TEAH)·PF₆** at 298 K with the saturation polarization (P_s) value of $0.95\text{ }\mu\text{C cm}^{-2}$ (Figure 4.3a). The origin of polarization in **(p-TEA)(p-TEAH)·PF₆** can be attributed to the stable charge-separated structure of the compound containing organic ammonium cations and octahedral PF₆⁻ anions and their involvement in rich non-classical H $\cdots$ F interactions in the co-crystal. Ferroelectric fatigue measurements on **(p-TEA)(p-TEAH)·PF₆** indicate no notable change in its P_r values up to 10^6 cycles confirming its robust polarization behavior (Figure 4.3b).

Temperature (T) and frequency (f) dependent permittivity measurements were performed on a compacted pellet of **(p-TEA)(p-TEAH)·PF₆** to obtain further insights

into its bulk polarization. These studies reveal the absence of any structural phase transition in $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$, as the real part of the dielectric permittivity (ϵ') remains constant in the temperature range of 298 to 440 K, close to its melting point. A sizable ϵ' value of 54.3 was noted at 298 K and 1 kHz frequency (Figure 4A.14a, Appendix 4). The plot of the dielectric loss factor ($\tan \delta$) vs. T indicates a low dielectric loss in $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ supporting its ferroelectric nature (Figure 4A.14b, Appendix 4). Similar observations were noted in the ϵ' vs. f and $\tan \delta$ vs. f plots as well (Figures 4A.15, Appendix 4).

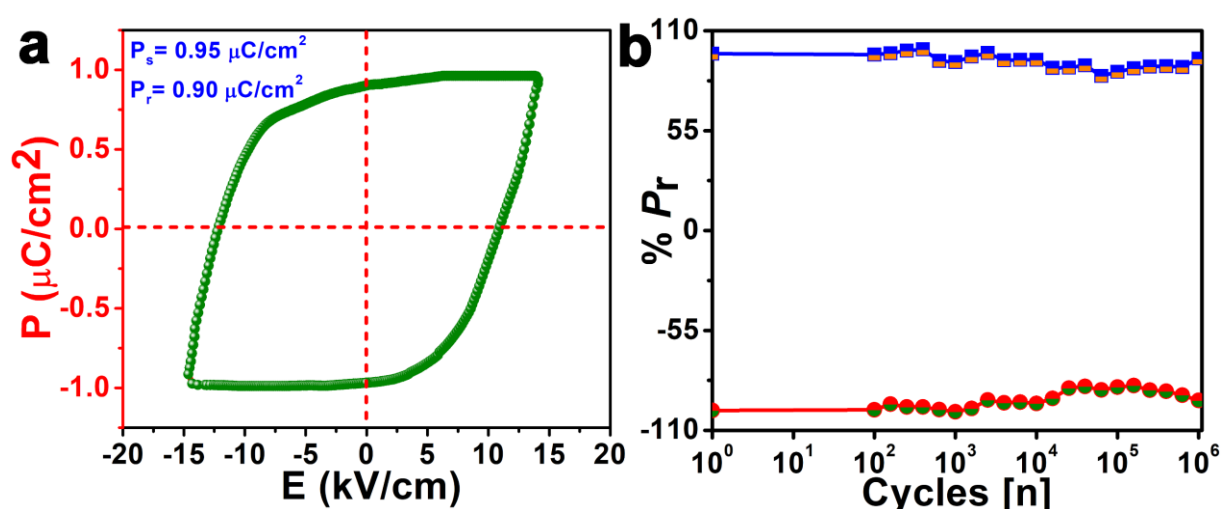


Figure 4.3: (a) The ferroelectric behavior of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ showing the rectangular P - E hysteresis loop at 298 K. (b) The fatigue test showing the retention of polarization of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ up to 10^6 cycles at 298 K.

Piezoresponse Force Microscopy (PFM) technique is utilized to investigate the ferro- and piezoelectric properties of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ at the nanoscale. Figure 4.4 shows the PFM studies performed on a single crystal grown on the drop-casted thin film of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$. Figure 4a is the domain structure showing the amplitude response of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ in the vertical-PFM measurements, while Figure 4.4b is the phase response showing the presence of domains with non-180° orientations. Subsequently, PFM spectroscopic measurements were performed on a single crystal of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ located on the surface of the film. These

measurements yield the signature butterfly-shaped amplitude-bias and the 180° domain switching phase-bias hysteresis loops, which reinforced the piezo- and ferroelectric nature of the material (Figures 4.4c-4.4d).

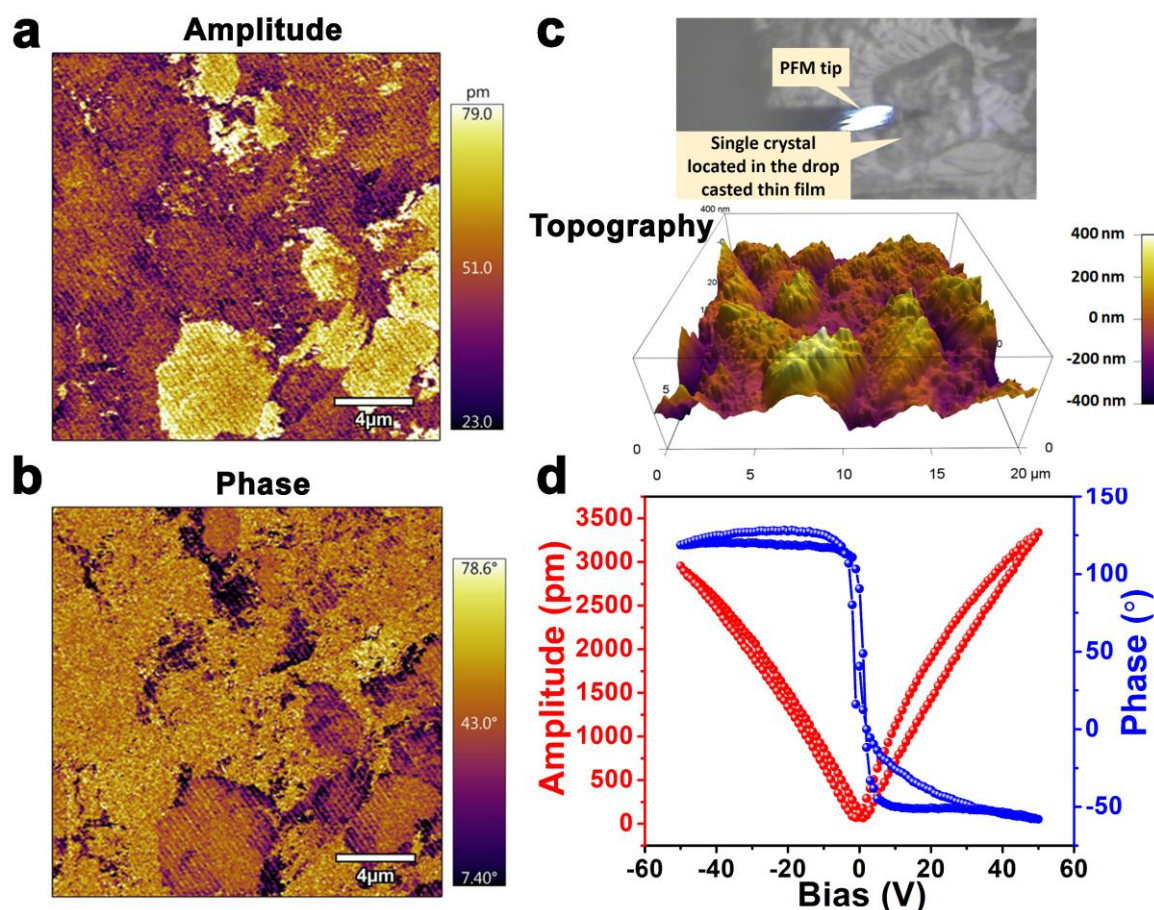


Figure 4.4: The PFM derived (a) amplitude, (b) phase images of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$. (c) The visualization of a single crystal of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ on the drop-casted thin film along with the PFM tip and its topography image. (d) The PFM amplitude-bias and phase-bias “butterfly” and “hysteresis” loops of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

Furthermore, piezoelectric measurements performed at an operating frequency of 110 Hz and applied stress of 0.25 N on $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ using the “Berlincourt” method gave the direct piezoelectric coefficient (d_{33}) of 4 pC N⁻¹. The piezoelectric voltage coefficient ($g_{33} = d_{33}/\epsilon_{33}$, where $\epsilon_r = \epsilon_{33}/\epsilon_0$, $\epsilon_0 = 8.854 \times 10^{-12}$ F m⁻¹ and $\epsilon_r =$

11.76 at 1 MHz) was calculated to be of $38.41 \times 10^{-3} \text{ V mN}^{-1}$. The transduction coefficient ($d_{33} \times g_{33}$), a measure of the power generation ability of any piezoelectric material, was calculated to be $153.64 \times 10^{-15} \text{ m}^3 \text{ J}^{-1}$ for **(p-TEA)(p-TEAH)·PF₆** suggesting its suitability for PENG applications. Moreover, materials with high piezoelectric voltage and electrostrictive coefficients are greatly desired for electromechanical applications via mechanical energy to electrical energy conversion. The electrostrictive coefficient ($Q_{33} = g_{33}/2P_s$) is calculated to be $2.02 \text{ m}^4 \text{ C}^{-2}$ for **(p-TEA)(p-TEAH)·PF₆**, where $P_s = 0.95 \text{ } \mu\text{C cm}^{-2}$. The calculated Q_{33} of **(p-TEA)(p-TEAH)·PF₆** is higher than those reported for several ceramic-based piezoelectric materials and is similar to that exhibited by PVDF.^{37, 38} Organic polymers with electrostrictive properties, such as polyvinylidene fluoride (PVDF), are recognized for their exceptional electromechanical coupling behavior, making them beneficial for piezoelectric nanogenerator (PENG) applications. However, it is uncommon to find polymers other than PVDF that demonstrate such high electrostrictive coefficients. Therefore, all-organic materials such as **(p-TEA)(p-TEAH)·PF₆** with a high electrostrictive coefficient ($Q_{33} = 2.02 \text{ m}^4 \text{ C}^{-2}$) are advantageous due to their easy synthesis and high moisture stability and are expected to provide significant PENG outputs with optimum mechanical-to-electrical conversion.

4.3.3 Fabrication and characterization of and **(p-TEA)(p-TEAH)·PF₆**-PCL composite films

To further investigate the application of **(p-TEA)(p-TEAH)·PF₆** for piezoelectric energy harvesting applications, its polymer composite films were prepared by incorporating 5, 10, 15, and 20 wt% of **(p-TEA)(p-TEAH)·PF₆** into polycaprolactone (PCL), a biodegradable polymer (Figure 4A.16, Appendix 4). These films were found to exhibit good flexibility for various mechanical motions as shown by their stability for bending and folding operations (Figure 4.5a). The FE-SEM analyses showed the presence of the piezoelectric crystallites of **(p-TEA)(p-TEAH)·PF₆** within the polymer matrix (FigureS 4.5b and 4A.17, Appendix 4). Powder X-ray diffraction (PXRD) analysis confirmed the structural stability and crystallinity of **(p-TEA)(p-TEAH)·PF₆** in the composite films, as evidenced by the presence of characteristic hkl peaks of **(p-TEA)(p-TEAH)·PF₆** in all wt% composites (Figure 4.5c). Also, the Raman spectral

analysis confirmed that the structural features of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ were preserved in all the $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ composites (Figure 4A.18, Appendix 4). Notably, the Raman active modes associated with neat PCL, C-C (1038 and 1109 cm^{-1}), CH_2 (1418 and 1439 cm^{-1}), and C=O (1722 cm^{-1}),³⁹ as well as that of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$, C-H (2952 , 3024 , 3064 cm^{-1}), C-C (809 cm^{-1}), C-N (1373 cm^{-1}), and N-H (2920 cm^{-1}), were found to be present in all the composite films. Furthermore, to validate the mechanical flexibility, stress-strain measurements were performed for neat PCL and those of 5, 10, 15, and 20 wt% of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ composites. The yield stress values of 9.8, 8.7, 7.5, and 5.8 MPa were observed for the 5, 10, 15, and 20 wt% composite films, respectively (for neat PCL, it is 12.6 MPa) (Figure 4A.19, Appendix 4). The values of Young's modulus were found to be 158, 144, 101, and 108 MPa for the 5, 10, 15, and 20 wt% composite films, respectively. Upon increasing the content of ferroelectric crystallites in the PCL matrix, a gradual reduction in both the tensile strength as well as Young's modulus can be noted, which could be attributed to the crystalline nature of the embedded materials. The observed stress values of all the films at 50% strain (the maximum these devices could experience during the PENG measurements) and the fact that they do not break even after 50% strain indicates the flexible nature of these composite materials. Finally, adhesive copper tapes were placed as upper and bottom electrodes to complete the nanogenerator device architecture and subsequently encapsulated with Kapton tape for electrical insulation.

4.3.4 Mechanical energy harvesting application and the outputs $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ composite devices

Spurred by the robust characteristics of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ films, the output performance of their corresponding PENG devices was tested under an external load of 21 N and at an optimized operating frequency of 10 Hz (Figure 4A.20, Appendix 4). The peak-to-peak open-circuit voltages ($V_{\text{OC-PP}}$) of the composite devices with 5, 10, 15, and 20 wt% of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ were measured to be 8, 13.1, 10.4, and 5 V, respectively (Figures 4.5d and 4A.21, Appendix 4). By contrast, for the device made up of neat PCL a $V_{\text{OC-PP}}$ of only 0.3 V was measured, indicating that the voltages generated from the composites were due to the piezoelectric nature of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

TEAH)·PF₆. Evidently, an increase in the V_{OC-PP} was observed for the particle loading up to the 10 wt% of **(p-TEA)(p-TEAH)·PF₆** in the composites and shows an abrupt decrease for the 15 and 20 wt% composites. The decrease in voltage outputs for higher concentrations of **(p-TEA)(p-TEAH)·PF₆** in PCL can be attributed to the agglomeration of **(p-TEA)(p-TEAH)·PF₆** crystallites in the polymer matrix, as observed from FE-SEM images of 15 and 20 wt% composites. It is to be noted that the agglomeration of the particles leads to Maxwell-Wagner-Sillars polarization.^{40, 41} This phenomenon is clear from the permittivity data measured for these **(p-TEA)(p-TEAH)·PF₆**-PCL composites. The frequency-dependence of ϵ' values of the composite films initially showed an increasing trend and reached the highest values for the 10 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL ($\epsilon' = 8.9$ at 1 MHz) composite (Figures 4.5e and 4A.22, Appendix 4). Afterwards, a reduction in ϵ' values for the 15 and 20 wt% composites was observed, indicating a reduction in the effective dipoles in the system.

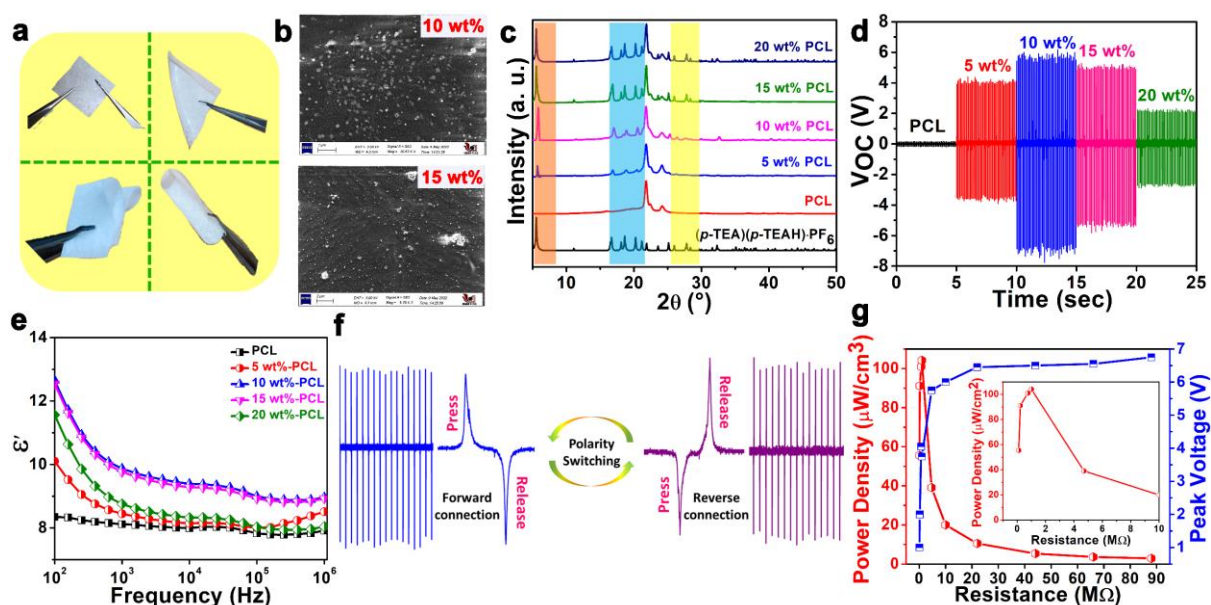


Figure 4.5: (a) Pictures of a representative **(p-TEA)(p-TEAH)·PF₆**-PCL composite film showing its flexibility, as demonstrated for stretching, bending, two-fold bending and rolling operations. (b) FE-SEM images of the 10 and 15 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL composite films. (c) Stacked PXRD profiles of **(p-TEA)(p-TEAH)·PF₆**-PCL films and their comparison with the diffraction patterns of as synthesized **(p-TEA)(p-TEAH)·PF₆**. (d) Open-circuit peak-to-peak voltages (V_{OC-PP}) of **(p-TEA)(p-TEAH)·PF₆**-

PCL composite devices. The shifted time axis provided here is a guide to the eyes. (e) Frequency-dependant permittivity for all **(p-TEA)(p-TEAH)·PF₆-PCL** composite films (f) The reversibility of obtained output signal upon forward and reverse connection of the electrode contacts to the oscilloscope. (g) The peak voltage drop and power density (PD) values of the 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** composite device under different external load resistances.

The piezoelectric nature of the composite device was confirmed by performing a polarity-switching test on the best-performing 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** device, which showed a maximum V_{OC-PP} value of 13 V. Thus, reversing the electrode connections to the oscilloscope during the press and release operations produced signals of equal magnitude and opposite directions, validating the true piezoelectric behavior of the device (Figures 4.5f and 4A.23, Appendix 4). Subsequently, a 4.7 MΩ resistor was employed to measure the voltages across the circuit to determine the calculated output currents. These measurements yielded the peak-to-peak current (I_{PP}) values of 1.21, 2.34, 1.86, and 1.11 μA for the 5, 10, 15, and 20 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** devices, respectively (Figures 4A.24-4A.25, Appendix 4). Notably, the 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** composite device yielded the highest V_{OC-PP} of 13.1 V and calculated I_{PP} value of 2.34 μA at 4.7 MΩ (Figure 4A.26, Appendix 4). In order to assess the effectiveness of composite devices for practical applications, their output peak voltage drops (by default the voltage generated during the compression cycles) were measured across a range of load resistances, spanning from 100 kΩ to 88 MΩ (Figure 4A.27, Appendix 4). The composite device containing 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** demonstrated the most promising performance, displaying a rise in voltage as the load resistance increased. At 1 MΩ, the peak voltage drop approached a value close to peak open-circuit voltage and ultimately attained saturation at higher resistances (Figure 4.5g). The power density (PD) values of all the **(p-TEA)(p-TEAH)·PF₆-PCL** devices at each of the load-resistance dependent measurements were calculated by the formula $VI/Vol.$, where V is the peak voltage drop, I is the peak current and $Vol.$ represents the volume of the device in cm³. The 10 wt% **1-PCL** composite device displayed the highest PD value of 104.2 μW cm⁻³ at

1 M Ω (Figure 4.5g). Also, the direct piezoelectric coefficient (d_{33}) value for the highest performing 10 wt% (p-TEA)(p-TEAH)·PF₆-PCL composite was measured to be 2 pC N⁻¹, validating the piezoelectric nature of the embedded crystallites of (p-TEA)(p-TEAH)·PF₆ inside the polymer matrix.

4.3.5 Construction of 3D printed 3DP-Gy composite films

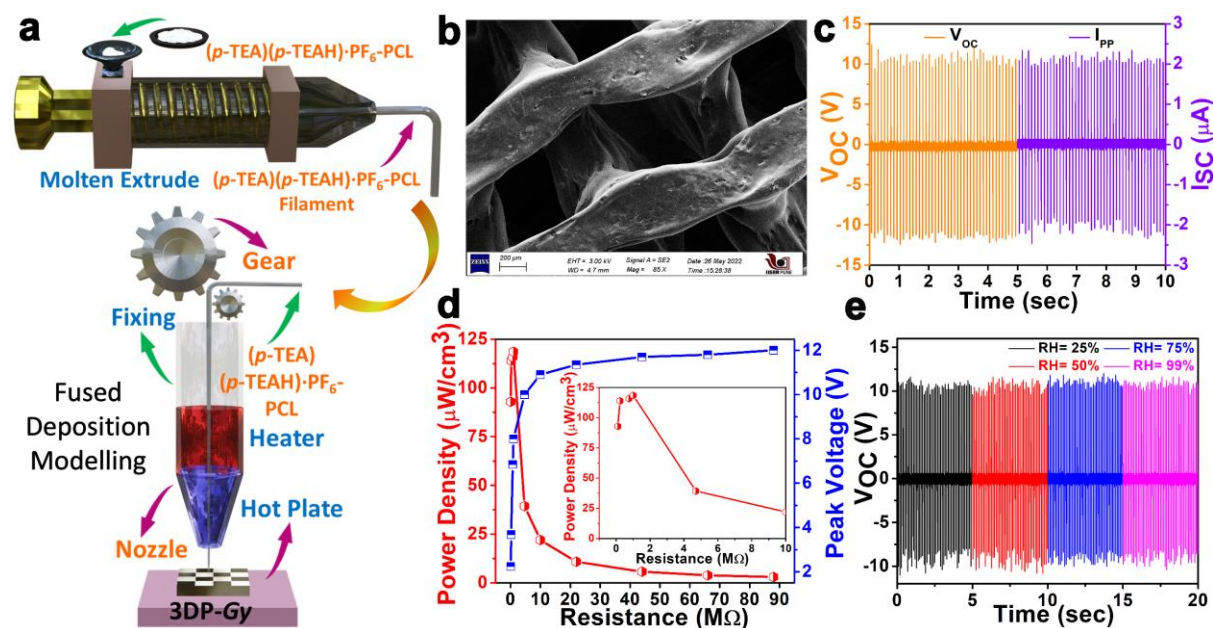


Figure 4.6: (a) Schematic showing the filament preparation and FDM printing of a (p-TEA)(p-TEAH)·PF₆-PCL composite slab, (b) FE-SEM images of the 3D printed 10 wt% 3DP-Gy composite slab. (c) Measured open-circuit peak-to-peak voltage V_{OC-PP} and calculated current I_{PP} for 3DP-Gy device (the shifted time axis provided here is a guide to the eye). (d) Calculated power density and voltage drop profile of 3DP-Gy with a range of load resistances. The inset depicts the maximum PD obtained at 1 M Ω resistance. (e) The RH-dependent open-circuit peak-to-peak voltage V_{OC-PP} of 3DP-Gy device.

Encouraged by our recent demonstration of fabricating a gyroid-shaped 3D printed PCL composite based on a two-component ammonium salt $\{[(Me)_3CCH(Me)NH_3][BF_4]\}$,³¹ we set out to investigate the scale-up capability of the

champion 10 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL device via 3D-printing technique. The fused deposition modeling (FDM) method was employed to shape the 10 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL composite into a 3D-printed device with gyroidal pores (**3DP-Gy**). Using the melt extruder equipment, composite filament wires of 10 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL suitable for 3D printing were first prepared from the corresponding as-made films (Figure 4.6a top and 4A.28, Appendix 4). The mechanical strengths of the filaments of neat PCL and 10 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL were checked to investigate the effect of **(p-TEA)(p-TEAH)·PF₆** particles on the composite filament. Similar observations as that of the thin film-based composites were noted for both the filaments of neat PCL and **(p-TEA)(p-TEAH)·PF₆**-PCL with the stress values of 8.31 and 7.45 MPa, respectively, at 50% strain (Figure 4A.29, Appendix 4). The values of Young's modulus were found to be 111 and 125 MPa for neat PCL and **(p-TEA)(p-TEAH)·PF₆**-PCL filaments, respectively. The filament was subsequently injected into the FDM 3D printer to produce gyroid-shaped composite slabs (Figure 4.6a bottom and 4A.30, Appendix 4). The microstructure analysis of the resulting **3DP-Gy** composite revealed a distinct Gy pore and an even dispersion of the crystallites of **(p-TEA)(p-TEAH)·PF₆** throughout the polymer matrix as observed from its FE-SEM image (Figures 4.6b and 4A.31, Appendix 4). The PENG device based on **3DP-Gy** composite was accomplished by sticking adhesive copper electrodes as top and bottom contacts and copper wires and Kapton tapes to enclose the device (Figure 4A.32, Appendix 4).

4.3.6 Mechanical energy harvesting applications of 3DP-Gy composite device

The **3DP-Gy** device was used for piezoelectric energy harvesting by applying an external load of approximately 21 N and operating at a frequency of 10 Hz. The V_{OC-PP} value of the device was measured to be 22.8 V, which indicates an increase in the output voltage by a value of 9.7 V in comparison with the 10 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL composite (Figures 4.6c left, 4A.33a and 4A.34, Appendix 4). The enhancement in the performance of the **3DP-Gy** device could be attributed to improved dipole alignments (achieved by the 3D printing process), reduced clamping effect and increased device area (from 3.6 to 6 cm²).

Likewise, the **3DP-Gy** device demonstrated a higher I_{PP} of 4.2 μA compared to the corresponding thin film-based device (2.34 μA) (Figure 4.6c right and 4A.33b, Appendix 4). Also, the voltage drop across the **3DP-Gy** device for the various external load resistances showed a trend similar to that observed for the thin-film-based device (Figure 4A.35, Appendix 4). The **3DP-Gy** device exhibited a maximum power density (PD) of 118.5 $\mu\text{W cm}^{-3}$ at 1 M Ω , which is comparable with many of the reported nanogenerator devices containing all-organic components (Figure 4.6d). The PENG cycling measurements showed that both the 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** and **3DP-Gy** devices maintained consistent voltage outputs beyond 10000 cycles, emphasizing their excellent durability with no signs of device degradation (Figures 4A.36-4A.37, Appendix 4).

As compound **(p-TEA)(p-TEAH)·PF₆** is stable in highly humid environments, we tested the PENG output performance of both the 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** and **3DP-Gy** devices after subjecting them to various RH conditions. Remarkably, the V_{OC-PP} value obtained from these devices remained uniform at all RH conditions ranging from 25 to 99% (Figures 4.6e and 4A.38, Appendix 4). The output voltages of these devices were found to be retained even after six months of storage under open air marking the stability of these devices for longer durations (Figure 4A.39, Appendix 4). These observations indicate that **(p-TEA)(p-TEAH)·PF₆-PCL** devices are compatible with scaling-up processes and are highly suitable for PENG applications under diverse environmental conditions. The sizable PENG outputs derived from both 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** and **3DP-Gy** devices can be attributed to the inherent piezoelectric nature of the ferroelectric **(p-TEA)(p-TEAH)·PF₆** crystallites with polarizable dipoles embedded in PCL matrix.

To assess the energy storage capabilities of the 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** and **3DP-Gy** devices, capacitor charging experiments were conducted using capacitors with different capacitance values. The devices were connected to a four-diode bridge rectifier circuit to convert the AC output voltages generated during impact measurements into DC voltages (Figure 4.7a). Thus, from the charging curves of a 100 μF capacitor, the maximum charge and energy stored were found to be 226.0 and 133.5 μC and 257.0 and 89.6 μJ , respectively, by employing the 10 wt% **(p-TEA)(p-**

TEAH)·PF₆-PCL and **3DP-Gy** devices (Figures 4A.40, Appendix 4). The voltage profiles during the charging process also show a similar trend for both these devices (Figure 4A.41, Appendix 4). The obtained results indicate that the large-scale 3D printed device has efficient energy harvesting and storage capabilities, as evidenced by the increased charge accumulation in the capacitors while using the **3DP-Gy** device. Notably, by using a lower-rated 22 μ F capacitor a higher storage capacity of 3.4 V was achieved, which in turn was sufficient to flash-light a green LED (Figure 4.7b). The corresponding maximum charge and energy stored in the 22 μ F were calculated to be 72.0 μ C and 121.0 μ J, respectively (Figure 4A.42, Appendix 4).

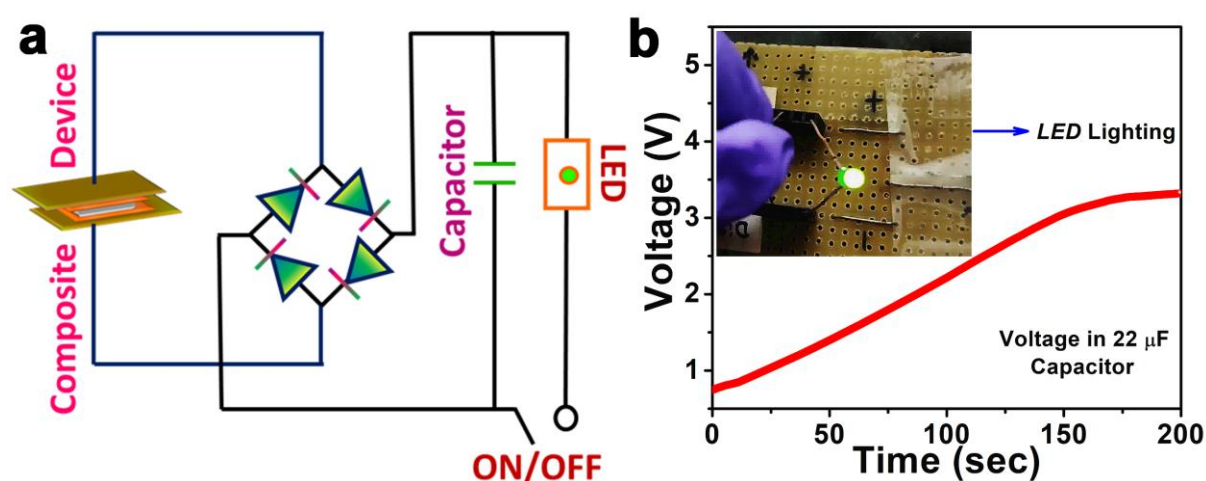


Figure 4.7: (a) The circuit diagram of the full-wave four-diode bridge rectifier circuit utilized for capacitor charging and LED lighting experiments. (b) The voltage accumulated in a 22 μ F capacitor by utilizing the **3DP-Gy**. Inset: the image of the lighted green LED by using the charge stored in the 22 μ F capacitor

4.4 Conclusion

The development of organic ferroelectric materials for piezoelectric energy harvesting requires structural asymmetry, polar order and long-term stability. In this work, the synthesized co-crystal **(p-TEA)(p-TEAH)·PF₆** exhibits these attributes by the respective presence of chiral ammonium cations, non-coordinating PF₆[−] anions and a neutral amine with additional H-bonding interactions. The *P-E* hysteresis loop

measurements on **(p-TEA)(p-TEAH)·PF₆** gave a saturation polarization (P_s) of 0.95 $\mu\text{C cm}^{-2}$. Remarkably, **(p-TEA)(p-TEAH)·PF₆** shows a higher electrostrictive coefficient (Q_{33}) value of 2.02 m^4C^{-2} , compared to well-known PVDF and ceramic-based piezoelectric materials. The polymer composites of varying weight percentages were then prepared by combining **(p-TEA)(p-TEAH)·PF₆** with biodegradable non-piezoelectric PCL polymer and studied for PENG applications. The optimal 10 wt % **(p-TEA)(p-TEAH)·PF₆**-PCL device produced a maximum output voltage of 13 V and a power density of 104.2 $\mu\text{W cm}^{-3}$. Furthermore, by utilizing the miniaturized 3D printing technique a gyroid-shaped device containing 10 wt% of **(p-TEA)(p-TEAH)·PF₆** (**3DP-Gy**) has been prepared, which not only retained the $V_{\text{OC-PP}}$ of the thin-film-based device but also improved the overall output performance to 22.8 V (increase by 9.8 V) and lead the improvement of the power density (118.5 $\mu\text{W cm}^{-3}$). The applicability of both 10 wt% **(p-TEA)(p-TEAH)·PF₆**-PCL and **3DP-Gy** under extremely humid conditions (99% RH) was then validated, as no degradation in performance was noted even after exposure to 99% RH. The generated output voltages were used to charge different rating capacitors. The 3D-printed device was found to accumulate more charge than that of the thin film-based device. Also, the charge accumulated in a 22 μF capacitor was utilized for flash-lighting a green LED. These findings suggest that combining a stable all-organic material with a biodegradable polymer such as PCL and modern 3D printing techniques provides an efficient strategy for fabricating less-toxic and less-expensive devices for applications in future wearable electronics.

4.5 References

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End of Chapter 4

Chapter 5



**A Chiral B-N Adduct as a New
Frontier in Ferroelectrics and
Piezoelectric Energy Harvesting**

5.1 Introduction

The exploration of boron-nitrogen (B-N) adducts, the classical example of a Lewis acid-base pair, has been a long journey in chemistry, driven by their potential to exhibit tailored molecular, solid state, and optical properties.¹ The genesis of this journey can be traced back to 1809 when Gay-Lussac first reported the B-N adduct $\text{H}_3\text{N}\cdot\text{BF}_3$.² Since then, a plethora of B-N adducts have been reported by using numerous synthetic procedures, each contributing to the rich diversity of B-N chemistry.³⁻⁶ The B-N bond, an isostere for the ubiquitous C-C bond, shares the same isoelectronic 8-electron configuration. However, the B-N bond distinguishes itself by its high polarity, a consequence of the electronegativity difference between nitrogen and boron atoms.⁷ These attributes have been widely exploited in various domains such as hydrogen storage, catalysis, polymer formulations, photographic applications, fuel additives, etc.^{1, 8-11} Recently, the well-known trimethylamine borane (TMAB) has been shown to exhibit plasticity and piezo- and pyroelectric energy harvesting properties.¹² The excellent mechanical properties of TMAB may be attributed to the flexibility of B-N bonds.

Spurred by these findings, we envisioned that judiciously designed B-N adducts could also exhibit ferroelectric properties. Ferroelectrics, a unique subclass of dielectrics, display switchable spontaneous polarization behavior upon changing the direction of the external electric fields.¹³ These materials find applications in ferroelectric random-access memories, ferroelectric field-effect transistors, memristors, infrared detectors, piezoelectric sensors, nonlinear optical devices, fast display electronics, capacitors, and so on.¹⁴⁻²⁰ Studies on ferroelectricity are primarily focused on the ceramic materials of inorganic oxides due to their robust polarization attributes.²¹⁻²⁴ However, these materials exhibit certain drawbacks associated with their heavy and toxic metal ions, high-temperature device processibility, and brittleness.^{25, 26} In contrast, organic and organic-inorganic hybrid materials can overcome the disadvantages possessed by traditional ceramic materials.²⁷⁻³⁰ Particularly, molecular ferroelectrics have the advantages of easy synthesis, solution processibility, and mouldable materials properties while maintaining environmental sustainability.^{13, 31, 32}

Ferroelectric salts containing organic cations and tetrafluoroborate anions are well-established and shown to exhibit substantial polarization values.^{27, 33, 34} Thus, strategically replacing the BH₃ unit in TMAB with a more polar BF₃ group can help generate highly polarizable donor-acceptor adducts with excellent ferroelectric properties. Since the use of chiral compounds guarantees material crystallization in an acentric point group, including polar ones,³⁵⁻³⁷ we embarked on a study of an enantiomeric pair of chiral B-N adducts containing *R*-(-)/*S*-(+)- α -methylbenzylamine and boron trifluoride. The compounds [^{*R*}C₆H₅CH(CH₃)NH₂BF₃] (^{*R*}**MBA-BF₃**) and [^{*S*}C₆H₅CH(CH₃)NH₂BF₃] (^{*S*}**MBA-BF₃**) were crystallized in the chiral monoclinic polar space group *P*2₁. Ferroelectric measurements on the compacted pellet of ^{*R*}**MBA-BF₃** yielded a rectangular *P-E* hysteresis loop with a saturation polarization (*P_s*) of 4.27 $\mu\text{C cm}^{-2}$. DFT-based computational analysis of the crystal structures corroborated the polar response and showed a calculated polarization value of 10.04 $\mu\text{C cm}^{-2}$, aligning well with the experiment. These calculations also elucidated the group-to-subgroup transition characteristic of the paraelectric-to-ferroelectric switch. Furthermore, the domain structures of the ^{*R*}**MBA-BF₃** adduct were visualized by piezoresponse force microscopic (PFM) images. The microscopic switchable ferroelectric domains were verified by characteristic PFM amplitude “butterfly” and phase hysteresis loops. One of the challenges associated with single-component (molecular) systems to show ferroelectricity is their weak dipole characteristics due to the absence of charge-separated structures. Thus, integrating B-N bonds with polar order could pave the way for designing molecular ferroelectric materials with large polarization values.

5.2 Experimental section

5.2.1 General remarks

R-(-)- or *S*-(+)- α methyl benzyl amine were purchased from Avra Chemicals and were used without further purification. BF₃·OEt₂ was purchased from Sigma Aldrich and was used as received. The thermogravimetric analyses were performed using the PerkinElmer STA-6000 analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a TA Q20 differential scanning calorimeter with heating and cooling rates of 10 °C/min under the nitrogen atmosphere. NMR spectra were recorded on a Bruker 400

MHz spectrometer (^1H NMR, 400.13 MHz; $^{13}\text{C}\{^1\text{H}\}$ NMR, 100.62 MHz) in CDCl_3 solvent. Melting point analyses were done using a Buchi M-560 melting point apparatus and were uncorrected. The powder X-ray diffraction (PXRD) data were measured in the 2-theta range of 5° to 50° on a Bruker-D8 Advance X-ray diffractometer.

Thermo Fisher Scientific UK Model K alpha+ spectrometer operating at 72 W power was used to analyze the X-ray photoelectron spectroscopy (XPS) spectrum of **$^{\text{R}}\text{MBA-BF}_3$** . The monochromatic Al K α anode (1486.6 eV) was used as the X-ray source. The sample loading and analyzer chambers were kept at vacuum pressures of 1.2×10^{-8} mbar and 2×10^{-9} mbar, respectively. 400 μm spot-size micro-focused X-ray sources were used for data acquisition. A 200 eV pass energy was used for the high-resolution survey scan, while a 50 eV pass energy was used to record individual core-level spectra. Charge compensation, maintained through ultra-low energy co-axial electron and Ar^+ ion beams, remained active during spectral acquisition. The binding energies of the different elements in the sample were determined by energy calibration using the C1s standard value of 284.6 eV. During the data collection process, the spectrometer base pressure was maintained at or above 5×10^{-9} mbar and 1×10^{-7} mbar with the flood cannon activated. Avantage software was utilized to handle raw data with an instrument resolution of ± 0.1 eV. Smart background subtraction was applied for peak fitting.

5.2.2 Synthesis

To a stirred solution of *R*-(-)- or *S*-(+)-alpha methyl benzylamine (1.2 g, 10 mmol) in hexane (50 mL), $\text{BF}_3 \cdot \text{OEt}_2$ (1.41 g, 10 mmol) was added slowly for 30 minutes at 0°C . The reaction mixture was subsequently stirred for 7 hours. The obtained white precipitates were then filtered and dried at room temperature. The dried precipitates of **$^{\text{R}}\text{MBA-BF}_3$** and **$^{\text{S}}\text{MBA-BF}_3$** were then dissolved in methanol and kept for crystallization at room temperature. White crystals of **$^{\text{R}}\text{MBA-BF}_3$** and **$^{\text{S}}\text{MBA-BF}_3$** were obtained after 2-3 days.

$^{\text{R}}\text{MBA-BF}_3$ Yield: 88 %. Melting point: 350-360 K. ^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.22 (m, 6H), 5.60 (s, 3H), 4.29 (q, $J = 6.8$ Hz, 1H), 1.48 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.82 (s), 129.11 (s), 51.75 (s), 19.81 (s). ^{11}B NMR (128 MHz,

CDCl_3) δ -1.16 (s). Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{BF}_3\text{N}$: C 50.84; H 5.87; N 7.41. Found: C 50.82; H 5.82; N 7.43.

$^{\text{S}}\text{MBA-BF}_3$ Yield: 89 %. Melting point: 350-360 K. ^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.21 (m, 6H), 5.40 (s, 4H), 4.29 (d, J = 6.8 Hz, 1H), 1.48 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 137.82 (s), 129.11 (s), 51.75 (s), 19.81 (s). ^{11}B NMR (128 MHz, CDCl_3) δ -1.16 (s). Anal. Calcd. for $\text{C}_8\text{H}_{11}\text{BF}_3\text{N}$: C 50.84; H 5.87; N 7.41. Found: C 50.85; H 8.85; N 7.42.

5.2.3 Crystallography

Using Mo $\text{K}\alpha$ radiation (λ = 0.71073 Å), the single-crystal X-ray diffraction data of $^{\text{R}}\text{MBA-BF}_3$ and $^{\text{S}}\text{MBA-BF}_3$ were collected at 120 K and 298 K, respectively, on a Bruker Smart Apex Duo diffractometer. The crystal structures were initially solved using the direct method and then refined by full-matrix least-squares against F^2 , utilizing SHELXL-2014/7 integrated in the Apex 3 program.³⁸ The crystallographic refinement data for $^{\text{R}}\text{MBA-BF}_3$ and $^{\text{S}}\text{MBA-BF}_3$ at different temperatures are listed in Table 5.1. The refinement of all non-hydrogen atoms was carried out anisotropically. The hydrogen atoms' positions were determined geometrically in relation to their parent atoms.³⁹ DIAMOND-3.1 software was utilized to prepare structural illustrations of the refined structures of $^{\text{R}}\text{MBA-BF}_3$ and $^{\text{S}}\text{MBA-BF}_3$.

Table 5.1: Details of crystallographic data collection and structure refinements for $^{\text{R}}\text{MBA-BF}_3$ and $^{\text{S}}\text{MBA-BF}_3$.

Crystallographic details	$^{\text{R}}\text{MBA-BF}_3$ (120 K)	$^{\text{R}}\text{MBA-BF}_3$ (298 K)	$^{\text{S}}\text{MBA-BF}_3$ (120 K)	$^{\text{S}}\text{MBA-BF}_3$ (298 K)
Chemical formula	$\text{C}_8\text{H}_{11}\text{BF}_3\text{N}$	$\text{C}_8\text{H}_{11}\text{BF}_3\text{N}$	$\text{C}_8\text{H}_{11}\text{BF}_3\text{N}$	$\text{C}_8\text{H}_{11}\text{BF}_3\text{N}$
Formula weight (g/mol)	188.99	188.99	188.99	188.99
Temperature	120(2)K	298(2)K	120(2)K	298(2)K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$
a (Å); α (°)	7.4462(6); 90	7.559(11); 90	7.4405(6); 90	7.67(2); 90

b (Å); β (°)	6.1141(5); 93.552(3)	6.330(9); 92.85(4)	6.1091(5); 93.554(5)	6.370(2); 93.23(7)
c (Å); γ (°)	10.3123(6); 90	10.296(15); 90	10.3297(8); 90	10.36(3); 90
V (Å ³); Z	468.58(6); 2	492.1(12); 2	468.63(6); 2	505.00(3); 2
ρ (calc.) g cm ⁻³	1.339	1.275	1.339	1.243
μ (Mo K α) mm ⁻¹	0.119	0.114	0.119	0.111
2 $\theta_{\max}$ (°)	56.502	50.014	56.838	50.048
R(int)	0.1178	0.1313	0.1289	0.1762
Completeness to θ	100	99.9	99.9	99.9
Data / param.	2308/120	1743/120	2344/120	1785/120
GOF	1.028	0.993	1.006	0.953
R1 [$F > 4\sigma(F)$]	0.0505	0.0994	0.0536	0.0997
wR2 (all data)	0.0956	0.3479	0.0991	0.3527
max. peak/hole (e.Å ⁻³)	0.245/-0.241	0.0574/-0.229	0.244/-0.255	0.475/-0.225
Flack parameters	0.5(14)	-4(6)	-0.4(7)	-0(7)

5.2.4 Hirshfeld surface analysis

To visualize the various types of interactions, present on the Hirshfeld surface, the Crystal Explorer 3.1 program was utilized to map the Hirshfeld surface analyses of **^RMBA-BF₃** and **^SMBA-BF₃** using normalized contact distance (d_{norm}), shape index, and curvedness. For this purpose, both compounds' single-crystal X-ray crystallographic information files (CIF) were employed. These interactions were depicted as 3D color mapping images, with intense interactions represented by the color red, medium interactions by blue, and weak interactions by white. The Hirshfeld surface of both compounds, **^RMBA-BF₃**, and **^SMBA-BF₃**, were color-coded using different colors to generate diverse surface color mappings. Additionally, 2D fingerprint plots were constructed for both compounds. These plots are histograms that compile the distances of given atoms closest to the interior (d_i) and exterior (d_e) of the

generated Hirshfeld surface. The different contours in the 2D fingerprint plots were represented by blue and grey colors, illustrating the various molecular interaction types.

5.2.5 Nonlinear optical measurements

Nonlinear optical measurements were performed by using a direct output from a Coherent Astrella Ti:Sapphire regenerative amplifier providing femtosecond laser pulses (800 nm, 75 fs) at a 1 kHz repetition rate. The output was used unfocused. Laser fluence at samples was equal to 0.28 mJ/cm².

In order to perform a Kurtz-Perry powder test, the single crystals ^RMBA-BF₃ and ^SMBA-BF₃ and KDP were crushed with a spatula and sieved through an Aldrich mini-sieve set, collecting a microcrystal size fraction of 125–177 μm. Next, size-graded samples were fixed in between microscope glass slides to form tightly packed, uniform layers, sealed, and mounted to the horizontally aligned sample holder. No refractive index matching oil was used. Under the same excitation conditions, the SHG signal was collected for ^RMBA-BF₃ and KDP for 6000 ms and 500 ms, respectively.

The employed measurement setup operates in the reflection mode. Specifically, the laser beam delivered from the regenerative amplifier, passed through a 5mm aperture, was directed onto the sample at 45 degrees to its surface. Emission collecting optics consisted of a Ø25.0 mm plano-convex lens of focal length 25.4 mm mounted to the 400 μm 0.22 NA glass optical fiber and was placed along the normal to the sample surface. The distance between the collection lens and the sample was equal to 30 mm. The spectra of SHG responses were recorded by an Ocean Optics Flame T fiber-coupled CCD spectrograph with a 200 μm entrance slit. Scattered pumping radiation was suppressed with the use of a Thorlabs 750 nm short-pass dielectric filter (FESH0750).

5.2.6 Ferroelectric, dielectric and piezoelectric measurements

The *P-E* hysteresis loop measurements for ^RMBA-BF₃ were carried out on a compact disc sample with a diameter of approximately 8 mm and thickness of 1.1 mm, which was electroded using Cu adhesive tapes. The ferroelectric polarization vs. electric field (*P-E*) measurements were conducted using the aixACCT TF-2000E model hysteresis

loop analyzer. The leakage currents were recorded dynamically during the hysteresis loop measurements. The ferroelectric fatigue measurements were performed at a frequency of 100 Hz and an applied voltage of 100 V, respectively.

For the dielectric permittivity and Impedance measurements, a powder-pressed pellet of **^RMBA-BF₃** was used. The measurements were performed using the Solartron Analytical Impedance Analyzer model 1260, which was coupled with a Dielectric Interface 1296A. The equipment was operated with a Janis 129610A cryostat sample holder and a Lakeshore 336 model temperature controller.

The resonance frequency (f) of an electrical circuit involving a constant-phase element (CPE) has been calculated using the following formula:

$$f = \frac{1}{2\pi(QR_2)^{1/\alpha}}$$

Where, Q (CPE-T) is related to effective capacitance, α (CPE-P) is related to the depressed semicircle, and R_2 is the Ohmic resistance.

Table 5.2. Impedance data fitting parameters for **^RMBA-BF₃**.

Element	^RMBA-BF₃
R1	28586
CPE1-T	1.722E-10
CPE1-P	0.81341
R2	1.8337E07
Wo1-R	3.7854E07
Wo1-T	0.86638
Wo1-P	0.51168
Chi-Squared Value	0.00026187

The Berlincourt Piezotest meter model PM300 was utilized to measure the piezoelectric coefficient (d_{33}) for $\text{R}^{\text{MBA}}\text{-BF}_3$. A compacted disc sample approximately 8 mm in diameter and 1.1 mm thick was used for the measurements.

5.2.7 Computational details

We conducted our calculations using first-principles methodology based on density functional theory (DFT)^{40, 41}, with the Vienna Ab initio Simulation Package (VASP)^{42, 43} serving as our computational tool. To model the exchange-correlation functional, we employed the generalized gradient approximation (GGA) functional revised for solids (PBEsol).⁴⁴ This choice of functional aligns the optimized lattice parameters well with experimental data, when compared to the standard PBE functional. In our simulations, we utilized the projector-augmented wave (PAW) potentials^{43, 45}, with the valence states as follows: B:(2s²2p¹, version 06Sep2000), C:(2s²2p², version 08Apr2002), H:(1s¹, version 15Jun2001), N:(2s²2p³, version 08Apr2002), F:(2s²2p⁵, version 08Apr2002). For the sampling of the Brillouin zone, we employed 7x7x7 Monkhorst–Pack⁴⁶ k-point meshes, the cut-off energy was set to 700 eV and the force convergence criterion was fixed within the error less than 0.001 eV/Å on each atom. To compute the spontaneous polarization (P_s), we employed the Berry-phase formalism.⁴⁷⁻⁵⁰ The Berry-phase method, is a key approach in understanding the process of spontaneous polarization changes in crystalline solids. This method was pioneered by Resta and further developed by King-Smith and Vanderbilt, which focuses on the geometric quantum phase, or Berry phase, of valence wave functions. Initially, Resta's theory involved the electronic contribution to the change in polarization (ΔP_e) due to a finite adiabatic change in the Kohn-Sham Hamiltonian of the crystalline solid as:

$$\Delta P_e = \int_{\lambda_1}^{\lambda_2} \frac{\partial P_e}{\partial \lambda} d\lambda \quad (1)$$

where $\frac{\partial P_e}{\partial \lambda}$ is dependent on the electronic mass (m_e) and charge (e), the number of unit cells, unit cell volume, occupied bands (M), momentum operator (p), and the Bloch solutions(ψ_{nk}^λ). The Kohn-Sham potential (V^λ), when parameterized by a

change (λ) such as the displacement of an atom in the unit cell, plays a crucial role. King-Smith and Vanderbilt modified the theory proposed by R. Resta by, eliminating explicit references to conduction band states (ψ_{mk}^λ). They demonstrate that the change in polarization along any path can be determined from information about the system at the end phases.

$$\Delta P_e = P_e^{\lambda_2} - P_e^{\lambda_1} \quad (2)$$

Where,

$$P_e^\lambda = -\frac{if|e|}{8\pi^3} \sum_{n=1}^M d^3k \langle u_{nk}^\lambda | \nabla_k | u_{nk}^\lambda \rangle \quad (3)$$

Here, f is the occupation number of states in the valence bands, u_{nk}^λ is the cell-periodic part of the Bloch function ψ_{nk}^λ , and the sum runs over all M-occupied bands.

In particular, in the analysis of ferroelectrics, the evolution path is denoted by the evolution of the polar phonon eigen displacements when going from the high-symmetry paraelectric phase ($P2_1/m$ in this case) towards the low-symmetry polar space group ($P2_1$ in our case of study). The visual representations of atomic structures were generated with the assistance of the VESTA (Visualization of Electronic and Structural Analysis) software.⁵¹

5.2.8 Piezoresponse force microscopy studies

The piezo- and ferroelectric properties of the crystal film of material **^RMBA-BF₃** prepared on ITO (Indium tin oxide) coated glass surface were studied using PFM measurements conducted with the Asylum Research MFP-3D atomic force microscopy (AFM) system. Contact mode AFM experiments were carried out using RMN-12PT300B cantilever probes, which had a spring constant of 1.12 N m⁻¹ and a tip diameter of less than 8 nm, to measure the piezoresponse of the crystal films. PFM data was obtained through vertical-PFM experiments, wherein an AC voltage was applied to the conductive AFM tip while the bottom electrode remained grounded. The PFM images were collected at a resonance frequency of 300 +/- 20 kHz, with an applied bias of 100 V. Additionally, PFM phase and amplitude contrast were recorded in areas measuring approximately 9 X 9 μm², using dual AC resonance tracking (DART) mode PFM.

5.2.9 Preparation of $^R\text{MBA-BF}_3$ Device for Piezoelectric Energy Harvesting Measurements

The tightly sandwiched nanogenerator devices of $^R\text{MBA-BF}_3$ crystallites were prepared by attaching small ($2 \times 5 \text{ mm}^2$) conductive adhesive copper tapes (Cu-lids in the schematic) at the corners of the ITO-coated PET sheets, which serve as the top and bottom. In the next step, adhesive Kapton tapes were placed on the borders of the ITO-coated PET sheets to avoid direct contact between the electrodes. Subsequently, $^R\text{MBA-BF}_3$ crystallites were deposited on one of the ITO surfaces and then the other ITO-coated sheet with Cu tape with the Kapton border was placed above the crystal layer. In the last step, copper wires were soldered on the Cu-lids and the device was fully encapsulated with another layer of adhesive Kapton tapes to keep the sandwiched structure intact during measurements and reduce the static charge developed during the continuous impact on the device.

5.2.10 Piezoelectric energy harvesting measurements

A periodic impact instrument, customized to operate at an impact force of 21 N and frequency of 10 Hz, was used to carry out the mechanical energy harvesting experiments. The output voltages and currents were measured using a Tektronix 2024 Mixed Signal Oscilloscope, which had an input impedance of 1 M Ω . The devices under test ($^R\text{MBA-BF}_3$) had a thickness of approximately 1 mm and an active area of 100 mm².

5.3 Results and discussion

5.3.1 Synthesis, characterization, crystal structures and SHG studies

The enantiomerically pure compounds $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$ were prepared by introducing $\text{BF}_3 \cdot \text{OEt}_2$ to a hexane solution of either *R*-($-$)- α -methylbenzylamine or *S*-($+$)- α -methylbenzylamine under a nitrogen atmosphere at 0 °C (Figure 5.1a). Rod-shaped single crystals of $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$, suitable for single-crystal X-ray diffraction studies, were obtained upon the slow evaporation of their corresponding methanolic solutions. The compounds $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$ crystallized in the chiral polar monoclinic $P2_1$ space group (Figures 5.1b-1c, 5A.7-5A.8, Appendix 5). The chirality of *R*-($-$)- or *S*-($+$)- α -methyl benzylamine was instrumental in the crystallization

of these noncentrosymmetric enantiomeric pairs. The homochiral characteristics of $^R\text{MBA-}$ and $^S\text{MBA-BF}_3$ were further verified by their circular dichroism (CD) spectra in methanol. These compounds give bisignate bands at 248, 254, 260, and 266 nm corresponding to the $n\text{-}\pi^*$ transitions (Figure 5.1d). The B-N distances in $^R\text{MBA-}$ and $^S\text{MBA-BF}_3$ were found to be 1.6063(46) and 1.6040(52) Å, consistent with those present in typical amine-borane donor-acceptor adducts. The average B-F distances of 1.3693(63) and 1.3707(67) Å in $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$, respectively, were also comparable with those found in other BF_3 adducts of amines.

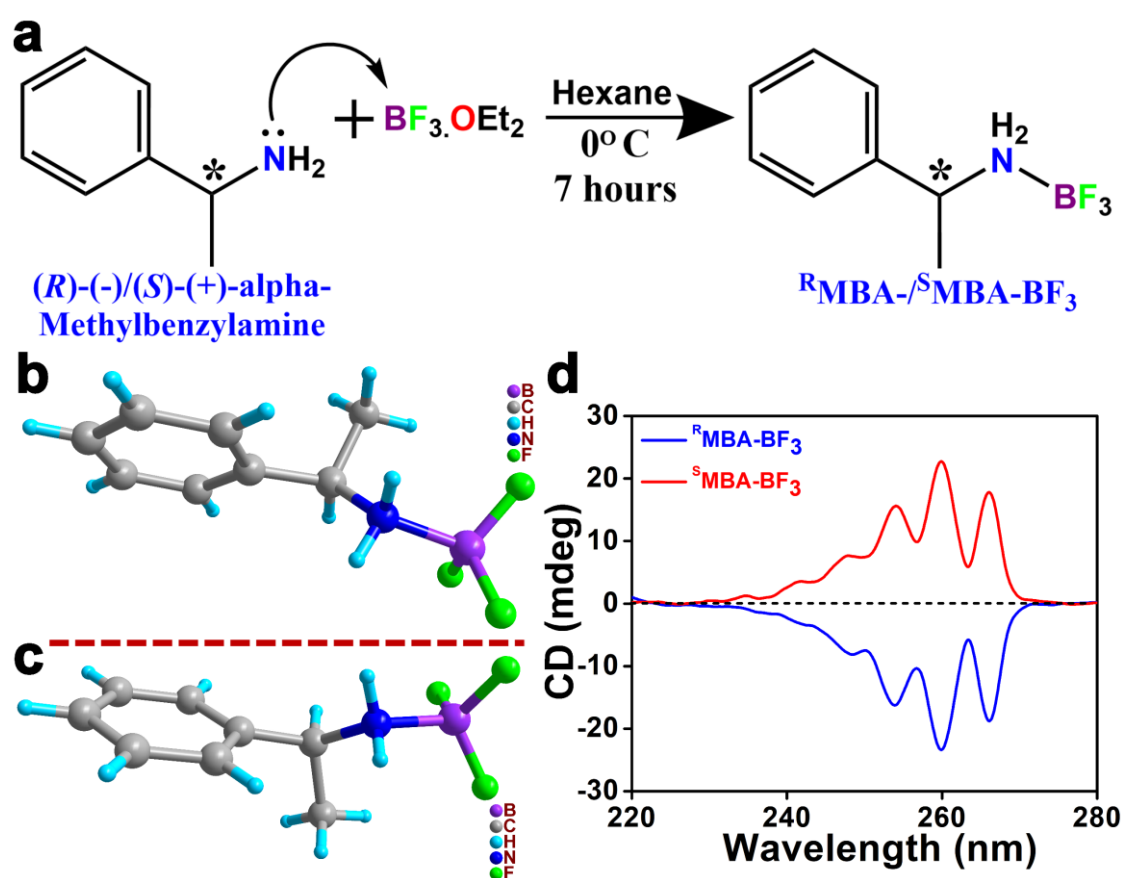


Figure 5.1: (a) Synthetic procedure for preparing $^R\text{MBA-}$ and $^S\text{MBA-BF}_3$. (b) Asymmetric unit of $^R\text{MBA-BF}_3$. (c) Asymmetric unit of $^S\text{MBA-BF}_3$. (d) The CD-spectra for $^R\text{MBA-}$ and $^S\text{MBA-BF}_3$.

The fluorine atoms of $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$ are involved in C-H...F type intermolecular hydrogen bonding interactions with the phenyl rings of the alpha-methylbenzyl groups. The cumulative effect of these interactions is the formation of a 1D chain-like structure along the polar b -axis (Figures 5.2a-5.2b, 5A.9-5A.10, and Tables 5A.1-5A.3, Appendix 5). The chain-like structures in these chiral assemblies foster the generation of long-range polar order, essential for ferroelectricity. The extent of various interactions (H...F/F...H, C...H/ H...C, H...H, F...F, F...C/C...F, etc.) within enantiomeric adducts were evaluated by Hirshfeld surface analysis using Crystal Explorer 3.1 software. The C-H...F hydrogen bonding interactions present in $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$ are represented by the dark red dots on the d_{norm} -mapped Hirshfeld surface (Figures 5A.11-5A.15, Appendix 5). Among all interactions present, the H...F/F...H interactions contribute around 43.1 % of the total interactions present in these enantiomeric pairs.

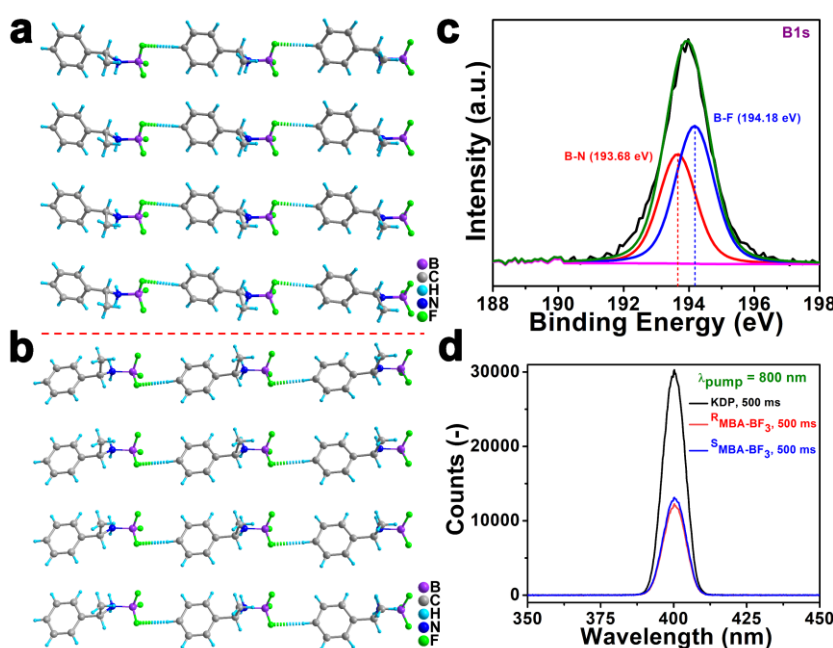


Figure 5.2: (a) H-bonding interactions present in $^R\text{MBA-BF}_3$. (b) H-bonding interactions in $^S\text{MBA-BF}_3$. (c) The B1s X-ray photoelectron spectrum of $^R\text{MBA-BF}_3$. (d) SHG profiles of $^R\text{MBA-BF}_3$ and $^S\text{MBA-BF}_3$ and their comparison with that of standard KDP sample.

To verify the adduct formation in the bulk material and to test the existence of various bonds present in these enantiomers, X-ray photoelectron spectroscopy (XPS) studies were performed on **^RMBA-BF₃**. The XPS composition analysis confirmed the presence of B, C, N, and F elements. The existence of two deconvoluted peaks of B(1s) with binding energies at 193.68 and 194.18 eV, indicated the presence of two different bonds corresponding B-N and B-F functionalities (Figures 5.2c and 5A.16a, Appendix 5). The C(1s) spectra comprise three peaks with binding energies of 284.52, 285.02 and 286.42 eV corresponding to C=C, C-C/C-H and C-N bonds, respectively (Figure 5A.16b, Appendix 5). The deconvoluted N(1s) spectra gave signature signals due to N-B (400.88 eV), N-H (401.28 eV), and N-C (402.28 eV) bonds, while only one peak in the F(1s) spectra confirmed the B-F bonds with a binding energy of 686.28 eV (Figures 5A.16c-5A.16d, Appendix 5).

Further, the bulk purity of these enantiomerically pure compounds was further established by powder X-ray diffraction (PXRD) analyses, which correspond well with the simulated peaks from their single-crystal X-ray data (Figure 5A.17, Appendix 5). The thermogravimetric analysis (TGA) of two enantiomeric B-N adducts confirmed their thermal stability up to 400 K with clear melting points around 350 K (Figure 5A.18, Appendix 5). The absence of any structural phase transition in both the molecules was then confirmed by differential scanning calorimetry (DSC) analyses. The noncentrosymmetric nature of both **^RMBA-** and **^SMBA-BF₃** was reaffirmed by second harmonic generation (SHG) experiments using Kurtz-Perry type nonlinear optical measurement setup. The compounds **^RMBA-BF₃** and **^SMBA-BF₃** exhibited relative SHG efficiencies of 0.41 and 0.44, respectively, vs. KDP reference at 293 K (Figure 5.2d).

5.3.2 Dielectric, Impedance, ferroelectric and piezoelectric studies

Due to the analogous physical and chemical properties of these enantiomeric compounds, only **^RMBA-BF₃** was used for further electrical studies. The dielectric nature of **^RMBA-BF₃** was confirmed by the frequency (f) and temperature (T) dependent dielectric permittivity (ϵ') measurements on its compacted powder pellet at a temperature range of 298 to 350 K and at a frequency range from 10 kHz to 1 MHz. From the real part of the dielectric permittivity (ϵ') vs. T profiles, an increase in the

permittivity with an increase in the temperature could be observed. This can be attributed to the increased thermal motion of dipoles at higher temperatures, especially near to their melting temperatures. A similar trend was observed for the frequency-dependent ϵ' profiles as well, and the higher dielectric permittivity values obtained at lower frequencies can be attributed to the contributions from all four types of polarization mechanisms at this frequency range. No heat anomalies were seen in the investigated temperature range (below its melting temperature). The ϵ' of $^R\text{MBA-BF}_3$ at 298 K were in the range from 317 to 9 in the frequency range from 1 kHz to 1 MHz (Figure 5A.19, Appendix 5). The temperature and frequency-dependent dielectric loss factors ($\tan \delta$) also followed similar trends with no heat anomalies (Figure 5A.20, Appendix 5).

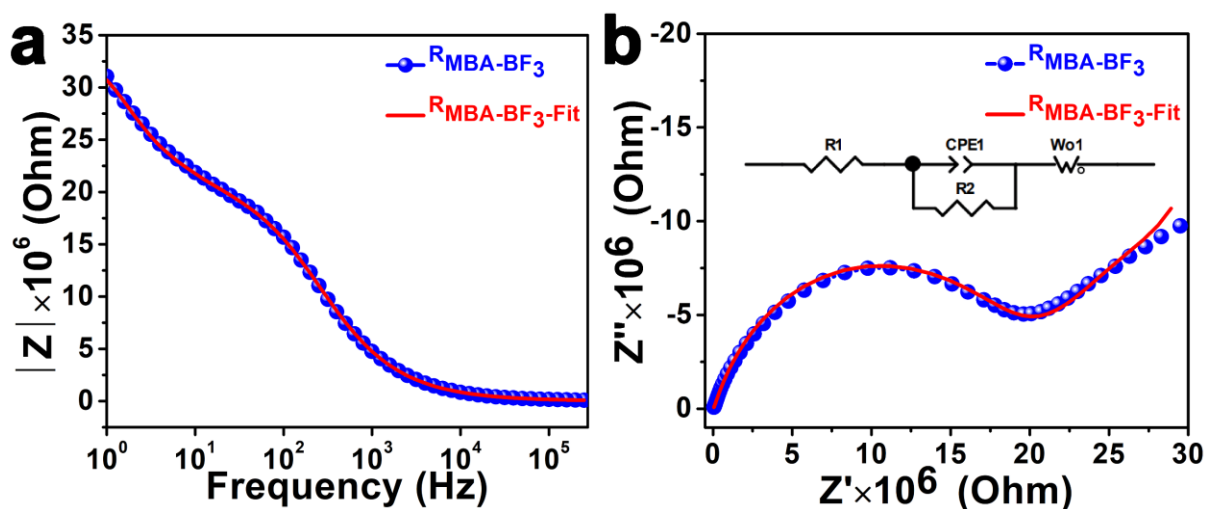


Figure 5.3: (a) Frequency-dependent total impedance (Z) for $^R\text{MBA-BF}_3$. (b) Nyquist plot for $^R\text{MBA-BF}_3$.

The impedance properties of $^R\text{MBA-BF}_3$ were examined through frequency-dependent impedance analysis conducted at room temperature. Analysis of the impedance magnitude (Z) against frequency (f) reveals a notable increase in impedance with decreasing frequency, analogous to the behavior observed in the frequency-dependent dielectric permittivity measurement (Figure 5.3a). Notably, the impedance magnitude stabilizes at higher frequencies, remaining relatively constant

and independent of frequency. The obtained data was further analyzed using the Warburg circuit model to fit the Z' vs. Z'' Nyquist plot (Figure 5.3b). From the fitted data, the resonance frequency of $^R\text{MBA-BF}_3$ adduct was calculated to be ~ 189 Hz.

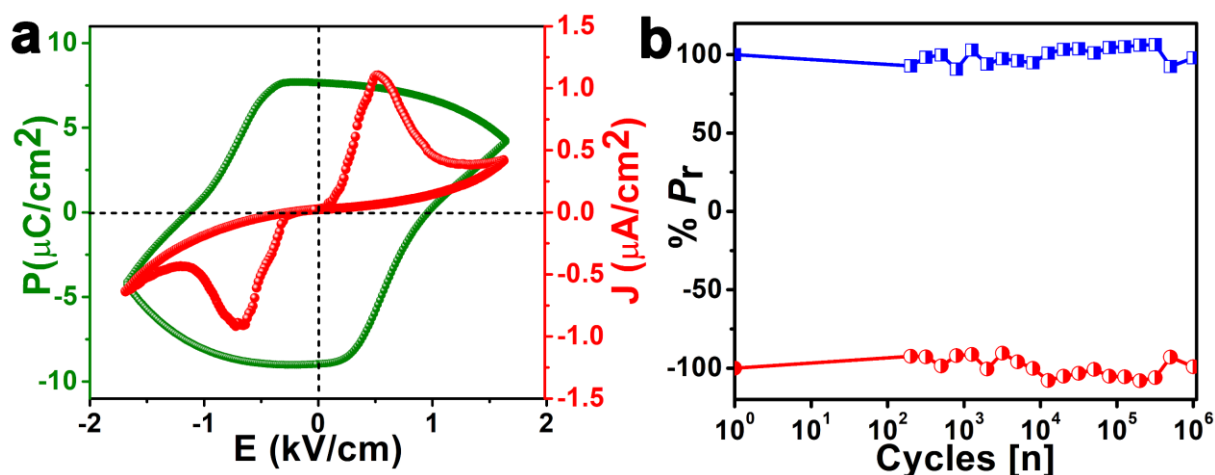


Figure 5.4: (a) P - E hysteresis loop for $^R\text{MBA-BF}_3$. (b) The fatigue test showing the retention of polarization of $^R\text{MBA-BF}_3$ up to 10^6 cycles.

The chiral nature of the molecule and its crystallization in polar point group C_2 , prompted us to further study its ferroelectric characteristics by P - E hysteresis loop measurements. The ensuing P - E loop took on a rectangular shape for $^R\text{MBA-BF}_3$ with a remnant polarization (P_r) value of $7.65 \mu\text{C cm}^{-2}$ and saturation polarization (P_s) of $4.27 \mu\text{C cm}^{-2}$ (Figure 5.4a). The coercive field (E_c) was found to be 0.95 kV cm^{-1} for $^R\text{MBA-BF}_3$. The polarization developed in $^R\text{MBA-BF}_3$ can be attributed to the dipoles formed by the dative bond-assisted charge transfer from the MBA group to the BF_3 moiety. Subsequent long-range polar order could occur due to the 1D-H-bonding interactions between the boron-bound fluorine atoms and the phenyl C-H protons in the amine unit along the polar b -axis. Furthermore, dynamic leakage current density (J) measurements were performed along the P - E loop trace as a function of the applied electric field (E). The obtained J - E profile supported the ferroelectric nature of the compound $^R\text{MBA-BF}_3$, exhibiting low leakage behavior with peak maxima at the domain switching points (Figure 5.4a). Ferroelectric fatigue measurements on $^R\text{MBA-}$

BF_3 indicate no notable change in its P_r values up to 10^6 cycles, validating its intact polarization behavior (Figure 5.4b).

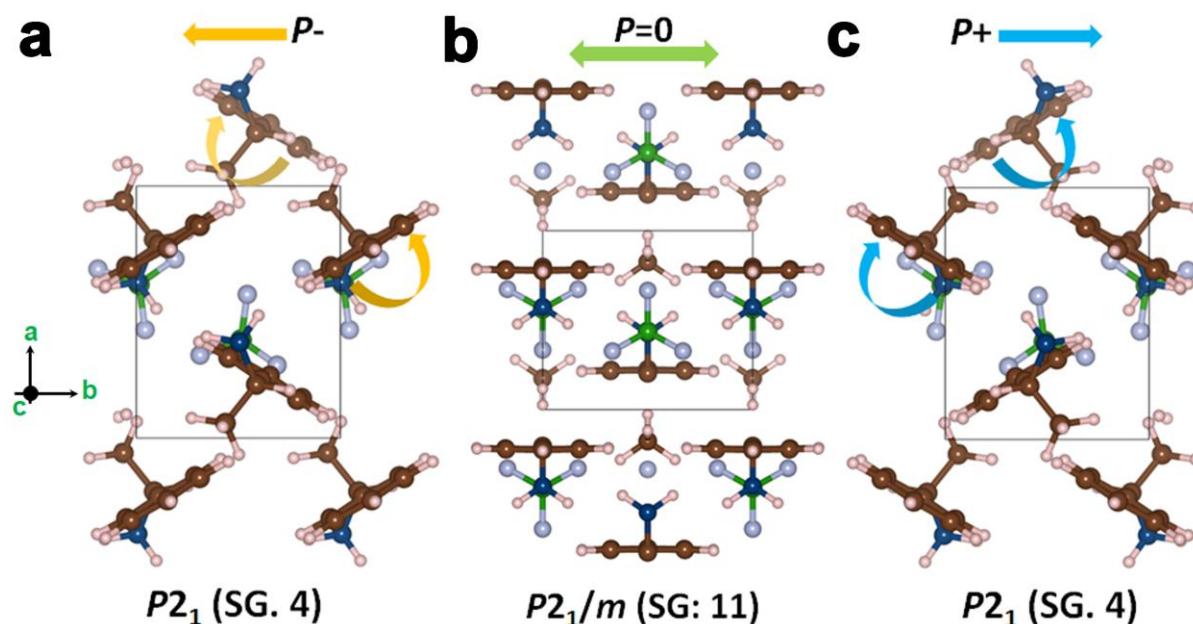


Figure 5.5: Structural evolution during ferroelectric polarization reversal. (a) Structure of R MBA-BF_3 with negative polarization direction ($P2_1$). (b) Hypothetical structure ($P2_1/m$) of R MBA-BF_3 with zero polarization. (c) Structure of R MBA-BF_3 with positive polarization direction ($P2_1$). The bent arrows in (a) and (c) show the molecular rotations around the c -axis that results in polar response along the b -axis associated with the Γ_1^- mode, while Γ_1^+ is an alignment (nonpolar) mode, which relates to the cell volume expansion.

To elucidate the underlying factors driving polarization generation in R MBA-BF_3 , we employed a first principles-based computational approach.^{52, 53} Initially, we identified the high-symmetry structure, assumed to be paraelectric, with a $P2_1/m$ symmetry (Figure 5.5b). Within this structure, we discerned two distinct symmetry distortions, denoted as Γ_1^- and Γ_1^+ , each involving displacements from the high-symmetry to the low-symmetry phase (Figures 5.5a and 5.5c). The Γ_1^- distortion involved the rotation of molecular chains, leading to the $P2_1$ phase from the $P2_1/m$ phase, representing the polar mode. Subsequently, following proper structural relaxation of the high-symmetry

structure, we observed all cationic amine groups aligning perfectly with the c -axis, albeit with a huge reduction in volume along the c -axis. This alignment mode, maintaining the $P2_1/m$ phase, can be classified as Γ_1^+ , constituting a non-polar mode. The entire phenomenon appears to be of geometric polarization mechanism, wherein Γ_1^- induces polarization; meanwhile, the Γ_1^+ preserves the high-symmetry structure, yet with an enhanced polar distortion. Employing both the high-symmetry and low-symmetry structures, using the Berry phase approach, the polarization (P_s) value was computed to be $10.04 \mu\text{C cm}^{-2}$, which aligns well with our experiments.

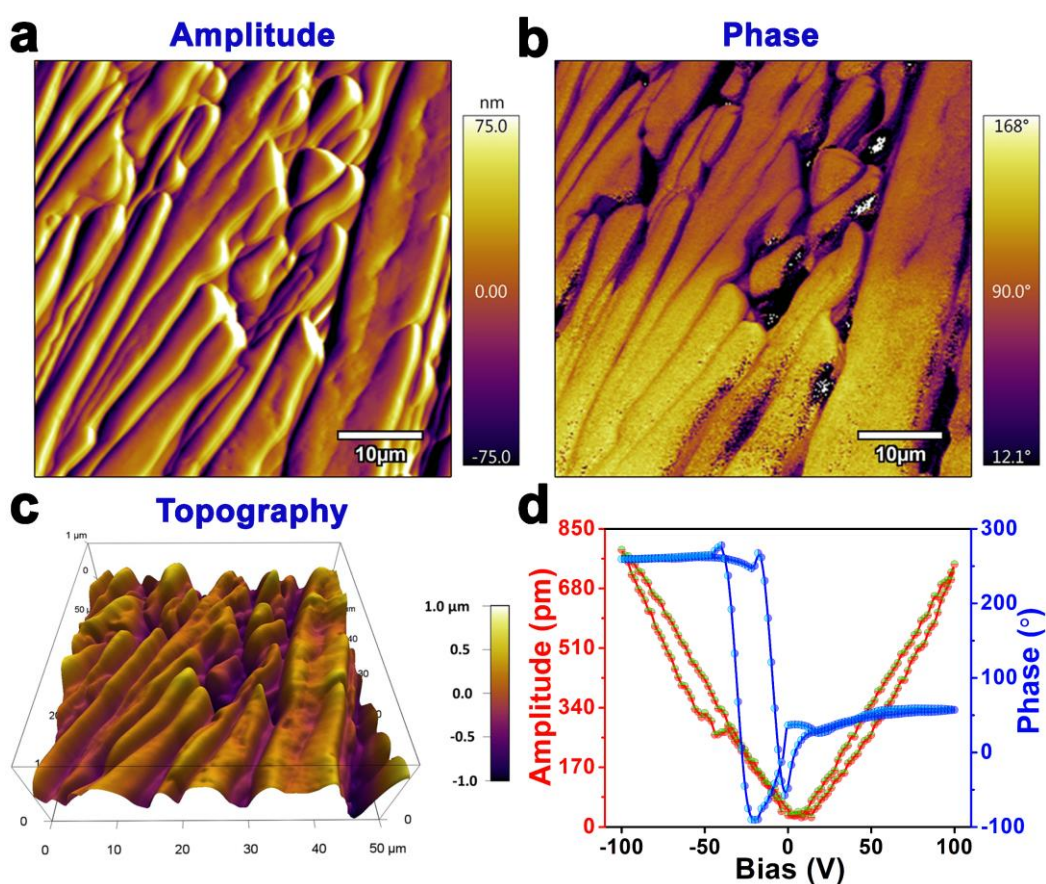


Figure 5.6: PFM-derived (a) Amplitude image (b) Phase image (c) 3D-topography (d) Amplitude- and phase-bias "butterfly" and "hysteresis" loops of $RMBF_3$.

The piezoresponse force microscopy (PFM) technique was employed to authenticate the microscopic polarization state and domain alignments of $RMBF_3$, providing

insights into the electromechanical coupling strength and the polarization direction of individual domains. Visualization of amplitude and phase domain structure of **^RMBA-BF₃** was achieved on a drop-casted thin film with distinct crystals of width ~10-20 μm . The PFM amplitude image of **^RMBA-BF₃** showed regions of distinct contrast, indicative of different piezoresponse domains. Clear domain walls separating the different domains can be seen in the amplitude image, as reflected in the phase image (Figure 5.6a-5.6b). PFM spectroscopy measurements were performed on a specific location on the surface of a single crystal (area ~ $9 \times 9 \mu\text{m}^2$) (Figures 5.6c and 5A.21, Appendix 5). A constant tip voltage of $\pm 100 \text{ V}$ was applied, giving characteristic amplitude-bias “butterfly” and phase-bias hysteresis loops typical for any ferroelectric material (Figure 5d). The observed near 180° phase difference between opposite signals verifies the inverse switching polarization behavior. Furthermore, the converse piezoelectric coefficient (d_{33}) was calculated to be $9\text{-}12 \text{ pm V}^{-1}$ from the slope of the amplitude-bias curve. This result substantiates the existing ferroelectric characteristics of the organic B-N adduct **^RMBA-BF₃**.

The piezoelectric coefficient (d_{33}) was also measured using the “Berlincourt” method at 110 Hz frequency and 21 N force. The measurements performed on the compacted pellet of **^RMBA-BF₃** yielded a d_{33} value of 3.46 pC N^{-1} (Figure 5A.22, Appendix 5). The piezoelectric voltage coefficient ($g_{33} = d_{33}/\epsilon_{33}$, where $\epsilon_r = \epsilon_{33}/\epsilon_0$, $\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$ and $\epsilon_r = 15.12$ at 100 kHz) was calculated to be of $25.85 \times 10^{-3} \text{ VmN}^{-1}$. The transduction coefficient ($d_{33} \times g_{33}$), a measure of the power generation ability of any piezoelectric material, was calculated to be $89.44 \times 10^{-15} \text{ m}^3 \text{ J}^{-1}$ for **^RMBA-BF₃**, suggesting its suitability for PENG applications. Moreover, materials with high piezoelectric voltage and electrostrictive coefficients are greatly desired for electromechanical applications involving the conversion of mechanical energy to electrical energy. The electrostrictive coefficient ($Q_{33} = g_{33}/2P_s$) is calculated to be $0.30 \text{ m}^4\text{C}^{-2}$ for **^RMBA-BF₃**, where $P_s = 4.27 \mu\text{C cm}^{-2}$. The calculated Q_{33} of **^RMBA-BF₃** surpasses those reported for several ceramic-based piezoelectric materials ($0.034\text{-}0.096 \text{ m}^4\text{C}^{-2}$).⁵⁴ All these attributes promise the utility of **^RMBA-BF₃** for various electromechanical applications.

5.3.3 Fabrication of $^R\text{MBA-BF}_3$ nanogenerator device and its piezoelectric energy harvesting outputs

Furthermore, we tested the ferroelectric $^R\text{MBA-BF}_3$ compound for energy harvesting applications. The device architecture was built by tightly sandwiching the crude crystals of $^R\text{MBA-BF}_3$ (~20 mg) between two ITO-coated PET sheets, ensuring direct contact with the conductive surfaces. The copper wires were used as electrodes from the top and bottom ITO contacts and were connected to an oscilloscope. The assembly was sealed with Kapton tape to mitigate any static charge interference during the measurements (Figure 5.7a).

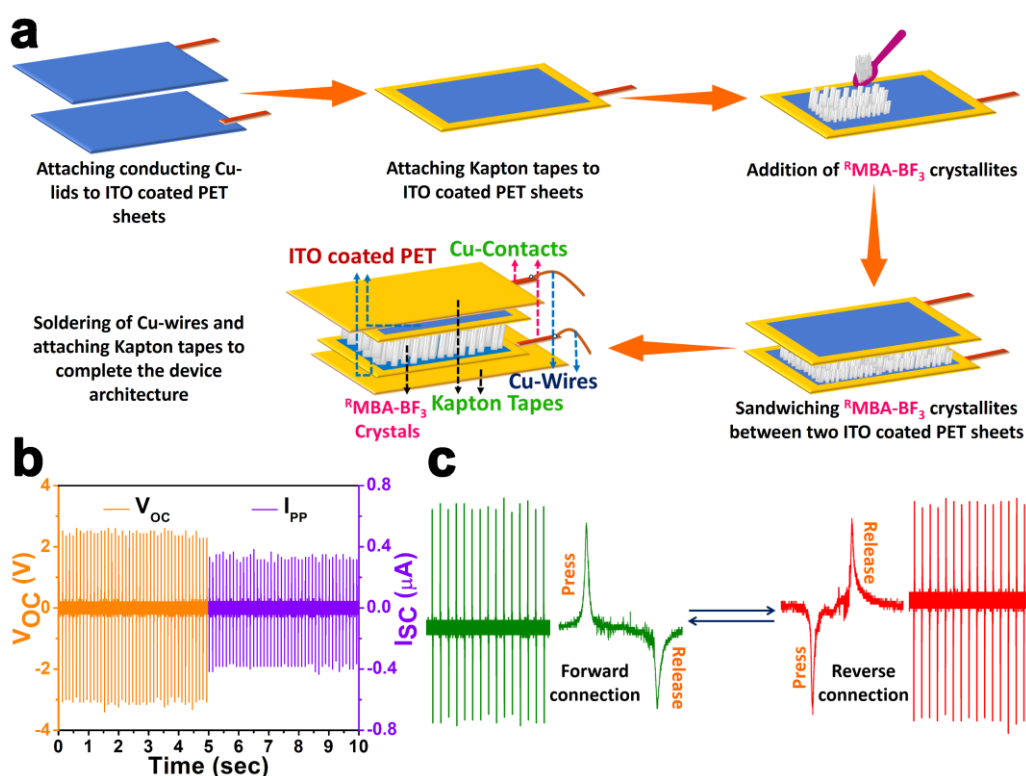


Figure 5.7: (a) Schematic showing the piezoelectric nanogenerator device preparation using $^R\text{MBA-BF}_3$ crystallites. (b) Open circuit peak-to-peak voltage (V_{PP}) for $^R\text{MBA-BF}_3$ and calculated short-circuit current (I_{PP}) of $^R\text{MBA-BF}_3$ device (the shifted time axis provided here is a guide to the eye). (c) Forward and reverse polarity peak-to-peak voltage profiles for $^R\text{MBA-BF}_3$.

The piezoelectric nanogenerator studies were performed by using a custom-built impact setup attached to an oscilloscope. These measurements were done at a constant applied force of 21 N and 10 Hz frequency (Figure 5A.23, Appendix 5). The **^RMBA-BF₃** device exhibited an open circuit peak-to-peak voltage of 6.2 V, while the peak-to-peak short circuit current was calculated to be 0.8 μ A upon connecting the device to a 4.7 M Ω resistor (Figure 5.7b). To quantify the reliability of the V_{PP} obtained by the **^RMBA-BF₃** device, we performed the polarity reversal measurements by changing the connections to the oscilloscope, which confirmed the retention of V_{PP} with the formation of reverse signals with opposite magnitudes (Figure 5.7c and 5A.24, Appendix 5). These observations further validate the piezoelectric origin of the obtained output signals.

5.4 Conclusion

In summary, our study delineates the design strategy for achieving sizable ferroelectricity in neutral donor-acceptor B-N adducts. The enantiomeric pair of adducts **^RMBA-BF₃** and **^SMBA-BF₃** crystallized in the chiral monoclinic polar space group $P2_1$, suitable for ferroelectric studies. The noncentrosymmetry of these adducts was spectroscopically verified by SHG studies. The P - E hysteresis measurements on the **^RMBA-BF₃** pellets revealed a remnant (P_r) polarization of 7.65 μ C cm⁻² at a coercive field of 0.95 kV cm⁻¹. Theoretical calculations on the chiral compounds elucidated the ferroelectric switching pathway, predicting polarization of ~ 10 μ C cm⁻² relative to a centrosymmetric structure derived from the averaged coordinates of the polar crystal structures. The PFM measurements done on the thin film of **^RMBA-BF₃** further confirm its ferro- and piezoelectric nature. Moreover, the **^RMBA-BF₃** pellets demonstrated piezoelectric characteristics with a macroscopic d_{33} value of ~ 3.5 pC N⁻¹ and a piezoelectric energy harvesting output voltage of ~ 6 V. These findings advocate for further studies on neutral small-molecule derived ferroelectrics in the quest for all-organic stable and nontoxic molecular systems for next-generation energy and electronic devices.

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End of Chapter 5

Chapter 6



Thesis Conclusion and Future Perspectives

In summary, this thesis presents the synthesis of ferroelectrically active non-centrosymmetric polar organic and organic-inorganic hybrid ammonium salts and Lewis acid-base pairs, which are utilized for piezoelectric energy harvesting applications. The noncentrosymmetry in all these systems were achieved by the strategic use of asymmetric amines and anions. The diverse H-bonding interactions present in all the synthesized organic and organic-inorganic hybrid materials gave rise to their notable polarization properties.

In this context, in [Chapter 2](#), we first prepared a chiral ammonium-based bismuth halide perovskite $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$. Interestingly, the material crystallized in the orthorhombic $P2_12_12_1$ space group, suitable for piezoelectric studies. The polymer composites of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ with polylactic acid (PLA) were prepared and utilized for mechanical energy harvesting applications. A maximum output open-circuit voltage of 10.4 V and a power density of $5.26 \mu\text{Wcm}^{-2}$ have been measured for the 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA polymer composite film. In addition, the 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device has been used for charging a 100 μF capacitor, storing the highest voltage of 1.16 V in 60 seconds.

In [Chapter 3](#), we synthesized the organoammonium salt $\{[\text{Me}_3\text{CCH}(\text{Me})\text{NH}_3][\text{BF}_4]\}$ (**DMBA**•**BF**₄), containing 3,3-dimethyl-2-butylammonium (DMBA) cation with a chiral carbon center and tetrafluoroborate anion. The compound **DMBA**•**BF**₄ crystallized in tetragonal $P4_2$ space group suitable for ferroelectric studies. *P-E* hysteresis loop measurements on **DMBA**•**BF**₄ showed sizable saturation polarization at room temperature. The characteristic amplitude-bias “butterfly” and phase-bias “hysteresis” behavior of **DMBA**•**BF**₄ was also tracked by piezoresponse force microscopy measurements. The composites of **DMBA**•**BF**₄ with biodegradable polycaprolactone (PCL) polymer were prepared and examined for piezoelectric nanogenerator applications. The 10 wt% **DMBA**•**BF**₄-PCL gave a maximum open-circuit peak-to-peak voltage ($V_{\text{OC-PP}}$) of 36.2 V with the corresponding power density of $48.1 \mu\text{W cm}^{-2}$. Subsequently, the scaling-up capabilities of **DMBA**•**BF**₄ were checked by preparing gyroid (Gy) shaped 3D-printed ensembles. The 10 wt% **Gy-DMBA**•**BF**₄-PCL composite resulted in an enhanced output voltage of 41 V and power density of 56.8

$\mu\text{W cm}^{-2}$ and, hence, validated the miniature device forming scaling up ability of compound **DMBA•BF₄**.

Furthermore, in [Chapter 4](#), we synthesized a highly moisture-stable ammonium salt co-crystal $[\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_2][\text{CH}_3\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_3][\text{PF}_6]$ (**(p-TEA)(p-TEAH)•PF₆**), by the combination of an ammonium salt and a neutral amine which crystallized in monoclinic *C2* space group. The compound **(p-TEA)(p-TEAH)•PF₆** was found to be extremely moisture stable even at 99% relative humidity (RH) conditions **(p-TEA)(p-TEAH)•PF₆** gave a saturation polarization (P_s) of $0.95 \mu\text{C cm}^{-2}$ at 298 K, and a direct piezoelectric (d_{33}) coefficient of 4 pC N^{-1} . Remarkably, these values resulted in a high electrostriction coefficient (Q_{33}) value of $2.02 \text{ m}^4 \text{ C}^{-2}$, higher than those exhibited by the piezoceramics and close to that of polyvinylidene difluoride (PVDF). The piezoelectric energy harvesting applications of **(p-TEA)(p-TEAH)•PF₆** have been established on its composites with biodegradable polycaprolactone (PCL) polymer. A maximum peak-to-peak open-circuit voltage ($V_{\text{OC-PP}}$) of 13.1 V and power density of $104.2 \mu\text{W cm}^{-3}$ were observed for the 10 wt% **(p-TEA)(p-TEAH)•PF₆**-PCL composite device. Spurred by its high moisture stability and sizable PENG output characteristics, the scaled-up device for the 10 wt% **(p-TEA)(p-TEAH)•PF₆**-PCL composite was prepared using the 3D-printing technique. Remarkably, the gyroid-shaped 3D-printed PENG device resulted in a doubled $V_{\text{OC-PP}}$ of 22.8 V and doubled power density of $118.5 \mu\text{W cm}^{-3}$. Moreover, these results specified that co-crystallizing two-component charge-separated systems with neutral organic compounds is an effective approach for obtaining highly moisture-stable organic ferroelectrics for next-generation energy harvesting devices.

Finally, in [Chapter 5](#), we demonstrated the preparation of an enantiomeric pair of ferroelectric materials **^RMBA•BF₃** and **^SMBA•BF₃**, which crystallize in monoclinic *P2₁* space group. Owing to the similar physical and chemical properties of **^RMBA•BF₃** and **^SMBA•BF₃**, further studies were done on one enantiomer, **^RMBA•BF₃**. **^RMBA•BF₃** gave a saturation polarization of $4.27 \mu\text{C cm}^{-2}$ at room temperature, and the PFM studies validated the existence of ferro- and piezoelectricity in **^RMBA•BF₃** with typical amplitude- and phase-bias loops. Further, the energy harvesting applications on the crude crystals of **^RMBA•BF₃** gave rise to an open circuit voltage (V_{PP}) of 6.2 V. These findings pave the way for the preparation of stable, nontoxic, small-molecule based

ferroelectric all-organic B-N adducts and their corresponding applications in ferro- and piezoelectric nanogenerators.

The research reported in this thesis has the potential to replace conventional ceramic systems that include heavy metals by promoting the development of flexible piezoelectric and ferroelectric energy harvesting devices. Piezoelectric energy harvesters still show low output compared to triboelectric nanogenerators with all their advantages. Therefore, in the near future, developing novel techniques for producing pyroelectric, thermoelectric, and triboelectric energy harvesting devices using low molecular weight organic and organic-inorganic hybrid materials will be a primary research priority. The simultaneous extraction of energy from several natural sources is made possible by integrating multiple energy harvesters, which also promises to enhance device performance. The interfacial interactions between the polymer matrix and piezoelectric particles are a critical component influencing the output of composite devices. Therefore, a more thorough investigation of materials, along with a thorough comprehension of the chemistry of the interfacial regions in polymeric composite materials, will surely improve device performance. These developing energy harvesting and storage systems are expected to find use in a number of fields in the future, such as molecular electronics, microsensors, batteries, capacitors, Internet of Things (IoT), and blue energy power systems. These developments can potentially have a significant impact on new-age electronics and can also open the door for future improvements in efficient and sustainable technology.



Appendix



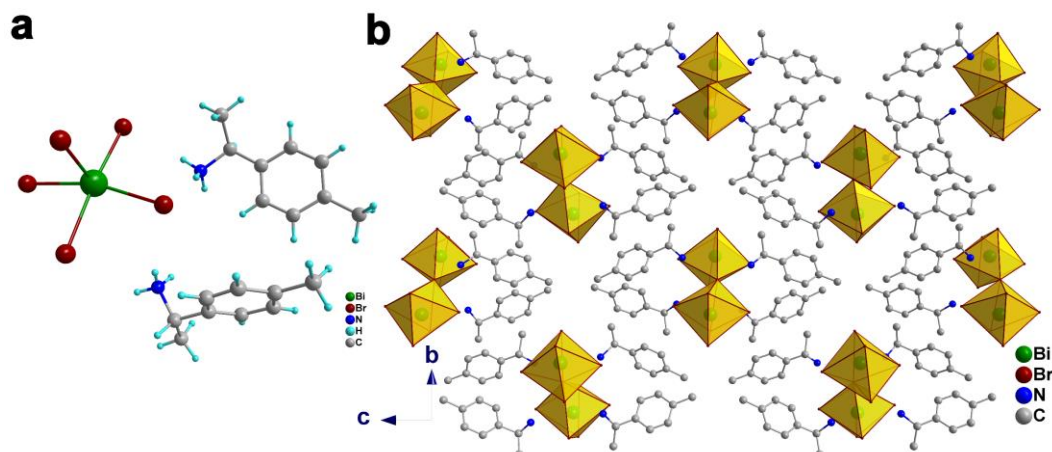


Figure 2A.1: (a) Asymmetric unit and (b) packing diagram of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ along *a*-axis at 100 K.

Table 2A.1. Hydrogen bonding parameters for $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$.

D-H...A	d(H...A) Å	d(D-A) Å	<(DHA) °	Symmetry transformations to generate equivalent atoms
N(11)-H(11D)...Br4	2.5205(25)Å	3.4234(238) Å	172.887(1492) °	-0.5+x, 0.5-y, 1-z
N(11)-H(11F)...Br2	2.5862(26)Å	3.4088(214) Å	150.45(129) °	0.5+x, 0.5-y, 1-z
N(21)-H(21D)...Br4	2.6226(26)Å	3.4911(255) Å	159.588(1597) °	-0.5+x, 0.5-y, 1-z
N(21)-H(21F)...Br1	2.5001(32)Å	3.3726(239) Å	161.443(1499) °	-0.5+x, 0.5-y, 1-z

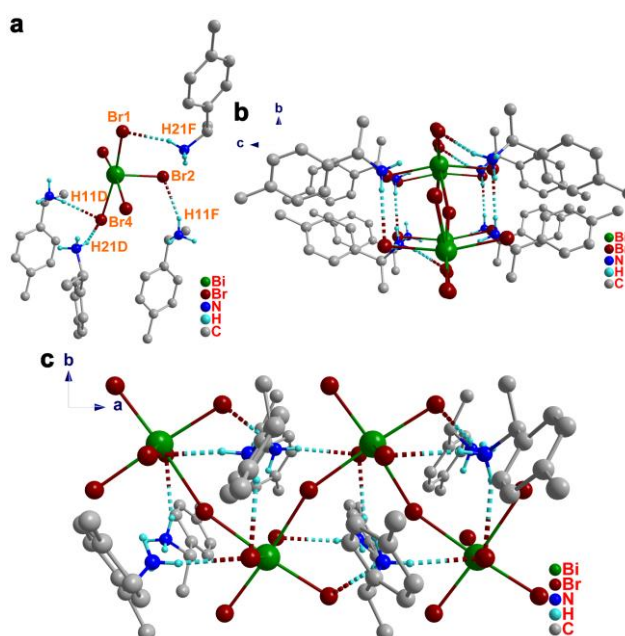


Figure 2A.2: Non-classical N-H...Br hydrogen bonding interactions in $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ at 100 K.

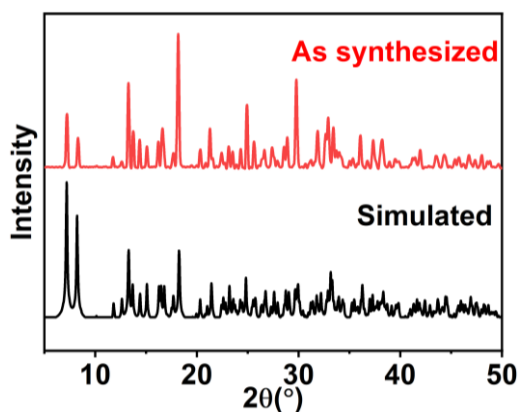


Figure 2A.3: The powder X-ray diffraction (PXRD) profile of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$.

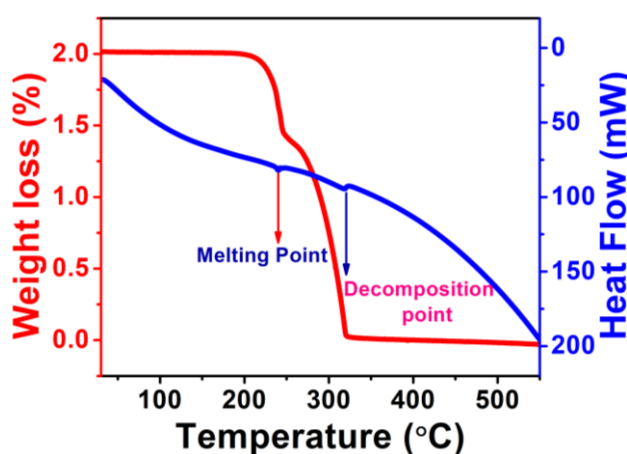


Figure 2A.4: The thermogravimetric and differential thermal analysis profiles of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$.

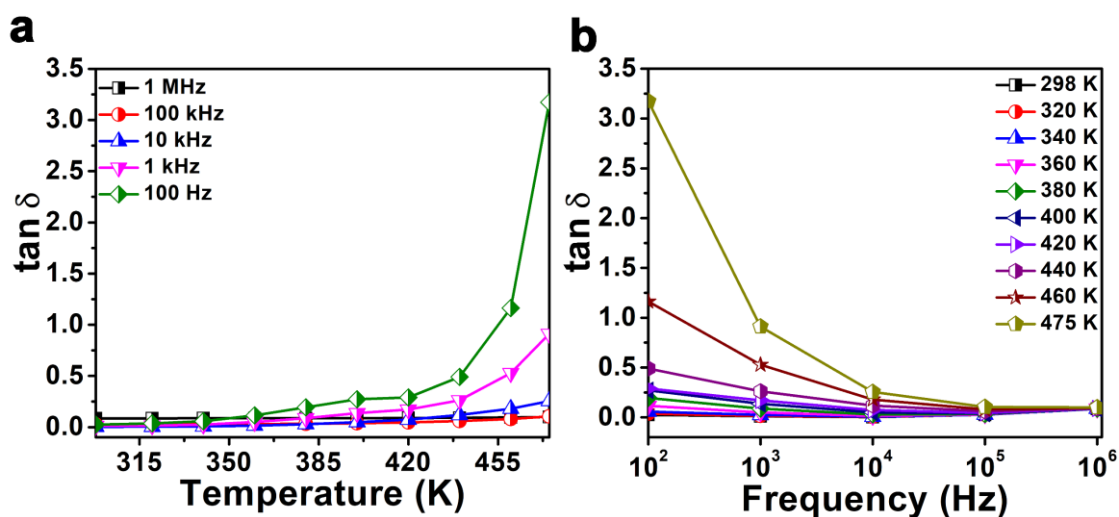


Figure 2A.5: (a) Temperature dependant dielectric loss plot and (b) Frequency dependant dielectric loss plot of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$.

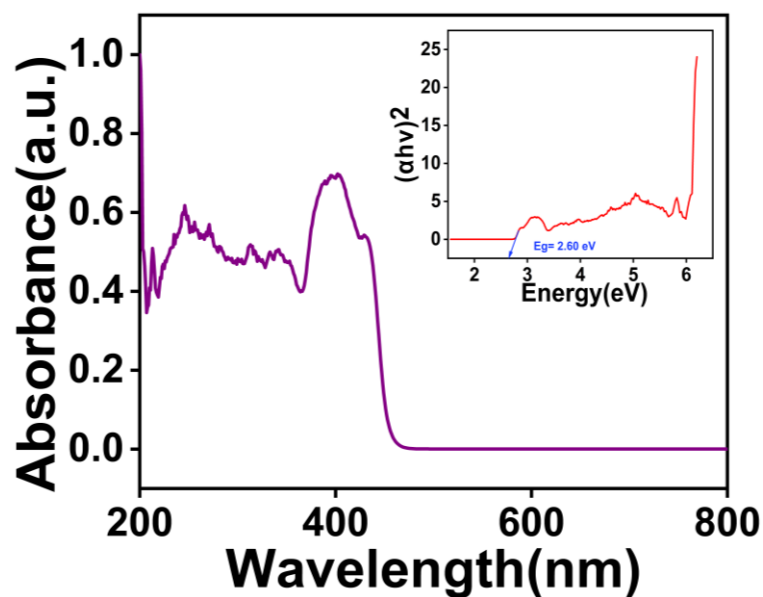


Figure 2A.6: UV-Visible diffuse reflectance spectrum of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$; its corresponding Tauc plot is displayed in the inset.

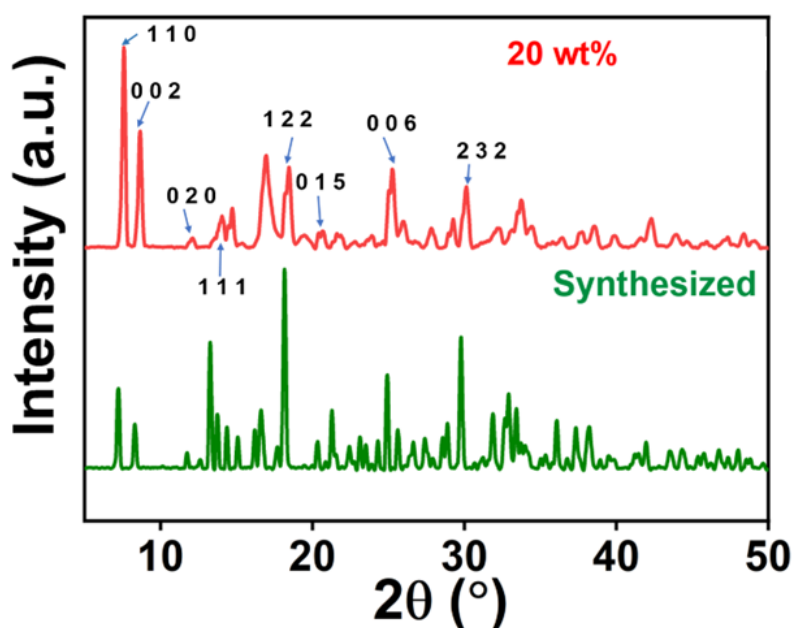


Figure 2A.7: The powder X-ray diffraction pattern and the characteristic hkl peaks for compound $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ and the 20 wt % $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA.

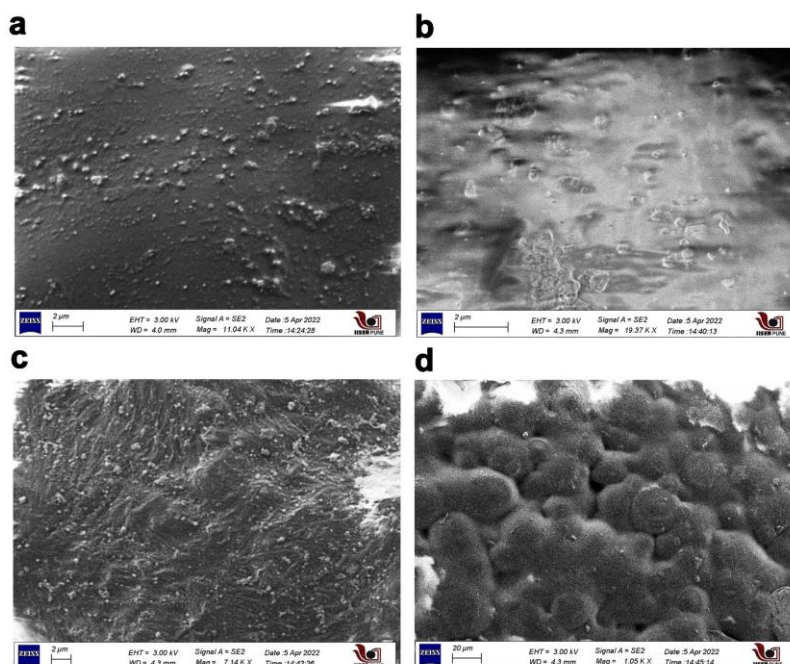


Figure 2A.8: The FE-SEM images of $\{[sCH(MePh)(Me)NH_3]_2[BiBr_5]\}_n$ -PLA composites. The figures a, b, c, and d correspond to 5, 10, 15, and 20 wt % $\{[sCH(MePh)(Me)NH_3]_2[BiBr_5]\}_n$ -PLA composites, respectively.

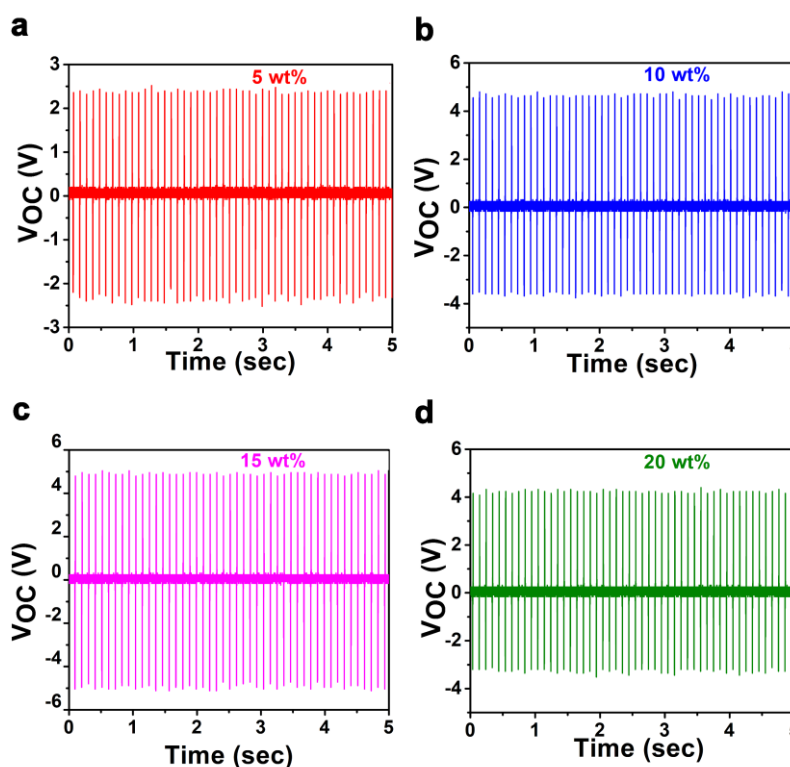


Figure 2A.9: Output voltage profiles of all the $\{[sCH(MePh)(Me)NH_3]_2[BiBr_5]\}_n$ -PLA composite films.

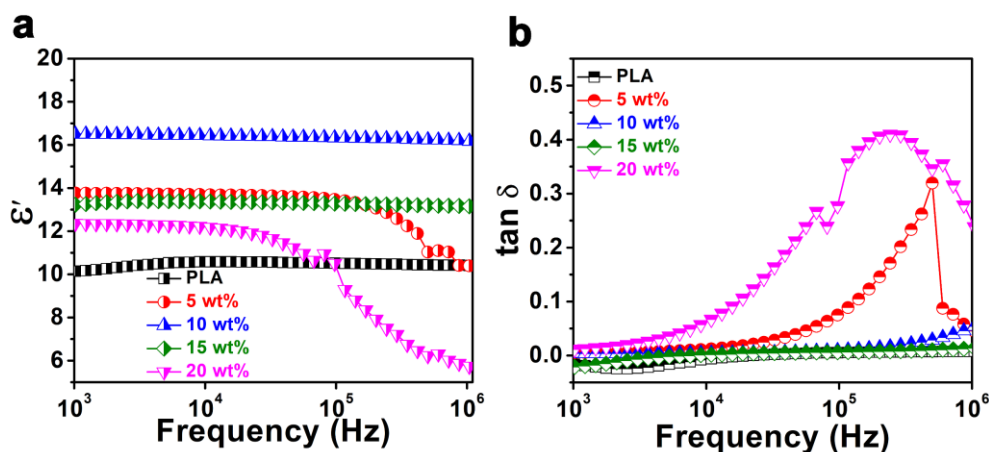


Figure 2A.10: Frequency dependent dielectric permittivity and (b) Frequency dependent dielectric loss plot of neat PLA and all $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA films.

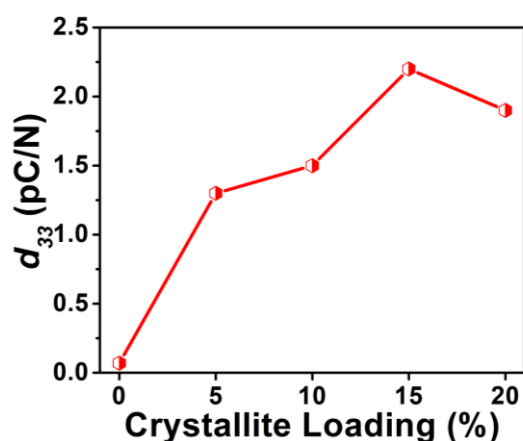


Figure 2A.11: The comparative d_{33} values for all $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite films and neat PLA film. The solid lines the connecting the points are a guide the eye.

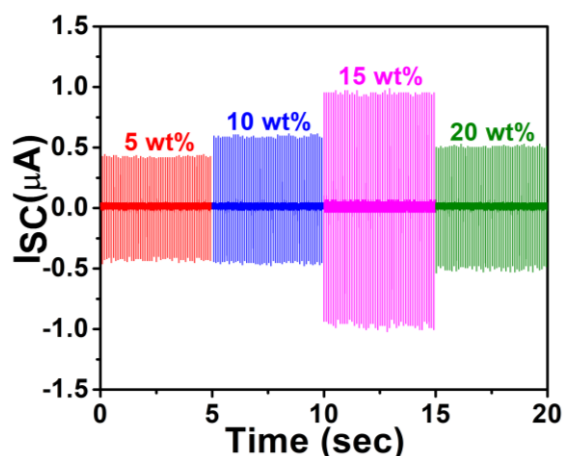


Figure 2A.12: Output current profile of $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite films.

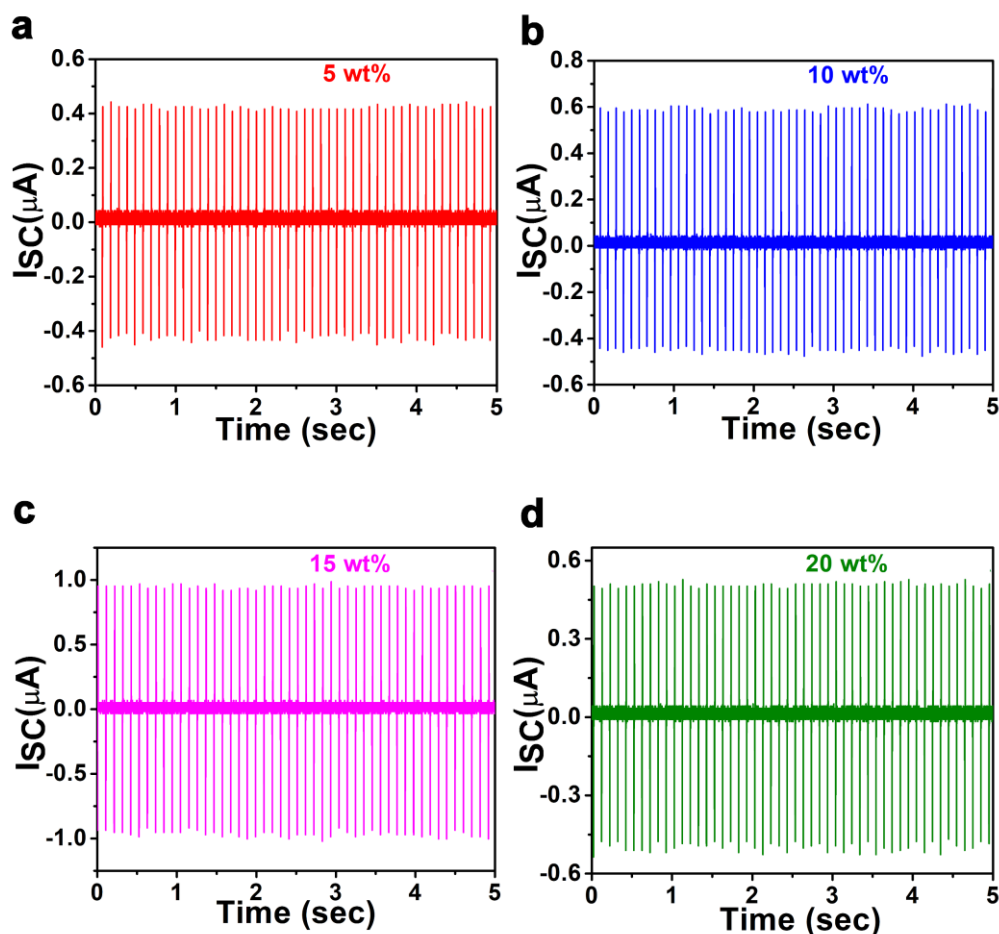


Figure 2A.13: The calculated output currents of all the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ composite films.

Table 2A.2: Summary of maximum piezoelectric energy harvesting outputs of 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n\text{-PLA}$ composite devices.

Parameters	Energy Harvesting Outputs
Area of the Device	3.6 cm ²
Maximum V_{PP}	10.4 V
Maximum I_{PP}	2.2 μA
Maximum CD	0.5 μA/cm ²
Maximum PD	5.26 μW/cm ²
Energy Stored in 100 μF Capacitor	58.25 μJ
Charge Stored in 100 μF Capacitor	116.5 μC

Table 2A.3: Comparison of output device performances of known energy harvesters based on polymer composites of organic-inorganic hybrid materials.

Hybrid Composite Devices	Output Voltages	Current/Current density	Power/Power density	Active area
MAPbI ₃ -PVDF	9.43	0.76 $\mu\text{A cm}^{-2}$	-	1 x 1 cm ²
MAPbBr ₃ -PVDF	5	60 nA	0.28 $\mu\text{W cm}^{-2}$	2.4 x 1.5 cm ²
MAPbI ₃ -PDMS	1.0	50 nA cm ⁻²	-	1 x 1 cm ²
FAPbBr ₃ -PDMS	4	-	-	1 x 1 cm ²
CsPbBr ₃ /PVDF	10.3	1.29 $\mu\text{A cm}^{-2}$	3.31 μW	1 x 1 cm ²
PVDF-PLLA-SnO ₂ NF-MAPbI ₃	4.82	29.7 nA	-	0.25 x 0.25 cm ²
SnO ₂ NF-MAPbI ₃	1.02	10.32 nA	-	0.25 x 0.25 cm ²
[BnNMe ₃] ₂ CdBr ₄ /PDMS	52.9	0.23 $\mu\text{A cm}^{-2}$	13.8 $\mu\text{W cm}^{-2}$	3 x 3 cm ²
[BnNMe ₂ ⁿ Pr] ₂ CdBr ₄ /PDMS	63.8	0.59 $\mu\text{A cm}^{-2}$	37.1 $\mu\text{W cm}^{-2}$	3 x 3 cm ²
(TMFM)FeBr ₄	2.2	-	-	-
[Ph ₃ MeP] ₄ [Ni(NCS) ₆]/TPU	19.29	3.59 $\mu\text{A cm}^{-2}$	2.51 mW cm ⁻³ (50.26 $\mu\text{W cm}^{-2}$)	1.3 x 3 cm ²
[Ph ₃ MeP] ₂ [CuCl ₄]/TPU	25	1.1 $\mu\text{A cm}^{-2}$	14.1 $\mu\text{W cm}^{-2}$	1.2 x 3 cm ²
15 wt% {[^s CH(MePh)(Me)NH ₃] ₂ [BiBr ₅]} _n - PLA	10.4	0.5 $\mu\text{A cm}^{-2}$	5.26 $\mu\text{W cm}^{-2}$	1.2 x 3 cm ²

Note: MAPbI₃ = methylammonium lead iodide; PVDF = polyvinylidene difluoride; PDMS = polydimethylsiloxane; FAPbBr₃ = formamidinium lead bromide; PLLA = poly(L-lactic acid); SnO₂ = tin oxide; NF = nanofiber; [BnNMe₃]₂CdBr₄ = N,N,N-trimethyl-1-phenylmethanaminium cadmium(II) bromide; [BnNMe₂ⁿPr]₂CdBr₄ = N-benzyl-N,N-dimethylpropan-1-aminium cadmium(II) bromide; (TMFM)FeBr₄ = trimethylfluoromethylammonium iron(III)bromide, TPU = thermoplastic polyurethane, PLA = polylactic acid .

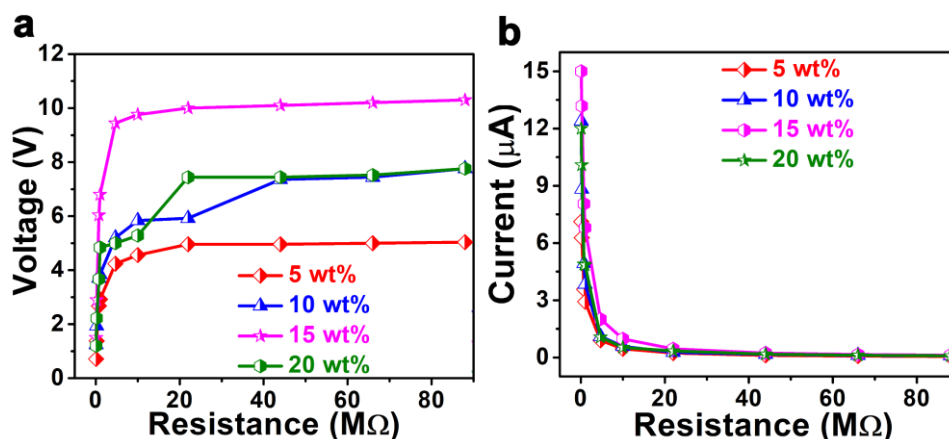


Figure 2A.14: The comparative output (a) voltage and (b) current data for all the $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite devices under various load resistances.

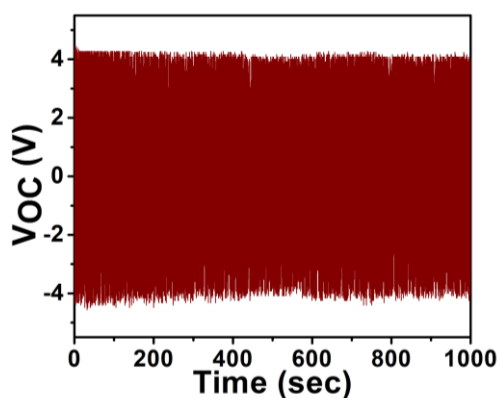


Figure 2A.15: Fatigue test for the 15 wt% $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device up to 10000 cycles.

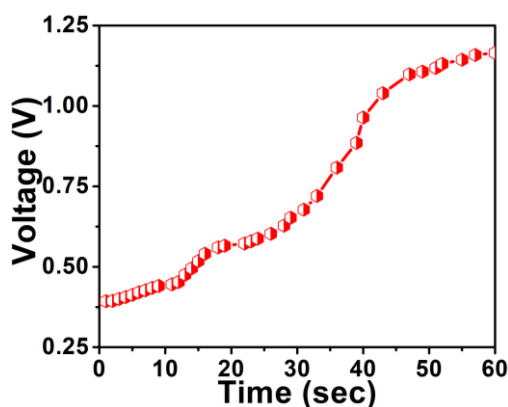
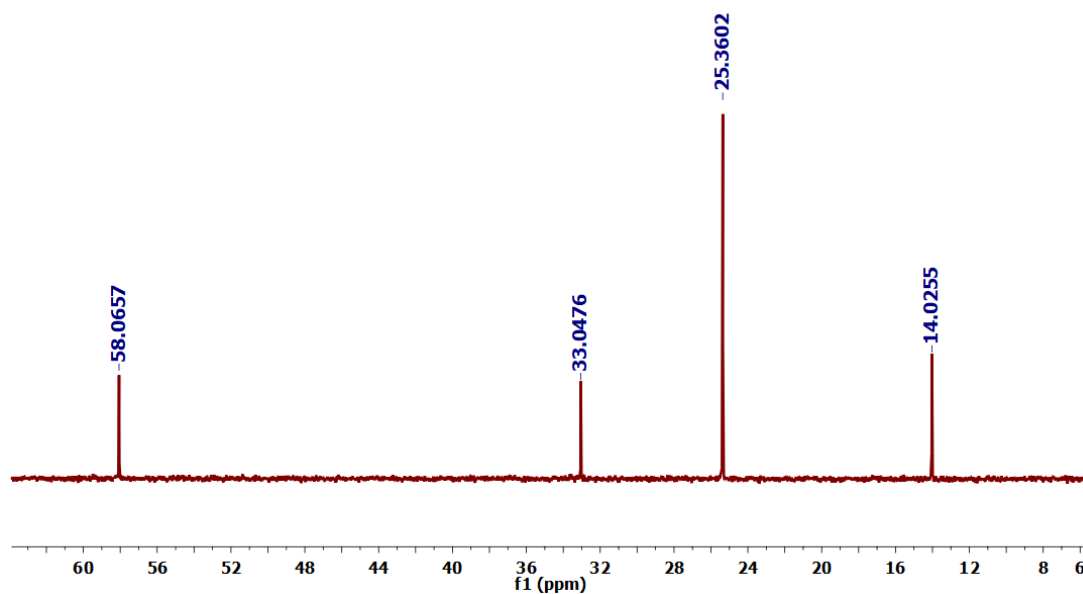
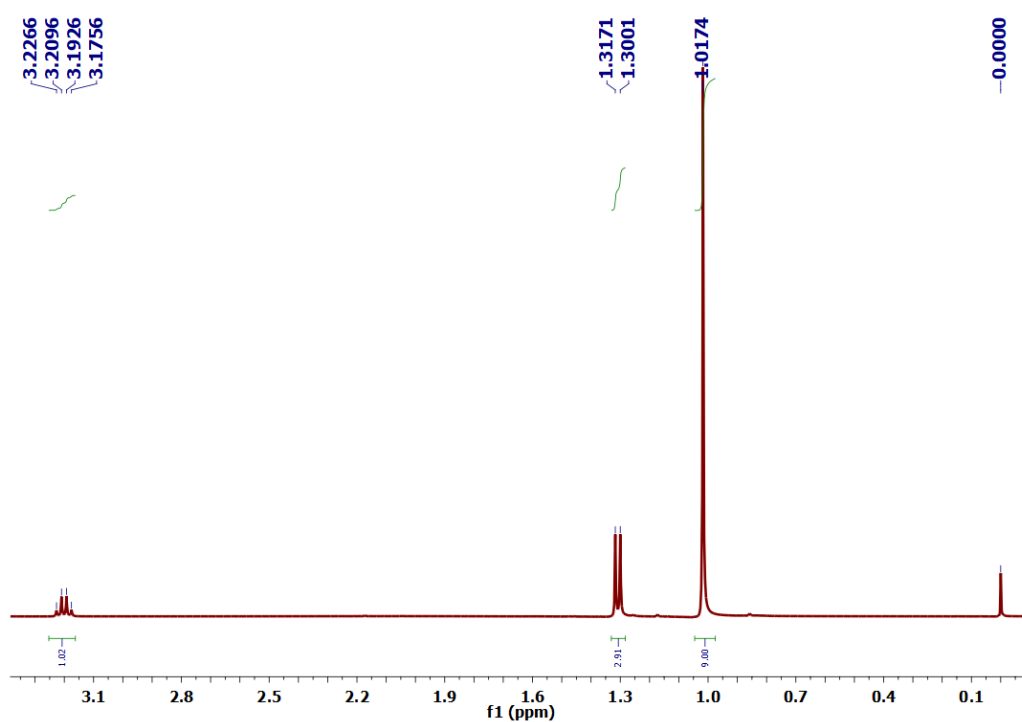


Figure 2A.16: Stored voltages in a 100 μF capacitor by employing the 15 wt % $\{[{}^s\text{CH}(\text{MePh})(\text{Me})\text{NH}_3]_2[\text{BiBr}_5]\}_n$ -PLA composite device at different time intervals.

Figure 3A.1: ^{13}C Spectrum of $\text{DMBA}\cdot\text{BF}_4$.Figure 3A.2: ^1H Spectrum of $\text{DMBA}\cdot\text{BF}_4$.

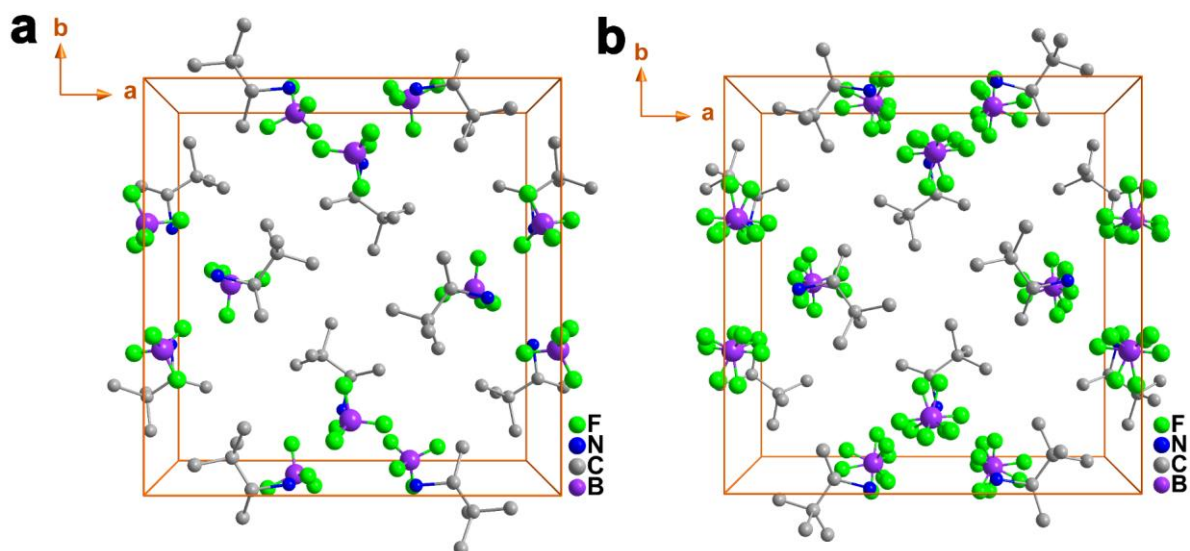


Figure 3A.3: Packing diagrams of **DMBA•BF₄** along *c*-axis at (a) 120 K and (b) 298 K.

Table 3A.1: Hydrogen bonding parameters for **DMBA•BF₄** at 120 K.

D-H...A	d(H...A) Å	d(D-A) Å	<(DHA)°	Symmetry transformations to generate equivalent atoms
N(11)-H(11A)···F21	1.9894(93)Å	2.7835(132) Å	144.975(654)°	<i>x</i> , <i>y</i> , 1+ <i>z</i>
N(21)-H(21C)···F12	2.0595(103)Å	2.8767(137) Å	148.911(639)°	1- <i>x</i> , 2- <i>y</i> , 1+ <i>z</i>
N(21)-H(21A)···F22	1.9522(65)Å	2.8576(135) Å	172.589(766)°	1- <i>x</i> , 2- <i>y</i> , 1+ <i>z</i>
N(11)-H(11C)···F14	2.0209(96)Å	2.9301(141) Å	176.445(703)°	<i>x</i> , <i>y</i> , 1+ <i>z</i>
N(21)-H(21B)···F13	1.9849(100)Å	2.8879(139) Å	170.784(643)°	<i>x</i> , <i>y</i> , 1+ <i>z</i>
N(11)-H(11B)···F24	2.1182(69)Å	2.9225(120) Å	151.374(324)°	1- <i>x</i> , 2- <i>y</i> , 1+ <i>z</i>

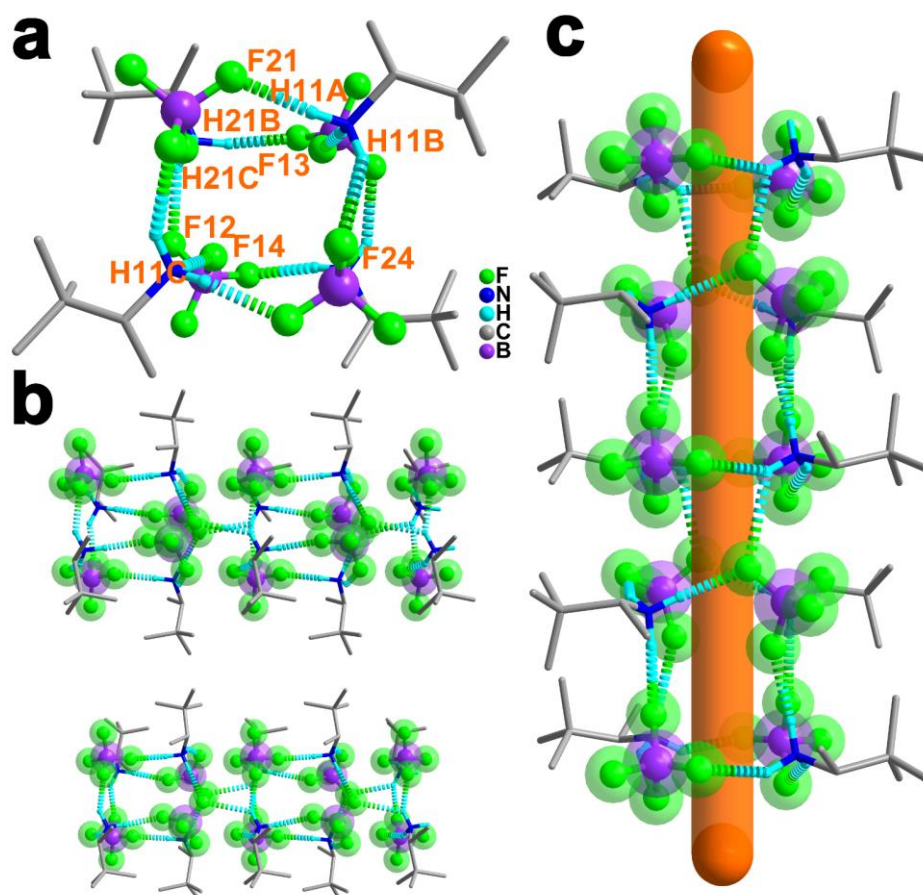


Figure 3A.4: N-H $\cdots$ F hydrogen bonding interactions in **DMBA•BF₄** at 120 K. (a) View of a tetrameric core of four cations and four anions in **DMBA•BF₄**. (b) Formation of a 1D-polymeric structure via the connection between the neighboring tetrameric motifs in the packing. (c) View of the 1D-helical structure present in **DMBA•BF₄**.

Table 3A.2: Hydrogen bonding parameters for **DMBA•BF₄** at 298 K.

D-H $\cdots$ A	d(H $\cdots$ A) Å	d(D-A) Å	$\angle$ (DHA) °	Symmetry transformations to generate equivalent atoms
N(1)-H(1A) $\cdots$ F11'	1.9696(263) Å	2.8289(317) Å	162.038(1292) °	1-x, 2-y, z
N(1)-H(1B) $\cdots$ F13'	2.1240(232) Å	2.9339(283) Å	150.938(1176) °	1-x, 2-y, z
N(1)-H(1C) $\cdots$ F24	2.1715(276) Å	3.0606(245) Å	175.873(1158) °	1-x, 2-y, z
N(2)-H(2A) $\cdots$ F23'	2.0099(247) Å	3.887(30) Å	168.465(1266) °	1-x, 2-y, 1+z
N(2)-H(2B) $\cdots$ F21'	1.9368(292) Å	2.7617(317) Å	153.368(1371) °	x, y, 1+z
N(2)-H(2C) $\cdots$ F14	2.1248(184) Å	2.9971(305) Å	166.353(1628) °	x, y, 1+z

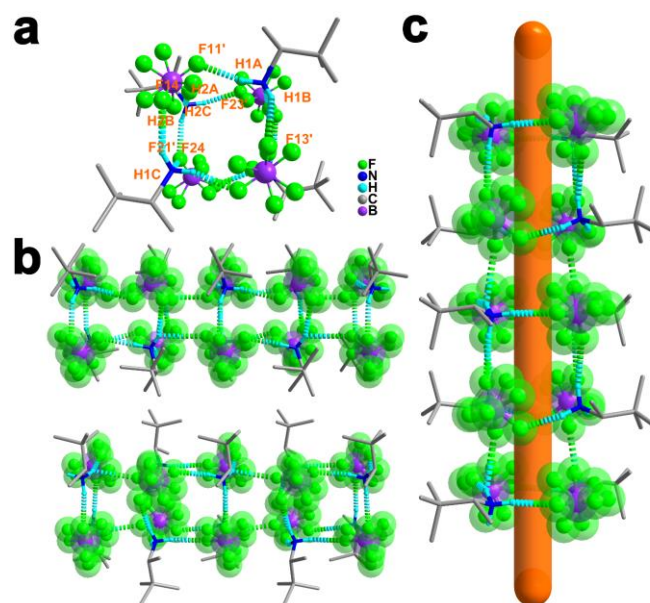


Figure 3A.5: N-H $\cdots$ F hydrogen bonding interactions in **DMBA•BF₄** at 298 K. (a) View of a tetrameric core of four cations and four anions in **DMBA•BF₄**. (b) Formation of a 1D-polymeric structure via the connection between the neighboring tetrameric motifs in the packing. (c) View of the 1D-helical structure present in **DMBA•BF₄**.

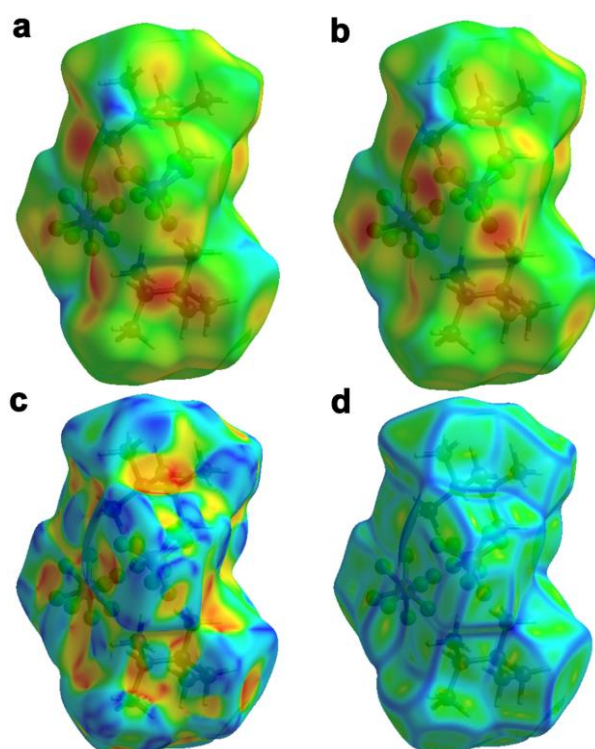


Figure 3A.6: The 3D color mapping derived from the Hirshfeld surface analysis of **DMBA•BF₄** (298 K) showing (a) d_i , (b) d_e , (c) shape index, and (d) curvedness.

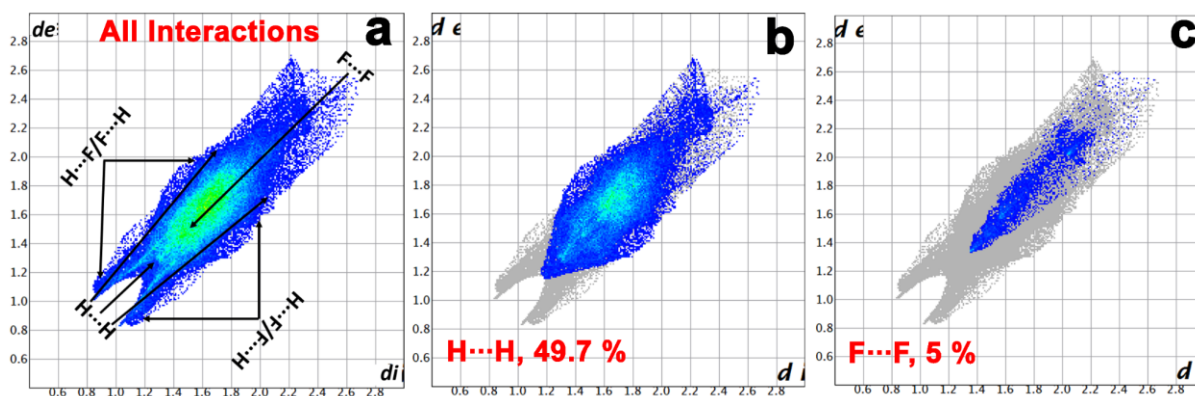


Figure 3A.7: 2D fingerprint (d_e vs d_i) plot of **DMBA•BF₄** (298 K) showing (a) all the possible interactions and the percentages of (b) H...H and (c) F...F interactions in the molecule.

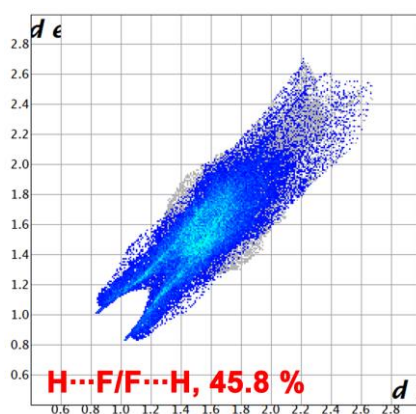


Figure 3A.8: 2D fingerprint (d_e vs d_i) plot of **DMBA•BF₄** (298 K) showing the H...F/F...H interactions in the molecule.

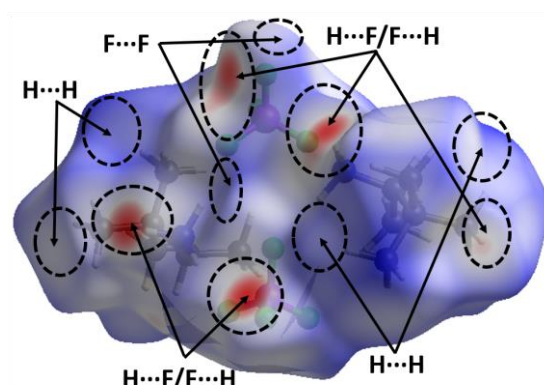


Figure 3A.9: The 3D color mapping derived from the Hirshfeld surface analysis showing all interactions present in **DMBA•BF₄** (120 K).

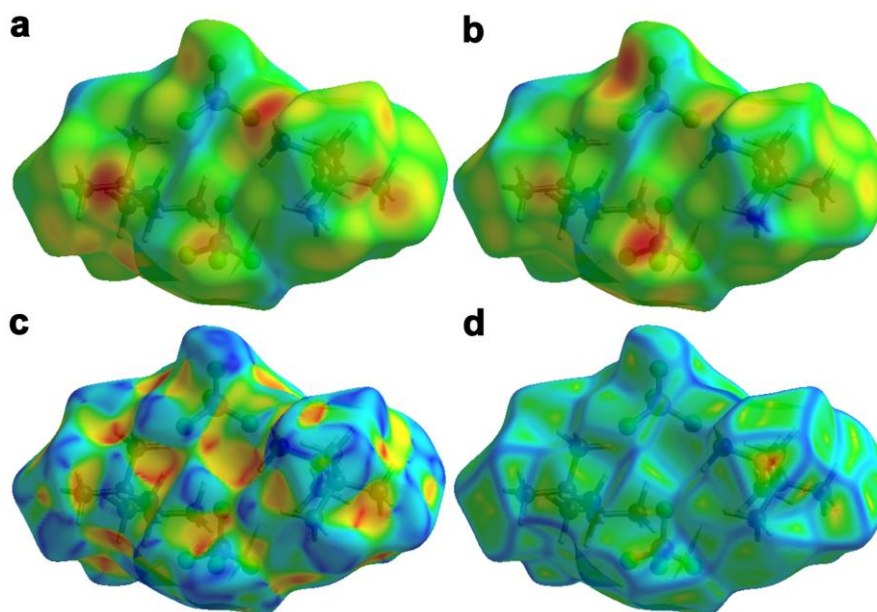


Figure 3A.10: The 3D color mapping derived from the Hirshfeld surface analysis of **DMBA•BF₄** (120 K) showing (a) d_i , (b) d_e , (c) shape index, (d) curvedness.

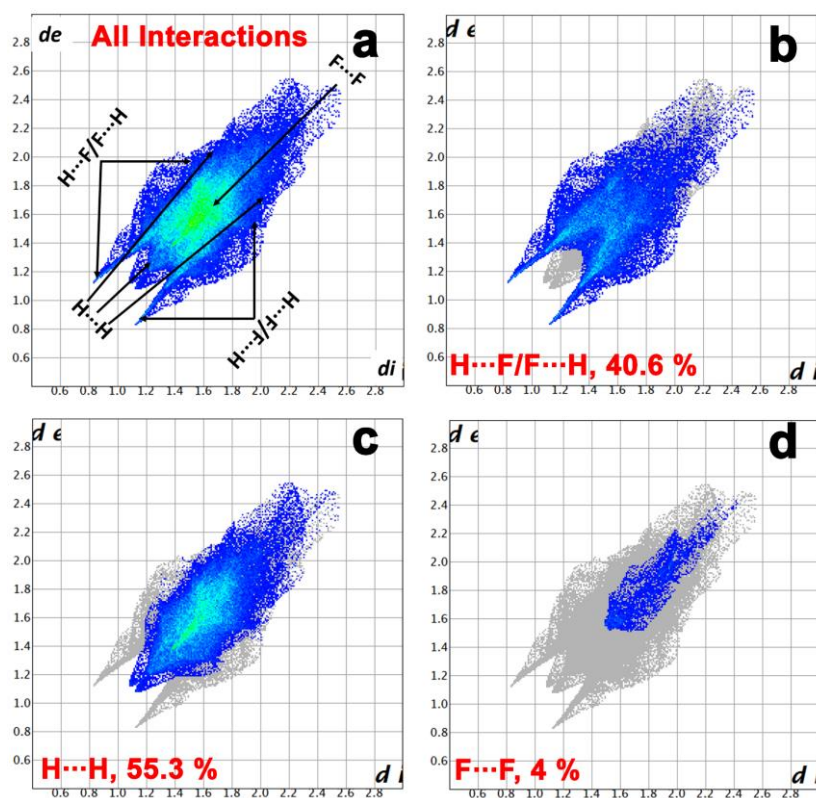


Figure 3A.11: 2D fingerprint (d_e vs. d_i) plot of **DMBA•BF₄** (120 K) showing (a) all the possible interactions and the percentages of (b) $\text{H}\cdots\text{H}$ and (c) $\text{F}\cdots\text{F}$ interactions in the molecule.

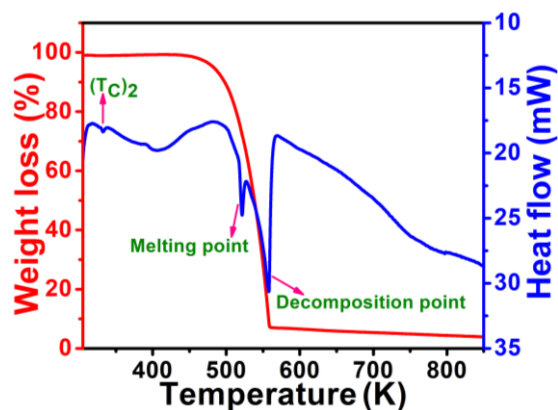


Figure 3A.12: The thermogravimetric-differential thermal analysis profile of **DMBA•BF₄**.

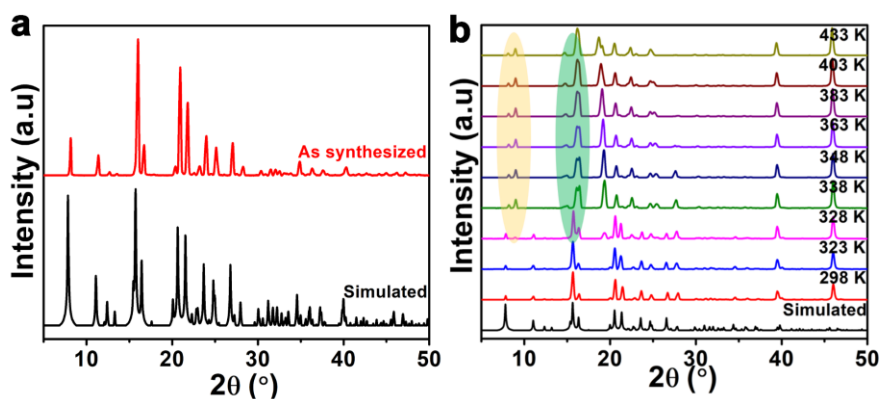


Figure 3A.13: The (a) room temperature and (b) variable temperature powder X-ray diffraction profile of **DMBA•BF₄** along with its simulated profiles from the 298 K single-crystal data.

Table 3A.3: Indexed PXRD unit cell parameters for **DMBA•BF₄** at HTP 348 K.

Crystal System	Tetragonal	
Space Group	$P4_22_12$	
Cell Parameters	ESDs	
a (Å)	11.65053	0.012
b (Å)	11.65053	0.012
c (Å)	13.90133	0.022
α (°)	90	0
β (°)	90	0
γ (°)	90	0
V (Å ³)	1886.896	0

The PXRD data of **DMBA•BF₄** at 348 K was analysed using Highscore Plus software suit. McMaille method was used to index the pattern and the cell parameters were refined for zero 2 θ shift.

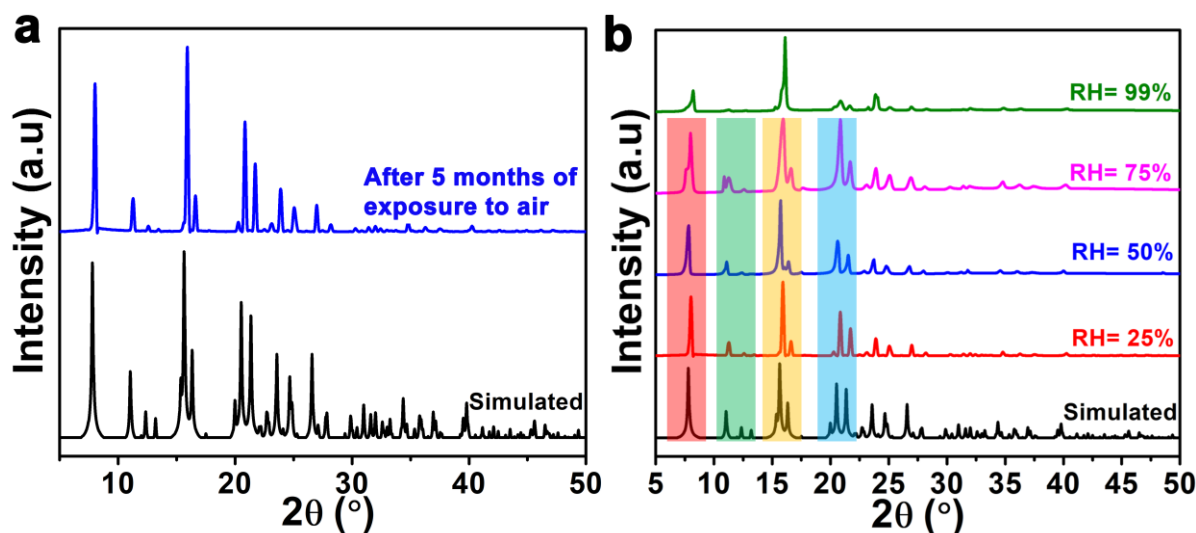


Figure 3A.14: PXRD profile of **DMBA•BF₄** (a) after 5 months of preparation and (b) kept at different humid conditions at 298 K.

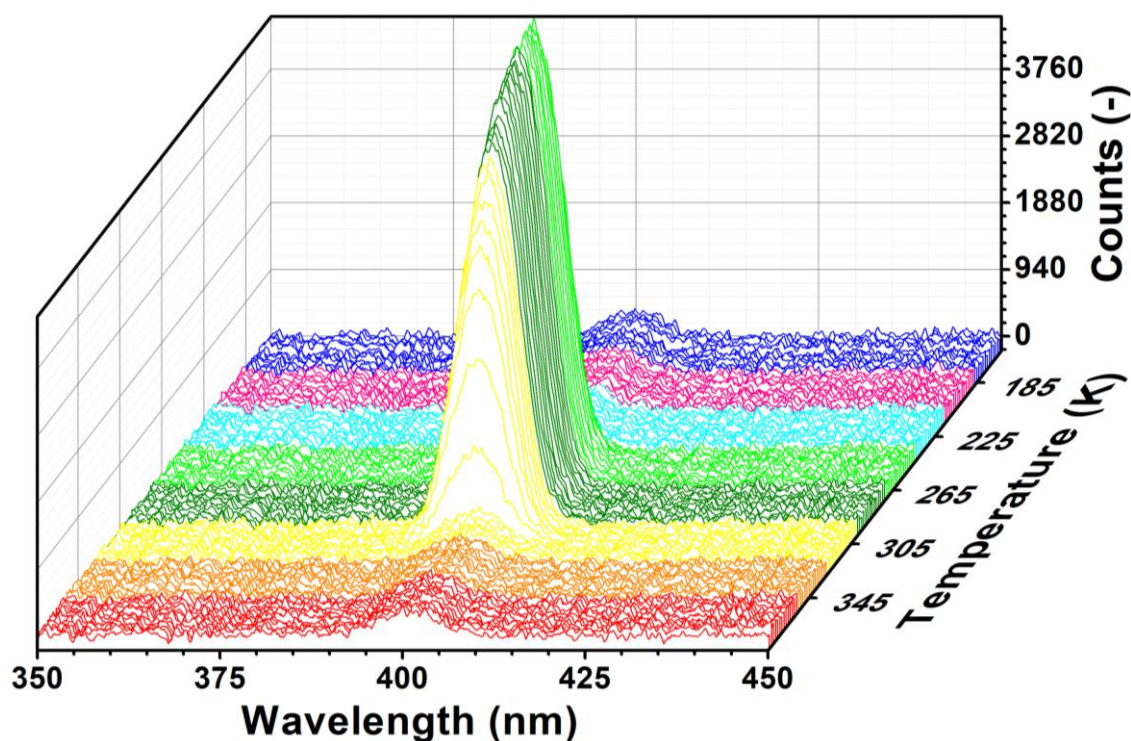


Figure 3A.15: The temperature dependent SHG activity of **DMBA•BF₄**.

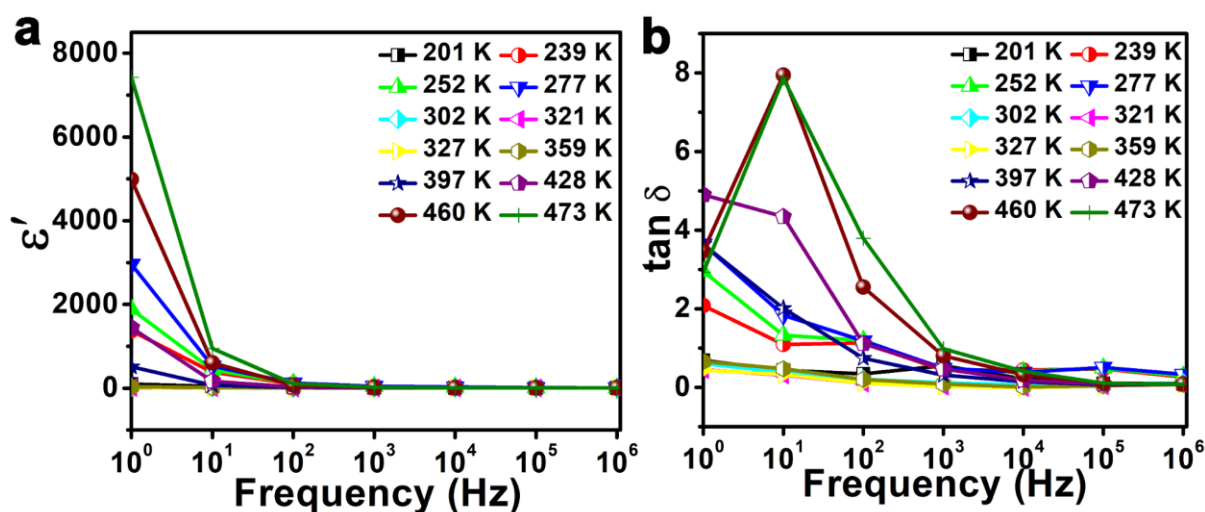


Figure 3A.16: Frequency dependent (a) dielectric permittivity and (b) dielectric loss plots of **DMBA•BF₄**.

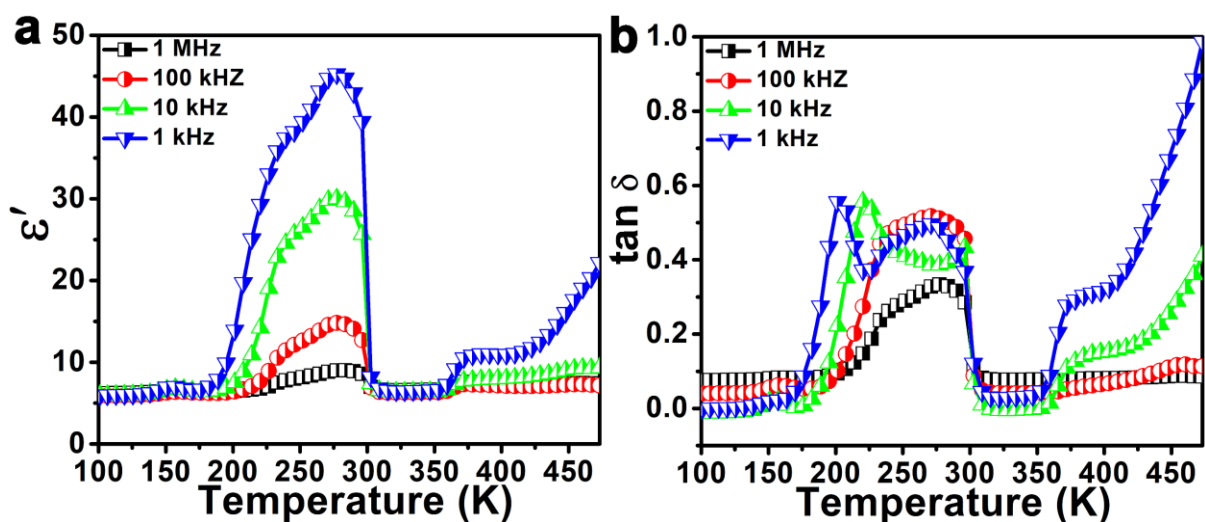


Figure 3A.17: Temperature dependent (a) dielectric permittivity and (b) dielectric loss plots of **DMBA•BF₄**.

Table 3A.4: Dipole moment calculation of **DMBA•BF₄**.

Temperature	Ferroelectric Material	Dipole moment in Debye unit (D)
120 K	DMBA•BF₄	18.4
298 K	DMBA•BF₄	17.7

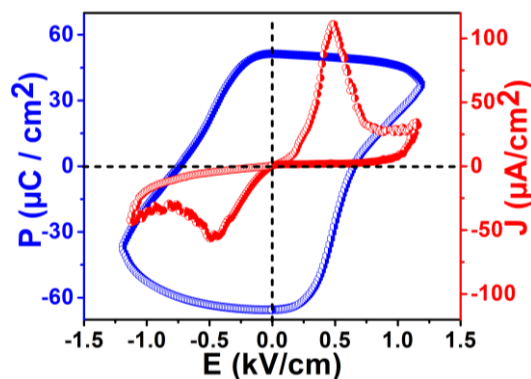


Figure 3A.18: The P-E hysteresis analysis of **DMBA•BF₄** at 218 K showing a higher polarization value of $37.90 \mu\text{C cm}^{-2}$ at 0.1 Hz frequency with a slightly higher E_c of 0.65 kV cm^{-1} .

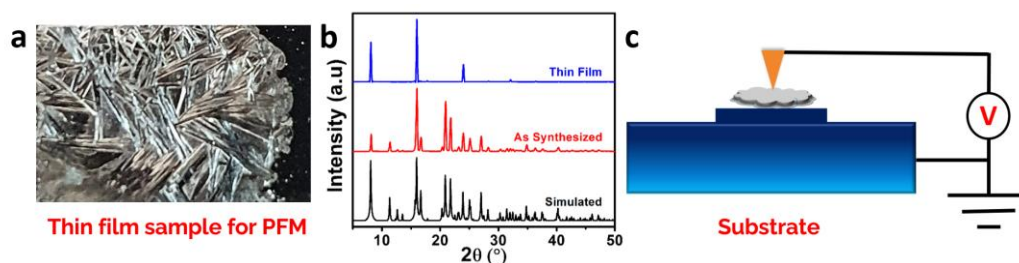


Figure 3A.19: The thin film sample of **DMBA•BF₄** (left) employed for the PFM measurement. The schematic diagram showing the PFM experiment (right).

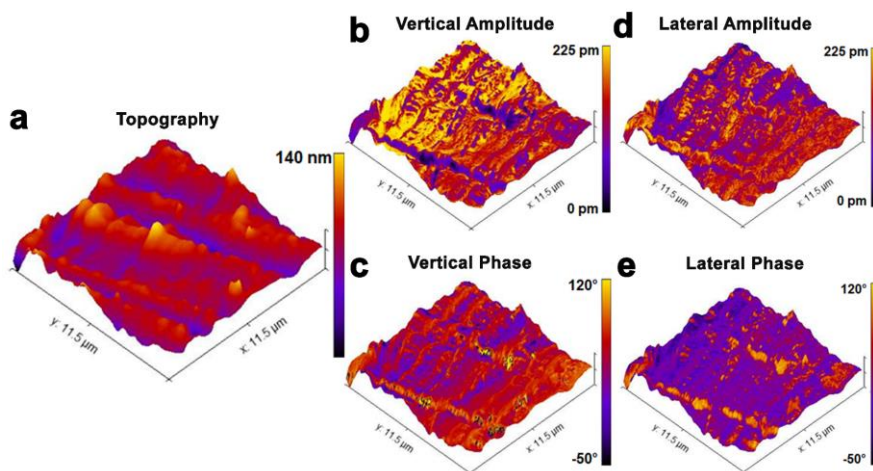


Figure 3A.20: The vector PFM data of a thin film sample of **DMBA•BF₄** showing the (a) blank 3D-topography image (b) 3D-vertical amplitude, (c) 3D-vertical phase, (d) 3D-lateral amplitude, (e) 3D-lateral phase images over laid on the corresponding topography.

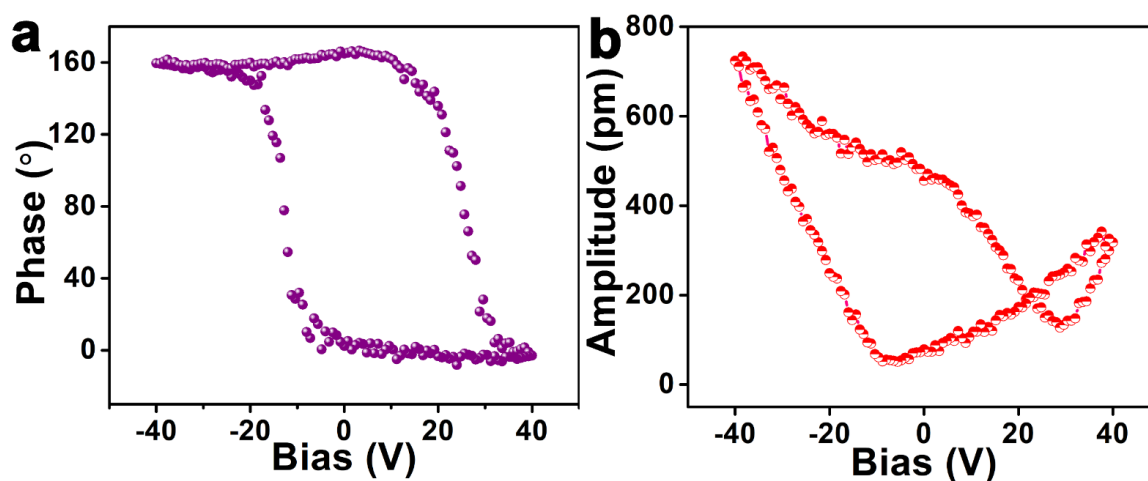


Figure 3A.21: The ± 40 V bias (a) Phase hysteresis loop and (b) Amplitude-bias butterfly loop of $\text{DMBA} \cdot \text{BF}_4$.

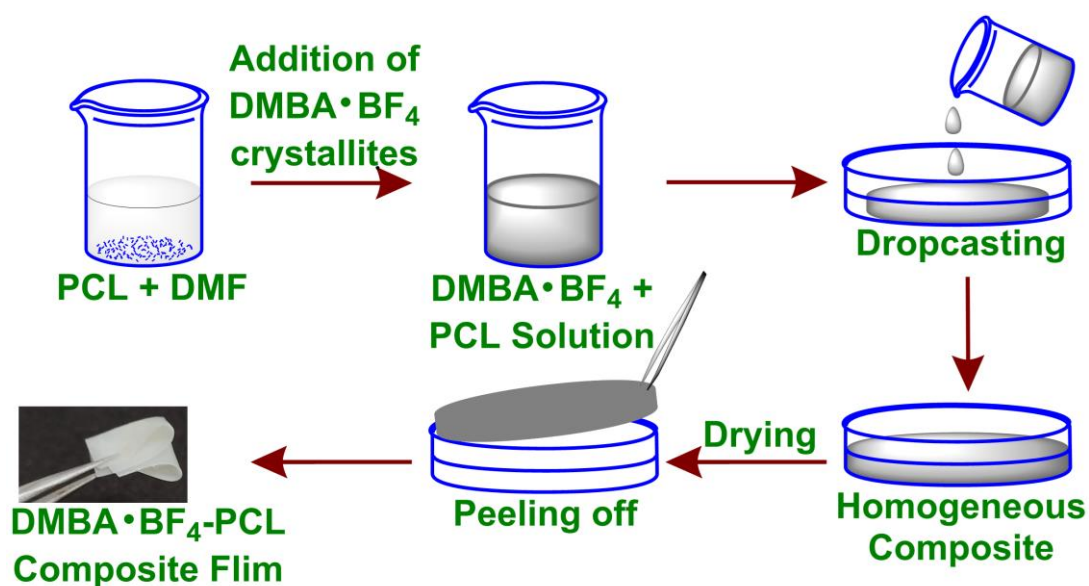


Figure 3A.22: Schematic for the preparation of $\text{DMBA} \cdot \text{BF}_4$ -PCL composite films.

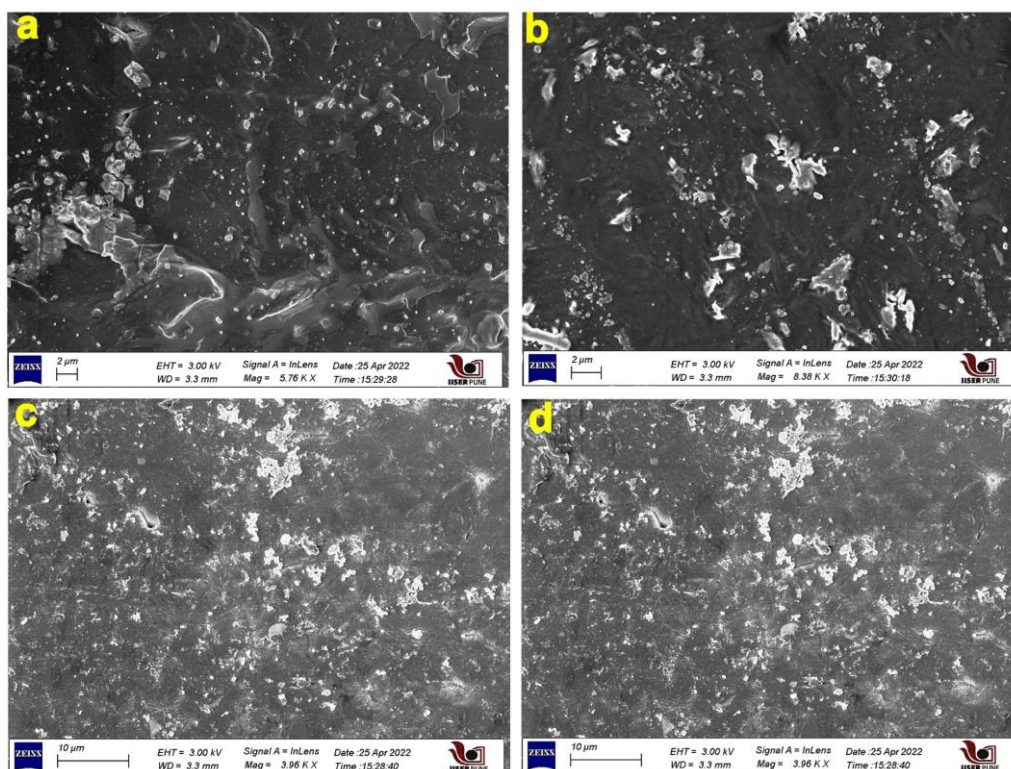


Figure 3A.23: SEM images of 5 wt% DMBA•BF₄-PCL composite.

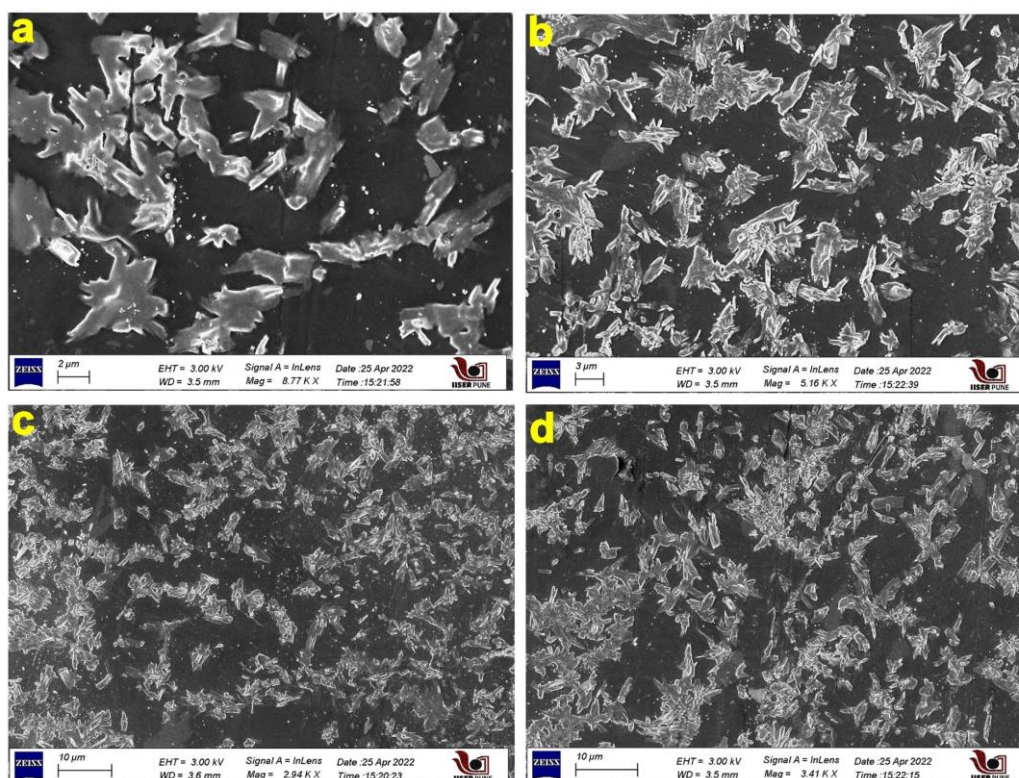


Figure 3A.24: SEM images of 10 wt% DMBA•BF₄-PCL composite.

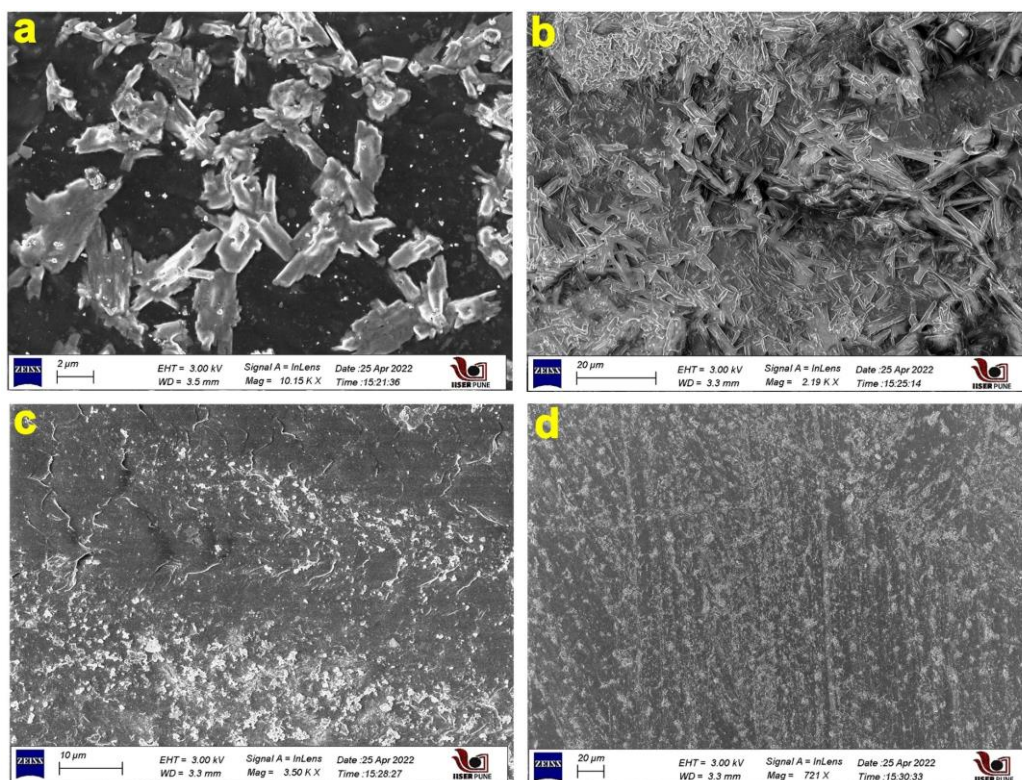


Figure 3A.25: SEM images of 15 wt% **DMBA•BF₄**-PCL composite.

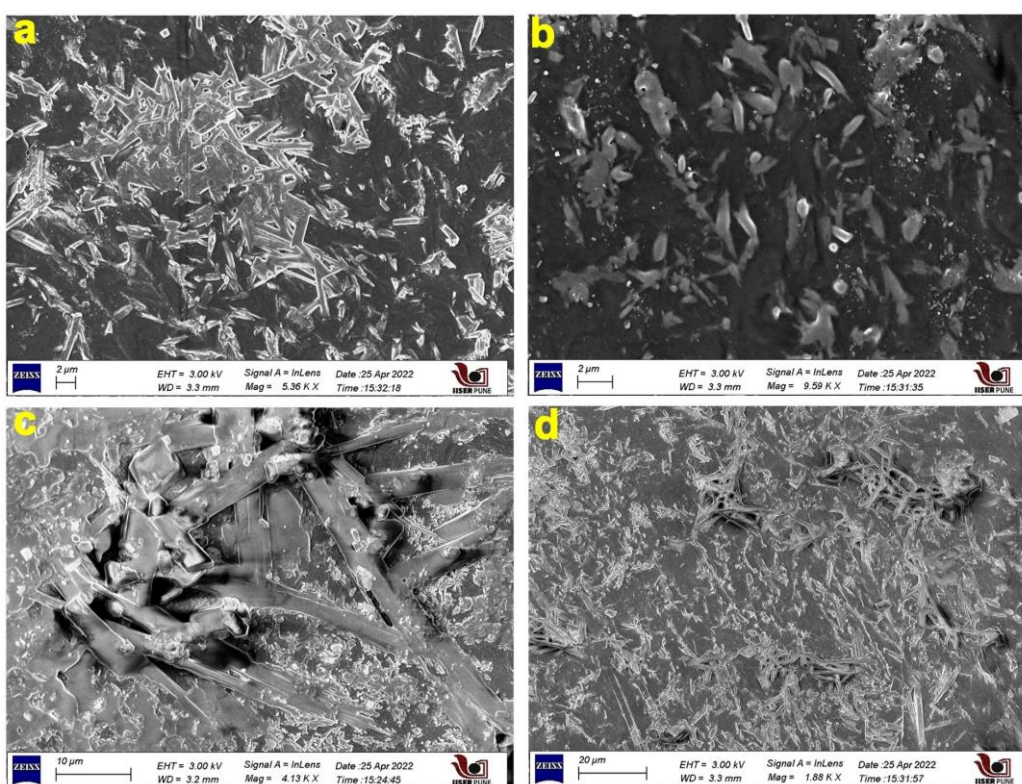


Figure 3A.26: SEM images of 20 wt% **DMBA•BF₄**-PCL composite.

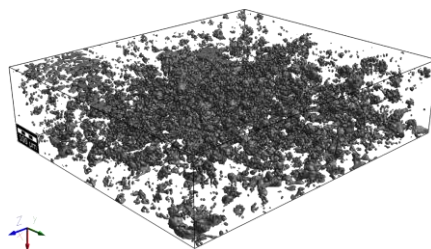


Figure 3A.27: The 3D visualization of the **DMBA•BF₄** crystallites in the polymer matrix of 10 wt% **DMBA•BF₄**-PCL composite film (the polymer background was corrected to visualize the spatial distribution of the crystallites of **DMBA•BF₄** in the matrix) (scale bar is 100 microns).

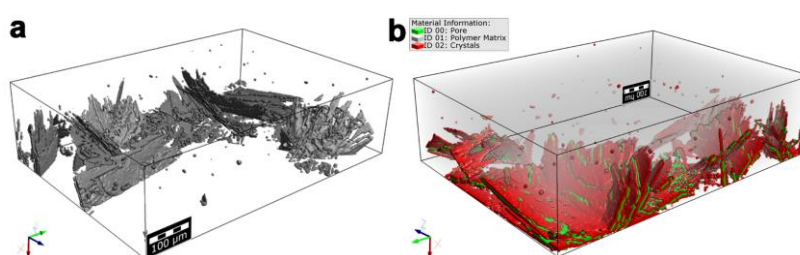


Figure 3A.28: The X-ray 3D-microtomography (a) 3D visualization of the **DMBA•BF₄** crystallites in the polymer matrix (the polymer background was corrected to visualize the spatial distribution of the crystallites of **DMBA•BF₄** in the matrix) and (b) 3D visualization of the **DMBA•BF₄** crystallites along with the polymer matrix in the 5 wt% **DMBA•BF₄**-PCL composite films (red colour represents crystals and green represents void volume) (scale bar is 100 microns).

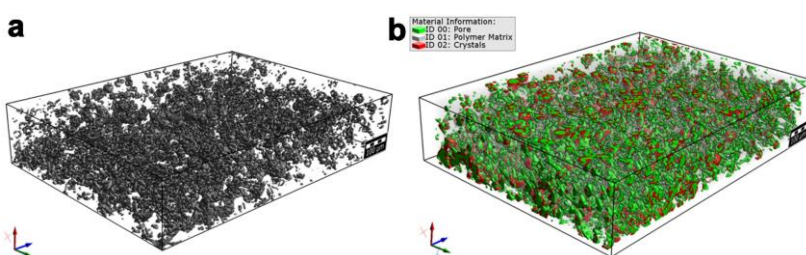


Figure 3A.29: The X-ray 3D-microtomography (a) 3D visualization of the **DMBA•BF₄** crystallites in the polymer matrix (the polymer background was corrected to visualize the spatial distribution of the crystallites of **DMBA•BF₄** in the matrix) and (b) 3D visualization of the **DMBA•BF₄** crystallites along with the polymer matrix in the 20 wt% **DMBA•BF₄**-PCL composite film (red colour represents crystals and green represents void volume) (scale bar is 100 microns).

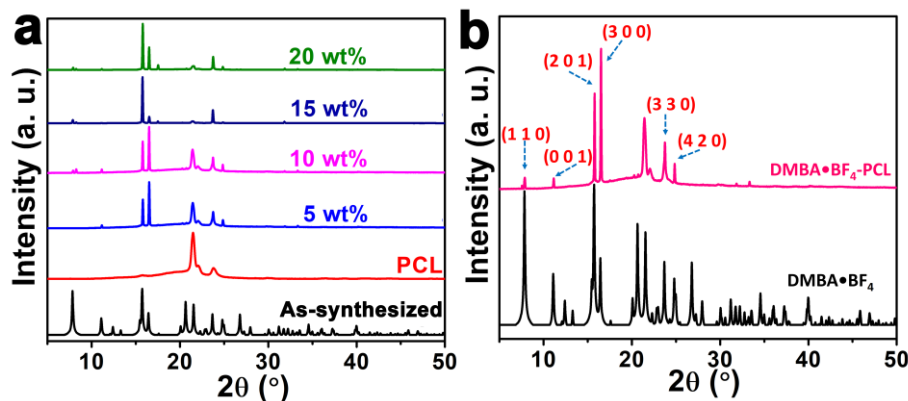


Figure 3A.30: The powder X-ray diffraction pattern and the characteristic hkl peaks for compound $\text{DMBA}\cdot\text{BF}_4$ and $\text{DMBA}\cdot\text{BF}_4$ -PCL composite film.

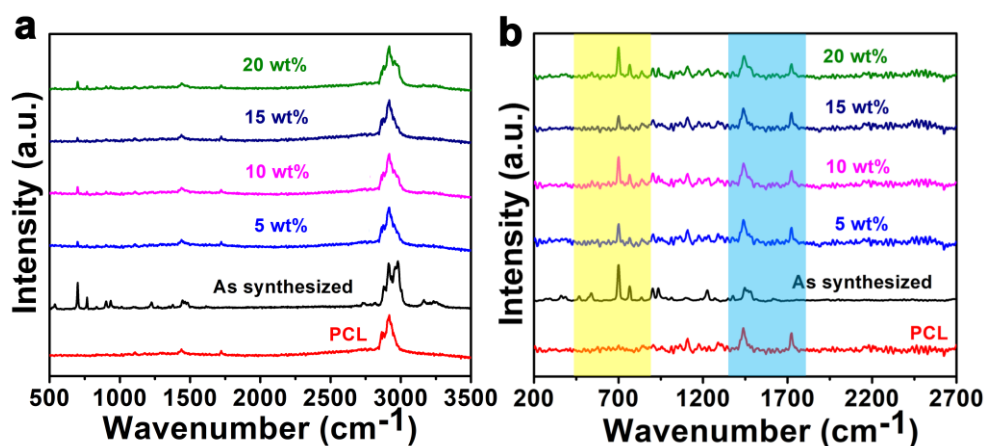


Figure 3A.31: Raman spectral profile of all the wt% $\text{DMBA}\cdot\text{BF}_4$ -PCL composite films compared to that of the neat compound $\text{DMBA}\cdot\text{BF}_4$ and polymer PCL.

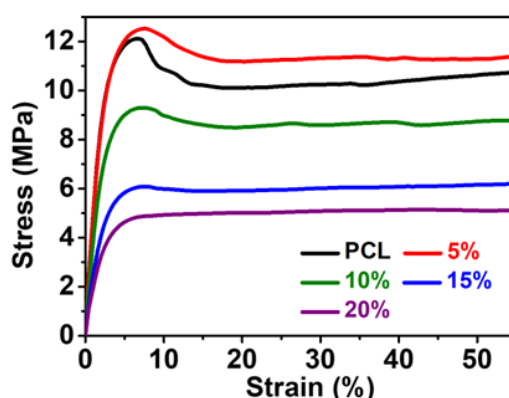


Figure 3A.32: The stress-strain profile of PCL and $\text{DMBA}\cdot\text{BF}_4$ -PCL composite films.

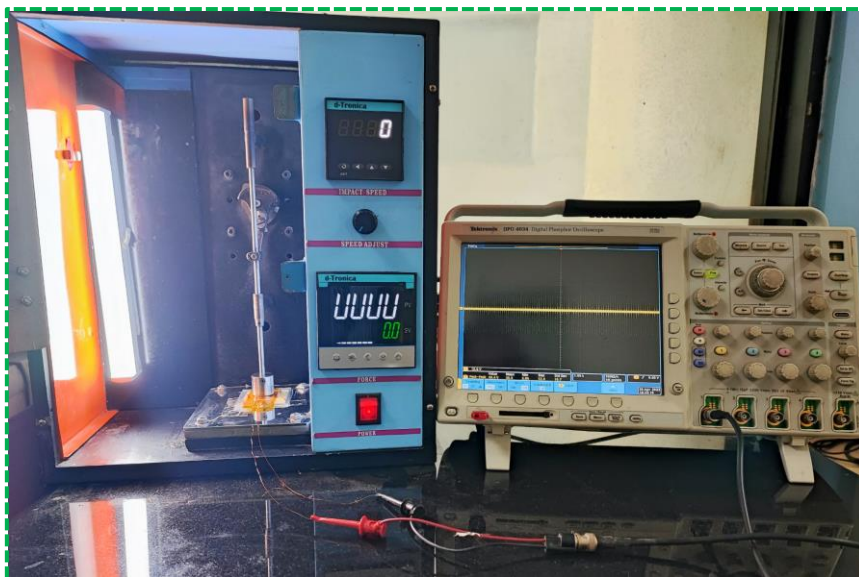


Figure 3A.33: Picture of the piezoelectric energy harvesting setup.

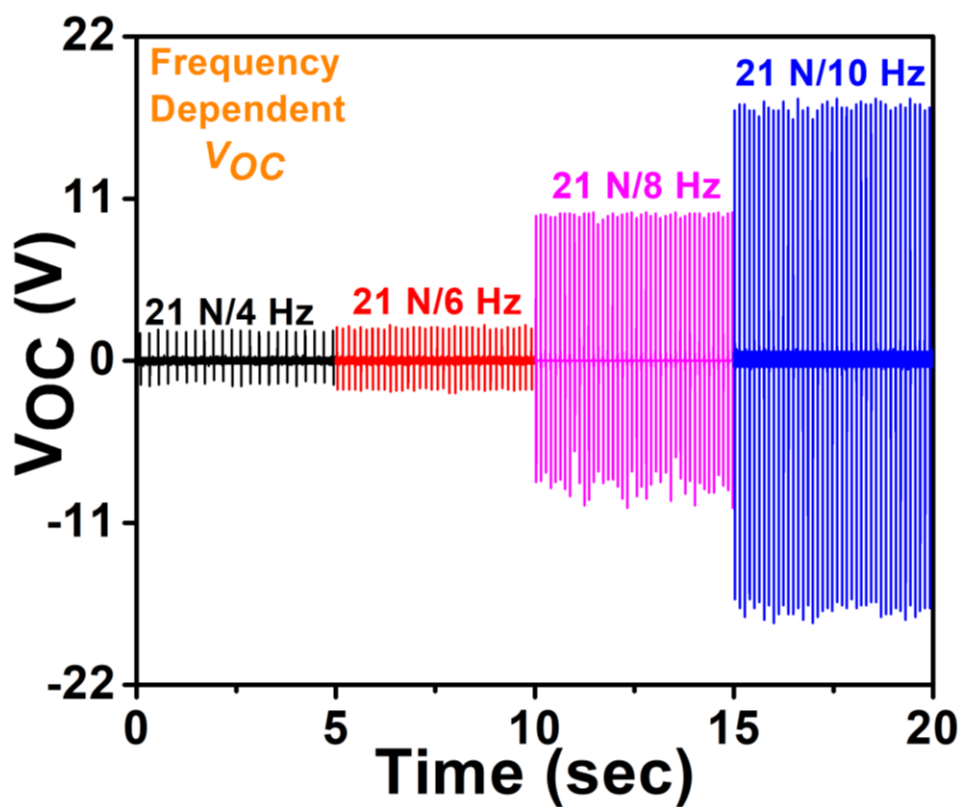


Figure 3A.34: Frequency dependent V_{OC-PP} of 10 wt% **DMBA•BF₄-PCL** under 21N applied force.

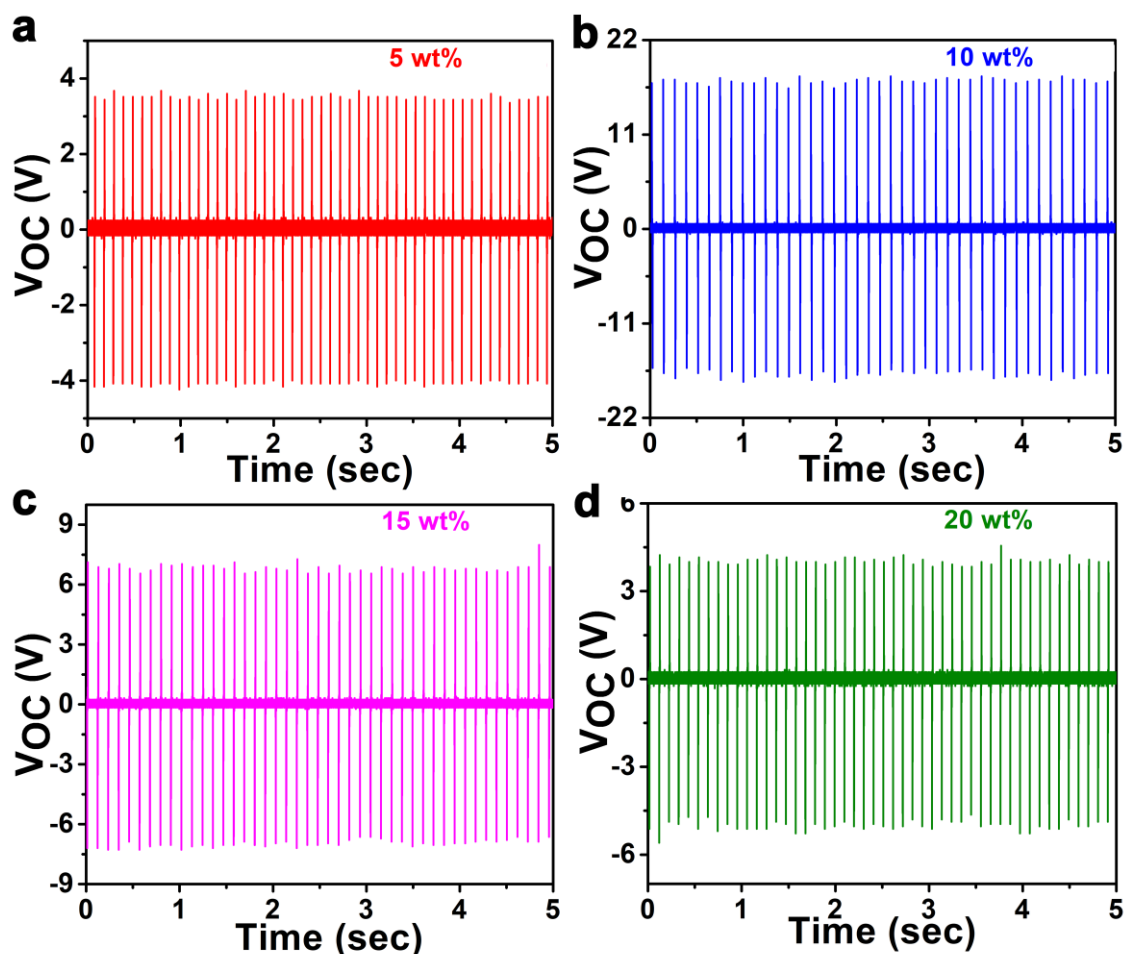


Figure 3A.35: Output voltage profiles of DMBA•BF₄-PCL composite devices.

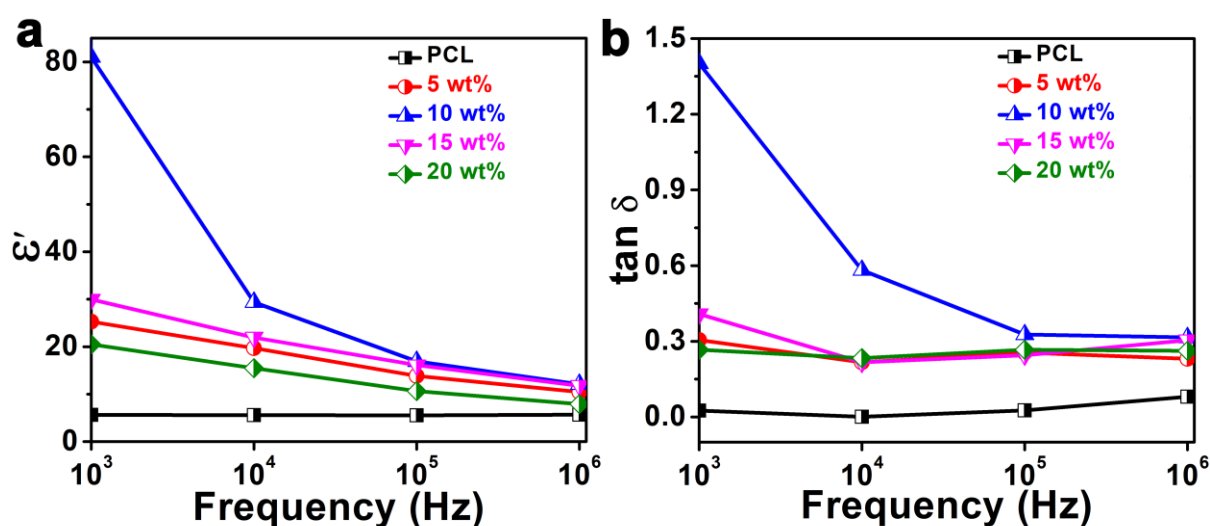


Figure 3A.36: Frequency dependant (a) real-part of dielectric permittivity and (b) dielectric loss data for all DMBA•BF₄-PCL composite films.

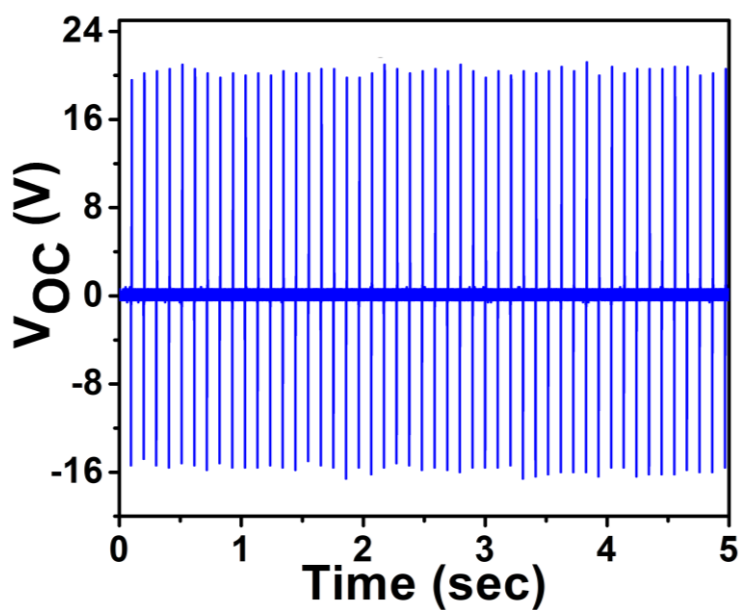


Figure 3A.37: The polarity-switching profile of 10 wt% **DMBA•BF₄**-PCL device.

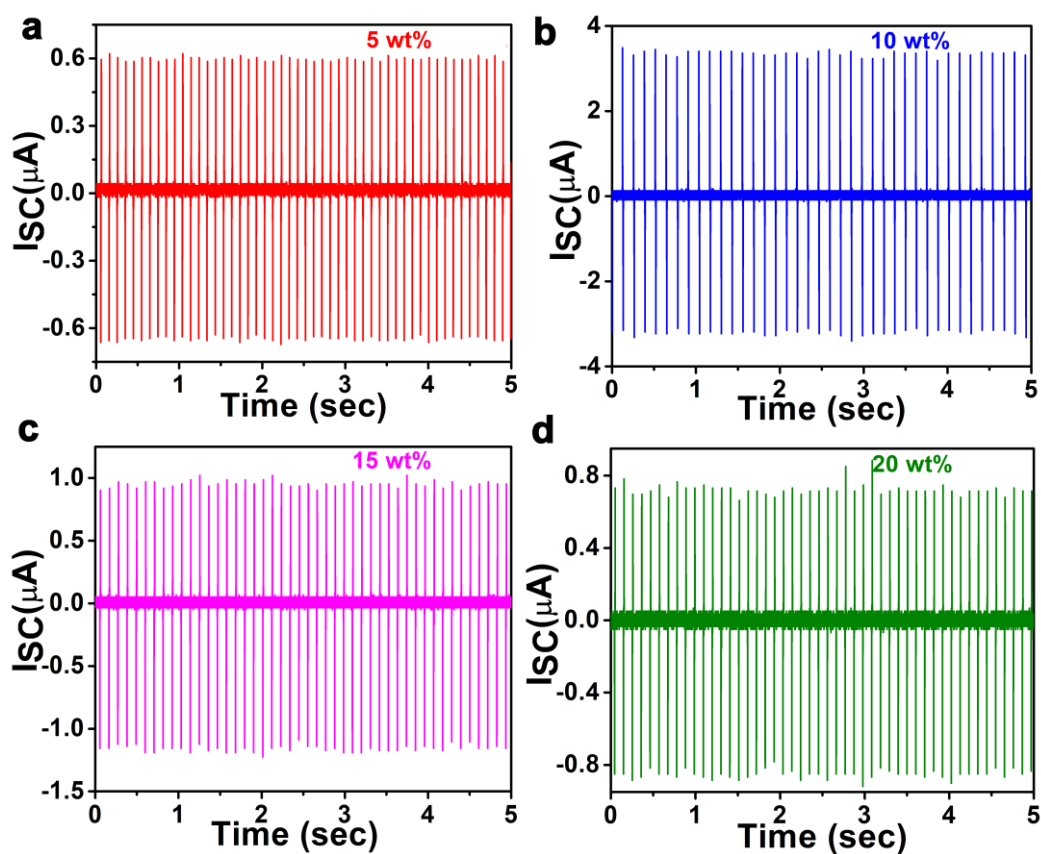


Figure 3A.38: The calculated output currents of all **DMBA•BF₄**-PCL composite devices.

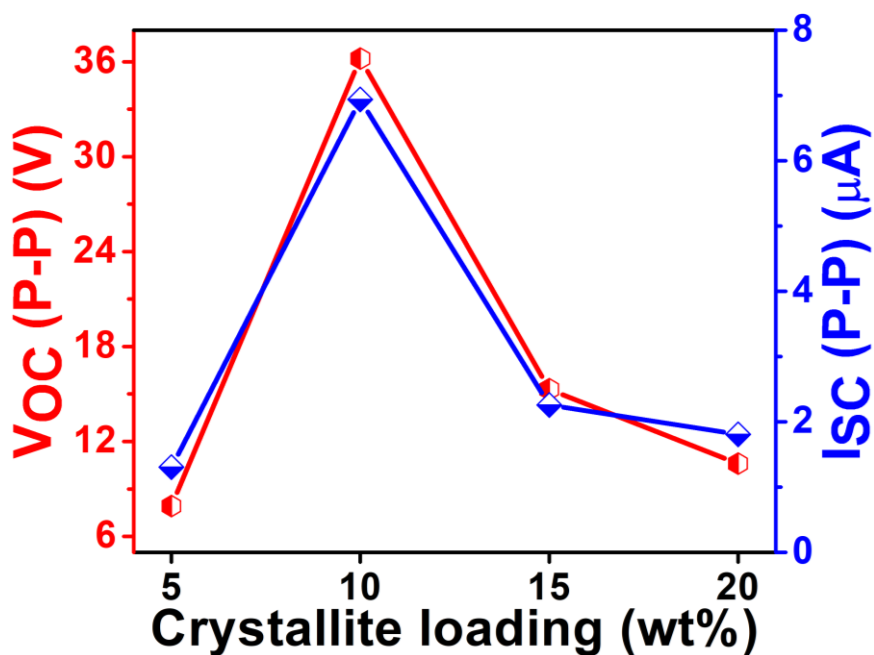


Figure 3A.39: Comparative diagram showing the observed trends in V_{OC-PP} and I_{PP} values of $DMBA \cdot BF_4$ -PCL composite devices.

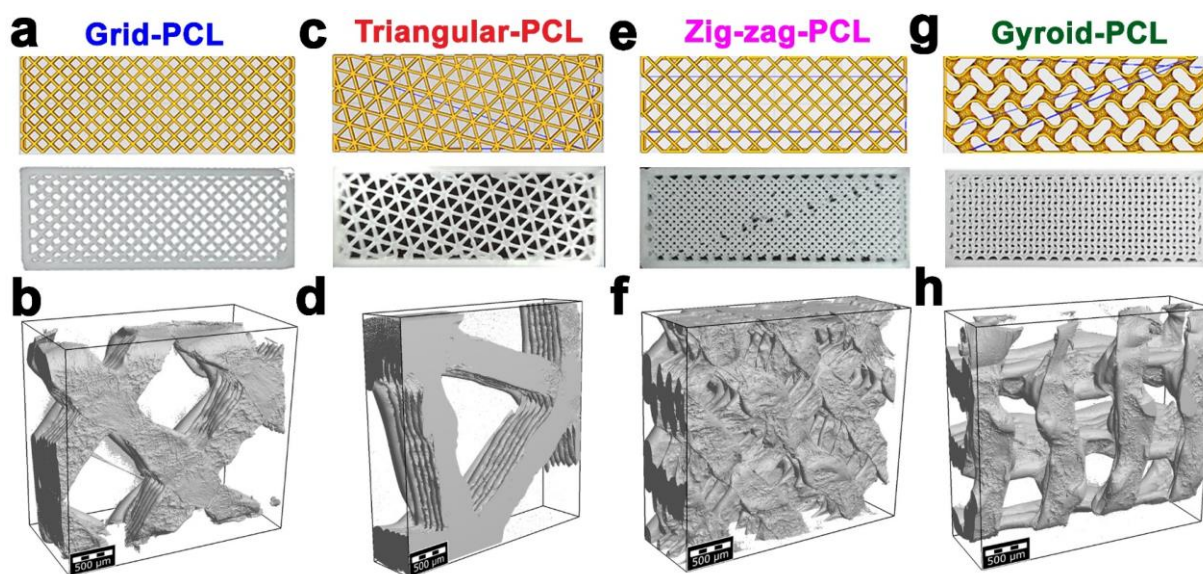


Figure 3A.40: The computerised pictorial representations and as made 3D-printed patterns of (a) Grid-PCL (c) Triangular-PCL (e) Zig-zag-PCL (g) Gyroid-PCL and the X-ray 3D-microtomography visualisation of (b) Grid-PCL (d) Triangular-PCL (f) Zig-zag-PCL (h) Gyroid-PCL 3D-printed shapes (scale bar is 500 microns).

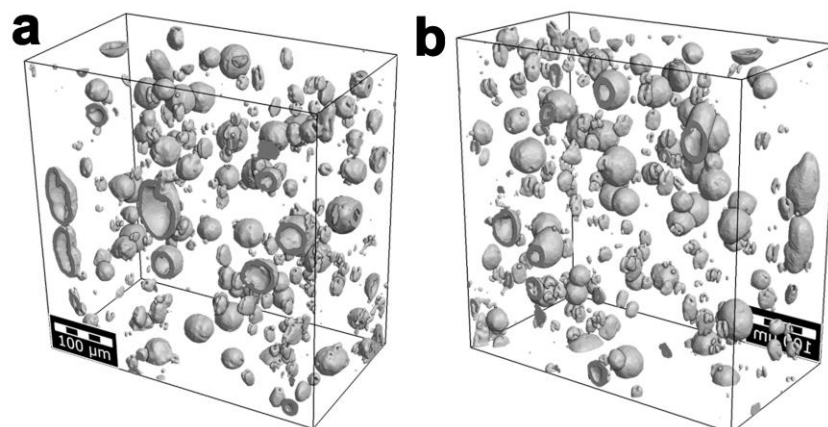


Figure 3A.41: (a) and (b) The X-ray 3D-microtomography visualization of the **DMBA•BF₄** crystallites in the 3D-printed **Gy-DMBA•BF₄-PCL** composite from the two opposite sides (the polymer background was corrected to visualize the spatial distribution of the crystallites of **DMBA•BF₄**) (scale bar is 100 microns).

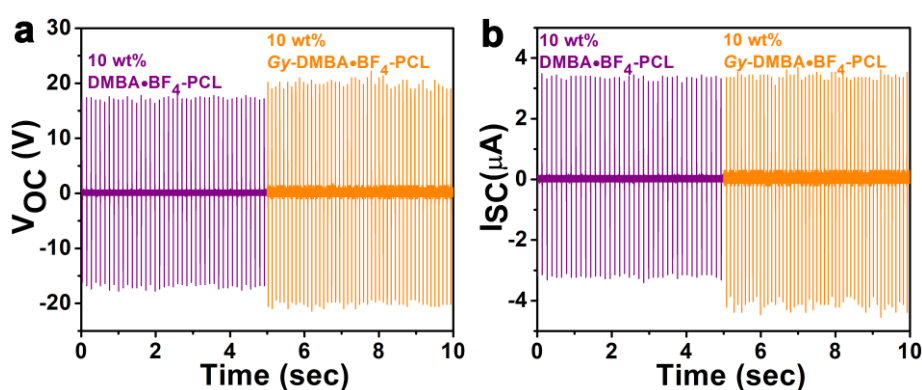


Figure 3A.42: The comparative (a) open-circuit voltage (V_{OC-PP}) and (b) calculated current (I_{PP}) profiles of 3D printed 10 wt% **Gy-DMBA•BF₄-PCL** to that of 10 wt% **DMBA•BF₄-PCL** thin film.

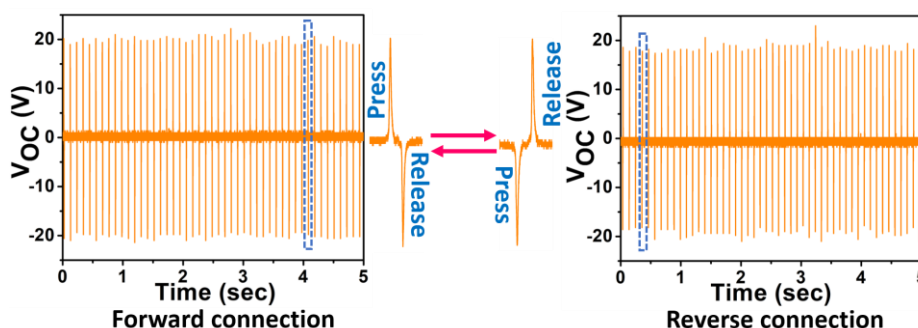


Figure 3A.43: The polarity-switching profile of 10 wt% **Gy-DMBA•BF₄-PCL**.

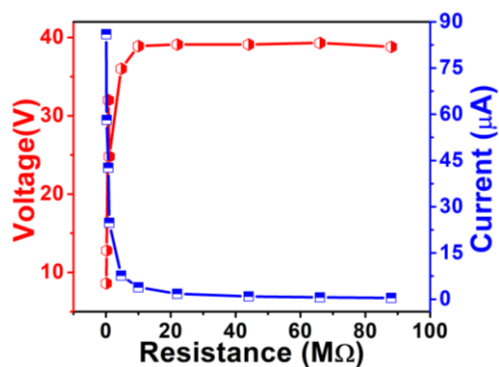


Figure 3A.44: The comparative output voltage and current data for 10 wt% **Gy-DMBA•BF₄-PCL** composite device under various load resistances.

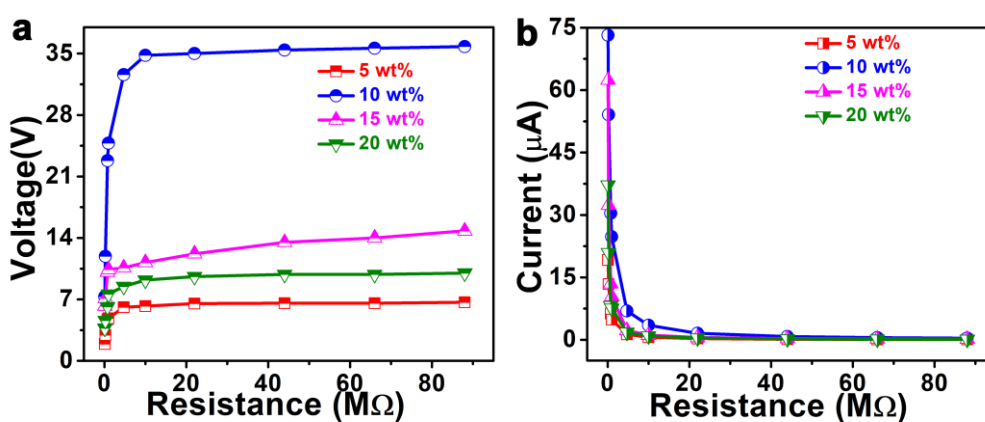


Figure 3A.45: The comparative output (a) voltage and (b) current data for all the **DMBA•BF₄-PCL** composite devices under various load resistances.

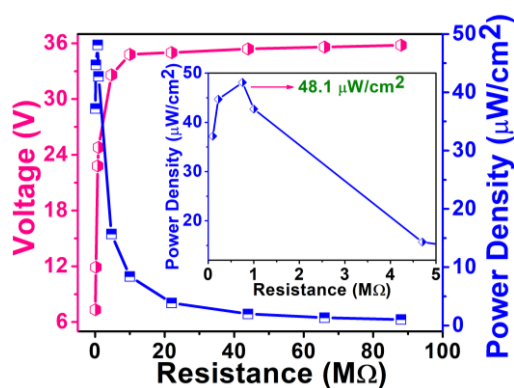


Figure 3A.46: Voltage (V) and power density (PD) values of the 10 wt% **DMBA•BF₄-PCL** composite device under different load resistances. The inset shows magnified view of the PD profile in the low resistance region showing the maximum value at 760 kΩ.

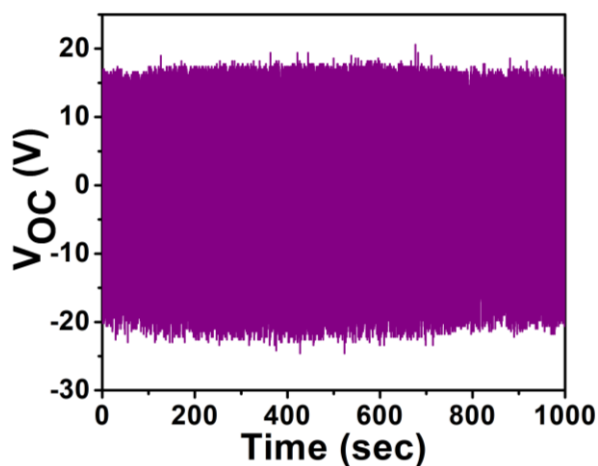


Figure 3A.47: The cyclic stability test of 10 wt% **Gy-DMBA•BF₄-PCL**.

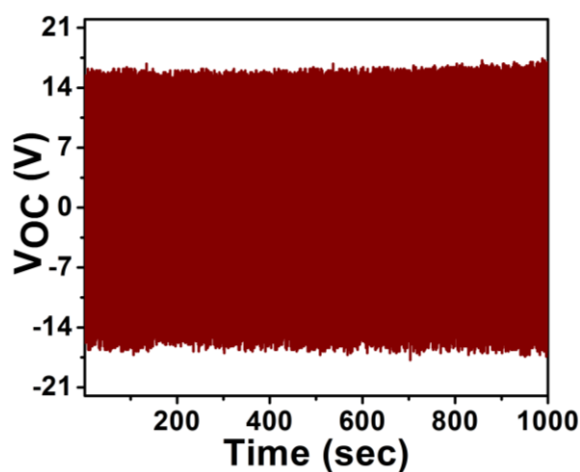


Figure 3A.48: The cyclic stability test of 10 wt% **DMBA•BF₄-PCL**.

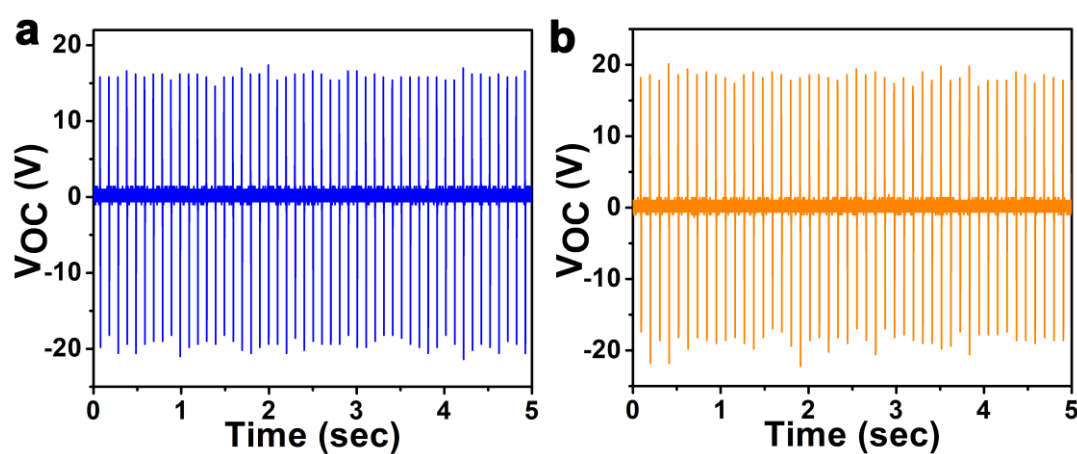


Figure 3A.49: Reproducibility of V_{OC-PP} of the (a) 10 wt% **DMBA•BF₄-PCL** and (b) 10 wt% **Gy-DMBA•BF₄-PCL** devices after 5 months.

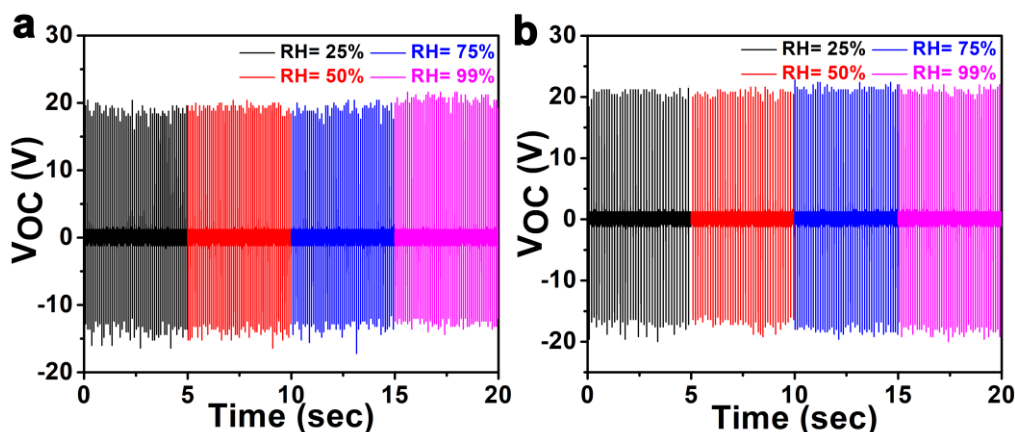


Figure 3A.50: V_{OC-PP} of (a) 10 wt% **DMBA•BF₄-PCL** and (b) 10 wt% **Gy-DMBA•BF₄-PCL** under different humid environments at 298 K.

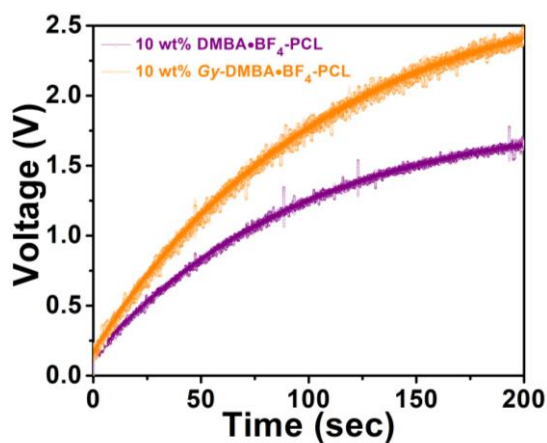


Figure 3A.51: The voltages stored in a 100 μ F capacitor by using the 10 wt% **Gy-DMBA•BF₄-PCL** and 10 wt% **DMBA•BF₄-PCL** devices.

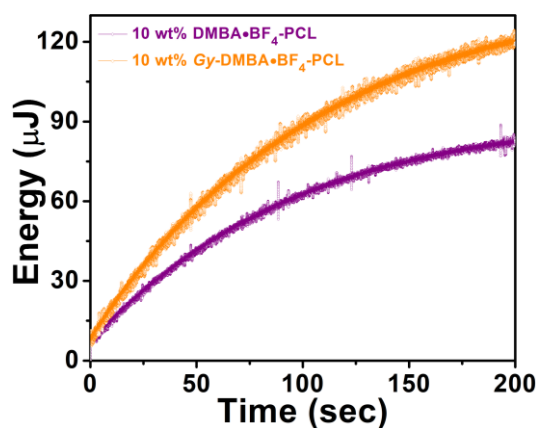


Figure 3A.52: The energies stored in a 100 μ F capacitor by using the 10 wt% **Gy-DMBA•BF₄-PCL** and 10 wt% **DMBA•BF₄-PCL** devices.

Table 3A.5: Comparison of output device performances of known composite energy harvesters made from organic and hybrid compounds.

Organic Composite Devices	Output Voltages	Current/Current density	Power/Power density	Active area
DPDP·PF ₆ /PDMS	8.5 V	0.28 $\mu\text{A cm}^{-2}$	0.14 $\mu\text{W cm}^{-2}$	1.8 x 1 cm^2
DPDP·PF ₆ /TPU	6.73 V	0.12 $\mu\text{A cm}^{-2}$	0.06 $\mu\text{W cm}^{-2}$	1.3 x 3 cm^2
DPDP·BF ₄ /TPU	8.95 V	0.23 $\mu\text{A cm}^{-2}$	0.20 $\mu\text{W cm}^{-2}$	1.3 x 3 cm^2
TPAP·BF ₄ /TPU	7.37 V	0.16 $\mu\text{A cm}^{-2}$	0.09 $\mu\text{W cm}^{-2}$	1.3 x 3 cm^2
TIAP·BF ₄ /TPU	4.75 V	0.11 $\mu\text{A cm}^{-2}$	0.04 $\mu\text{W cm}^{-2}$	1.3 x 3 cm^2
TMAB	10 V	4.46 μA	-	-
[Bn(4-BrBn)NMe ₂].BF ₄	20 V	4 μA	21.1 $\mu\text{W cm}^{-2}$	1750 mm^2
3NA@PCL	7 V	70 nA	21.1 nW cm^{-2}	4.0 cm^2
Boc-FF_PCL	22 V	-	-	4.0 cm^2
Boc-FF_PLLA	8 V	-	-	4.0 cm^2
Boc-FF_PMMA	8 V	-	-	4.0 cm^2
[Ph ₃ PMe] ₄ [CuCl ₄]	25 V	1.1 $\mu\text{A cm}^{-2}$	14. $\mu\text{W cm}^{-2}$	1.2 x 3 cm^2
{[^s CH(MePh)(Me)NH ₃][BiBr ₅]} _n	10.4 V	0.5 $\mu\text{A cm}^{-2}$	5.26 $\mu\text{W cm}^{-2}$	1.2 x 3 cm^2
[Ph ₃ MeP] ₄ [Ni(NCS) ₆]/TPU	19.29 V	3.59 $\mu\text{A cm}^{-2}$	2.51 mW cm^{-3} (50.26 $\mu\text{W cm}^{-2}$)	1.3 x 3 cm^2
(TMFM)FeBr ₄	2.2 V	-	-	-
[BnNMe ₃] ₂ CdBr ₄ /PDMS	52.9 V	0.23 $\mu\text{A cm}^{-2}$	13.8 $\mu\text{W cm}^{-2}$	3 x 3 cm^2
[BnNMe ₂ ⁿ Pr] ₂ CdBr ₄ /PDMS	63.8 V	0.59 $\mu\text{A cm}^{-2}$	37.1 $\mu\text{W cm}^{-2}$	3 x 3 cm^2
MAPbBr ₃ -PVDF	5 V	60 nA	0.28 $\mu\text{W cm}^{-2}$	2.4 x 1.5 cm^2
FAPbBr ₃ /PVDF	26.2 V	2.1 μA	18.4 $\mu\text{W cm}^{-2}$	3 cm^2
FAPbBr ₃ -PDMS	8.5 V	3.4 $\mu\text{A cm}^{-2}$	12 $\mu\text{W cm}^{-2}$	1 x 3 cm^2
CsPbBr ₃ @PVDF	103 V	170 $\mu\text{A cm}^{-2}$	14 $\mu\text{W cm}^{-2}$	0.80 cm^2
MASnI ₃ -PVDF	12 V	4.0 $\mu\text{A cm}^{-2}$	21.6 $\mu\text{W cm}^{-2}$	1 x 1 cm^2
PVDF-PLLA-SnO ₂ NF- MAPbI ₃	4.82 V	29.7 nA	-	0.25 x 0.25 cm^2
SnO ₂ NF-MAPbI ₃	1.02 V	10.32 nA	-	0.25 x 0.25 cm^2
MAPbI ₃ -PVDF	9.43 V	0.76 $\mu\text{A cm}^{-2}$	-	1 x 1 cm^2

10 wt% DMBA · BF₄ -PCL	36.2 V	6.9 μ A	48.1 μ W cm ⁻²	1.2 x 3 cm ²
10 wt% Gy-DMBA · BF₄ -PCL	41 V	7.6 μ A	56.8 μ W cm ⁻²	1.5 x 4 cm ²

Note: The overall energy harvesting performance of the composite devices depend on multiple factors, such as the ratio of the piezoelectric particles and the polymer used, materials dimensions (width, length and thickness), amount of piezoelectric crystallites in the film, phase purity of piezoelectric material, selection of polymer matrix, choice of electrode, active surface area between electrode and material, the magnitude of the applied mechanical force and operating frequency and the structural morphologies of the ferroelectric particles in the composite materials.

Note: DPDP·PF₆ = diphenyl diisopropylamino phosphonium hexafluorophosphate; TPU = thermoplastic polyurethane; DPDP·BF₄ = diphenyl diisopropylaminophosphonium tetrafluoro borate; TPAP·BF₄ = triphenyl isopropylaminophosphonium tetrafluoro borate; TIAP·BF₄ = tetraisopropylaminophosphonium tetrafluoro borate; TMAB = trimethylamine borane; PCL = polycaprolactone; PLLA = poly-L-lactic acid; PMMA = poly (methyl methacrylate); MAPbI₃ = methylammonium lead iodide; PVDF = polyvinylidene difluoride; PDMS = polydimethylsiloxane; FAPbBr₃ = formamidinium lead bromide; PLLA = poly(L-lactic acid); SnO₂ = tin oxide; NF = nanofiber; [BnNMe₃]₂CdBr₄ = N,N,N-trimethyl-1-phenylmethanaminium cadmium(II) bromide; [BnNMe₂ⁿPr]₂CdBr₄ = N-benzyl-N,N-dimethylpropan-1-aminium cadmium(II) bromide; (TMFM)FeBr₄ = trimethylfluoromethylammonium iron(III)bromide.

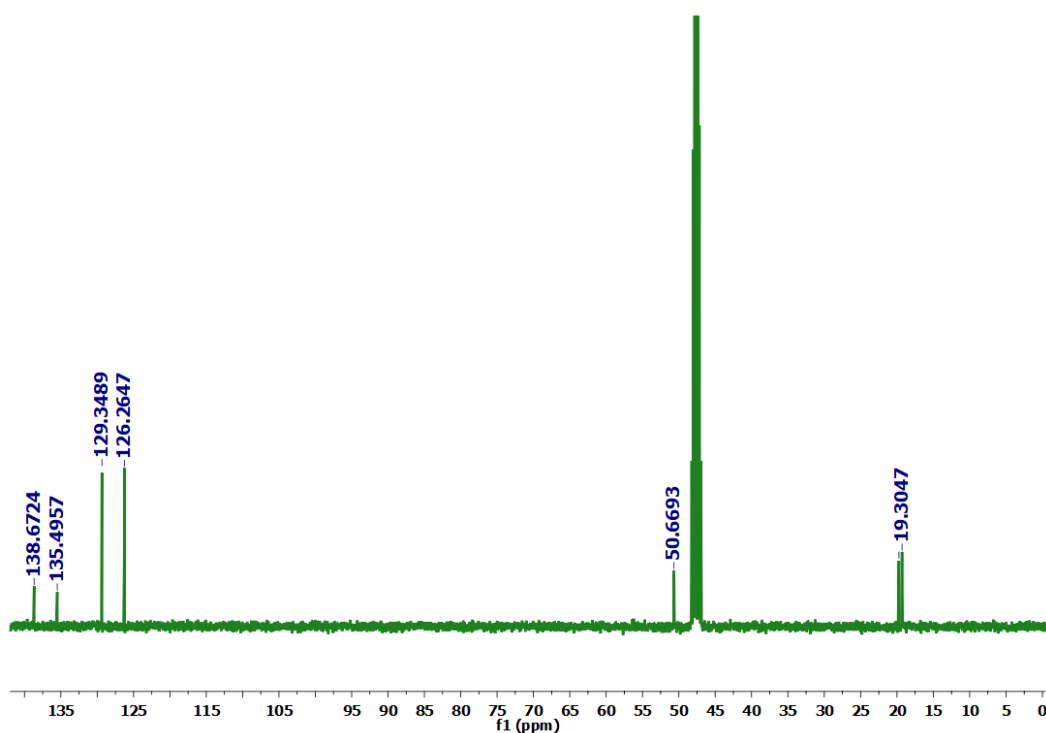


Figure 4A.1. The ^{13}C -NMR Spectrum of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

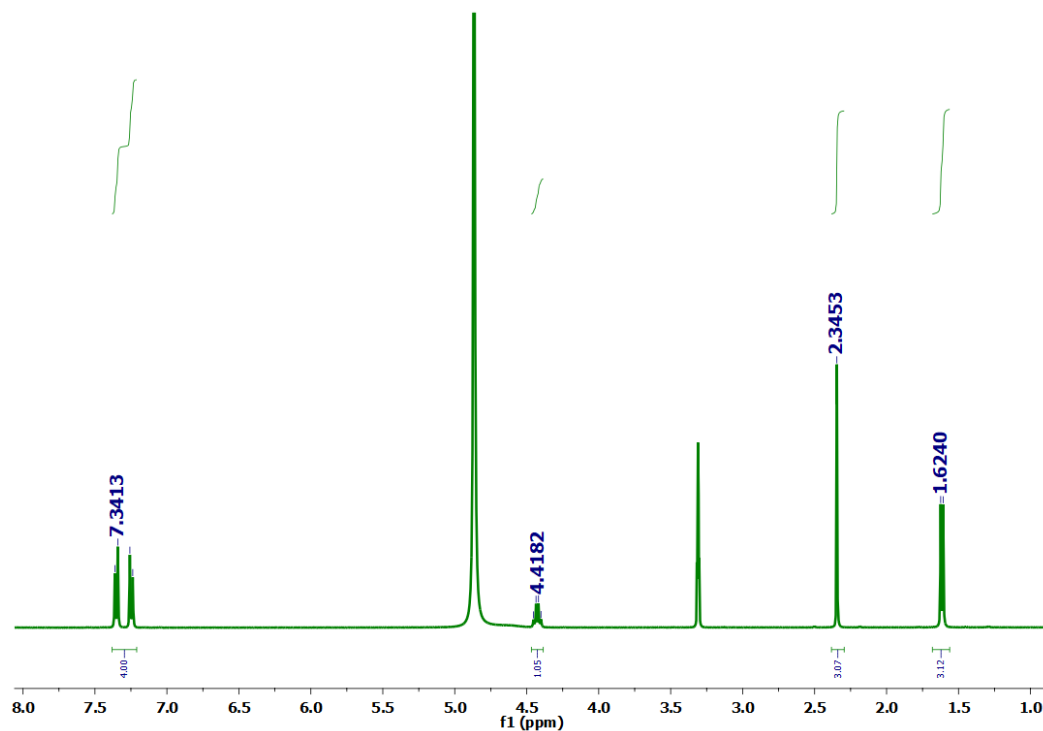


Figure 4A.2. The ^1H -NMR Spectrum of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

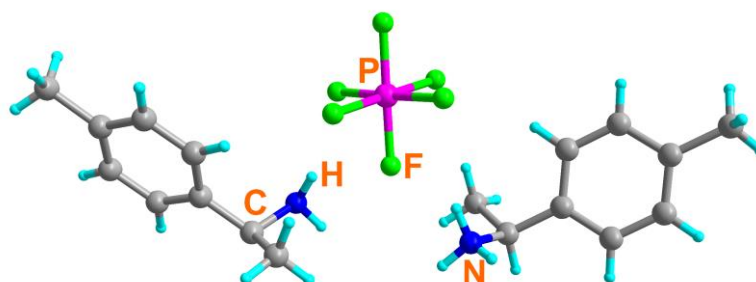


Figure 4A.3. The molecular structure of **(p-TEA)(p-TEAH)·PF₆** at 298 K. The disordered F-atoms are omitted for clarity.

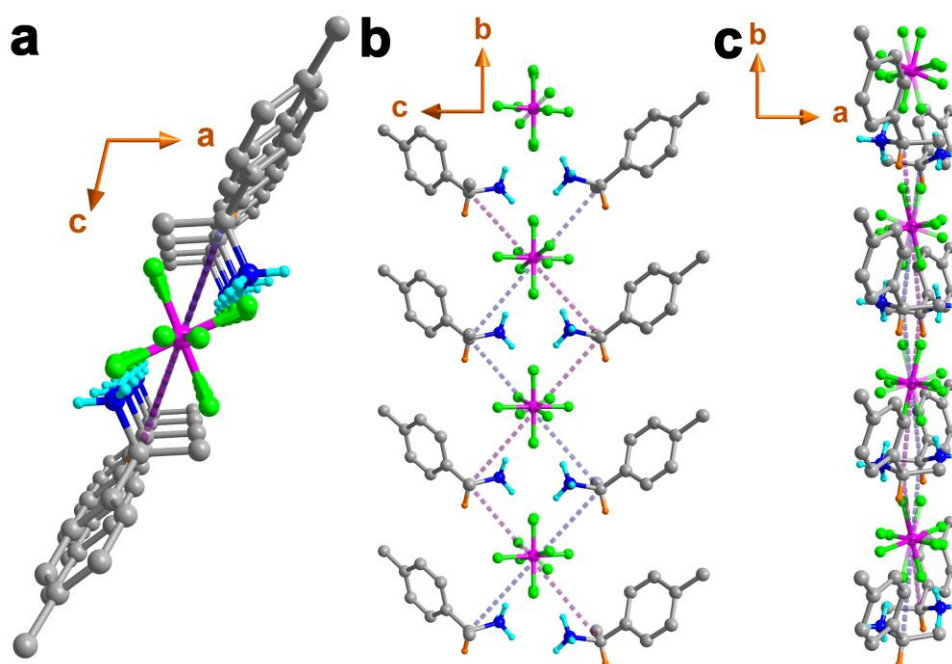


Figure 4A.4. The packing diagram of **(p-TEA)(p-TEAH)·PF₆** along (a) *a*-axis, (b) *b*-axis (c) *c*-axis at 100 K including the disordered F-atoms.

Table 4A.1. Hydrogen bonding parameters for **(p-TEA)(p-TEAH)·PF₆** at 100 K (without disorder).

D-H...A	d(H...A) Å	d(D-A) Å	<(DHA) °	Symmetry transformations to generate equivalent atoms
N(1)-H(1A)···F1	1.8394(21)Å	2.7401(38) Å	169.853(207) °	-1.5+x, -1.5+y, z
N(1)-H(1B)···F2	1.7576(83)Å	2.6116(95) Å	155.237(305) °	-1-x, -1+y, 1-z
N(1)-H(1C)···F3	1.7856(91)Å	2.5666(95) Å	142.274(298) °	-1+x, -2+y, z

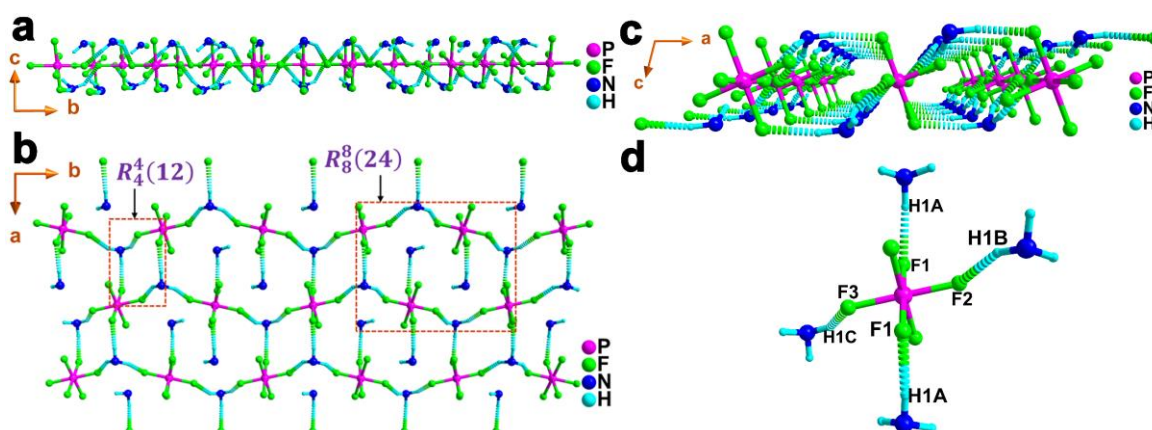


Figure 4A.5. The N-H...F hydrogen bonding interactions in $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ at 100 K. (a) along a -axis. (b) along b -axis. (c) along c -axis. (d) Repeating unit of the H-bonding sheet (C, H and disordered F-atoms are omitted for clarity).

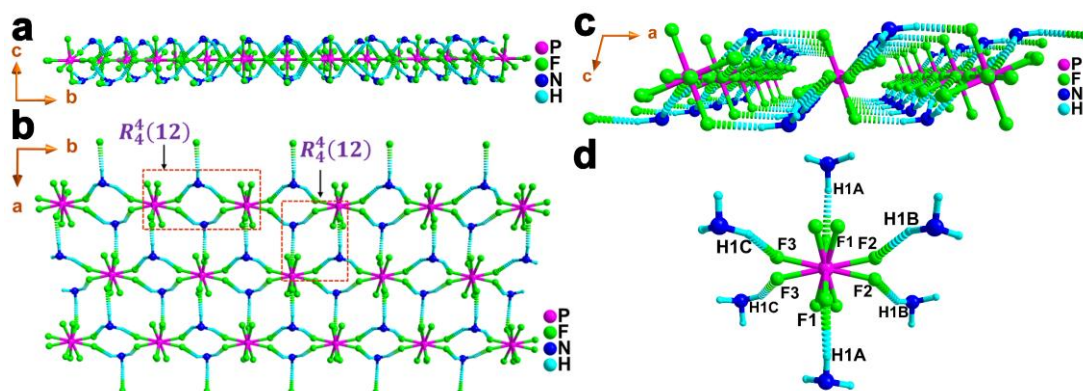


Figure 4A.6. The N-H...F hydrogen bonding interactions in $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ at 100 K including the interactions from the disordered F-atoms. (a) along a -axis. (b) along b -axis. (c) along c -axis. (d) Repeating unit of the H-bonding sheet (C and H atoms are omitted for clarity).

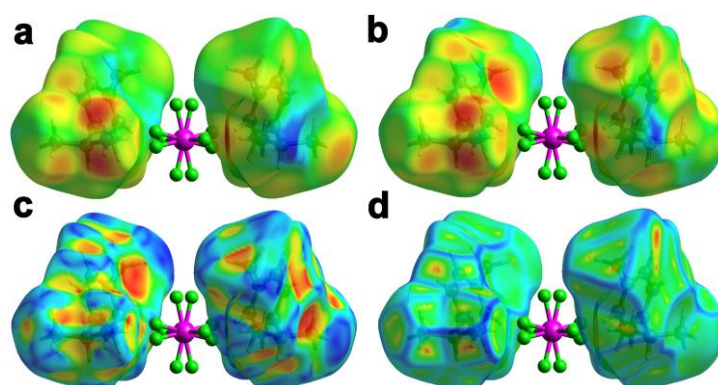


Figure 4A.7. The 3D color mapping derived from the Hirshfeld surface analysis of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ (100 K) (including the interactions from the disordered F-atoms) showing (a) d_i , (b) d_e , (c) shape index, and (d) curvedness.

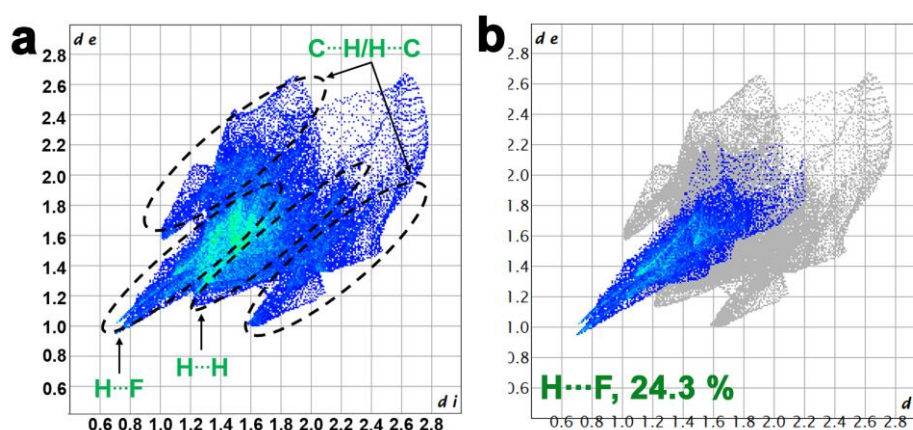


Figure 4A.8. 2D fingerprint (d_e vs d_i) plot of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ (100 K) showing the percentages of (a) all interactions and (b) $\text{H}\cdots\text{F}$ interactions in the molecule.

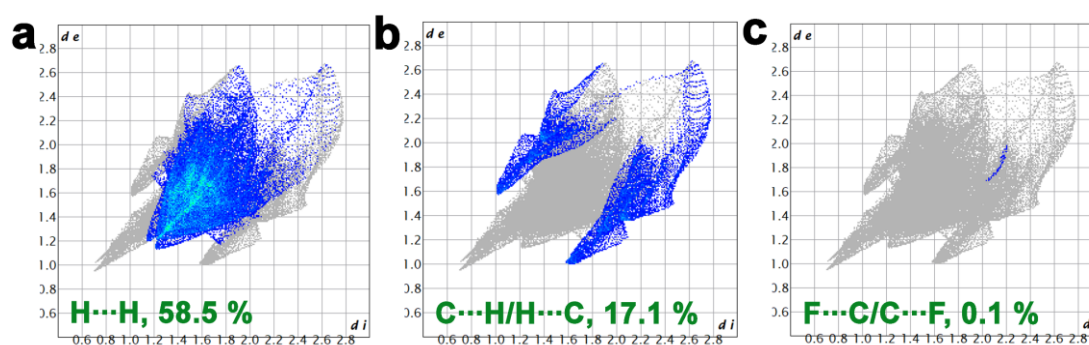


Figure 4A.9. 2D fingerprint (d_e vs d_i) plot of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ (100 K) showing the percentages of (a) $\text{H}\cdots\text{H}$, (b) $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$ and (c) $\text{C}\cdots\text{F}/\text{F}\cdots\text{C}$ interactions in the molecule.

Table 4A.2. Percentage interactions present in $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ at 100 K.

Interactions	$(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ (100 K) (%)
$\text{H}\cdots\text{F}$	24.3
$\text{H}\cdots\text{H}$	58.5
$\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$	17.1
$\text{C}\cdots\text{F}$	0.1

Table 4A.3. Hirshfeld surface analysis of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ at 100 K.

Temperature	Surface Property	Range (Minimum/Maximum)	Globularity and Asphericity	Surface Volume and Area
$(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ (100 K)	d_i	0.7077/2.7844	0.653 and 0.349	411.03 Å ³ and 409.48 Å ²
	d_e	0.9618/2.7163		
	d_{norm}	-0.6960/1.5901		
	Shape index	-0.9952/0.9974		
	Curvedness	-3.3837/0.3661		

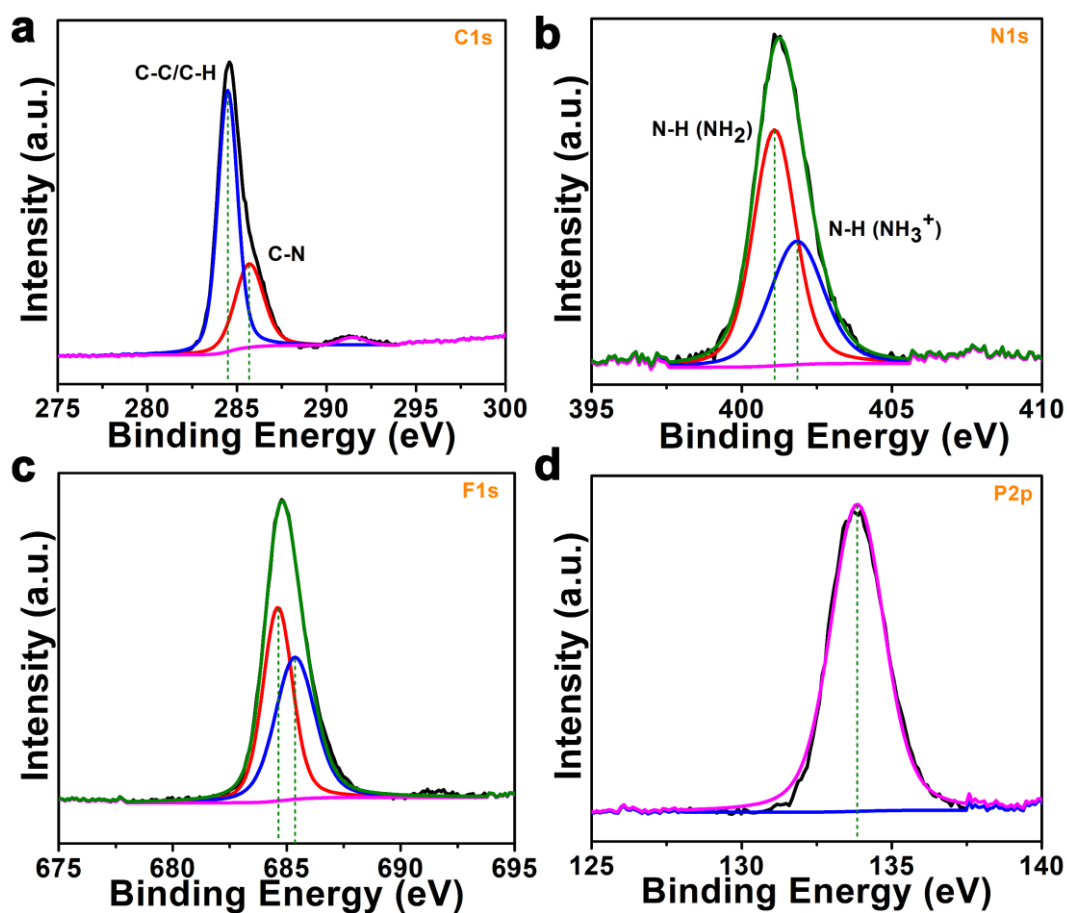


Figure 4A.10. The X-ray photoelectron spectrum (a-d) of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

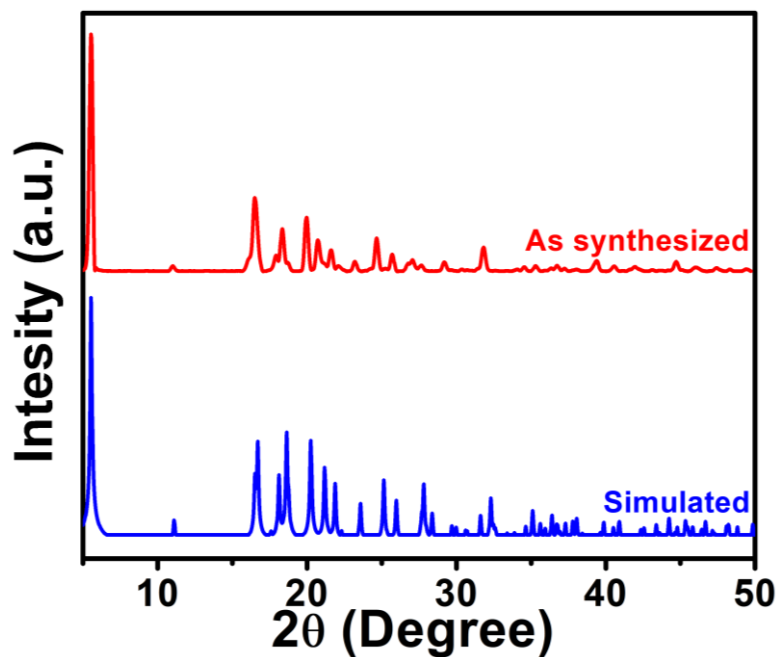


Figure 4A.11. The room temperature PXRD profiles of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ along with its simulated profile from the 298 K single-crystal data.

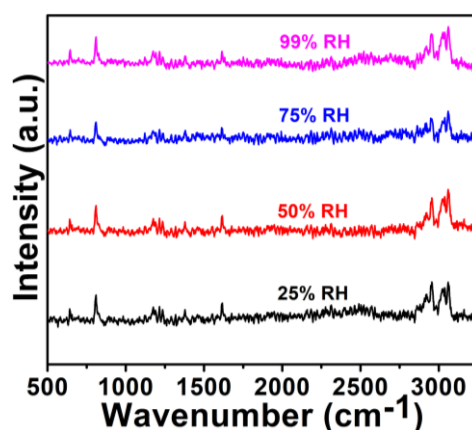


Figure 4A.12. The Raman spectral profile of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ upon exposure to various humidity conditions showing its high stability.

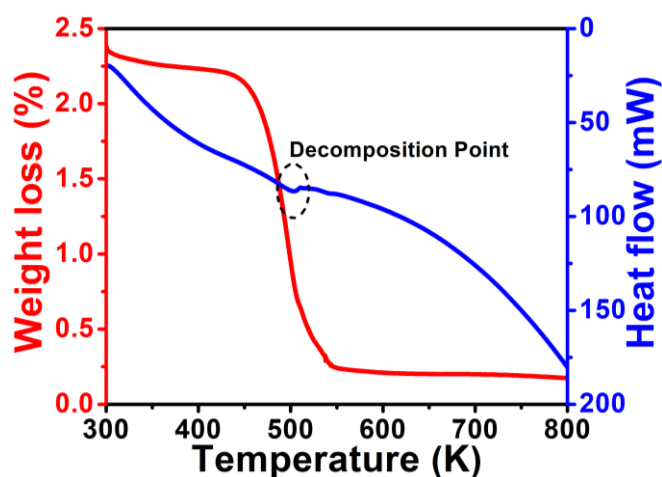


Figure 4A.13. The thermogravimetric-differential thermal analysis profile of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

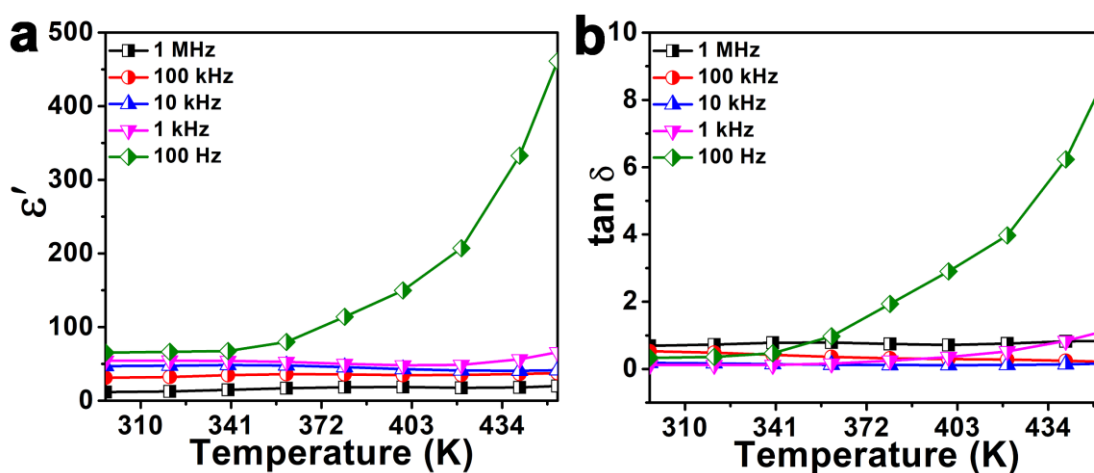


Figure 4A.14. The temperature dependant (a) dielectric permittivity and (b) dielectric loss plots of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

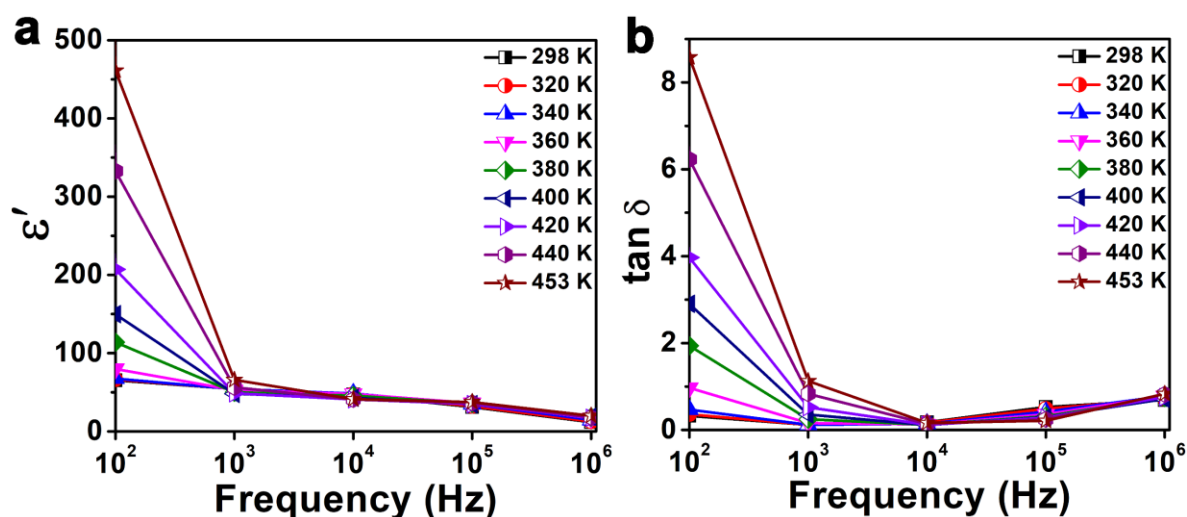


Figure 4A.15. The frequency dependant (a) dielectric permittivity and (b) dielectric loss plots of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$.

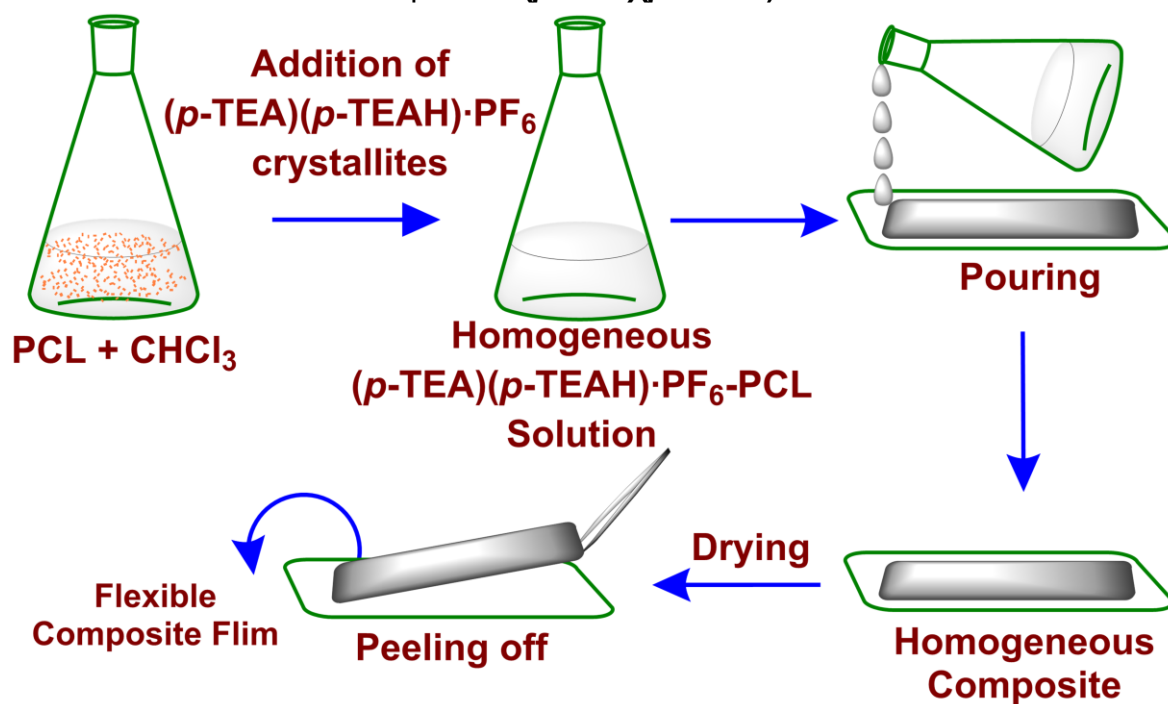


Figure 4A.16. Schematic for the preparation of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ -PCL composite films.

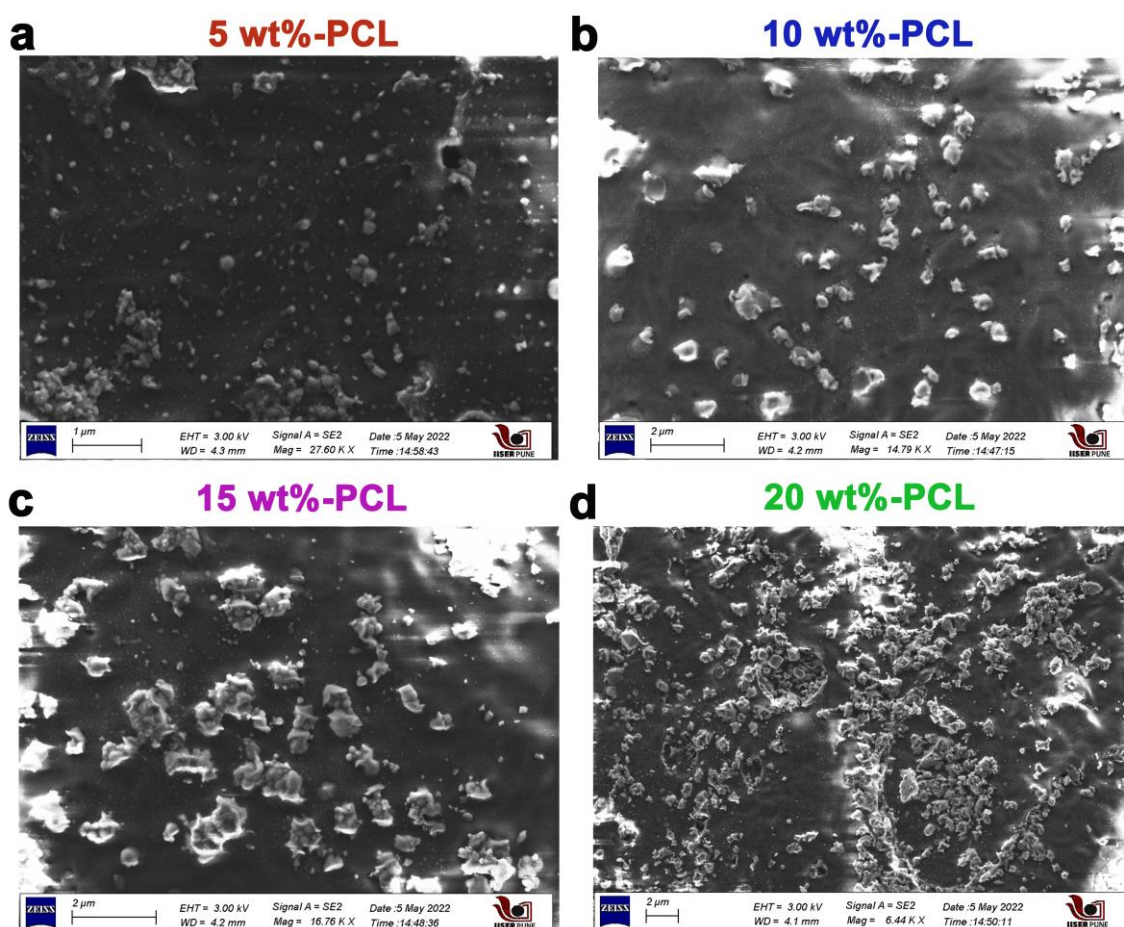


Figure 4A.17. The FE-SEM images of 5, 10, 15, and 20 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ -PCL composites.

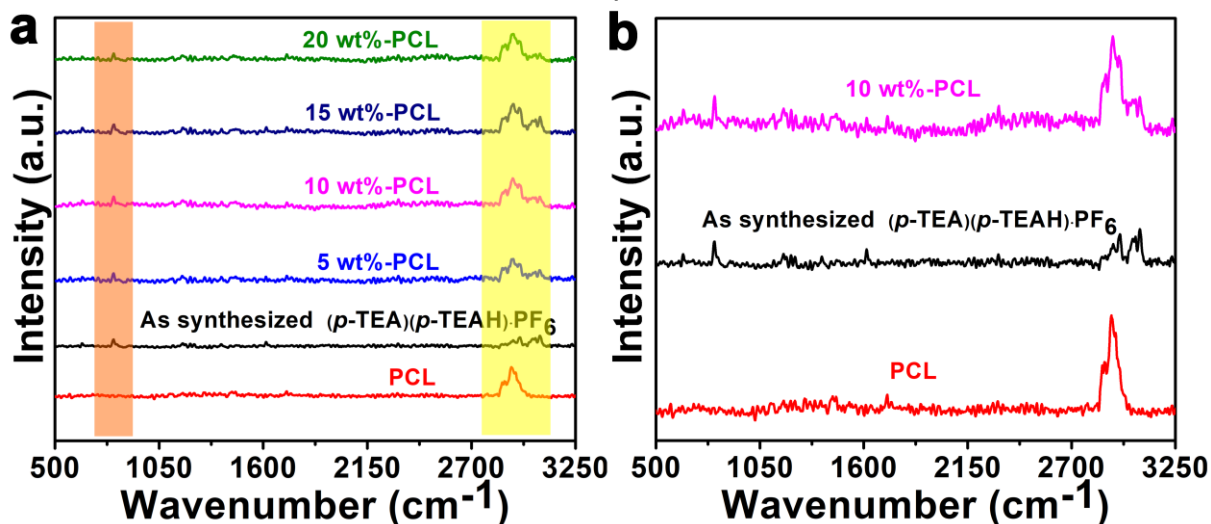


Figure 4A.18. The Raman spectral profile of all the wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ -PCL composite films compared to that of the neat compound $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ and polymer PCL.

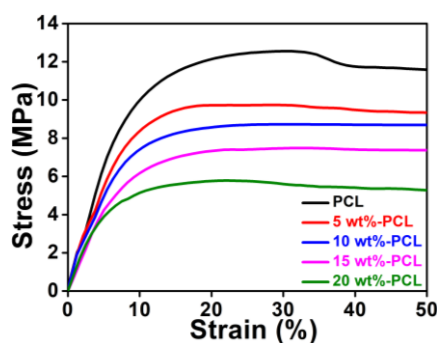


Figure 4A.19. The stress-strain profile of PCL and $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ -PCL composite films.

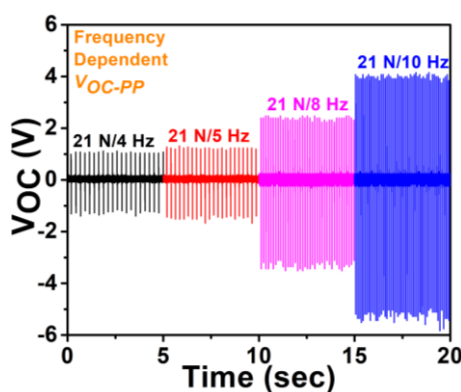


Figure 4A.20. The frequency-dependent open-circuit peak-to-peak voltage ($V_{\text{OC-PP}}$) data of 10 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ -PCL composite device.

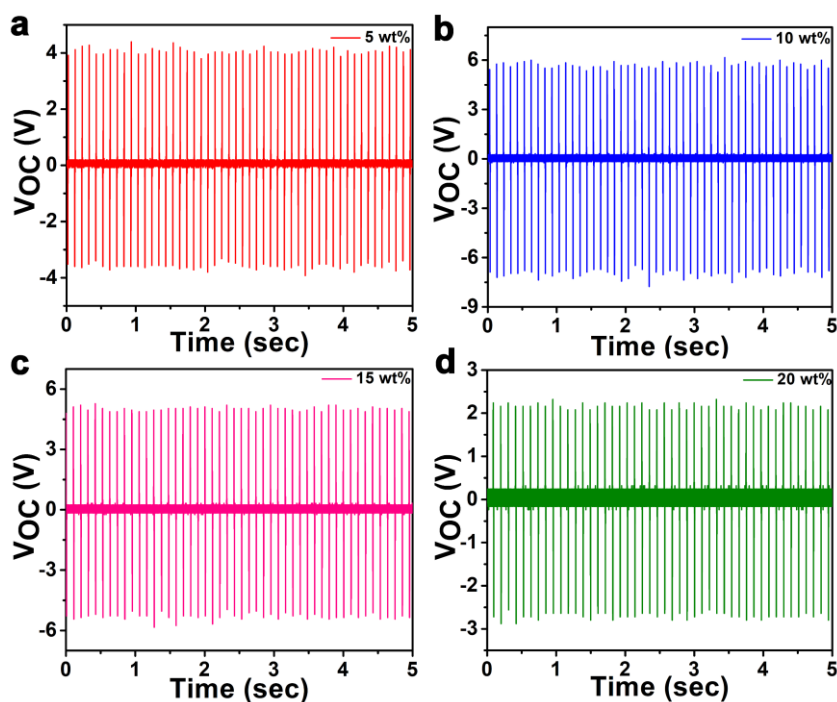


Figure 4A.21. The open-circuit peak-to-peak voltage ($V_{\text{OC-PP}}$) profiles of $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6$ -PCL composite devices.

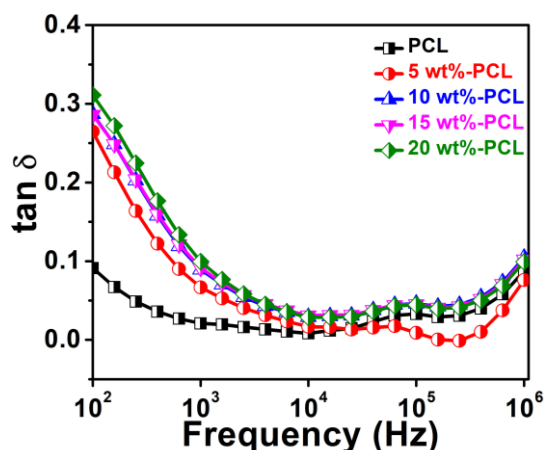


Figure 4A.22. The frequency-dependant dielectric loss data for all $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ composite films.

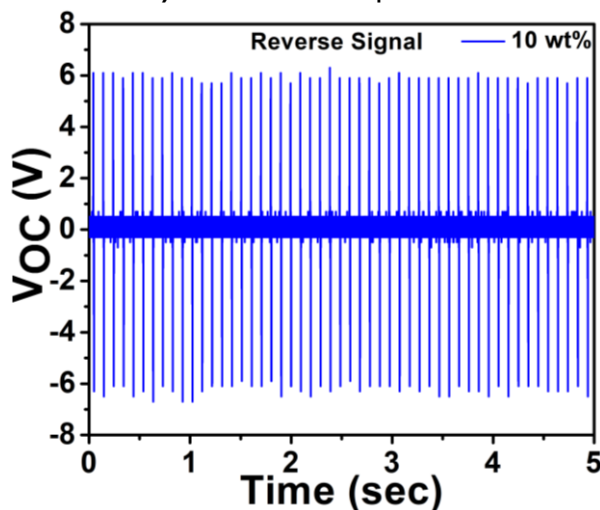


Figure 4A.23. The open-circuit peak-to-peak voltage (V_{OC-PP}) obtained from of 10 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ upon reversing the connections.

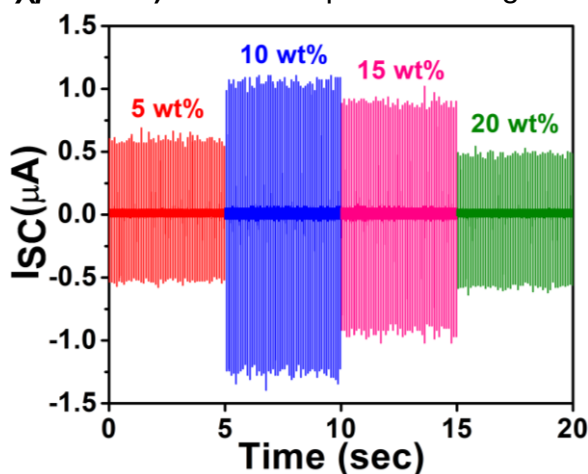


Figure 4A.24. The output peak-to-peak current (I_{PP}) profile calculated from the voltage drop obtained by attaching a $4.7\text{ M}\Omega$ resistor across the circuit for the $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ composite devices.

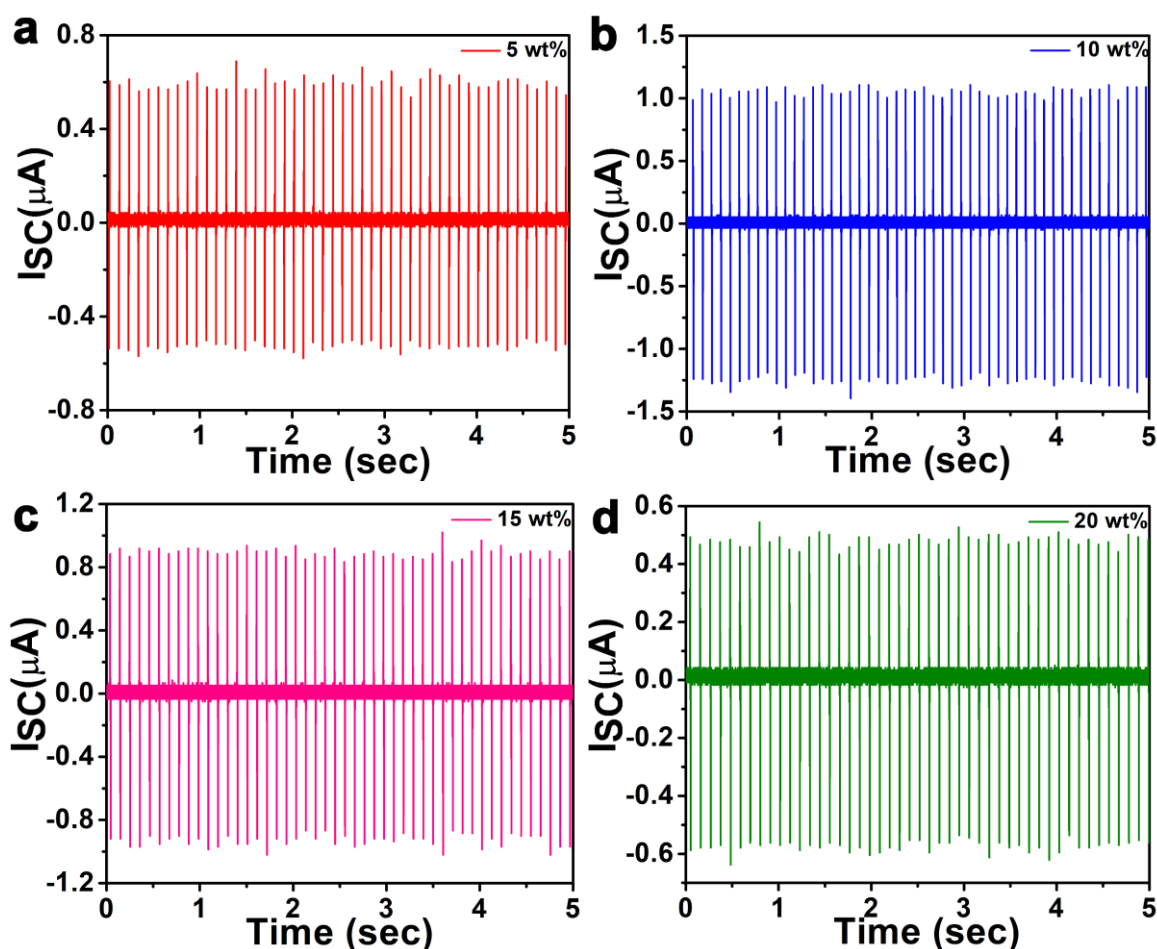


Figure 4A.25. The output peak-to-peak current (I_{PP}) profile calculated from the voltage drop obtained by attaching a 4.7 M Ω resistor across the circuit for the (p-TEA)(p-TEAH)·PF₆-PCL composite devices.

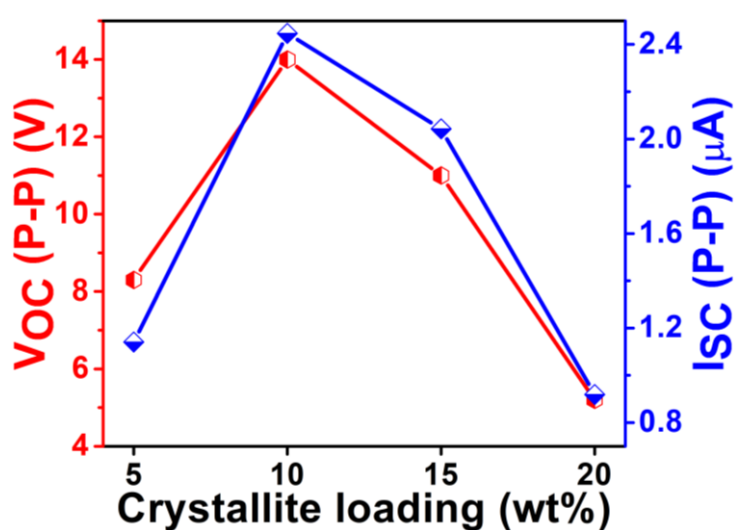


Figure 4A.26. Comparative diagram showing the observed trends in V_{OC-PP} and I_{PP} values of (p-TEA)(p-TEAH)·PF₆-PCL composite devices.

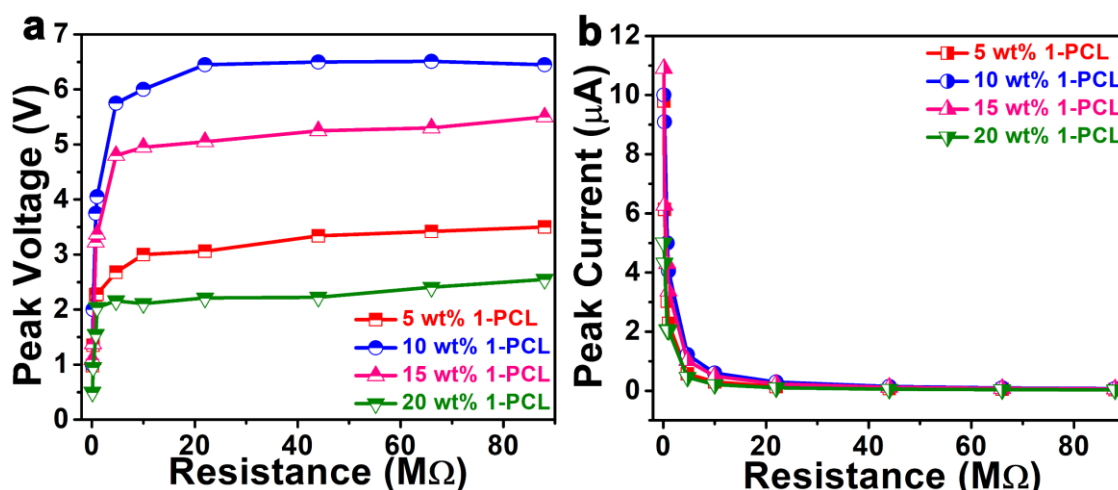


Figure 4A.27. The comparative peak (a) voltage drop and (b) current data for all the $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ composite devices under various load resistances (by default the voltage and current generated during the compression cycles).

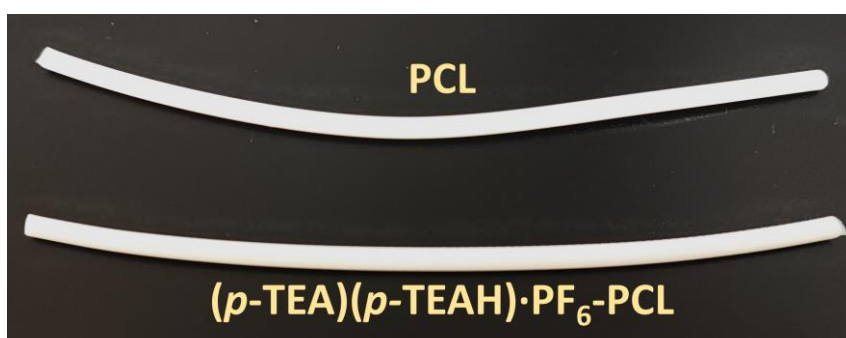


Figure 4A.28. Pictures of the raw filaments.

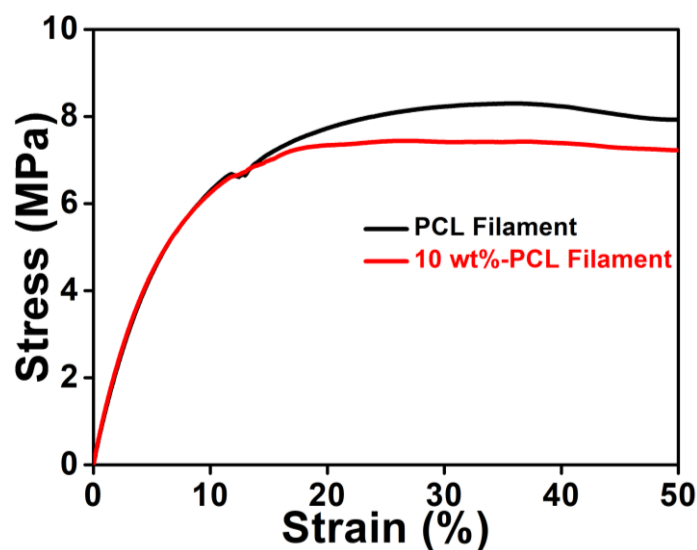


Figure 4A.29. The stress-strain profile of PCL and $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ composite filaments.

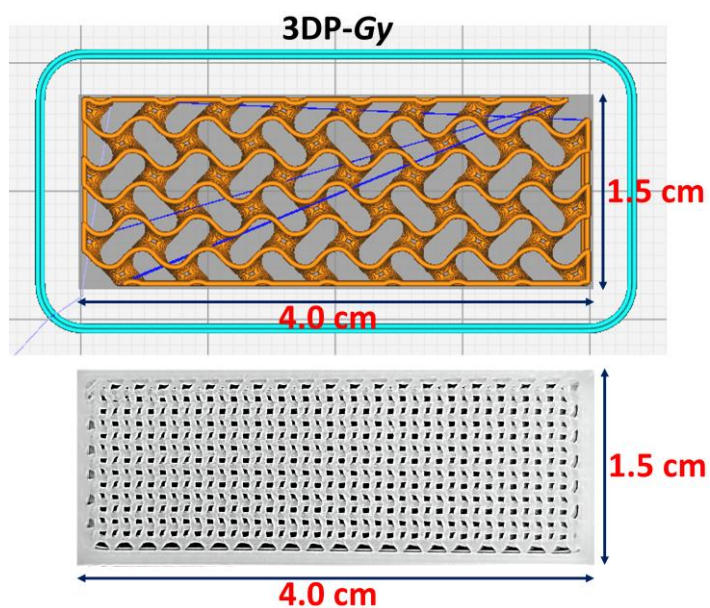


Figure 4A.30. Pictures of the computerized and as-made **3DP-Gy** slabs with dimensions.

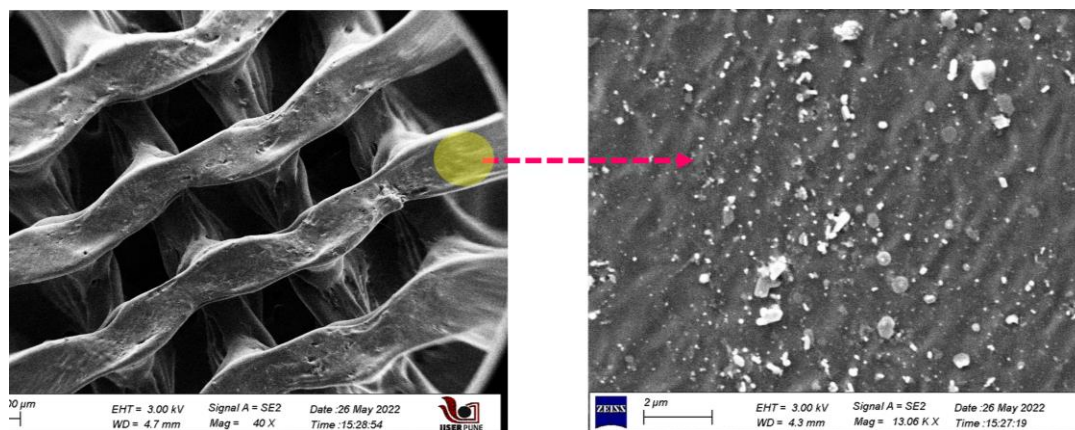


Figure 4A.31. SEM images of 10 wt% **3DP-Gy** composite.



Figure 4A.32. Pictures of the computerized and as-made **3DP-Gy** slab with dimensions.

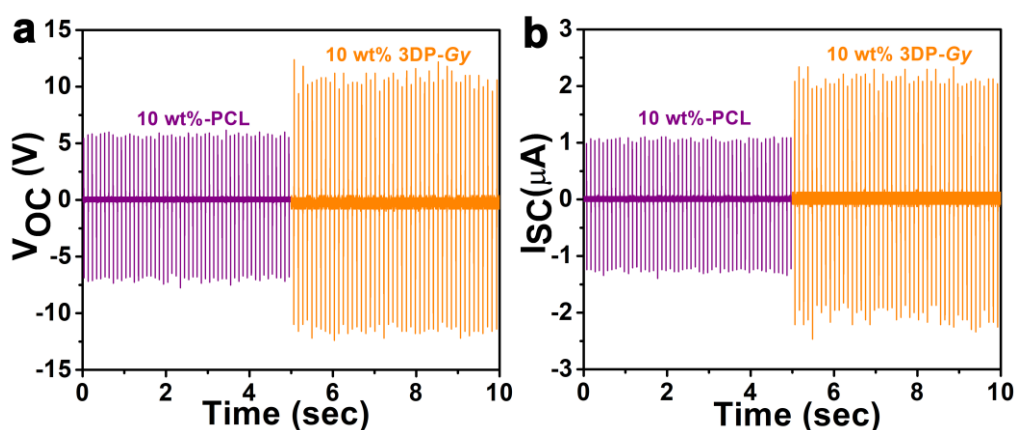


Figure 4A.33. The comparative peak-to-peak (a) open-circuit voltage (V_{OC-PP}) and (b) calculated current (I_{PP}) profiles of 3D printed 10 wt% **3DP-Gy** to that of 10 wt% **(p-TEA)(p-TEAH)·PF₆-PCL** thin film.

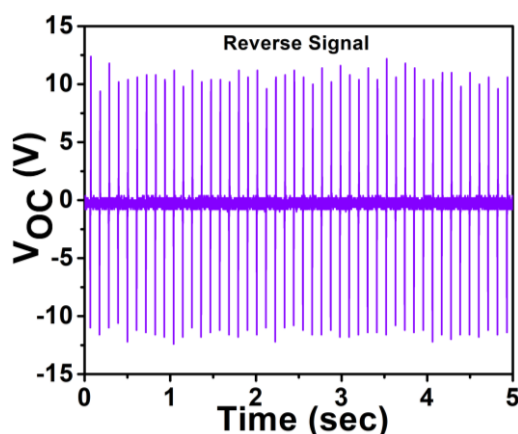


Figure 4A.34. The open-circuit peak-to-peak voltage (V_{OC-PP}) obtained from 10 wt% **3DP-Gy** upon reversing the connections.

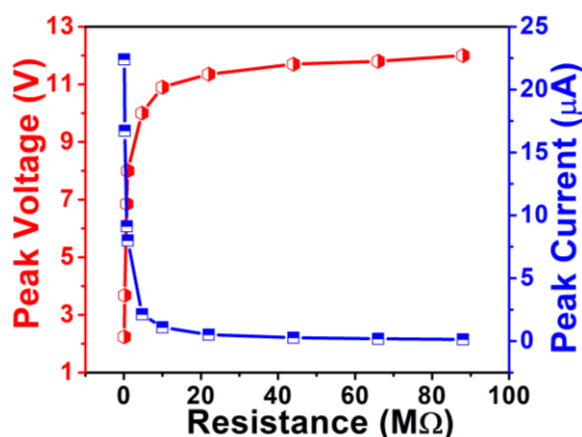


Figure 4A.35. The comparative peak (a) voltage drop and (b) current data for 10 wt% **3DP-Gy** composite device under various load resistances (by default the voltage and current generated during the compression cycles).

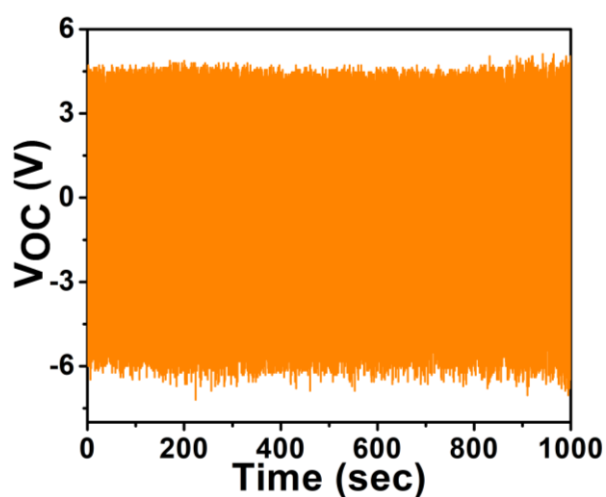


Figure 4A.36. The cyclic stability test of 10 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ showing the retention of $V_{\text{OC-PP}}$ up to 10000 cycles.

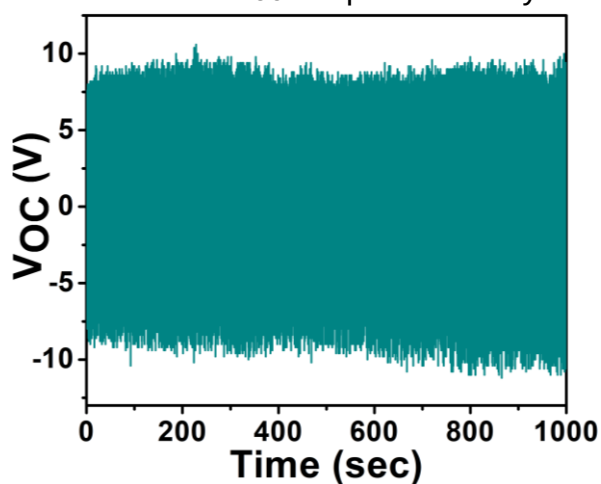


Figure 4A.37. The cyclic stability test of 10 wt% **3DP-Gy** showing the retention of $V_{\text{OC-PP}}$ up to 10000 cycles.

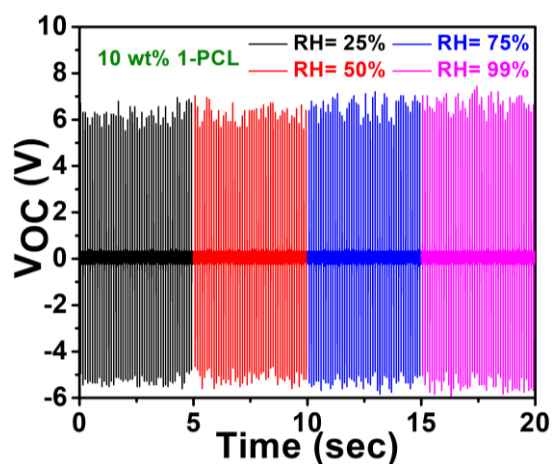


Figure 4A.38. The RH dependent open-circuit peak-to-peak voltage ($V_{\text{OC-PP}}$) of 10 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ device.

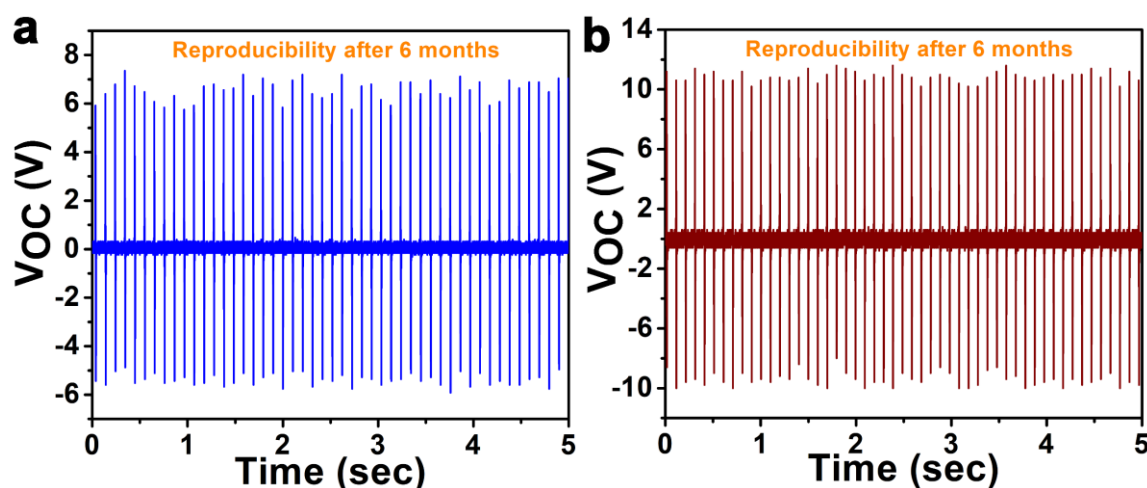


Figure 4A.39. The reproducibility of open-circuit peak-to-peak voltage (V_{OC-PP}) of 10 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ and 3DP-Gy after 6 months.

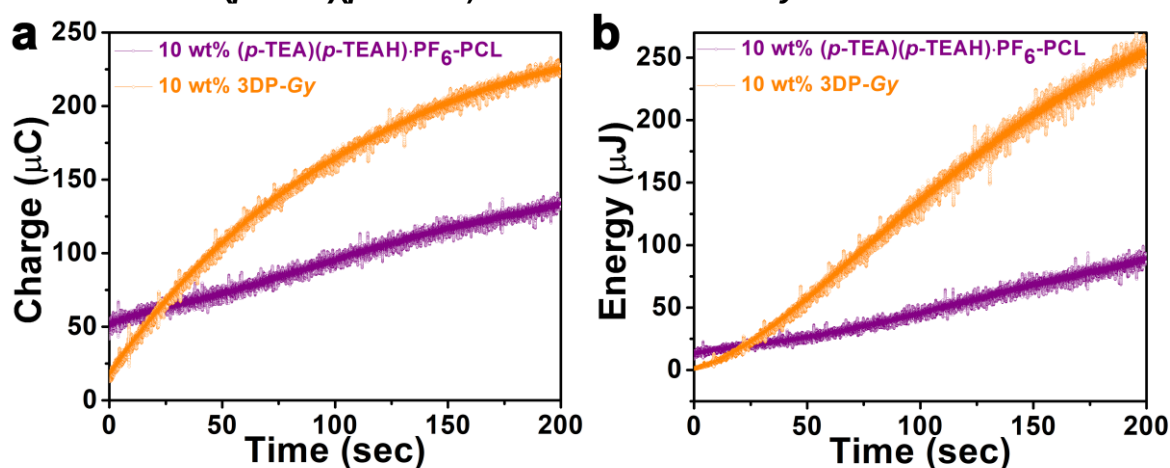


Figure 4A.40. The (a) charges stored and (b) energies stored in a 100 μF capacitor by using the 10 wt% 3DP-Gy and 10 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ devices.

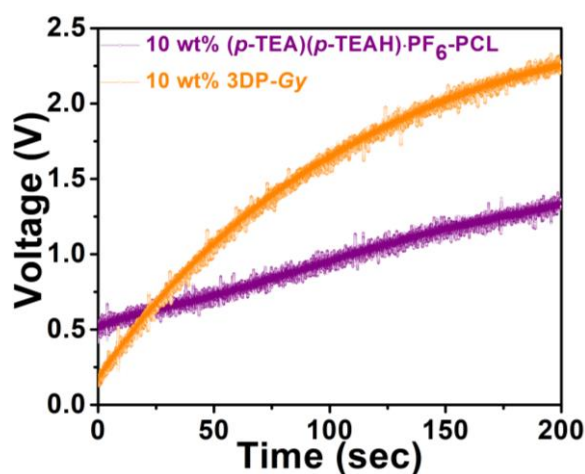


Figure 4A.41. The voltages stored in a 100 μF capacitor by using the 10 wt% 3DP-Gy and 10 wt% $(p\text{-TEA})(p\text{-TEAH})\cdot\text{PF}_6\text{-PCL}$ devices.

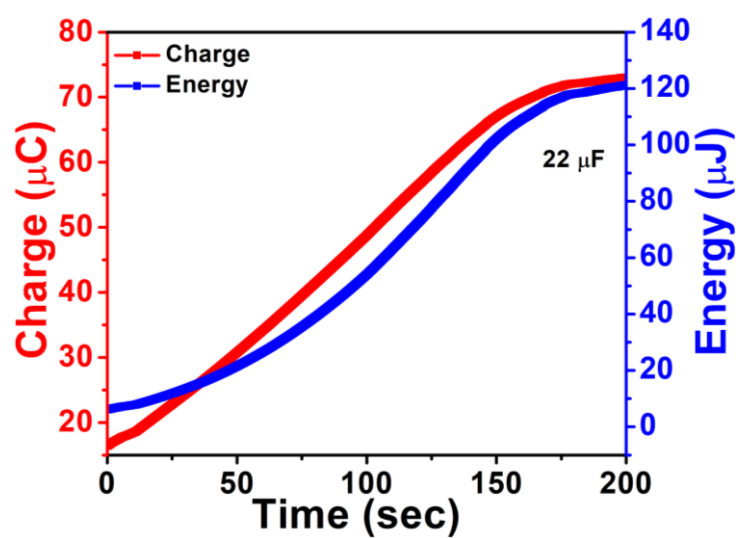
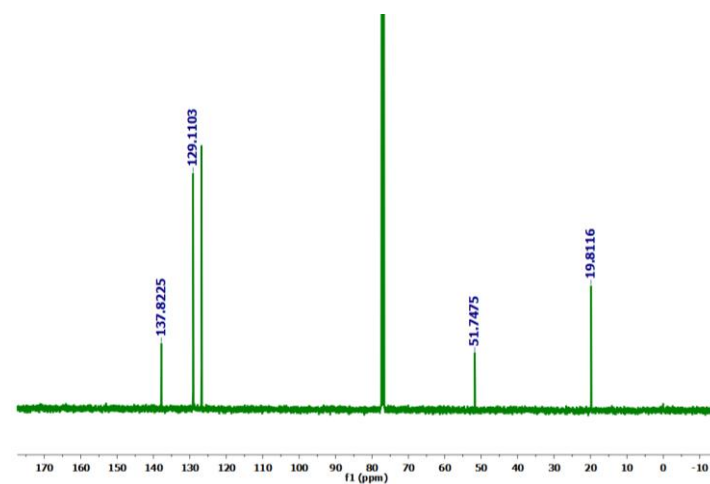
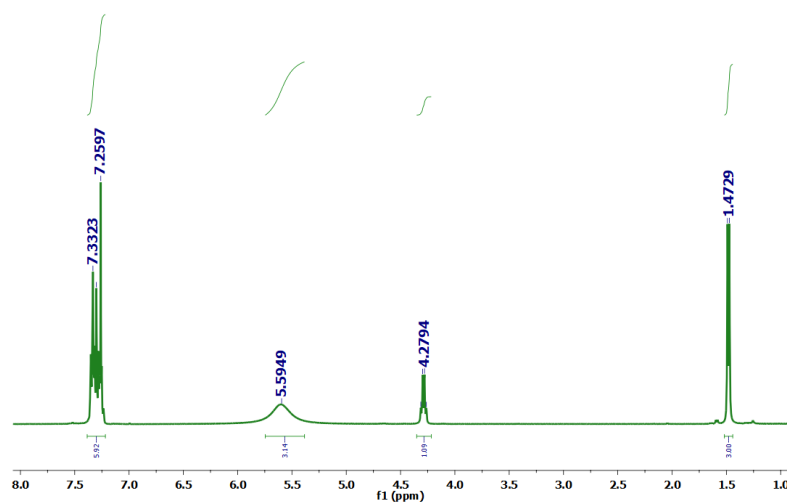
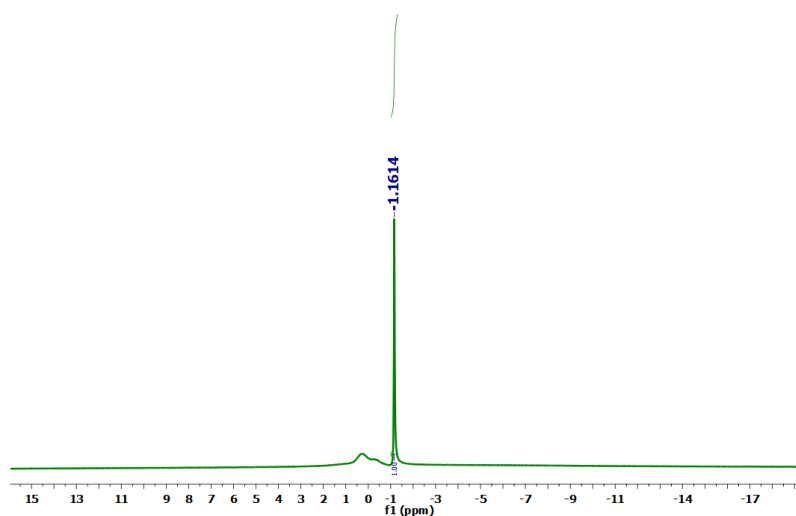
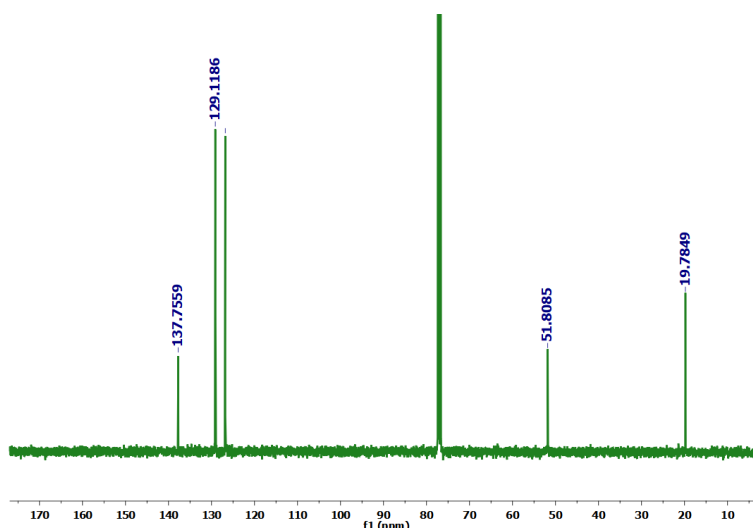
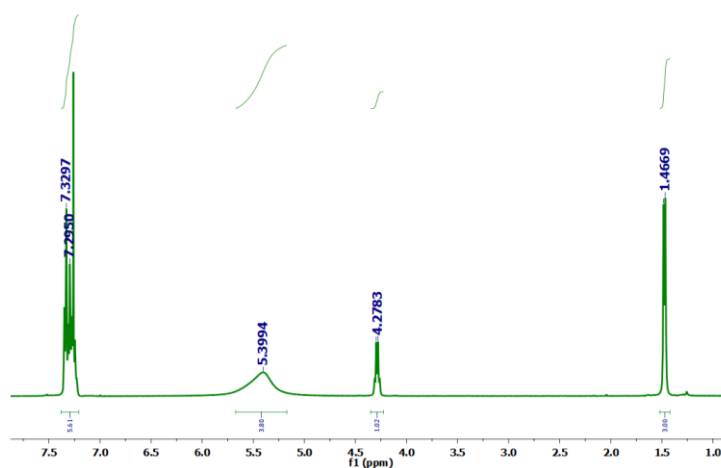
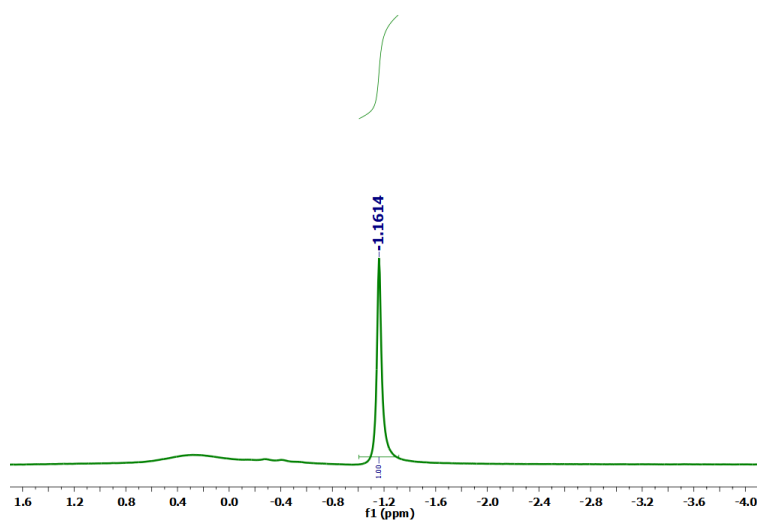


Figure 4A.42. The (a) charge and (b) energy stored in a 22 μF capacitor by using the 10 wt% **3DP-Gy** device.

Figure 5A.1. ^{13}C Spectrum of RMBa-BF_3 .Figure 5A.2. ^1H Spectrum of RMBa-BF_3 .Figure 5A.3. ^{11}B Spectrum of RMBa-BF_3 .

Figure 5A.4. ^{13}C Spectrum of $^5\text{MBA-BF}_3$.Figure 5A.5. ^1H Spectrum of $^5\text{MBA-BF}_3$.Figure 5A.6. ^{11}B Spectrum of $^5\text{MBA-BF}_3$.

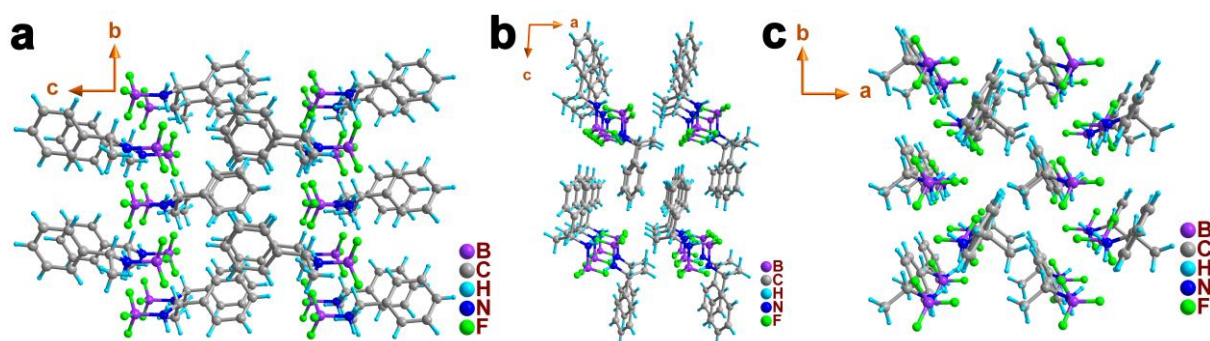


Figure 5A.7. Packing diagrams of $^R\text{MBA-BF}_3$ along (a) a -axis (b) b -axis and (c) c -axis at 120 K.

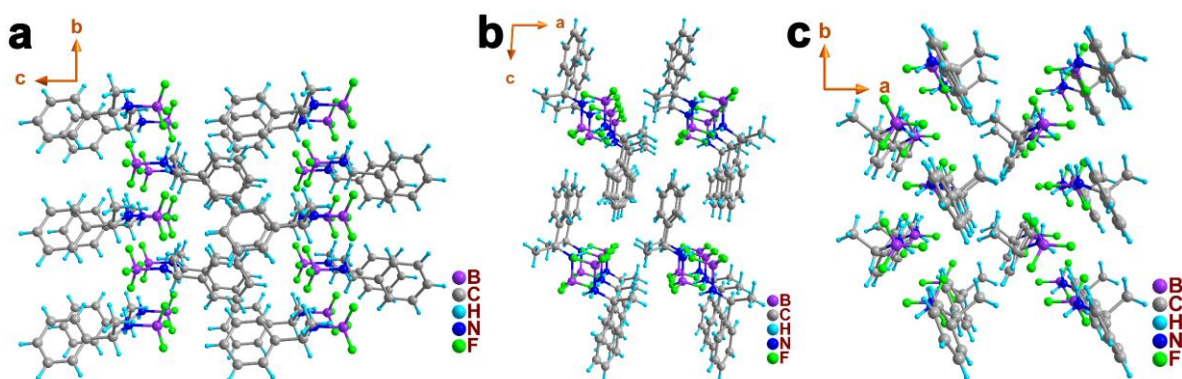


Figure 5A.8. Packing diagrams of $^S\text{MBA-BF}_3$ along (a) a -axis (b) b -axis and (c) c -axis at 120 K.

Table 5A.1. Hydrogen bonding parameters for $^R\text{MBA-BF}_3$ at 120 K.

D-H...A	d(H...A) Å	d(D-A) Å	<(DHA)°	Symmetry transformations to generate equivalent atoms
N(11)-H(11A)...F21	1.9894(93)Å	2.7835(132) Å	144.975(654)°	$x, y, 1+z$

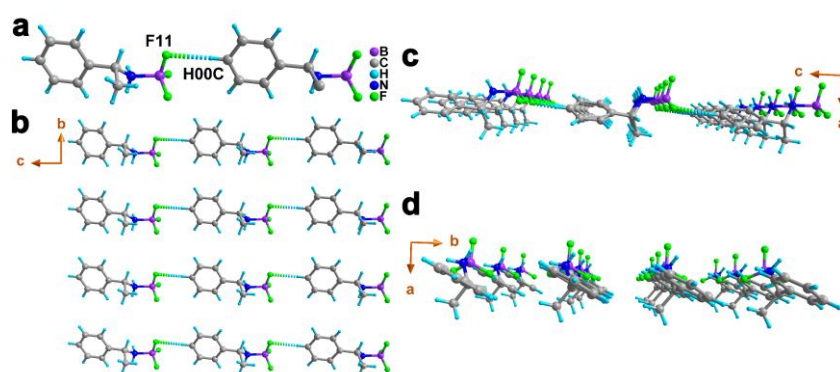


Figure 5A.9. N-H...F hydrogen bonding interactions in $^R\text{MBA-BF}_3$ at 120 K. (a) View of a repeating unit forming 1D-H-bonding interactions in $^R\text{MBA-BF}_3$. (b) Formation of a 1D-H-bonded chain structure via the connection between the neighbouring $^R\text{MBA-BF}_3$ moieties along a -axis. (c) H-bonding interactions along b -axis. (d) H-bonding interactions along b -axis.

Table 5A.2. Hydrogen bonding parameters for ^sMBA-BF₃ at 120 K.

D-H...A	d(H...A) Å	d(D-A) Å	<(DHA)°	Symmetry transformations to generate equivalent atoms
C(15)-H(000C)···F11	2.4799(21)Å	3.4087(132) Å	176.552(259)°	x, y, 1+z

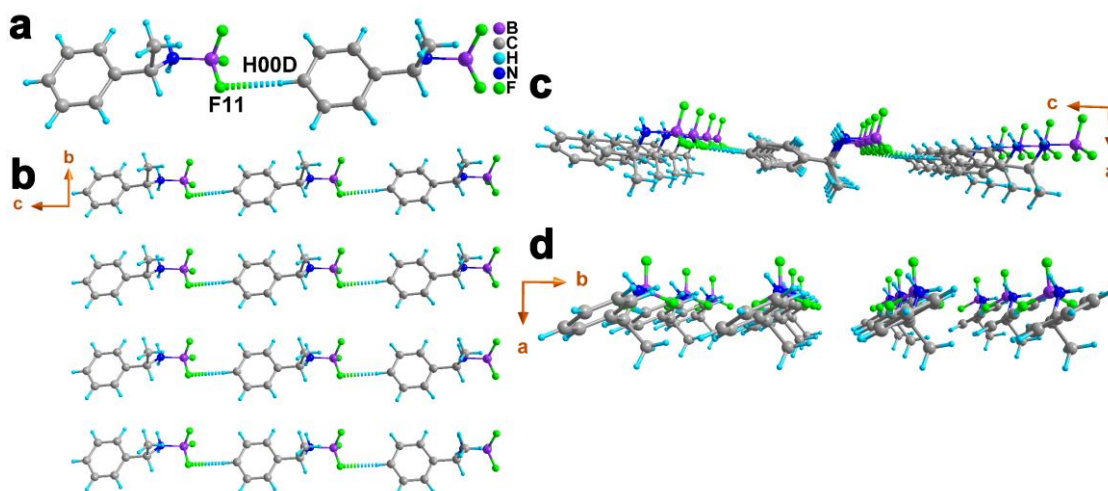


Figure 5A.10. N-H...F hydrogen bonding interactions in ^sMBA-BF₃ at 120 K. (a) View of a repeating unit forming 1D-H-bonding interactions in ^sMBA-BF₃. (b) Formation of a 1D-H-bonded chain structure via the connection between the neighbouring ^sMBA-BF₃ moieties along a-axis. (c) H-bonding interactions along b-axis. (d) H-bonding interactions along b-axis.

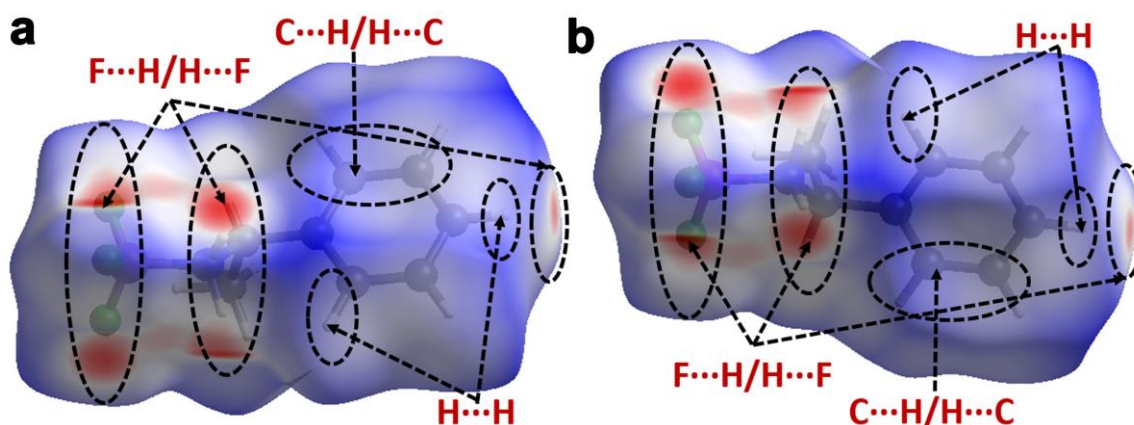


Figure 5A.11. (a) *d*-norm mapped Hirshfeld surface of ^sMBA-BF₃ showing all interactions present in the molecule. (b) The *d*-norm mapped Hirshfeld surface of ^sMBA-BF₃, showing all interactions present in the molecule.

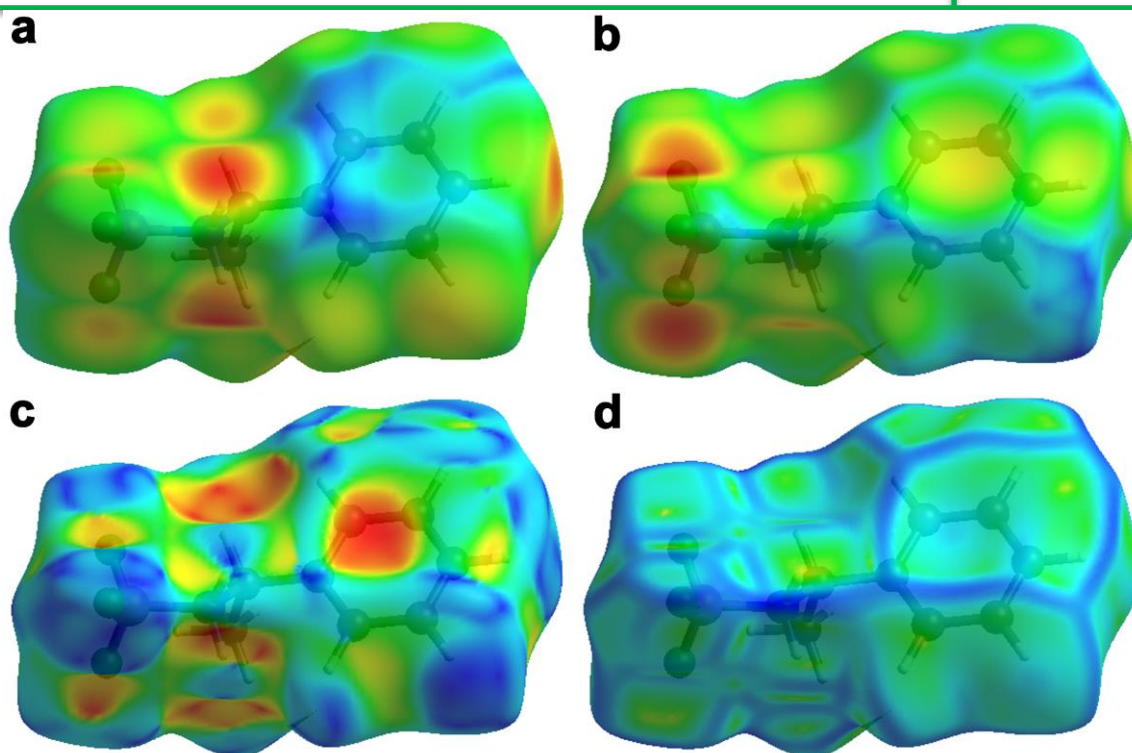


Figure 5A.12. The 3D color mapping derived from the Hirshfeld surface analysis of R^MBA-BF_3 showing (a) d_i , (b) d_e , (c) shape index, and (d) curvedness.

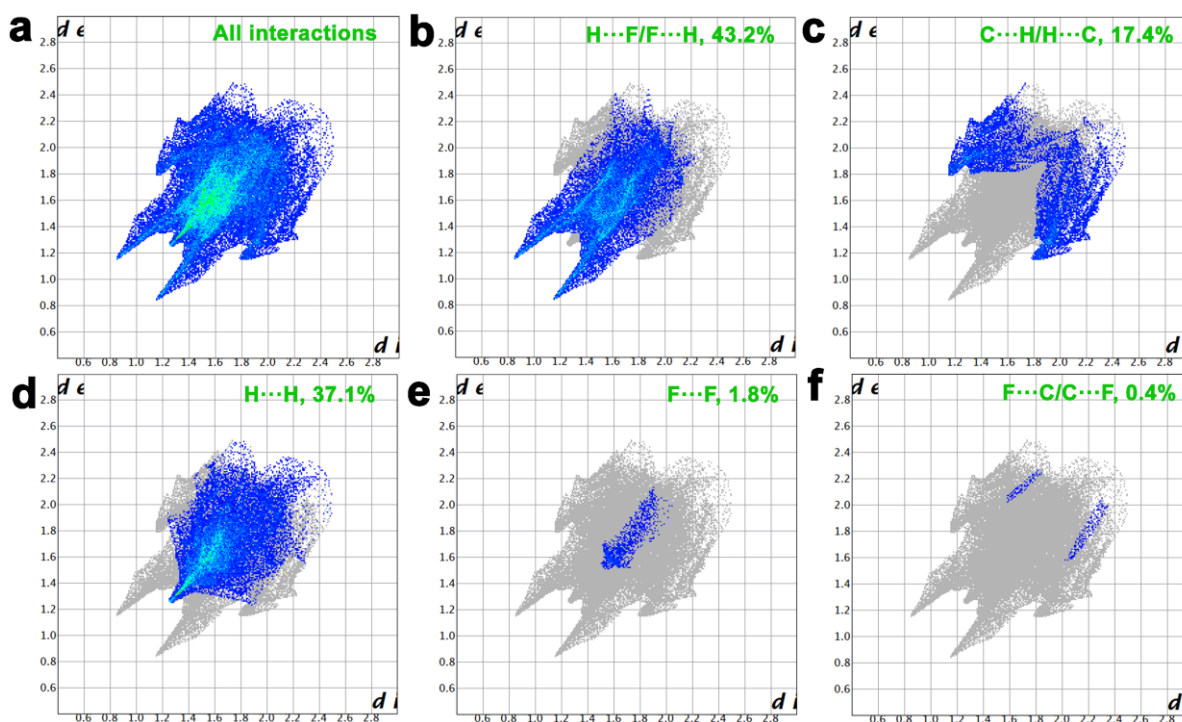


Figure 5A.13. 2D fingerprint (d_e vs d_i) plot of R^MBA-BF_3 showing (a) all the possible interactions and the percentages of (b) $H\cdots F/F\cdots H$, (c) $C\cdots H/H\cdots C$, (d) $H\cdots H$, (e) $F\cdots F$ and (f) $F\cdots C/C\cdots F$ interactions in R^MBA-BF_3 .

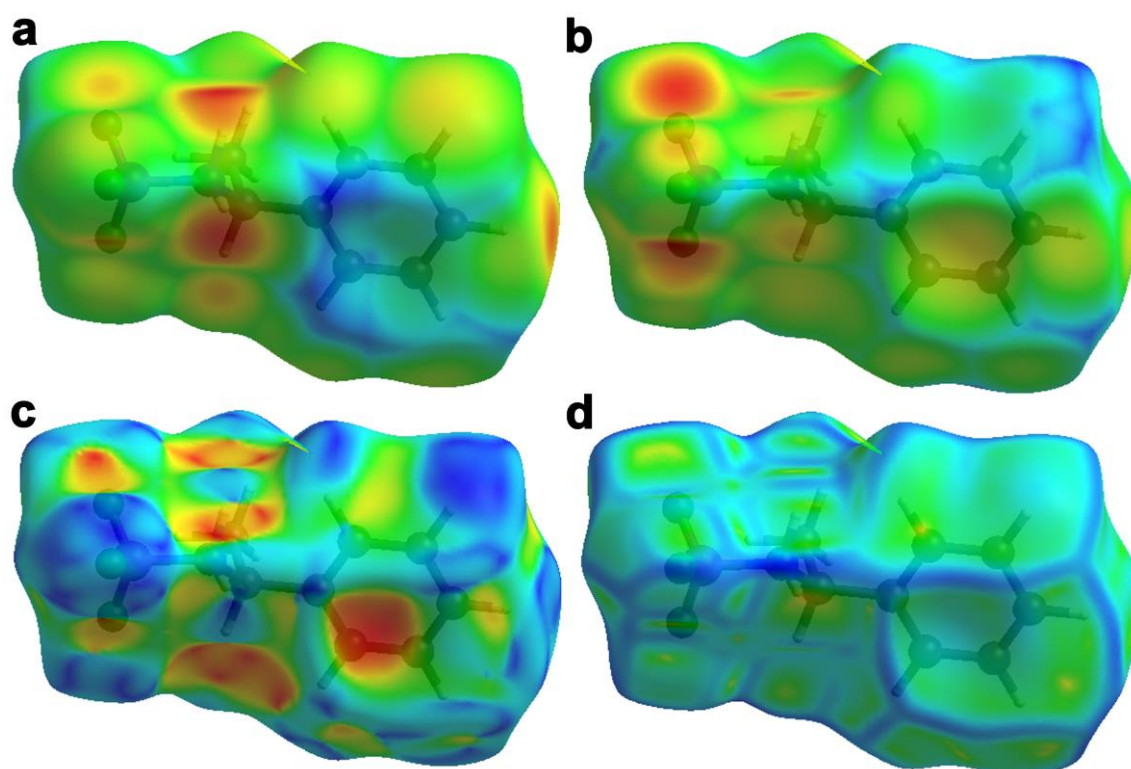


Figure 5A.14. The 3D color mapping derived from the Hirshfeld surface analysis of $^s\text{MBA-BF}_3$ (298 K) showing (a) d_i , (b) d_e , (c) shape index, (d) curvedness.

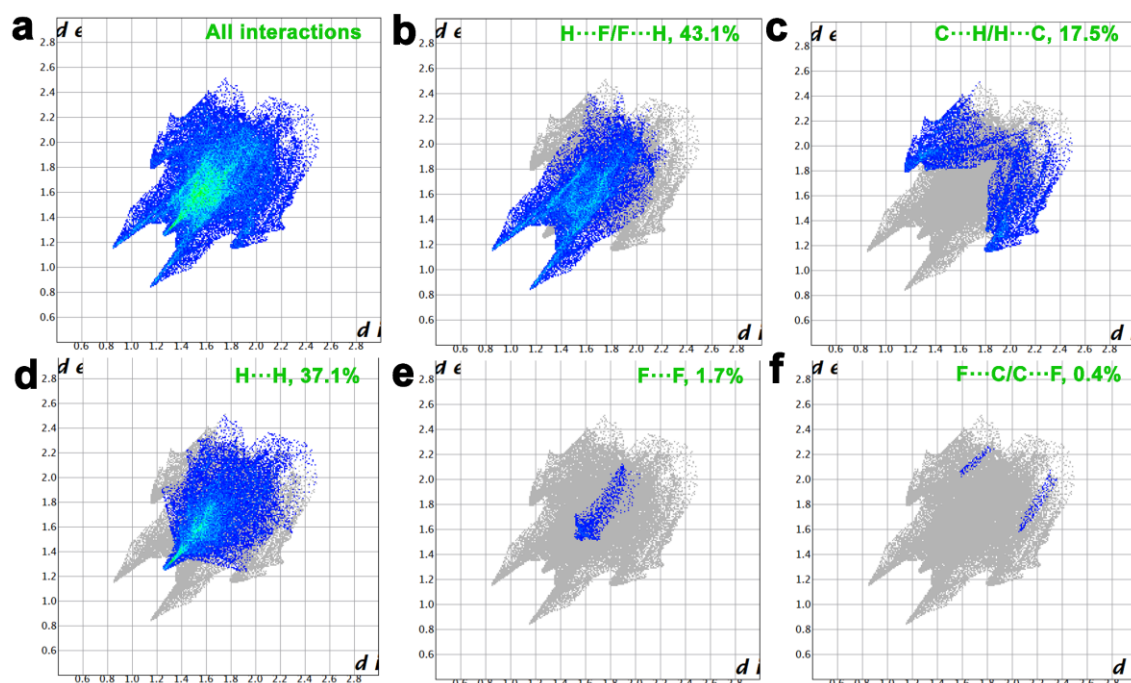


Figure 5A.15. 2D fingerprint (d_e vs d_i) plot of $^s\text{MBA-BF}_3$ showing (a) all the possible interactions and the percentages of (b) $\text{H}\cdots\text{F}/\text{F}\cdots\text{H}$, (c) $\text{C}\cdots\text{H}/\text{H}\cdots\text{C}$, (d) $\text{H}\cdots\text{H}$, (e) $\text{F}\cdots\text{F}$ and (f) $\text{F}\cdots\text{C}/\text{C}\cdots\text{F}$ interactions in $^s\text{MBA-BF}_3$.

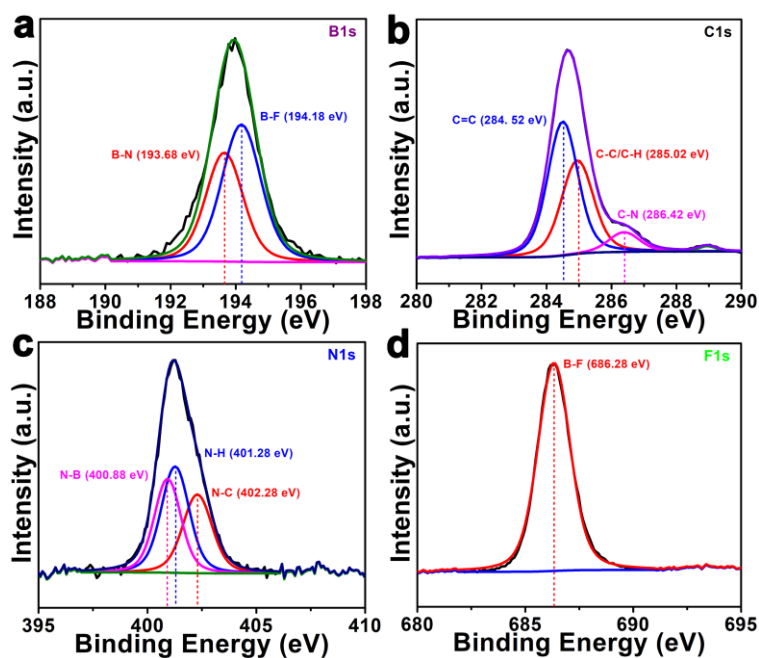


Figure 5A.16. The X-ray photoelectron spectrum (a-d) of $^R\text{MBA-BF}_3$.

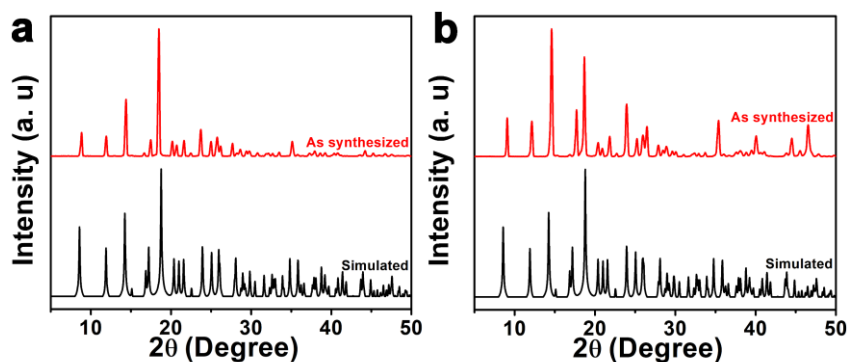


Figure 5A.17. The room temperature powder X-ray diffraction profiles of (a) $^R\text{MBA-BF}_3$ and (b) $^S\text{MBA-BF}_3$ along with their simulated profiles from the 298 K single-crystal data.

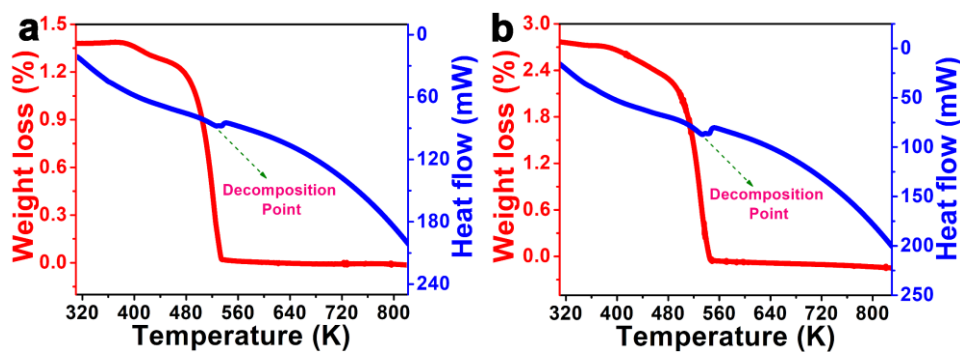


Figure 5A.18. The thermogravimetric-differential thermal analysis profiles of (a) $^R\text{MBA-BF}_3$ and (b) $^S\text{MBA-BF}_3$.

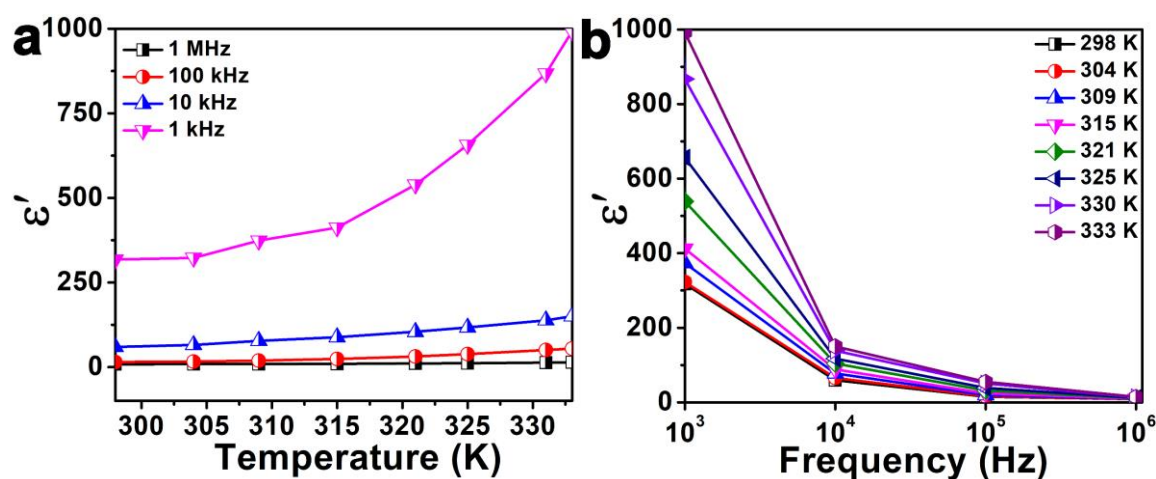


Figure 5A.19. The (a) temperature and (b) frequency dependant dielectric permittivity plot of R^{MBA-BF_3} .

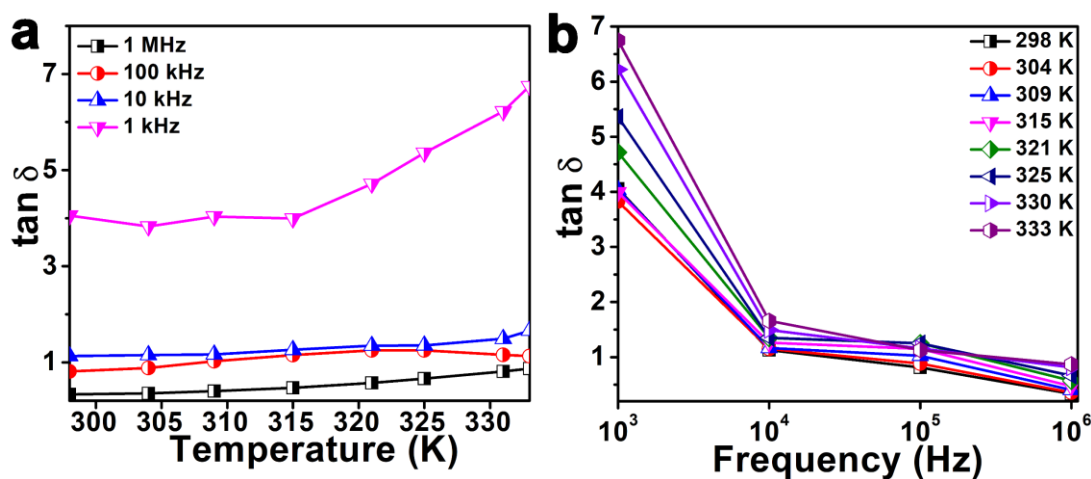


Figure 5A.20. The (a) temperature and (b) frequency dependant dielectric loss plot of R^{MBA-BF_3} .

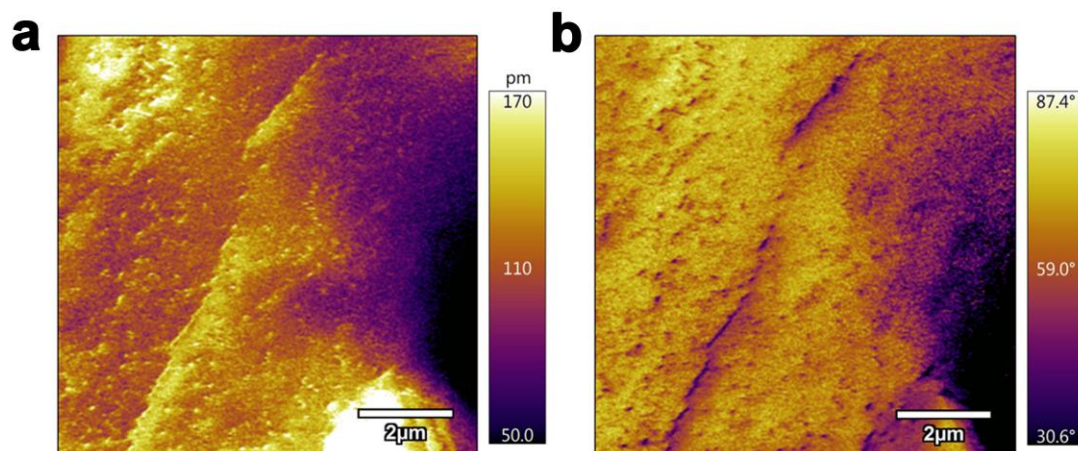


Figure 5A.21. PFM derived (a) Amplitude image (b) Phase image of a 9 X 9 area on the drop casted thin film of R^{MBA-BF_3} .

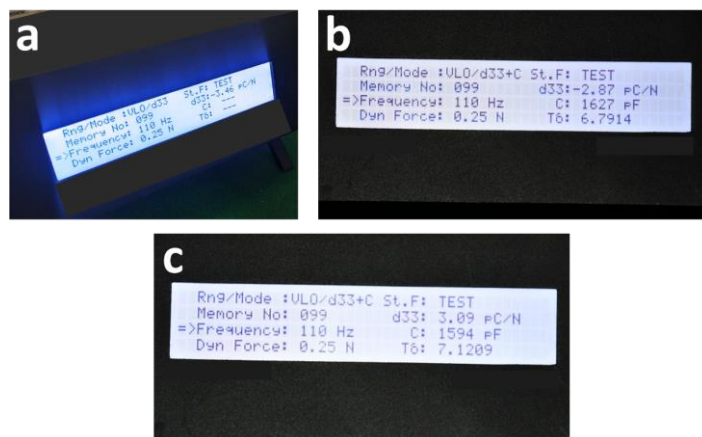


Figure 5A.22. d_{33} values for compacted pellet of $^R\text{MBA-BF}_3$ on both sides and at different surface points.

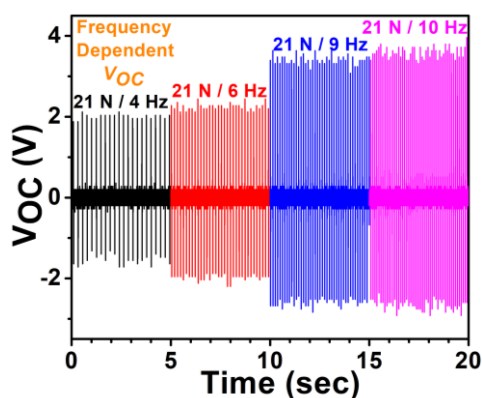


Figure 5A.23. Frequency dependent trend in V_{OC-PP} values of $^R\text{MBA-BF}_3$ device.

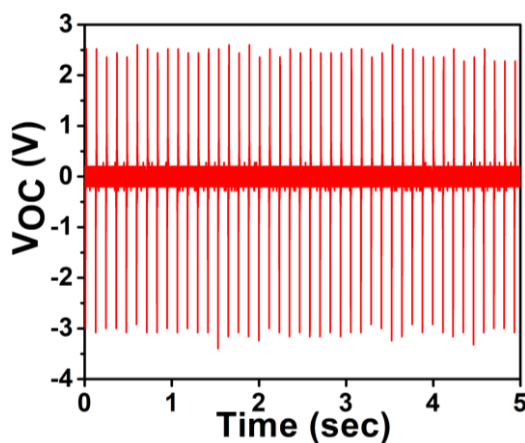


Figure 5A.24. The polarity-switching profile of $^R\text{MBA-BF}_3$ device.
