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A Flexible Composite Mechanical Energy Harvester from a Ferroelectric Organo-amino Phosphonium Salt

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Abstract: A new binary organic salt diphenyl diisopropylamino phosphonium hexaflurophosphate (DPDP·PF₆) was shown to exhibit a good ferroelectric response and employed as a mechanical energy harvester. The phosphonium salt crystallizes in the monoclinic noncentrosymmetric space group Cc and exhibits an H-bonded 1Dchain structure due to N-H...F interactions. Ferroelectric measurements on the single crystals of DPDP PF6 gave a well saturated rectangular hysteresis loop with a remnant (Pr) polarization value ~6 µCcm⁻². Further, composite devices based on polydimethylsiloxane (PDMS) films for various weight percentages (3, 5, 7, 10 and 20 wt %) of DPDP·PF₆ were prepared and examined for power generation by using a force-measurement setup. A maximum output peak to peak voltage (VPP) of 8.5 V and an output peak to peak current (IPP) of 0.5 µA was obtained for the non-poled composite film with 10 wt% of DPDP·PF₆. These results promise the efficacy of organic ferroelectric substances as potential mechanical energy harvesters.

Ferroelectric materials derived from organic and organicinorganic hybrid assemblies have been the topic of intense research in the past decade as alternate choice of materials for high-technique applications in the areas of energy and electronics.¹ In addition to their traditional utility as ferroelectric random access memories, capacitors, sensors, actuators and electromechanical transducers, they exhibit applications in the domains of photovoltaics and mechanical energy harvesters.² Harvesting energy from sustainable and renewable sources such as solar, thermal, vibrational and mechanical energy have attracted immense attention to meet the global demands of energy consumption in everyday life.³ Among various approaches, converting mechanical energy into electrical energy is of tremendous interest because of the simplicity of its generation via the forces derived from pressure, bending, folding and stretching motions.⁴ Inspired from the earlier discovery of

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 E-mail: praveenkumar@arde.drdo.in Supporting information for this article is given via a link at the end of the document. CCDC 1842608-1842612 contains the crystallographic data.

nanogenerators based on ZnO nanowires, several piezoelectric and ferroelectric materials including inorganic perovskite ceramic materials such as barium titanate, lead titanate, lithium niobate, sodium niobate and lead zirconate titanate have been employed for energy harvesting applications.⁵ Ferroelectrics are the subgroup of piezoelectric materials in which the electric dipoles can be reoriented or flipped by the application of an external electric field.⁶ Since the piezoelectric coefficient is directly proportional to the electric polarization ($d_{33} \alpha \epsilon P_r$), ferroelectric materials with intrinsic permanent dipole moment, high spontaneous polarization, and piezoelectric response is expected to increase the performance of the nanogenerator.^{7,8} In this context, it is desirable to prepare non-ceramic and heavymetal free power generators for addressing certain issues pertaining to heavier elements such as high-temperature processing, high-voltage poling, toxicity and to impart improved flexibility for the devices.⁹ Although polyvinylidene fluoride (PVDF) and its copolymers based composite materials have attracted greatly as energy harvesters due to their high piezoelectric response, achieving polar ferroelectric and piezoelectric order in these materials are still challenging.10 Moreover, PVDF requires mechanical stretching, hightemperature annealing or poling and requires external additives to obtain polar ferroelectric β phase.¹¹ Alternatively, polymer composites made up of ferro- and piezoelectric organic compounds offer an attractive approach for this application. Herein, we report a flexible mechanical energy harvester derived from a simple ferroelectric phosphorus based organic salt $Ph_2(PrNH)_2PPF_6$ (DPDP·PF_6) embedded in a PDMS matrix. The organo-aminophosphonium salt DPDP-PF₆ retains its polar symmetry for a wide range of temperatures from 100 to 463 K. The ferroelectric measurements on the single crystals of this compound gave a remnant polarization (P_r) of 6.32 μ Ccm⁻². The fabricated composites with polymeric PDMS films were shown to harvest electrical energy with a maximum output voltage of 8.5 V and output current of 0.5 µA (at 15 N impact force and 10 Hz frequency) for the composite with 10 wt% of DPDP·PF₆. To the best of our knowledge, this is the first report for a flexible energy harvester based on a binary organic ferroelectric salt.



Scheme 1. Synthesis of the phosphonium salts DPDP.Br and DPDP.PF $_{6}$.

The organoamino-phosphonium salt $[Ph_2({}^{i}PrNH)_2P] \cdot PF_6$, DPDP·PF₆, was synthesized from diphenylchlorophosphine (Ph₂PCI) as shown in Scheme 1 (Figures S1-S14, Supporting Information). Crystals of DPDP·PF₆ were directly obtained by the anion exchange reaction of DPDP·Br with KPF₆ and were solved

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in the acentric monoclinic space group Cc (Table S1, Supporting Information). The asymmetric unit consists of a phosphonium cation and a non-coordinating hexafluorophosphate anion while the unit-cell contains four DPDP PF₆ motifs (Figures 1a and 1b). The coordination environment around the cationic phosphorus center is distorted tetrahedral. The measured distances of 1.6210(18) and 1.6242(19) Å for P1-N1 and P1-N2, respectively, were in the expected range typically observed for amino-P(V) scaffolds. The N-H protons of the two amino groups are pointing opposite to each other and involved in an intermolecular Hbonding with the PF₆⁻ anions. As a result, the N1-P-N2 angle is wider (avg. 120.76 (10)°) than the ideal tetrahedral angle. Concomitantly, other angles were marginally distorted ranging from 104.93(10) to 108.34(10)° within the cationic segment (Tables S2 and S3, Supporting Information). Each amino proton is hydrogen bonded to two F-atoms of PF6- anion in a chelating fashion (with one strong and one weak interaction) and resulting in the formation of a 1D-chain like structure (Figure 1c, Figure S15, Supporting Information).



Figure 1. (a) Molecular structure of DPDP·PF₆ and (b) its packing diagram along the b-axis. (c) The 1D-chain structure of DPDP·PF₆ mediated by N-H...F hydrogen bonding.

A closer look at the structure of DPDP·PF₆ reveals that the organo- and amino groups around the central phosphonium cation presumably has played a key role for imparting asymmetry in the system.¹² To probe the presence of any centrosymmetric phase in the structure of DPDP·PF₆, single crystal X-ray diffraction analysis was performed in the temperature range between 100 and 463 K with an incremental step of 25 K between the measurements. A detailed structural analysis confirmed no change in symmetry and space group at all the measured temperatures albeit with a marginal increase in the lattice distances and cell volume (Figures S18 and S19, Supporting Information). The powdered unsieved sample of this salt shows a second harmonic generation (SHG) efficiency of 0.2, with respect to the reference KDP which confirms the noncentrosymmetric nature of DPDP·PF₆ at room temperature. The variable-temperature powder X-ray diffraction (VT-PXRD) profile of DPDP·PF₆ did not exhibit any phase change or the systematic absence of peaks upon increasing the temperatures from 298 to 463 K (Figure S20, Supporting Information). The thermogravimetric analysis coupled with differential thermal studies indicated that there are two heat anomalies, one for the melting at 471 K and a subsequent one at 603 K for decomposition (Figure S21, Supporting Information).

The point group symmetry for the structure of DPDP·PF₆ is C_s which belongs to one of the ten polar point groups (C₁, C_s, C₂, C_{2v}, C₃, C_{3v}, C₄, C_{4v}, C₆, and C_{6v}) that are suitable for ferroelectric measurements.¹³ The polarization (P) vs. electric field (E) measurements were performed on the single crystals of DPDP·PF₆ by using a Sawyer-Tower circuit at an operating frequency of 0.1 Hz (Figure 2 and Figure S22, Supporting Information). These crystals gave a remnant (P_r) and saturation (P_s) polarization values of 6.32 and 3.50 μ Ccm⁻², respectively (Figure 2a). The coercive fields (E_c) obtained in these studies were found to be 4.27 kVcm⁻¹.



Figure 2. (a) P-E hysteresis loop and the corresponding leakage current plot of DPDP-PF₆ and (b) Ferroelectric fatigue measurements up to 10^4 cycles and P-E loop after the fatigue cycles. Temperature dependent (c) dielectric constant (ϵ ') and (d) dielectric loss (tan δ) for various frequencies.

While the Pr for DPDP·PF₆ is comparable with some of the wellknown molecular ferroelectrics, the obtained Ec value is much lower than most of them.¹⁴ The observed Pr values are much higher than certain other phosphonium stabilized ferroelectric materials.¹⁵ Also, several metal-organic materials stabilized by related N-donor functionalized amido-P(V) ligands have shown to exhibit ferroelectric behavior.¹⁶ The leakage current density measurements indicate low leakage behavior which are of the order of 1.2 µAcm⁻² along with peaks associated with domain switching typical for ferroelectric materials (Figure 2a). Further, fatique measurements exemplified the retention of ferroelectric polarization for several switching cycles as 90% of its Pr as well as the rectangular shape of the hysteresis loop is retained even after 10⁴ cycles (Figure 2b). The high and stable polarization in this species can be attributed to its asymmetric ionic nature coupled with its H-bond assisted 1D-chain like alignment of bipolar phosphonium cations and PF₆⁻ anions along the b-axis (which is the direction of measurements) with a net long-range polar order.

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Further, we performed temperature dependent dielectric permittivity studies for DPDP.PF₆ on its compacted polycrystalline sample. The real part of the dielectric constant (ε) initially increases slowly with an onset of anomalous behaviour at 390 K (Figure 2c). However, no dielectric peak maxima were attained up to the temperature close to its melting point. These results are consistent with the crystallographic (both VT-SCXRD and VT-PXRD) data and with certain recent reports pertaining to molecular ferroelectrics. $^{17}\mbox{ The observed }\epsilon'$ values were found to vary between 7 and 27 upon sweeping the temperature from 200 to 463 K. The sharp rise in the ϵ ' values can be attributed to its ionic structure that shows increase in charge carriers and ion mobility at higher temperatures. A similar trend has also been observed in the corresponding dielectric loss (tan δ) plot as well (Figure 2d). The frequency dependent dielectric measurements gave higher ɛ' values at lower frequencies indicating the involvement of all the polarization (interface, dipolar, ionic and atomic) mechanisms (Figure S23-S25. Supporting Information).¹⁸ A preliminary piezo measurements on the single crystals of DPDP·PF₆ gave a piezoelectric coefficients (d₃₃) of 8 pC/N under the applied force of 0.20 N. The observed piezoresponse may be attributed to the oriented domain configurations in the single crystals.¹⁹ These values are consistent with some of the known molecular and polymeric ferro- and piezoelectric materials (Table S4, Supporting Information).



Figure 3. Images of (a) neat PDMS, (b) DPDP·PF₆/PDMS (10 wt%) and (c) the corresponding device. (d) The 3D-Xray tomography images of DPDP·PF₆/PDMS (10 wt%; grid scale: 50µm).

Owing to a greater attention for flexible mechanical energy harvesters and nanogenerators based on piezo- and ferroelectric materials, we examined the power generator response of DPDP·PF₆ in its composite form with the polydimethylsiloxane (PDMS) polymer (Figures 3a, 3b and 3c). The composite devices with 3, 5, 7, 10 and 20 wt% of DPDP·PF₆ in PDMS (DPDP·PF₆/PDMS) were prepared by the dispersion of appropriate quantities of DPDP·PF₆ into a homogeneous solution of PDMS precursors (Scheme S3 and Table S5, Supporting Information). All the obtained films unveiled exceptional flexibility as demonstrated by its ease for twisting, two-fold bending and rolling operations (Figure S26, Supporting Information). The morphologies of all the DPDP·PF₆/PDMS composites were investigated by X-ray 3D-tomography analysis. The magnified cross-sectional views of 3D-Xray tomography

images show a random distribution of the DPDP·PF₆ particles in the PDMS matrix (Figure 3d and Figures S27 and S28, Supporting Information). A comparative analysis revealed a much higher particle distribution and density for the 20 wt% composite than the 10 wt% composite. Furthermore, the presence of ferroelectric particles and the crystallite purity of DPDP·PF₆ in the composites was identified by using Raman spectroscopy. Pure PDMS matrix has characteristic peaks at 487 and 708 cm⁻¹ for the symmetrical Si-O-Si and Si-C stretching modes, respectively.²⁰ For DPDP·PF₆, major peaks are found for aromatic, and aliphatic Raman active modes at 1590, 1316, 1117, 998 cm⁻¹. These peaks were present in the DPDP·PF₆/PDMS (10 wt %) composite as well in addition to the peaks due to Si-O-Si and Si-C bonds in PDMS (Figure S29, Supporting Information).



Figure 4. The mechanical generator output voltages (a) and currents (c) for all the DPDP·PF $_{\theta}$ /PDMS devices. The output voltage (b) and current (d) obtained in a one cycle of measurement for the 10 wt % device.

The performances of the devices (with electrodes) have been tested by using an in-house fabricated impact machine and an oscilloscope. The output voltage and output currents for nonpoled DPDP·PF₆/PDMS materials with different ratios (3%, 5%, 7%, 10% and 20 wt%) of ferroelectric DPDP PF₆ fillers are generated from a periodically applied mechanical force. The performance of the DPDP·PF₆/PDMS devices improved with increase in concentration of DPDP·PF₆ upto 10 wt% and decreased for the 20 wt% composite. The obtained maximum output peak to peak voltage (VPP) and output peak to peak current (IPP) of DPDP·PF6/PDMS were found to be 8.5 V and 0.5 µA, respectively, for the 10 wt% composite under an optimized 15 N compressive force and 10 Hz frequency (Figures 4a and 4c, Figures S30 and S31, Supporting Information). These observations are consistent with a few ceramic oxide-polymer composite nanogenerators which show particle agglomeration at higher oxide concentrations with a net reduction in the dipole moments.²¹ The 3D-Xray tomography images support this claim, where the higher 20 wt% composite shows some aggregations

(Figure S27 and S28, Supporting Information). A closer view of the output voltage and current plots confirm a single piezoelectric response generated from each press and release cycle of the composite film (Figures 4b and 4d). The maximum current density (CD) and power density (PD) values of 0.28 μ Acm⁻² and 1.74 μ Wcm⁻³, respectively, were observed for the 10% composite (Figure S32, Supporting Information). The performance of the DPDP·PF₆/PDMS system is fairly comparable to several composites derived from ferroelectric (organic-inorganic and inorganic)-nonpiezoelectric polymer materials.^{88,21c,23b, 22}

The observed room temperature ε' values for the neat PDMS, 3%, 5%, 10% and 20% DPDP·PF₆/PDMS were found to be 5.6, 5.8, 6.9, 7.3 and 7.5, respectively, at 1 kHz (Figure S33, Supporting Information). A linear increase in ɛ' values from 3 to 20 wt % indicates the contribution from the ferroelectric particles for the overall dipole moment of the composite films.²³ Similarly, a marginal increase in the piezoelectric coefficient (d₃₃) values from 3 to 5 pC/N has been observed upon increasing the wt% of the ferroelectric component from 3% to 20% (Figure S34, Supporting Information). This clearly indicates that the organicpolymer matrix interface plays a vital role in determining the dielectric and piezoelectric properties of the DPDP·PF6/PDMS composites. Furthermore, it is to be noted that the effective energy harvesting performance of these materials depends on the layer thickness, strength of the mechanical force applied, structural morphologies and the weight ratio between polymer and piezoelectric filler.24

In summary, we have reported the synthesis of a new ferroelectric polar organic binary salt of DPDP·PF₆ containing organo- and amino functionalities. Ferroelectric measurements on the single crystals of this salt gave a P_r value ~6 μ Ccm⁻². The 1D-arrangement of organo aminophosphonium cations and PF₆ anions aided by the presence of N-H...F intermolecular hydrogen bond in its asymmetric lattice helps in the effective alignment of dipoles responsible for ferroelectric behaviour. Also, it exhibits high thermal and phase stability and sharp polarization response. In combination with polymeric PDMS films, device structures with excellent mechanical flexibility for various wt% (3, 5, 7, 10, 20%) of DPDP·PF₆ were prepared. The mechanical energy harvesting performance of these devices show the current density of 0.28 µAcm⁻², and power density of 1.74 μ Wcm⁻³ for the 10 wt% DPDP·PF₆/PDMS composite. These results demonstrate the effectiveness of organic ferroelectric materials for energy harvesting applications and promise their potential utility in future wearable electronics.

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Keywords: binary phosphonium salts • H-bonding • polar order • ferroelectricity • polymer composites • energy harvesters

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A noncentrosymmetric binary organic salt $Ph_2(^{i}PrNH)_2P$]·PF₆ was synthesized and found to exhibit excellent thermal and phase stabilities. Ferroelectric measurements on this salt gave remnant polarization value ~6 µCcm⁻². Further in combination with PDMS polymer it was utilized as a composite mechanical energy harvester that shows a highest output voltage of 8.5 V.



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A Flexible Composite Mechanical Energy Harvester from a Ferroelectric Organo-amino Phosphonium Salt