

Supporting information

Piezoelectric Energy Harvesting of a Bismuth Halide Perovskite Stabilised by Chiral Ammonium Cations

Supriya Sahoo, Nilotpal Deka, Ramamoorthy Boomishankar*

Department of Chemistry and Centre for Energy Science, Indian Institute of Science Education and Research (IISER), Pune, Dr. Homi Bhabha Road, Pune – 411008, India
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Table of contents

S.No.	Details	Page No.
1	X-ray crystallographic information	2-3
2	Characterisations	4-5
3	Dielectric studies	4
4	1-S -PLA composites and their Piezoelectric studies	5-10
5	References	11

Table S1. X-ray Crystallographic data for **1-S**.

Crystallographic details	1-S	1-S
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> ₂₁₂₁₂₁	<i>P</i> ₂₁₂₁₂₁
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

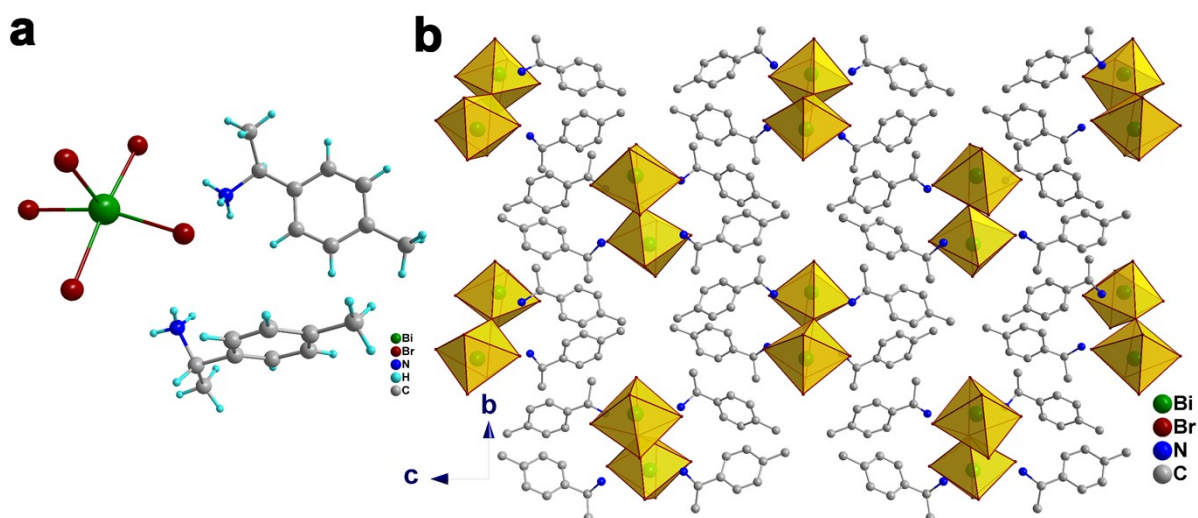
**Figure S1.** (a) Asymmetric unit and (b) packing diagram of **1-S** along a-axis at 100 K.

Table S2. Hydrogen bonding parameters for **1-S**.

D-H...A	d(H...A) Å	d(D-A) Å	$\angle(\text{DHA})$	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

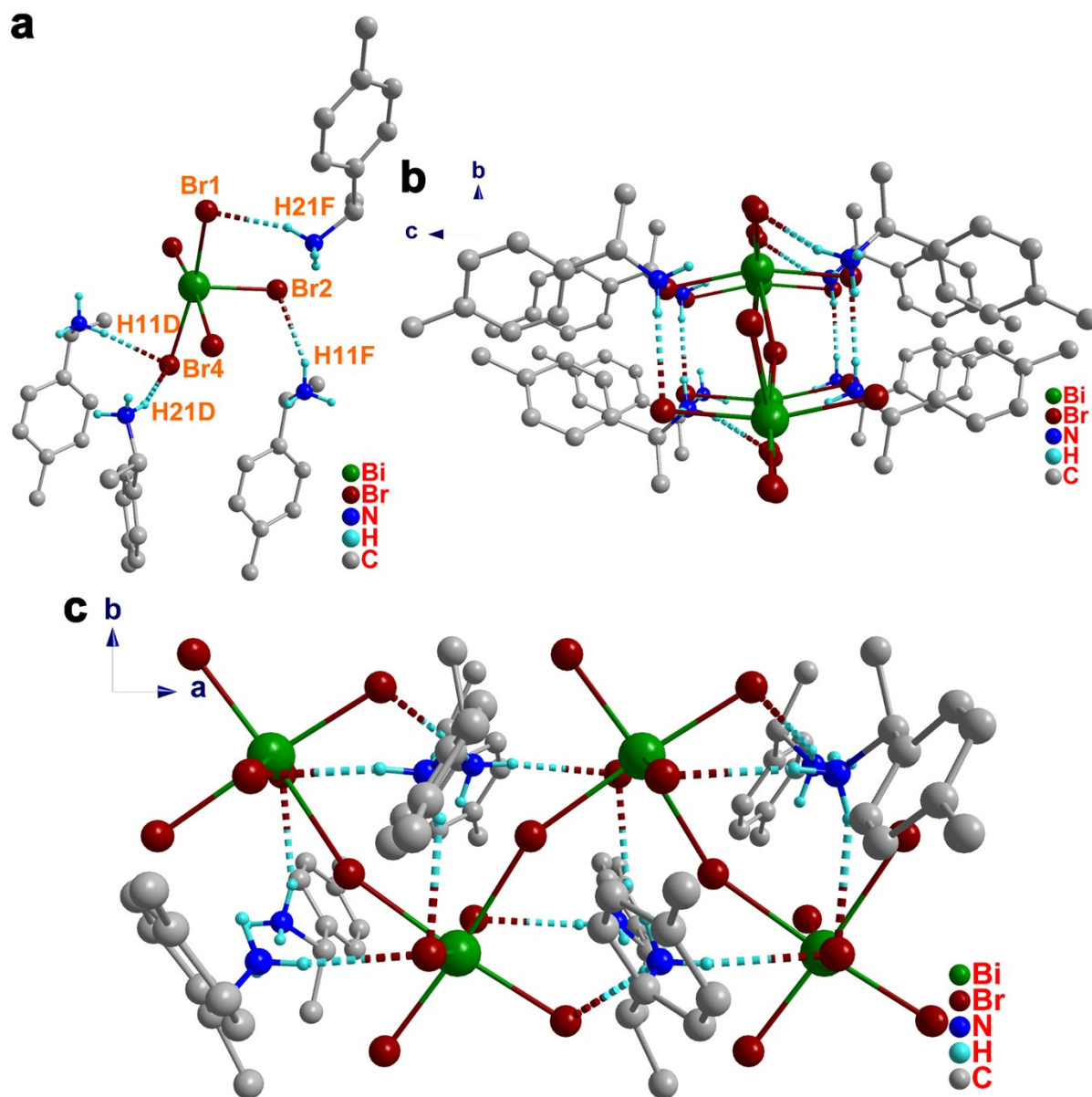


Figure S2. Non-classical N-H...Br hydrogen bonding interactions in **1-S** at 100 K.

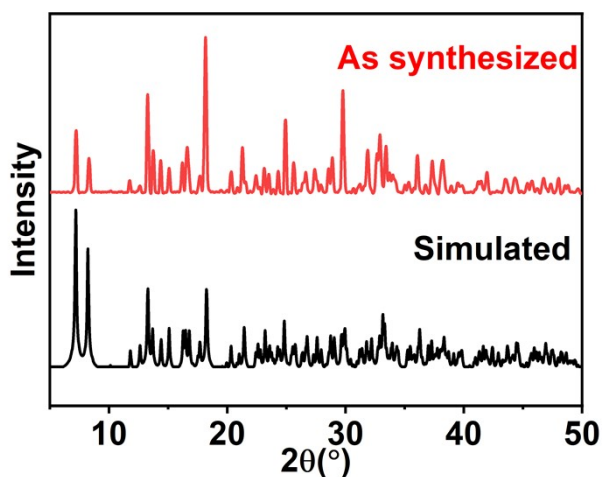


Figure S3. The powder X-ray diffraction (PXRD) profile of 1-S.

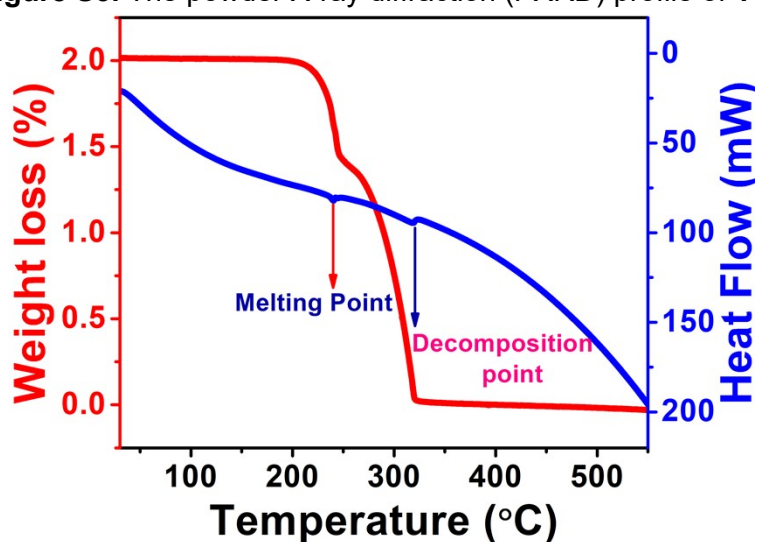


Figure S4. The thermogravimetric and differential thermal analysis profiles of 1-S.

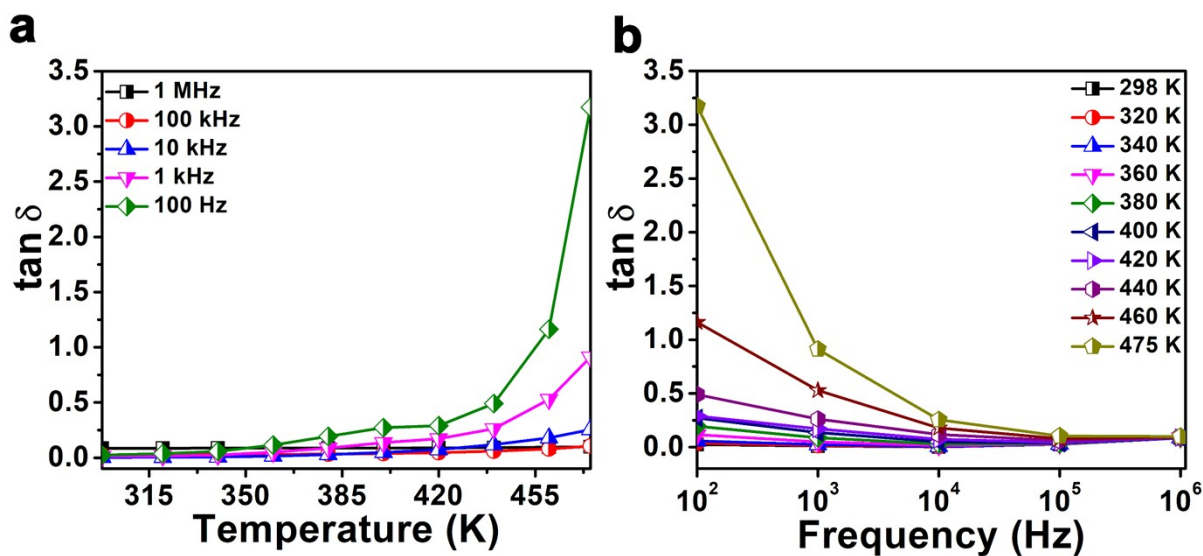


Figure S5. (a) Temperature dependant dielectric loss plot and (b) Frequency dependant dielectric loss plot of 1-S.

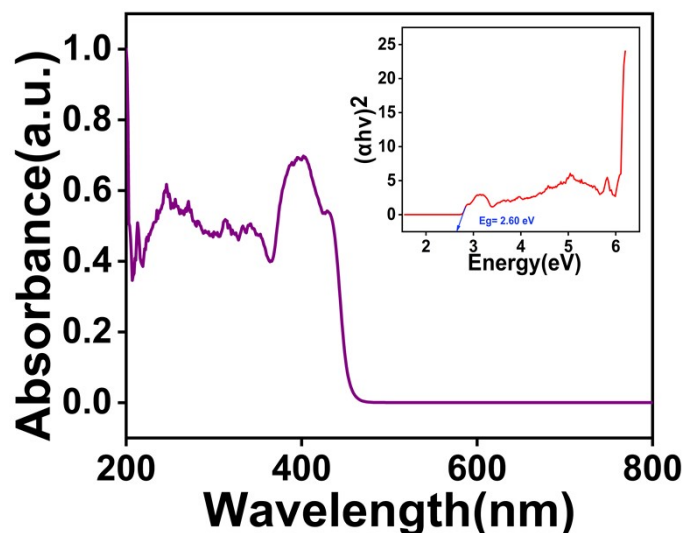


Figure S6. UV-Visible diffuse reflectance spectrum of **1-S**; its corresponding Tauc plot is displayed in the inset.

Table S3. Details about the preparation of various weight percentage (wt %) **1-S**-PLA composites.

Composite (wt%)	1-S (in mg)	1-S + 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

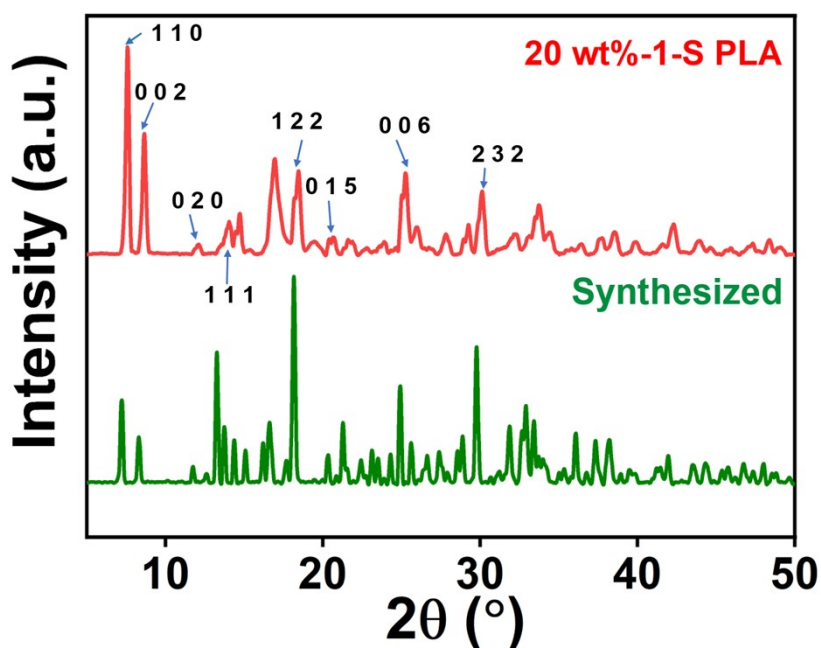


Figure S7. The powder X-ray diffraction pattern and the characteristic hkl peaks for compound **1-S** and the 20 wt % **1-S**-PLA.

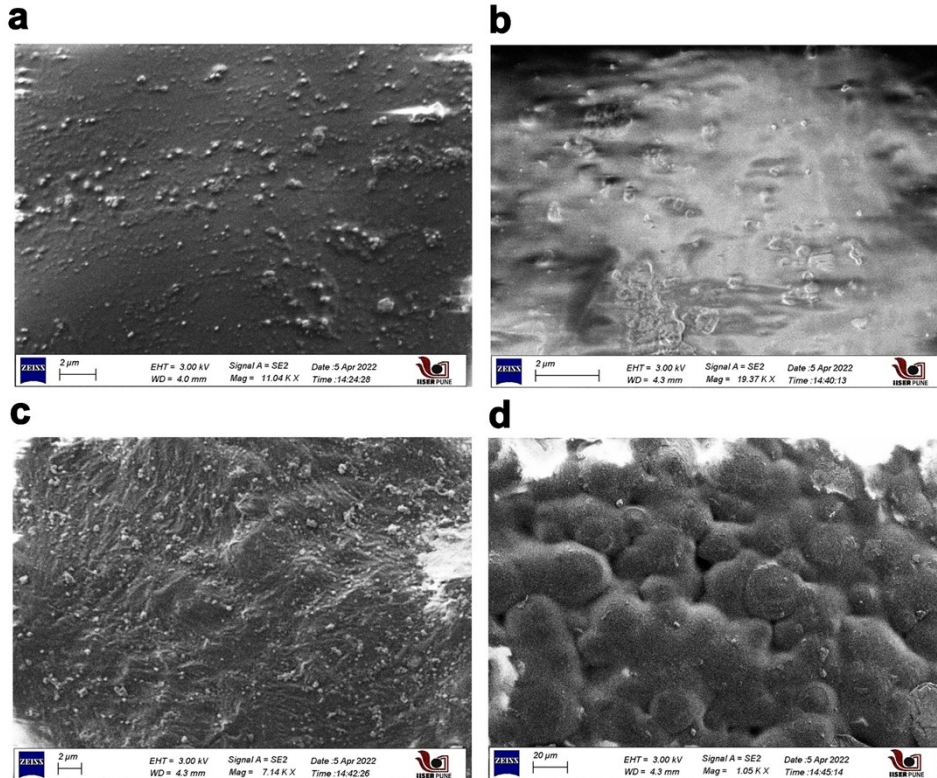


Figure S8. The FE-SEM images of 1-S-PLA composites. The figures a, b, c, and d correspond to 5, 10, 15, and 20 wt % 1-S-PLA composites respectively.

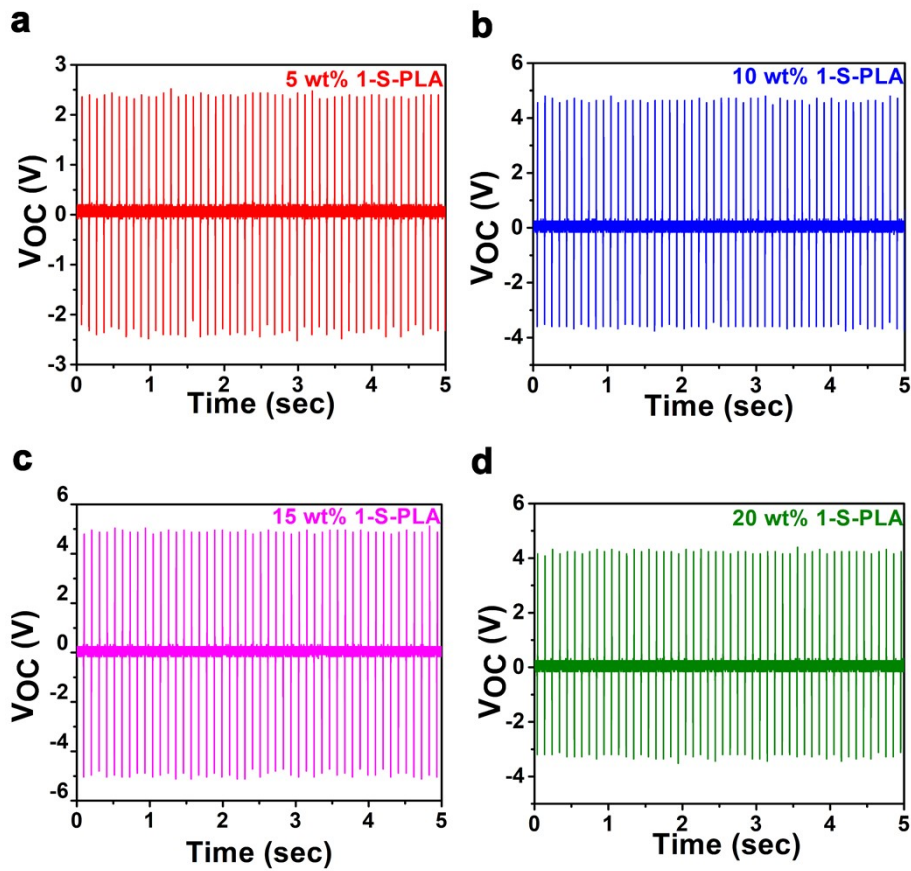


Figure S9. Output voltage profiles of all the 1-S-PLA composite films.

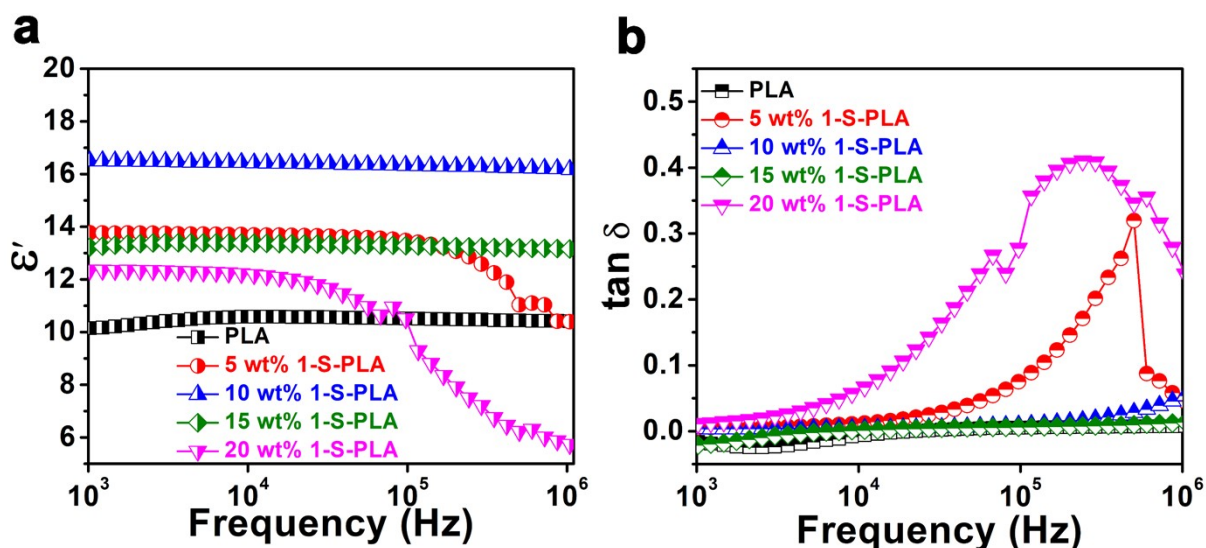


Figure S10. Frequency dependent dielectric permittivity and (b) Frequency dependent dielectric loss plot of neat PLA and all 1-S-PLA films.

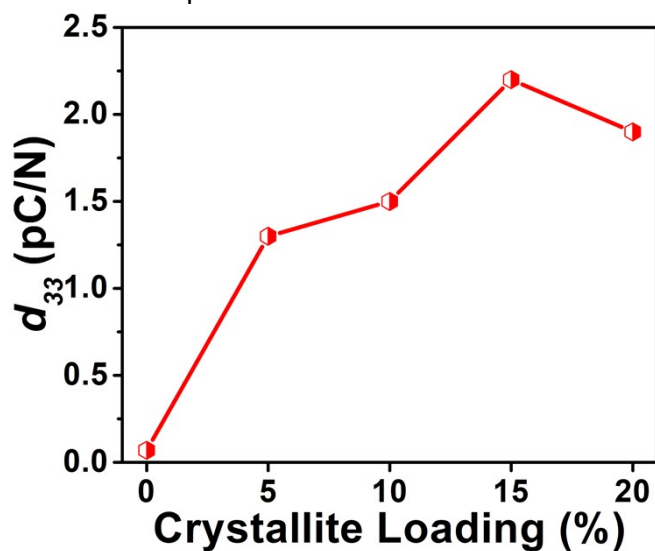


Figure S11. The comparative d_{33} values for all 1-S-PLA composite films and neat PLA film. The solid lines the connecting the points are a guide the eye.

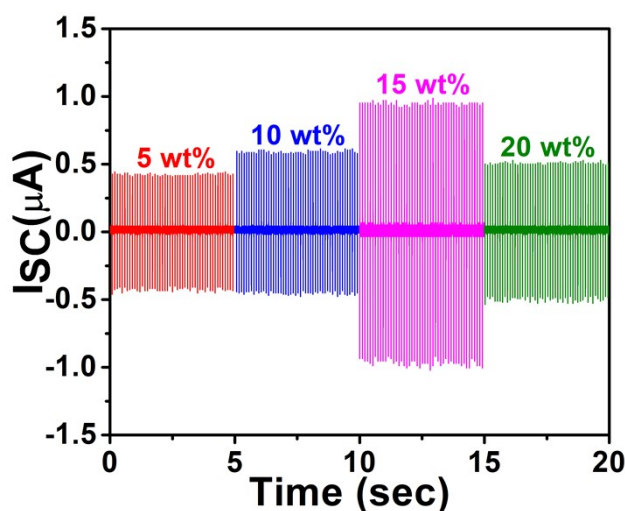


Figure S12. Output current profile of 1-S-PLA composite films.

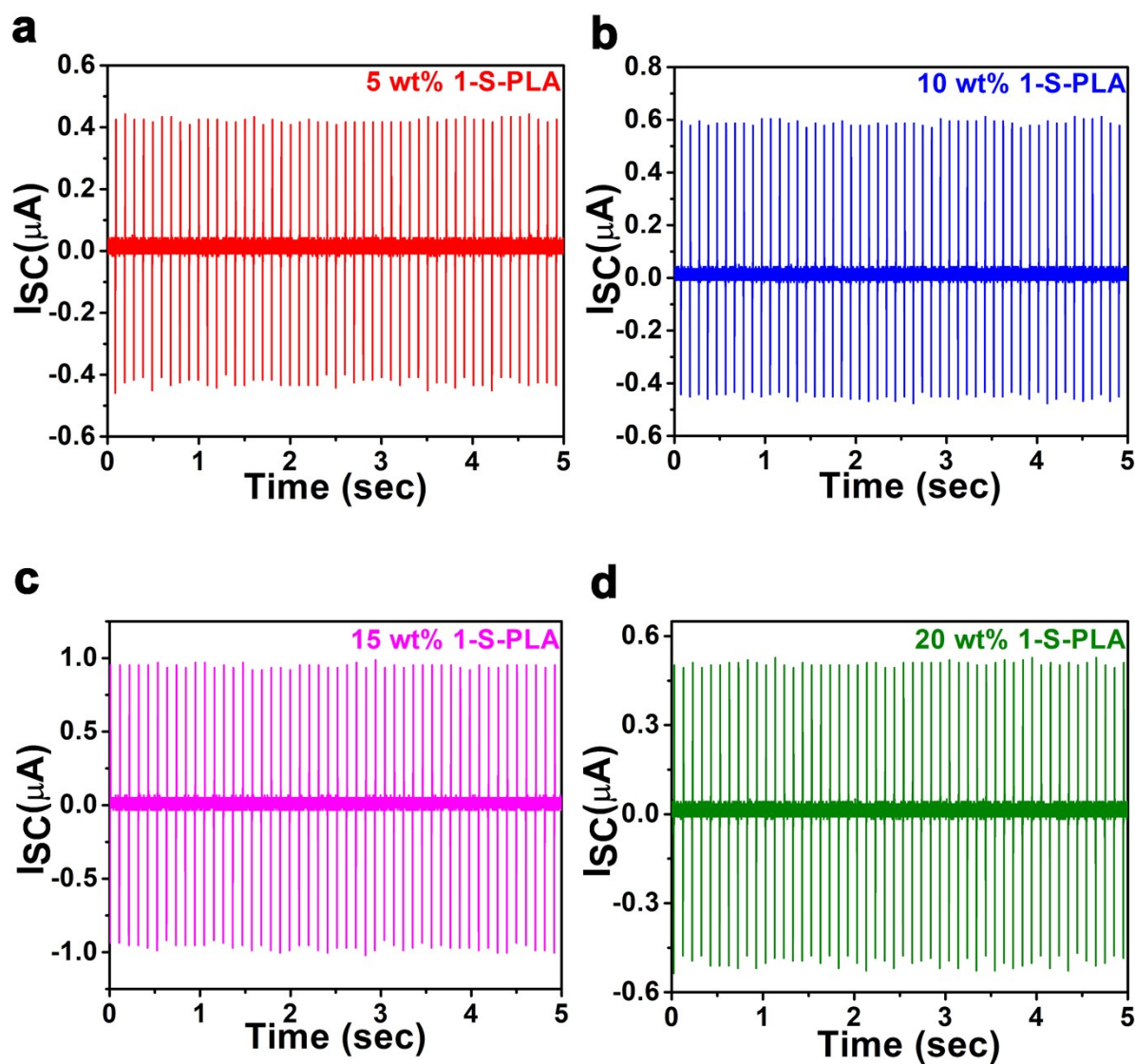


Figure S13. The calculated output currents of all the 1-S-PLA composite films.

Table S4. Summary of maximum piezoelectric energy harvesting outputs of 15 wt% 1-S-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 μ A
Maximum CD	0.5 μ A/cm ²
Maximum PD	5.26 μ W/cm ²
Energy Stored in 100 μ F Capacitor	58.25 μ J
Charge Stored in 100 μ F Capacitor	116.5 μ C

Table S5. 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	References
MAPbI ₃ -PVDF	9.43	0.76 $\mu\text{A cm}^{-2}$	-	1 x 1 cm ²	¹
MAPbBr ₃ -PVDF	5	60 nA	0.28 $\mu\text{W cm}^{-2}$	2.4 x 1.5 cm ²	²
MAPbI ₃ -PDMS	1.0	50 nA cm ⁻²	-	1 x 1 cm ²	³
FAPbBr ₃ -PDMS	4	-	-	1 x 1 cm ²	⁴
CsPbBr ₃ /PVDF	10.3	1.29 $\mu\text{A cm}^{-2}$	3.31 μW	1 x 1 cm ²	⁵
PVDF-PLLA-SnO ₂ NF-MAPbI ₃	4.82	29.7 nA	-	0.25 x 0.25 cm ²	⁶
SnO ₂ NF-MAPbI ₃	1.02	10.32 nA	-	0.25 x 0.25 cm ²	⁶
[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	⁷
[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	⁷
(TMFM)FeBr ₄	2.2	-	-	-	⁸
[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	⁹
[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	¹⁰
15 wt% 1-S-PLA	10.4	0.5 $\mu\text{A cm}^{-2}$	5.26 $\mu\text{W cm}^{-2}$	1.2 x 3 cm²	This work

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 .

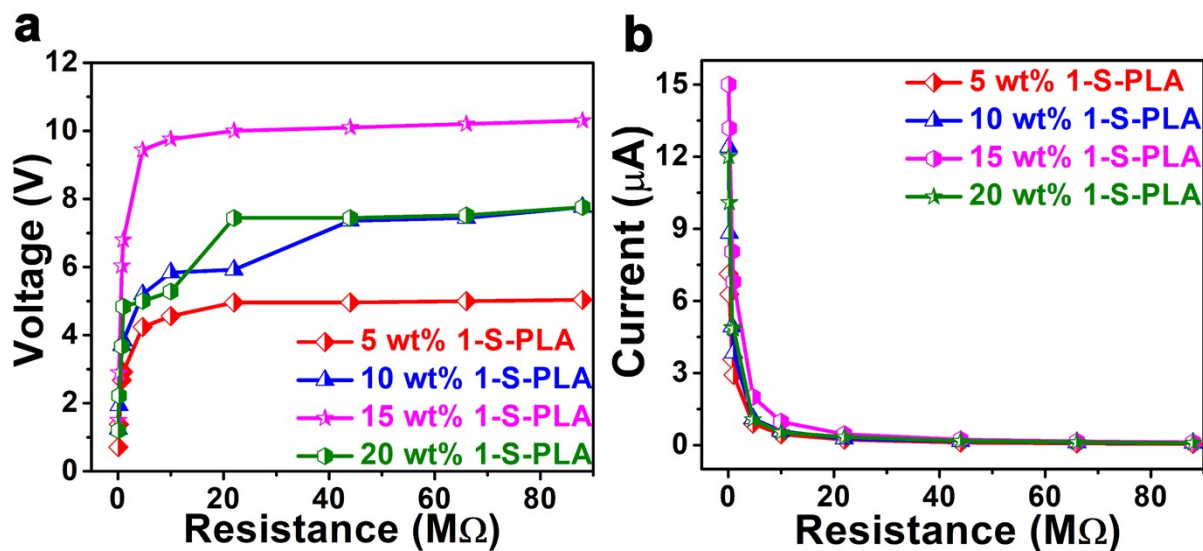


Figure S14. The comparative output (a) voltage and (b) current data for all the 1-S-PLA composite devices under various load resistances.

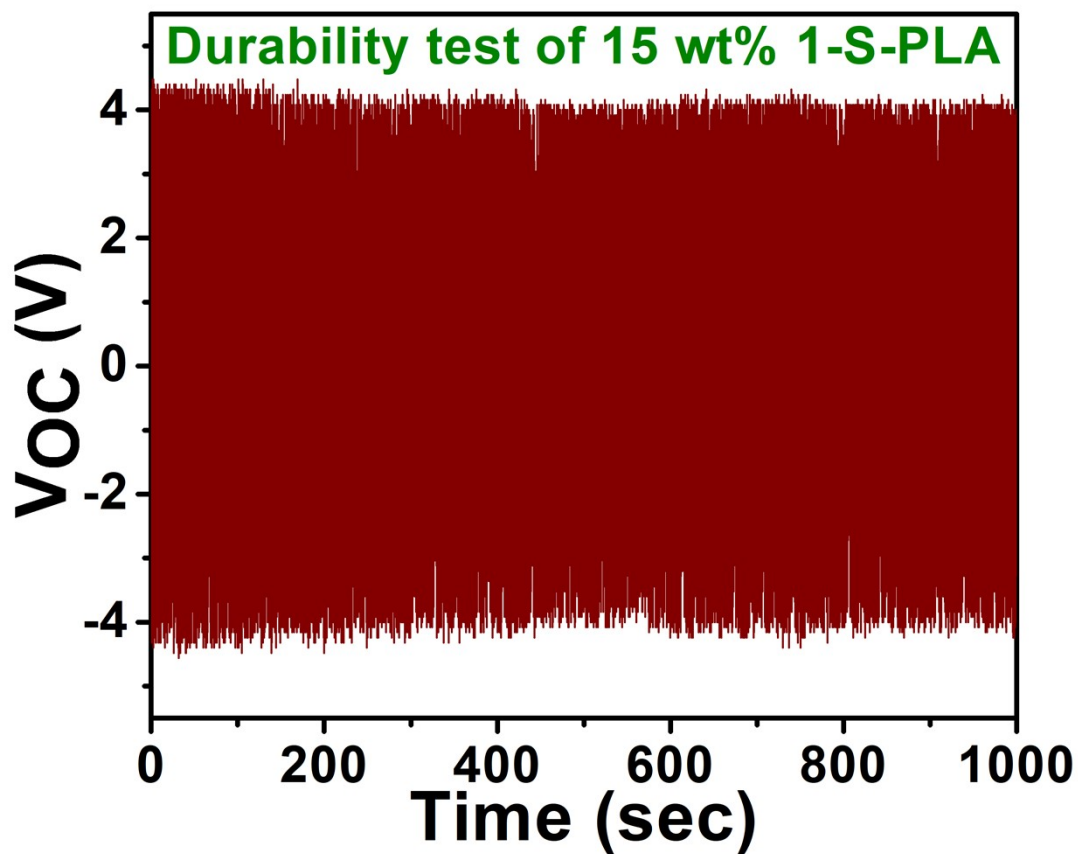


Figure S15. Fatigue test for the 15 wt% 1-S-PLA composite device up to 10000 cycles.

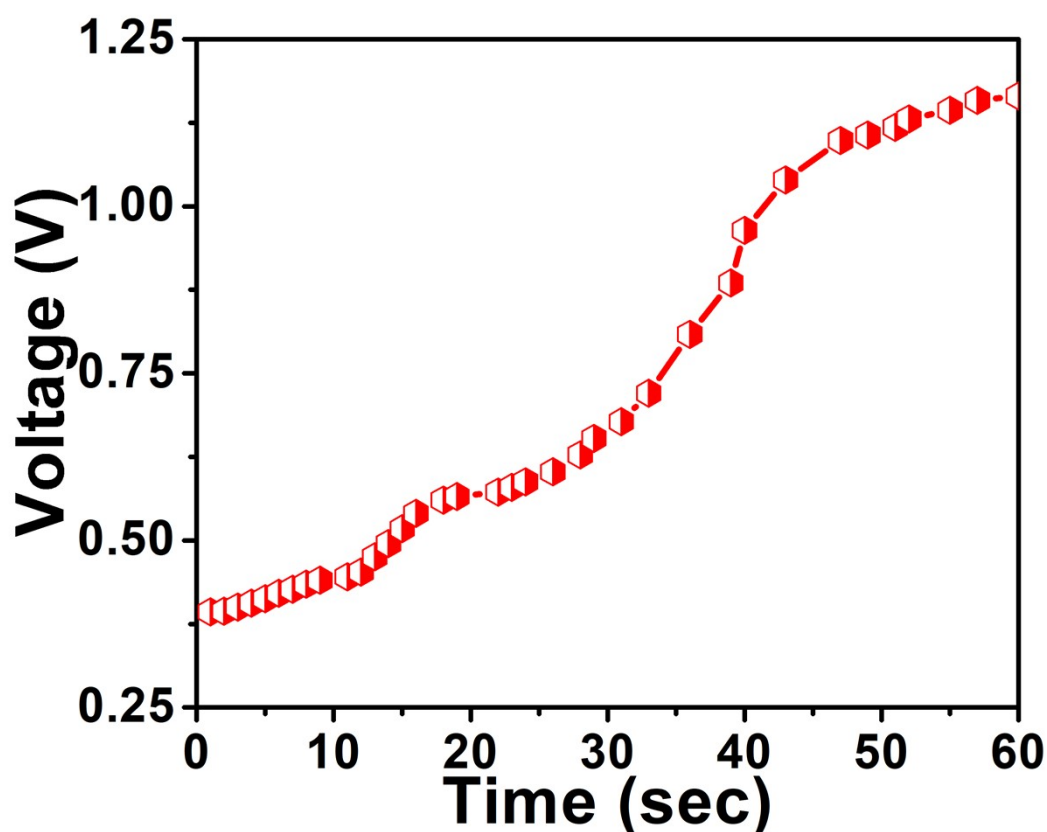


Figure S16. Stored voltages in a 100 μF capacitor by employing the 15 wt % 1-S-PLA composite device at different time intervals.

References

1. V. Jella, S. Ippili, J.-H. Eom, J. Choi and S.-G. Yoon, *Nano Energy*, 2018, **53**, 46-56.
2. A. Sultana, M. M. Alam, P. Sadhukhan, U. K. Ghorai, S. Das, T. R. Middy and D. Mandal, *Nano Energy*, 2018, **49**, 380-392.
3. Y.-J. Kim, T.-V. Dang, H.-J. Choi, B.-J. Park, J.-H. Eom, H.-A. Song, D. Seol, Y. Kim, S.-H. Shin, J. Nah and S.-G. Yoon, *Journal of Materials Chemistry A*, 2016, **4**, 756-763.
4. R. Ding, H. Liu, X. Zhang, J. Xiao, R. Kishor, H. Sun, B. Zhu, G. Chen, F. Gao, X. Feng, J. Chen, X. Chen, X. Sun and Y. Zheng, *Advanced Functional Materials*, 2016, **26**, 7708-7716.
5. Y. Li, M.-h. Xu, Y.-s. Xia, J.-m. Wu, X.-k. Sun, S. Wang, G.-H. Hu and C.-x. Xiong, *Chemical Engineering Journal*, 2020, **388**, 124205.
6. R. Tusiime, F. Zabihi, M. Tebyetekerwa, Y. M. Yousry, Y. Wu, M. Eslamian, S. Yang, S. Ramakrishna, M. Yu and H. Zhang, *Journal of Materials Chemistry C*, 2020, **8**, 2643-2658.
7. S. Deswal, S. K. Singh, P. Rambabu, P. Kulkarni, G. Vaitheeswaran, B. Praveenkumar, S. Ogale and R. Boomishankar, *Chemistry of Materials*, 2019, **31**, 4545-4552.
8. Y. Zhang, X.-J. Song, Z.-X. Zhang, D.-W. Fu and R.-G. Xiong, *Matter*, 2020, **2**, 697-710.
9. T. Vijayakanth, F. Ram, B. Praveenkumar, K. Shanmuganathan and R. Boomishankar, *Angewandte Chemie International Edition*, 2020, **59**, 10368-10373.
10. S. Sahoo, T. Vijayakanth, P. Kothavade, P. Dixit, J. K. Zaręba, K. Shanmuganathan and R. Boomishankar, *ACS Materials Au*, 2022, **2**, 124-131.