



HAL
open science

Achieving Ultrahigh Piezoelectricity in Organic–Inorganic Vacancy-Ordered Halide Double Perovskites for Mechanical Energy Harvesting

Guangguang Huang, Asif Abdullah Khan, Md Masud Rana, Chao Xu, Shuhong Xu, Resul Saritas, Steven Zhang, Eihab Abdel-Rahmand, Pascal Turban, Soraya Ababou-Girard, et al.

► **To cite this version:**

Guangguang Huang, Asif Abdullah Khan, Md Masud Rana, Chao Xu, Shuhong Xu, et al.. Achieving Ultrahigh Piezoelectricity in Organic–Inorganic Vacancy-Ordered Halide Double Perovskites for Mechanical Energy Harvesting. *ACS Energy Letters*, 2021, 6 (1), pp.16-23. 10.1021/acsenergylett.0c02200 . hal-03124235

HAL Id: hal-03124235

<https://univ-rennes.hal.science/hal-03124235v1>

Submitted on 22 Feb 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Achieving Ultrahigh Piezoelectricity in Organic-
2 Inorganic Vacancy-Ordered Halide Double
3 Perovskites for Mechanical Energy Harvesting

4 *Guangguang Huang^a, Asif Abdullah Khan^a, Md Masud Rana^a, Chao Xu^a, Shuhong Xu^c, Resul*
5 *Saritas^d, Steven Zhang^a, Eihab-Abdel Rahman^d, Pascal Turban^f, Soraya Ababou-Girard^f, Chunlei*
6 *Wang^{*c}, Dayan Ban^{*a,b,e}*

7 ^a Waterloo Institute for Nanotechnology, University of Waterloo, 200 University Ave West,
8 Waterloo, ON, Canada

9 ^b Department of Electrical and Computer Engineering, University of Waterloo, 200 University
10 Ave, Waterloo, ON, Canada

11 ^c Advanced Photonics Center, School of Electronic Science and Engineering, Southeast
12 University, Nanjing, 210096, P. R. China

13 ^d Department of Systems Design Engineering, University of Waterloo, 200 University Ave,
14 Waterloo, N2L 3G1 ON, Canada

15 ^e School of Physics and Electronics, Henan University, No. 1 Jinming street, Kaifeng, Henan, P.
16 R. China

17 ^f Univ Rennes, CNRS, IPR (Institut de Physique de Rennes) - UMR 6251, F-35000 AUTHOR

18 **Corresponding Author**

19 E-mail: wangchl@seu.edu.cn and dban@uwaterloo.ca

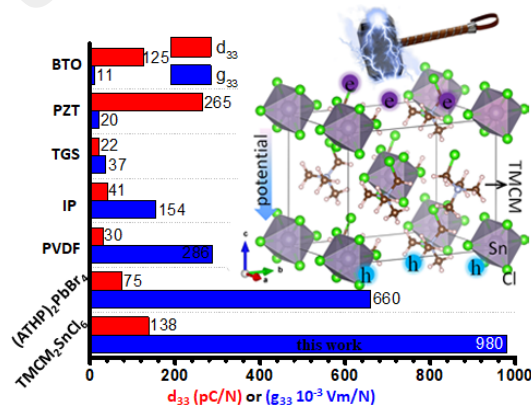
20

21

1 ABSTRACT

2 Piezoelectric charge coefficient (d_{33}) and piezoelectric voltage coefficient (g_{33}) are the two most
3 critical parameters that define output performance of piezoelectric nanogenerators (PNGs). Herein,
4 we propose a vacancy-ordered double perovskite of $\text{TMCM}_2\text{SnCl}_6$ (where TMCM is
5 trimethylchloromethyl ammonium) with a large d_{33} of 137 pC/N and g_{33} of $980 \times 10^{-3} \text{ V} \cdot \text{m/N}$. The
6 piezoelectric coefficients are considered from the halogen-bonding mediated synergistic
7 movements of atomic displacement in inorganic $[\text{SnCl}_6]^{2-}$ octahedrons, as well as the molecular
8 rotation of organic TMCM^+ , which is revealed by a combined density functional theory (DFT) and
9 experimental study. The $\text{TMCM}_2\text{SnCl}_6$ possesses a high saturated polarization (P_s) of $8.7 \mu\text{C}/\text{cm}^2$,
10 a high Curie temperature (T_c) of 365 K, and a low coercive field (E_c) of 0.6 kV/cm. The output
11 voltage (V_{oc}) and current (I_{sc}) of the PNGs are 81 V and $2 \mu\text{A}$ at an applied mechanical excitation
12 of (4.9 N, 40 Hz). We hope this work will provide guidance in energy harvesting by innovatively
13 designing highly piezoelectric perovskites for the PNGs.

14 TOC GRAPHICS



15

16

1 Piezoelectric nanogenerators (PNGs) have been emerging as a promising power source for self-
2 powered electronics owing to their direct power conversion from mechanical to electrical energy.¹⁻
3 ⁵ To maximize the output power of PNGs, both the d_{33} and g_{33} of the piezoelectric host are
4 important, which determines the output current ($I_{sc}=(d_{33}\times\Delta F)/\Delta t$, where ΔF is the applied force
5 and Δt is the time) and voltage ($V_{oc}=g_{33}\times\Delta P\times L$, where ΔP is the applied pressure and L is the
6 original film thickness), respectively.⁶⁻⁹ In the past decade, a wide range of piezoelectric materials,
7 targeting high g_{33} or d_{33} , have been synthesized for the efficient PNGs. For example, the organic
8 polyvinylidene fluoride (PVDF) possesses a high g_{33} ($\sim 286 \times 10^{-3} \text{ V}\cdot\text{m/N}$), leading to a high output
9 piezoelectric voltage. Unfortunately, the resultant current is limited due to its relatively-low d_{33}
10 ($\sim 30 \text{ pC/N}$).¹⁰⁻¹³ Conversely, inorganic perovskite oxide ceramics, including $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT)
11 and BaTiO_3 (BTO), exhibit a high d_{33} ($>100 \text{ pC/N}$) but their g_{33} is rather low ($\sim 20 \times 10^{-3} \text{ V}\cdot\text{m/N}$).¹⁴⁻
12 ¹⁸ Considering the relation between d_{33} and g_{33} ($g_{33}=d_{33}/(\epsilon_0\times\epsilon_r)$), where ϵ_r is material relative
13 permittivity, it is challenging to improve d_{33} while maintaining a high g_{33} because the increase of
14 d_{33} is usually associated with an even larger increase of ϵ_r .¹⁹

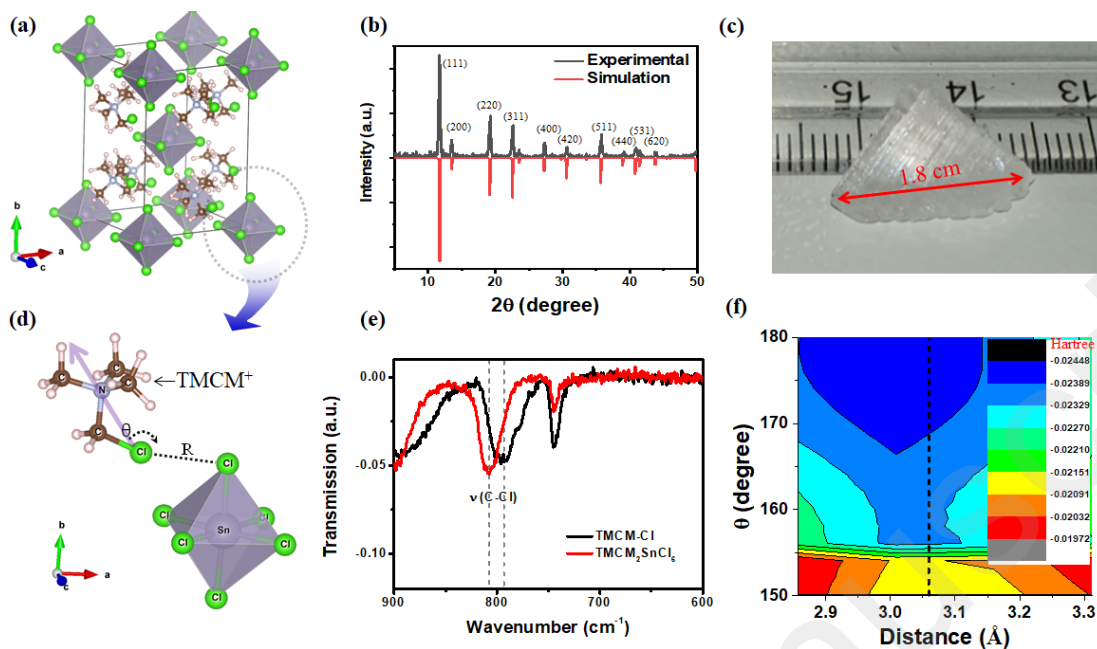
15 Organic-inorganic hybrid perovskites (OIHPs) combine the merits of both organic molecules
16 and crystalline inorganic solids at a molecular level. The OIHPs were firstly introduced to solar
17 cells (SCs) due to their excellent optical properties in 2009 and then adopted in piezoelectric
18 research.²⁰⁻²⁵ In 2015, the MAPbI_3 was firstly employed in PNGs which yielded an output voltage
19 and current density of 2.7 V and 140 nA/cm^2 at a pressure of 0.5 MPa.²⁶ Subsequently, a series of
20 perovskites, including MASnBr_3 , FAPbBr_2I and Cl/Br-MAPbI_3 , have been developed for efficient
21 PNGs via the piezoelectric composite films.²⁷⁻³¹ However, the aforementioned OIHPs evolved
22 from the shadows of the SCs possess limited piezoelectric coefficients. Therefore, extensive efforts
23 have been devoted to searching for highly piezoelectric OIHPs. Remarkably, one-dimensional

1 ABX₃-type OIHPs with high d₃₃, including the TMCM-MnCl₃ and A-site mixed
2 (TMFM)_x(TMCM)_{1-x}CdCl₃, were synthesized in 2017 and 2019, respectively.^{32, 33} Two-
3 dimensional (ATHP)₂PbBr₄ OIHPs with large d₃₃ of 75 pC/N and giant g₃₃ of 660 × 10⁻³ V•m/N
4 were reported in 2019.³⁴ In 2020, the OIHPs were further developed and successfully employed in
5 energy harvesting applications, including (FMTMA)PbCl₂I, HETMA-CdCl₃, (TMFM)FeBr₄ and
6 [Ph₃MeP]₄[Ni(NCS)₆].³⁵⁻³⁸ Despite their large piezoelectric coefficients, the newly-developed
7 OIHPs may suffer substantial difficulties in mass production and implementation. For example,
8 the TMCM-MnCl₃ has intrinsic chemical instability as the bivalent Mn is prone to be oxidized to
9 tetravalent, while the Cd (or Pb) in (TMFM)_x(TMCM)_{1-x}CdCl₃ (or (ATHP)₂PbBr₄) is not
10 environmental-friendly. Unlike the ABX₃-type OIHPs, the A₂BX₆ OIHPs (such as K₂PtCl₆) are
11 potentially more chemically stable because their B-site is already in the tetravalent state.³⁹⁻⁴¹

12 Herein, we proposed an alternative crystal model, which was vacancy-ordered double OIHPs,
13 for novel piezoelectric material design. The chemical formula was confirmed as TMCM₂SnCl₆ via
14 powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The large d₃₃ of
15 137 pC/N and giant g₃₃ of 980 × 10⁻³ V•m/N were experimentally measured for the prepared
16 TMCM₂SnCl₆ crystal, which was further confirmed by the DFT study and the outputs of PNGs.
17 The PNGs were fabricated via sandwiching the TMCM₂SnCl₆@PDMS composite film into two
18 copper electrodes, where PDMS represents Poly(dimethylsiloxane). A self-powered wireless
19 communication node (SWCN) was successfully driven by the PNG. The detailed material
20 synthesis and device fabrication processes are shown in the supporting information.

21

22



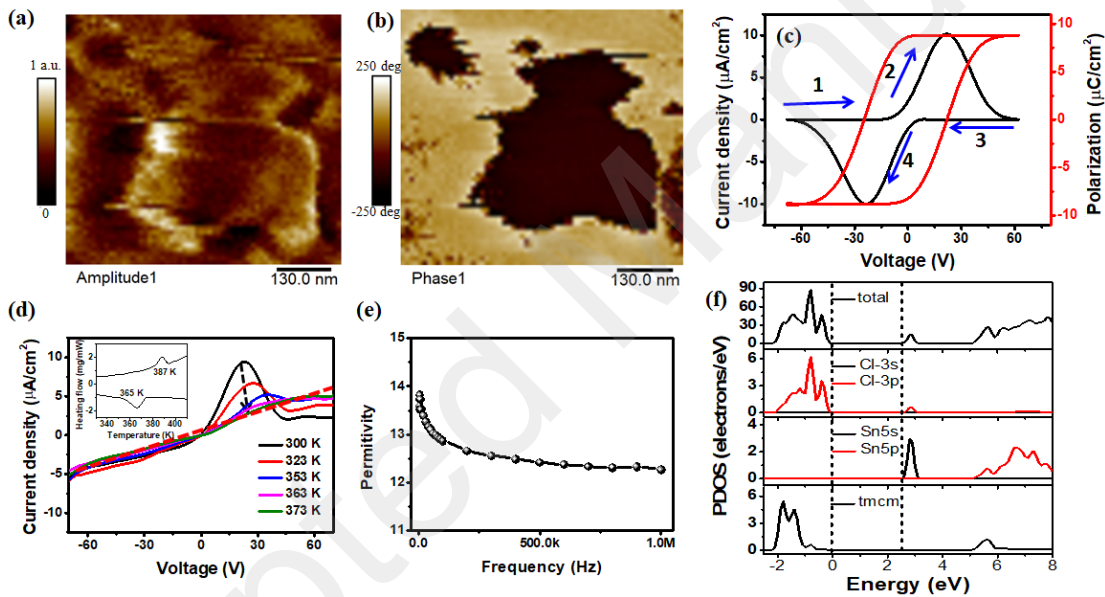
1
 2 **Figure 1. Crystal structure of $\text{TMCM}_2\text{SnCl}_6$ double perovskites:** (a) structural model; (b)
 3 calculated and experimental XRD patterns; (c) digital photograph of single crystal; (d) halogen
 4 bonding interaction. The arrow from Cl to N indicates the dipole direction of TMCM^+ ; (e) FTIR
 5 spectra of pure TMCM-Cl molecules and $\text{TMCM}_2\text{SnCl}_6$; (f) calculated energy mapping of halogen
 6 bond for the simplified model in Figure 1d.

7
 8 $\text{TMCM}_2\text{SnCl}_6$ is a vacancy-ordered double perovskite because its 50% $[\text{SnCl}_6]^{2-}$ octahedrons
 9 are replaced by periodic vacancies, in which the asymmetric TMCM^+ takes the A sites (**Figure**
 10 **1a**). This is different from the reported vacancy-ordered double perovskites with spherical
 11 symmetric cations like trimethylmethyl ammonium (TMA) or monovalent alkali metals (Na, K,
 12 Cs...) taking the A sites.⁴²⁻⁴⁴ **Figure 1b** shows the XRD measured from the $\text{TMCM}_2\text{SnCl}_6$ single
 13 crystals (black curve) in comparison to the simulated XRD (red curve) from the projected structure
 14 in Figure 1a. The single crystal of $\text{TMCM}_2\text{SnCl}_6$ with a length of 1.8 cm is shown in **Figure 1c**.

1 The agreement of XRD peaks confirms the crystal structure and its high phase purity. The
2 $\text{TMCM}_2\text{SnCl}_6$ was aged to 6 months in an ambient atmosphere and the XRD was measured in
3 **Figure S1a**. The reflection peaks of $\text{TMCM}_2\text{SnCl}_6$ almost remained unchanged and no new
4 reflection peaks appeared. These indicate the $\text{TMCM}_2\text{SnCl}_6$ crystals have not degraded into other
5 chemicals and exhibit good stability. The $\text{TMCM}_2\text{SnCl}_6$ also exhibits good thermal stability, as
6 indicated by a negligible change in the measured permittivity at 340K for one hour (**Figure S1d**).
7 The chemical states of $(\text{TMCM})_2\text{SnCl}_6$ were measured via XPS in **Figure S2**. The peaks at binding
8 energy of 495.8 eV and 487.3 eV are assigned to Sn^{4+} and corresponding to its $3d_{3/2}$ and $3d_{5/2}$
9 orbitals, respectively. The peaks at 200.6 eV and 198.8 eV are assigned to $3p_{1/2}$ and $3p_{3/2}$ orbitals
10 of Cl^- . This is well consistent to the chemical states in $[\text{SnCl}_6]^{2-}$ octahedrons, where Sn is in
11 tetravalent state and Cl in minus state.

12 A halogen bond has been considered as an efficient driving force to achieve the well-defined
13 structures during crystal growth for piezoelectric properties.^{45, 46} In $\text{TMCM}_2\text{SnCl}_6$, there is a net
14 attractive interaction between an electrophilic region associated with the Cl atom in TMCM^+ and
15 the nucleophilic Cl^- in the $[\text{SnCl}_6]^{2-}$ octahedron (**Figure 1d**). The attractive nature of the halogen
16 bond is determined by the bond distance (R, in the range of 2-6 Å) and the bond angle (θ , in the
17 range of 150-180°), especially when R is shorter than the sum of Van der Waals radii (~ 3.5 Å).
18 The halogen bond in the $\text{TMCM}_2\text{SnCl}_6$ was reflected by Fourier transform infrared spectroscopy
19 (FTIR) in **Figure 1e**. The absorption peak at 793 cm^{-1} (black line) is attributed to the stretching
20 vibration of Cl-C bond of TMCM^+ . For the $\text{TMCM}_2\text{SnCl}_6$, the absorption peak has a red-shift of
21 14 cm^{-1} to 807 cm^{-1} (red line). The red shift should be attributed to the increased force constant
22 when the electrophilic Cl in TMCM^+ is attracted by the nucleophilic Cl in $[\text{SnCl}_6]^{2-}$ octahedron
23 according to harmonic motion for diatomic model.^{47, 48} The halogen bond energy was calculated

1 by using DFT as a function of the bond distance (R) and the bond angle (θ) in **Figure 1f and**
 2 **Figure S3**. With the decreasing of R, the calculated system energy of $\text{TMCM}^+ \cdots [\text{SnCl}_6]^{2-}$
 3 decreases as the increased Coulomb attraction, and followed by a quick increase afterwards due to
 4 the dominating nuclear repulsion. The halogen bond energy is evaluated from the absolute value
 5 of valley energy. The lowest energy of halogen bond is observed to be 0.021 Hartree at a $\text{Cl} \cdots \text{Cl}$
 6 bond distance of 3.06 Å for a certain $\text{C}-\text{Cl} \cdots \text{Cl}$ bond angle ($\theta = 150^\circ$). The bond energy increases
 7 from 0.021 to 0.024 Hartree (dash line) as θ increases from 150° to 180° .

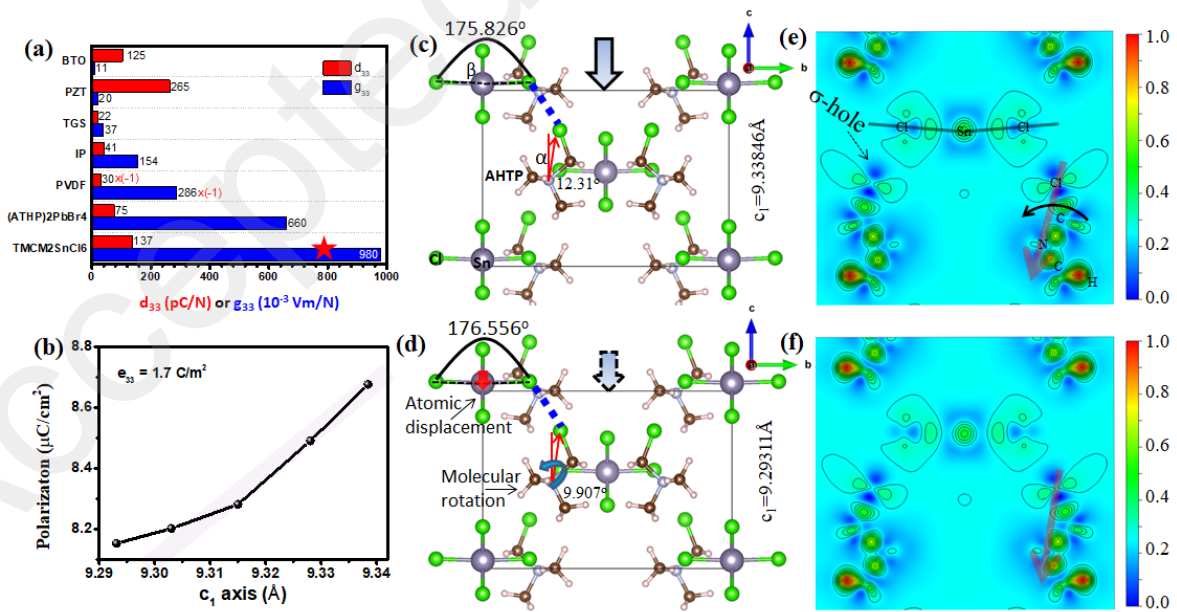


8
 9 **Figure 2. Piezoelectric and ferroelectric properties of $\text{TMCM}_2\text{SnCl}_6$ double perovskite:**
 10 vertical PFM amplitude (a) and phase (b) images; (c) current density-voltage (J-V) curve and the
 11 integrated polarization-voltage (P-V) hysteresis loop of the $\text{TMCM}_2\text{SnCl}_6$ film at room
 12 temperature (25°C) by using the double-wave method; (d) temperature-dependent J-V curves.
 13 Voltage was swept from -70 to 70 V. The inset is the differential scanning calorimetry (DSC) curves

1 of $\text{TMCM}_2\text{SnCl}_6$ crystals with the scanning rate of 10 K/min; (c) frequency-dependent permittivity
2 tested from 0.01 to 1 MHz; (f) calculated density of states of $\text{TMCM}_2\text{SnCl}_6$.

3 The d_{33} of $\text{TMCM}_2\text{SnCl}_6$ perovskites was measured to be 137 pC/N by using a quasi-static
4 method in **Figure S4**. The ferroelectric domains were confirmed by a clear contrast in amplitude
5 and phase images of vertical piezoelectric force microscopy (V-PFM) in **Figure 2a-b**. There was
6 no crosstalk between the topography (**Figure S5b**) and the V-PFM phase. Meanwhile, the lateral
7 PFM (L-PFM) was recorded in **Figure S5c-d** where the signal strength was found relatively weak,
8 indicating that the spontaneous polarization was almost along the out-of-plane direction.³³ The P-
9 V hysteresis loop was measured for $\text{TMCM}_2\text{SnCl}_6$ films with the thickness of 400 μm by using
10 the double-wave method (DWM) in **Figure 2c**.^{49, 50} The arrows in the J-V curve indicate the
11 voltage sweep directions (-60 V \rightarrow 0 V \rightarrow 60 V \rightarrow 0 V \rightarrow -60 V). The J-V curve exhibits two
12 apparent current peaks at the ferroelectric switching voltage of ± 23 V. The E_c of $\text{TMCM}_2\text{SnCl}_6$,
13 expressed by the ratio of switching voltage to the film thickness, is 0.6 kV/cm. This value is
14 comparable to that of conventional piezo-ceramics such as bulk BTO single crystals (1 kV/cm).⁵¹
15 The P_s from the P-V hysteresis loop is up to 8.7 $\mu\text{C}/\text{cm}^2$, close to the calculated value of 8.4 ± 0.3
16 $\mu\text{C}/\text{cm}^2$. When the temperature is higher than T_c , the ferroelectric material will undergo a phase
17 transition and lose its spontaneous polarization. The phase transition of $\text{TMCM}_2\text{SnCl}_6$ was
18 considered from orthorhombic to cubic, as indicated by some disappearing diffraction peaks at
19 around 26.3°, 33.5° and 36.5° in temperature-dependent XRD (**Figure S1b**). The T_c of
20 $\text{TMCM}_2\text{SnCl}_6$ was studied via monitoring the change of peak intensity at 23 V in the temperature-
21 dependent J-V curves. As indicated in **Figure 2d**, the current peaks disappear when the
22 temperature rises to 353-363 K. This is consistent to a pair of thermal anomalies at 365/387 K in
23 the differential scanning calorimetry (DSC) curves (the inset of Figure 2d) and an increase at 350-

1 380 K in the temperature dependent permittivity (**Figure S1c**). The $\text{TMCM}_2\text{SnCl}_6$ possesses a T_c
 2 above room temperature, making it suitable for PNG applications. The ϵ_r of perovskite oxide
 3 ceramics, such as PZT, is observed as thousands, which stems from the hopping polaron within
 4 semiconducting grains and interfacial polarization at the insulating grain boundary.⁵² The
 5 $\text{TMCM}_2\text{SnCl}_6$ exhibits a relative low ϵ_r of 14-12 with the frequency from 0.01 to 1 MHz in **Figure**
 6 **2e**. This should be attributed to the insulating properties of $\text{TMCM}_2\text{SnCl}_6$: where the calculated
 7 bandgap of above 3.2 eV and a narrow conduction band width are defined by the 5s orbits of Sn
 8 and the 3p orbits of Cl, as indicated in **Figure 2f** and **Figure S6**. According to $g_{33} = d_{33} / (\epsilon_0 \times \epsilon_r)$,
 9 where ϵ_0 is the permittivity of free space and $\epsilon_r = 16$, the calculated g_{33} is $980 \times 10^{-3} \text{ V} \cdot \text{m/N}$. Notably,
 10 a higher ϵ_r was chosen to match the following PNG working frequency at 40 Hz. In comparison to
 11 traditional metal oxides and other molecular materials listed in **Figure 3a** (or **Table S1**), the
 12 $\text{TMCM}_2\text{SnCl}_6$ perovskites are more favorable for the PNG applications due to the both large d_{33}
 13 and giant g_{33} .



14

15 **Figure 3. Origin of piezoelectricity in the $\text{TMCM}_2\text{SnCl}_6$ double perovskite:** (a) the d_{33} and g_{33}

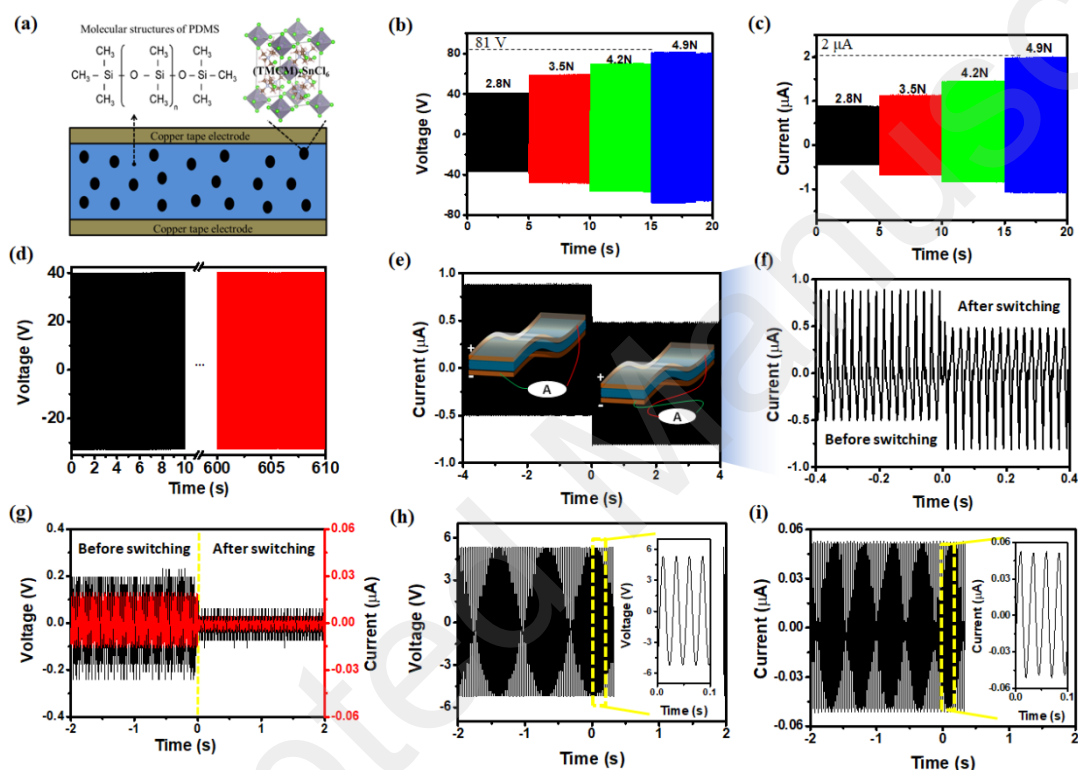
1 of $\text{TMCM}_2\text{SnCl}_6$ compared with the reported inorganic and molecular materials, including BTO,
2 PZT, Triglycine sulfate (TGS), Imidazolium perchlorate (IP), PVDF, and $(\text{ATHP})_2\text{PbBr}_4$; (b) the
3 calculated polarization as a function of c_1 by using Berry phase method; (c) side views of the
4 unstrained structure and (e) corresponding deformation charge density for $c = 9.33864 \text{ \AA}$; (d) the
5 strained structure and (f) deformation charge density for $c = 9.29311 \text{ \AA}$. The above deformation
6 charge density is in the [001] planes including the Sn-Cl \cdots Cl-C chain. The blue and red colors
7 represent the electron loss and gain, respectively.

8
9 To investigate the piezoelectric origin of $\text{TMCM}_2\text{SnCl}_6$ double perovskites, the polarization
10 (P_{total}) was calculated by the Berry phase method as a function of c_1 , where c_1 is the lattice constant
11 during the applied strain along the c axis (**Figure 3b**). The slope of the linear P_{total} vs. c_1 curve
12 yields the piezoelectric stress coefficient (e_{33}).^{53, 54} By fitting the P_{total} vs. c_1/c_0 curve in Figure 3b,
13 e_{33} is evaluated as 1.7 C/m^2 . According to the calculated elastic modulus tensor ($c_{33} = 187.7 \text{ kBar}$)
14 in **Table S2**, the d_{33} is calculated as 90 pC/N by using the expression of $d_{33} = e_{33}/c_{33}$. The calculated
15 d_{33} is lower than the experimental value of 137 pC/N as the P_{total} contribution resulted from lateral
16 strain was neglected.⁵⁵ **Figure 3c** and **3d** show the crystal structure (side view) of unstrained
17 $\text{TMCM}_2\text{SnCl}_6$ with a lattice constant c_1 of 9.33846 \AA and that of strained $\text{TMCM}_2\text{SnCl}_6$ with c_1 of
18 9.29311 \AA (corresponding to a strain of -0.4%), respectively. Under the applied strain, the angle
19 (α) in the dipole direction of TMCM^+ with respect to c axis decreases from 12.31° to 9.907° .
20 According to the equation of $P_{\text{TMCM}} = \mu \times \cos(\alpha) / V_u$, where μ is the dipole moment of TMCM^+ (4.65
21 Debye) and V_u is the cell volume, the polarization from the TMCM^+ increases when α decreases.
22 The deformation charge density profiles of the unstrained and strained crystal were shown in
23 **Figure 3e** and **3f**, respectively. The Cl atom in TMCM^+ is involved in the formation of the covalent

1 bond. In addition, there is a region of lower electron density (σ -hole) where the potential is positive,
2 which generates a cap of depleted electron density on the elongation of the covalent bond. Thus, a
3 halogen-bonding interaction will be formed between the Cl of TMCM^+ and the electron-rich Cl
4 atoms in $[\text{SnCl}_6]^{2-}$. Therefore, the rotation of TMCM^+ can trigger the atomic displacement in
5 $[\text{SnCl}_6]^{2-}$ octahedrons simultaneously, indicated by the increased angle (β) of Cl-Sn-Cl in
6 $[\text{SnCl}_6]^{2-}$ octahedrons from 175.6° to 176.5° . The polarization from $[\text{SnCl}_6]^{2-}$ is calculated by the
7 equation of $P_{\text{Sn}} = P_{\text{total}} - P_{\text{TMCM}}$. Via fitting the decomposed polarization P_{TMCM} and P_{Sn} in **Figure S7**,
8 the e_{33} of $[\text{SnCl}_6]^{2-}$ and TMCM^+ is 1.5 C/m^2 and 0.2 C/m^2 , respectively. It is clear that the $[\text{SnCl}_6]^{2-}$
9 contributes nearly all of the piezoelectricity. After replacing the asymmetric TMCM^+ by spherical
10 symmetric TMA^+ , the $[\text{SnCl}_6]^{2-}$ in $\text{TMA}_2\text{SnCl}_6$ is not distorted (**Figure S8**). The polarization from
11 $\text{TMA}_2\text{SnCl}_6$ is 0 and not changed under an applied strain, indicated the loss of piezoelectricity.
12 Unlike the traditional perovskite ceramics where the piezoelectricity is primarily arising from the
13 atomic displacement (**Figure S9**), (i) the organic TMCM^+ in $\text{TMCM}_2\text{SnCl}_6$ can break its crystal
14 symmetry and (ii) the piezoelectricity in $\text{TMCM}_2\text{SnCl}_6$ is from the halogen bond-mediated
15 synergistic movement of atomic displacement in inorganic $[\text{SnCl}_6]^{2-}$ octahedrons and the
16 molecular rotation of TMCM^+ .

17 The piezoelectricity in the $\text{TMCM}_2\text{SnCl}_6$ was further demonstrated by the outputs of fabricated
18 PNGs. The precursor of piezoelectric composite films was prepared via dispersing 10 wt. %
19 $\text{TMCM}_2\text{SnCl}_6$ nanoparticles (NPs) uniformly in the PDMS by mechanical stirring (**Figure S10**).
20 The size of the NPs was in the range of 200-1000 nm, as shown in the SEM and elemental mapping
21 (Figure S11b-c). The films were grown via drop-casting the above precursor solution on a glass
22 substrate (Figure S11a). After the drop-casting, NPs with a larger size tended to precipitate to the
23 bottom of central area rather than diffuse to the marginal area (**Figure S11a, d-f**). The fraction of

1 TMCM₂SnCl₆ NPs in the composite film for the PNG integration was 18 wt. % measured in the
 2 dotted circle in Figure S11d by the SEM-EDS. The film thickness at the central area was 300 μm.
 3 Finally, the TMCM₂SnCl₆@PDMS composite film was sandwiched between two copper
 4 electrodes for PNG fabrication (**Figure 4a** and **Figure S12**) (see the experimental details in the
 5 supporting information).



6
 7 **Figure 4. The piezoelectric output of single PNG:** (a) device structure of PNGs via inserting
 8 TMCM₂SnCl₆@PDMS composite film between copper electrodes; (b) V_{oc} and (c) I_{sc} of PNGs with
 9 the force from 2.8 to 4.9 N (40 Hz); (d) the device reliability tested for 10 mins; (e) I_{sc} and (f)
 10 enlarged view of the PNGs under forward and reverse electrical connections. The inset is schematic
 11 diagrams of the PNGs under forward and reverse connections; (g) polarity switching test of V_{oc}
 12 (black curve) and I_{sc} (red curve) of pure PDMS based devices; (h) V_{oc} and (k) I_{sc} of PNGs based
 13 on TMCM₂SnCl₆@PDMS film (without poling). For the Figures 4d-i, the applied mechanical

1 excitation is (2.8 N, 40 Hz).

2 The outputs of the $\text{TMCM}_2\text{SnCl}_6$ @PDMS based PNGs was measured by mounting the device
3 on a shaker in a vertical compressing and releasing process (**Figure S13**). For the PNGs with 18
4 wt. % $\text{TMCM}_2\text{SnCl}_6$ in the composite film, the output V_{oc} and I_{sc} of 40 V and 0.9 μA was achieved
5 under the force of 2.8 N at a frequency of 40 Hz. The device output is reproducible as indicated
6 by the statistical analysis of V_{oc} in **Figure S14**. With the applied force increased from 2.8 to 4.9
7 N, the piezoelectric outputs (V_{oc} and I_{sc}) of the PNGs increase linearly in **Figure 4b-c**. The V_{oc}
8 and I_{sc} reach 81 V and 2 μA , respectively, at an applied force of 4.9 N. The frequency-dependent
9 V_{oc} and I_{sc} are shown in **Figure S15** as the force keeps 2.8N. Meanwhile, the device outputs were
10 also recorded at low frequency (3 Hz) via a cylindrical hammer mounted on a linear motor and a
11 metallic stopper. The V_{oc} and current density (J_{sc}) were measured as 11.6 V and 1.17 $\mu\text{A}/\text{cm}^2$,
12 respectively, at an applied pressure of 0.032 MPa (**Figure S16**). The concentration of
13 $\text{TMCM}_2\text{SnCl}_6$ on the electricity generation capacity of the PNGs was optimized in **Figure S18**.
14 The output voltage and current gradually increase to 72 V and 1.3 μA with the increasing mass
15 fraction of $\text{TMCM}_2\text{SnCl}_6$ NPs up to 29 wt. %, under an applied force of 2.8 N. In comparison with
16 traditional inorganic perovskite ceramics in **Table S3**, the $\text{TMCM}_2\text{SnCl}_6$ were prepared at room
17 temperature and the PNGs exhibit the competitive piezoelectric outputs. The reliability of the
18 PNGs was explored by continually testing the device for 10 minutes and the amplitude of the
19 output voltage shows a negligible degradation (**Figure 4d** and Video S1), confirming its excellent
20 mechanical durability. Finally, the PNGs were used as an integrated power source to meet up the
21 energy demand of practical electrical loads via harvesting energy from local environment, such as
22 SWCN (see the details in **Figure S17** and Video S2).

1 To demonstrate the generated outputs were originating from the piezoelectric phenomenon, the
2 following experiments were conducted: (i) the measured current output of the PNGs switched its
3 polarity during the electrical connection reversal (**Figure 4e-f** and Video S3), indicating that the
4 outputs were produced from the PNGs; (ii) For comparison, the output V_{oc} and I_{sc} of PNGs made
5 from pure PDMS were merely 0.2 V and 0.02 μ A and lacking of the polarity switching property in
6 **Figure 4g**. The V_{oc} is enhanced with the loading $\text{TMCM}_2\text{SnCl}_6$ NPs in the composite film as shown
7 in **Figure S18**. These verify the claim that - the high performance of PNGs is determined by the
8 incorporation of $\text{TMCM}_2\text{SnCl}_6$; (iii) the effect of electrical poling on the PNG outputs was
9 investigated (see the poling procedures in the experimental section). Compared with the outputs
10 of unpoling PNGs (**Figure 4h-k**), the PNGs after poling at 4.5 kV (Figure 4b-c) exhibited drastic
11 increase in V_{oc} (from 5.4 to 40 V) and I_{sc} (from 0.05 to 0.9 μ A) under the same measurement
12 conditions (2.8 N, 40 Hz). A detailed comparison of output voltage of PNGs measured under
13 various applied poling fields is shown in **Figure S19**.

14 In summary, a novel vacancy-ordered double perovskite of $\text{TMCM}_2\text{SnCl}_6$ with a large d_{33} of
15 137 pC/N and giant g_{33} of $980 \times 10^{-3} \text{ V}\cdot\text{m/N}$ was proposed for the energy harvesting applications.
16 The $\text{TMCM}_2\text{SnCl}_6$ perovskite possesses a high P_s of 8.7 $\mu\text{C}/\text{cm}^2$, a high T_c of 365 K, and a low E_c
17 of 0.6 kV/cm. The ultrahigh piezoelectricity in $\text{TMCM}_2\text{SnCl}_6$ is attributed to the halogen bonding-
18 mediated synergistic movements of atomic displacement in the inorganic $[\text{SnCl}_6]^{2-}$ octahedron and
19 the dipole alignment of organic TMCM^+ . The piezoelectric coefficients from the $\text{TMCM}_2\text{SnCl}_6$
20 was firstly experimentally measured, then verified by DFT study, and finally confirmed by the
21 piezoelectric output of the PNGs. The piezoelectric composite films were prepared by dispersing
22 $\text{TMCM}_2\text{SnCl}_6$ NPs into the PDMS matrix. The peak values of V_{oc} and I_{sc} of the fabricated PNGs
23 reached up to 81 V and 2 μ A at an applied mechanical excitation of (4.9 N, 40 Hz). The SWCN

1 was successfully driven by the PNG. This work not only opens up a door for designing novel
2 piezoelectric OIHPs with ultrahigh d_{33} and g_{33} , but also paves the way for its real applications in
3 self-powered electronics.

4 **Supporting Information**

5 The Supporting Information is available free of charge at <https://pubs.acs.org/doi/...>
6 Experimental methods, computational details, XRD, XPS, d_{33} , and calculated band structure of
7 $\text{TMCM}_2\text{SnCl}_6$ crystals, digital photograph, SEM images and piezoelectric potential simulation of
8 $\text{TMCM}_2\text{SnCl}_6$ @PDMS composite films, digital photos, frequency-dependent outputs of single
9 PNG, real application of PNG for SWCN, output performance comparison of PNGs based on
10 PDMS matrix, table for calculated elastic modulus, and Videos (MP4) for device stability, output
11 switching, and SWCN.

12 **Notes**

13 The authors declare no competing financial interest.

14 **Acknowledgements**

15 This work is supported by Natural Science and Engineering Research Council of Canada,
16 Ontario Centers of Excellence, and University of Waterloo. The authors thank to Prof. Ning Yan
17 and Dr. Nicolas Tanguy from University of Toronto for their help with the DSC measurement.

18

19 **References**

20
21 (1) Pan, C.; Zhai, J.; Wang, Z. L., Piezotronics and Piezo-phototronics of Third Generation
22 Semiconductor Nanowires. *Chem. Rev.* **2019**, *119* (15), 9303-9359.

- 1 (2) Kim, I.; Roh, H.; Yu, J.; Jayababu, N.; Kim, D., Boron Nitride Nanotube-Based Contact
2 Electrification-Assisted Piezoelectric Nanogenerator as a Kinematic Sensor for Detecting the
3 Flexion-Extension Motion of a Robot Finger. *ACS Energy Lett.* **2020**, *5* (5), 1577-1585.
- 4 (3) Niu, X.; Jia, W.; Qian, S.; Zhu, J.; Zhang, J.; Hou, X.; Mu, J.; Geng, W.; Cho, J.; He, J.;
5 Chou, X., High-Performance PZT-Based Stretchable Piezoelectric Nanogenerator. *ACS*
6 *Sustainable Chem. Eng.* **2018**, *7* (1), 979-985.
- 7 (4) Biswas, P.; Hoque, N. A.; Thakur, P.; Saikh, M. M.; Roy, S.; Khatun, F.; Bagchi, B.; Das, S.,
8 Highly Efficient and Durable Piezoelectric Nanogenerator and Photo-power cell Based on
9 CTAB Modified Montmorillonite Incorporated PVDF Film. *ACS Sustainable Chem. Eng.*
10 **2019**, *7* (5), 4801-4813.
- 11 (5) Pandey, R.; Sb, G.; Grover, S.; Singh, S. K.; Kadam, A.; Ogale, S.; Waghmare, U. V.; Rao,
12 V. R.; Kabra, D., Microscopic Origin of Piezoelectricity in Lead-Free Halide Perovskite:
13 Application in Nanogenerator Design. *ACS Energy Lett.* **2019**, *4* (5), 1004-1011.
- 14 (6) Deutz, D. B.; Mascarenhas, N. T.; Schelen, J. B. J.; de Leeuw, D. M.; van der Zwaag, S.;
15 Groen, P., Flexible Piezoelectric Touch Sensor by Alignment of Lead-Free Alkaline Niobate
16 Microcubes in PDMS. *Adv. Funct. Mater.* **2017**, *27* (24), 1700728.
- 17 (7) Gao, X.; Zheng, M.; Yan, X.; Fu, J.; Hou, Y.; Zhu, M., High Performance Piezocomposite
18 for Flexible Device Application. *Nanoscale* **2020**, *12*, 5175-5185
- 19 (8) Hinchet, R.; Khan, U.; Falconi, C.; Kim, S., Piezoelectric Properties in Two-Dimensional
20 Materials: Simulations and Experiments. *Materials Today* **2018**, *21* (6), 611-630.
- 21 (9) Li, W.; Wu, N.; Zhong, J.; Zhong, Q.; Zhao, S.; Wang, B.; Cheng, X.; Li, S.; Liu, K.; Hu, B.;
22 Zhou, J., Theoretical Study of Cellular Piezoelectret Generators. *Adv. Funct. Mater.* **2016**, *26*
23 (12), 1964-1974.

- 1 (10) Dutta, B.; Kar, E.; Bose, N.; Mukherjee, S., NiO@SiO₂/PVDF: A Flexible Polymer
2 Nanocomposite for a High Performance Human Body Motion-Based Energy Harvester and
3 Tactile e-Skin Mechanosensor. *ACS Sustainable Chem. Eng.* **2018**, *6* (8), 10505-10516.
- 4 (11) Lee, J.-H.; Yoon, H.-J.; Kim, T. Y.; Gupta, M. K.; Lee, J. H.; Seung, W.; Ryu, H.; Kim, S.-
5 W., Micropatterned P(VDF-TrFE) Film-Based Piezoelectric Nanogenerators for Highly
6 Sensitive Self-Powered Pressure Sensors. *Adv. Funct. Mater.* **2015**, *25* (21), 3203-3209.
- 7 (12) Mao, Y.; Zhao, P.; McConohy, G.; Yang, H.; Tong, Y.; Wang, X., Sponge-Like
8 Piezoelectric Polymer Films for Scalable and Integratable Nanogenerators and Self-
9 Powered Electronic Systems. *Adv. Energy Mater.* **2014**, *4* (7), 1301624.
- 10 (13) Pi, Z.; Zhang, J.; Wen, C.; Zhang, Z.-b.; Wu, D., Flexible Piezoelectric Nanogenerator
11 Made of Poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) Thin Film. *Nano*
12 *Energy* **2014**, *7*, 33-41.
- 13 (14) Meng, X.; Wen, X.; Qin, G., DFT Study on Elastic and Piezoelectric Properties of
14 Tetragonal BaTiO₃. *Comput. Mater. Sci.* **2010**, *49* (4), S372-S377.
- 15 (15) Jeong, C. K.; Kim, I.; Park, K. I.; Oh, M. H.; Paik, H.; Hwang, G. T.; No, K.; Nam, Y. S.;
16 Lee, K. J., Virus-Directed Design of a Flexible BaTiO₃ Nanogenerator. *ACS Nano* **2013**, *7*
17 (12), 11016-25.
- 18 (16) Zhang, G.; Liao, Q.; Zhang, Z.; Liang, Q.; Zhao, Y.; Zheng, X.; Zhang, Y., Novel
19 Piezoelectric Paper-Based Flexible Nanogenerators Composed of BaTiO₃ Nanoparticles and
20 Bacterial Cellulose. *Adv. Sci.* **2016**, *3* (2), 1500257.
- 21 (17) Wu, W.; Bai, S.; Yuan, M.; Qin, Y.; Wang, Z. L.; Jing, T., Lead Zirconate Titanate
22 Nanowire Textile Nanogenerator for Wearable Energy-Harvesting and Self-Powered
23 Devices. *ACS Nano* **2012**, *6* (7), 6231-5.

- 1 (18) Bowen, C. R.; Kim, H. A.; Weaver, P. M.; Dunn, S., Piezoelectric and Ferroelectric
2 Materials and Structures for Energy Harvesting Applications. *Energy Environ. Sci.* **2014**, *7*
3 (1), 25-44.
- 4 (19) Yan, Y.; Zhou, J. E.; Maurya, D.; Wang, Y. U.; Priya, S., Giant Piezoelectric Voltage
5 Coefficient in Grain-Oriented Modified PbTiO₃ Material. *Nat. Commun.* **2016**, *7*, 13089.
- 6 (20) Li, W.; Wang, Z.; Deschler, F.; Gao, S.; Friend, R. H.; Cheetham, A. K., Chemically
7 Diverse and Multifunctional Hybrid Organic-Inorganic Perovskites. *Nat. Rev. Mater* **2017**,
8 *2* (3), 16099.
- 9 (21) Zhao, X. G.; Yang, J. H.; Fu, Y.; Yang, D.; Xu, Q.; Yu, L.; Wei, S. H.; Zhang, L., Design of
10 Lead-Free Inorganic Halide Perovskites for Solar Cells via Cation-Transmutation. *J. Am.*
11 *Chem. Soc.* **2017**, *139* (7), 2630-2638.
- 12 (22) Xiao, Z.; Meng, W.; Wang, J.; Mitzi, D. B.; Yan, Y., Searching for Promising New
13 Perovskite-Based Photovoltaic Absorbers: the Importance of Electronic Dimensionality.
14 *Mater. Horiz.* **2017**, *4* (2), 206-216.
- 15 (23) Huang, G.; Wang, C.; Xu, S.; Zong, S.; Lu, J.; Wang, Z.; Lu, C.; Cui, Y., Postsynthetic
16 Doping of MnCl₂ Molecules into Preformed CsPbBr₃ Perovskite Nanocrystals via a Halide
17 Exchange-Driven Cation Exchange. *Adv. Mater.* **2017**, *29* (29), 1700095.
- 18 (24) Manser, J. S.; Saidaminov, M. I.; Christians, J. A.; Bakr, O. M.; Kamat, P. V., Making and
19 Breaking of Lead Halide Perovskites. *Acc. Chem. Res.* **2016**, *49* (2), 330-8.
- 20 (25) Bernasconi, A.; Malavasi, L., Direct Evidence of Permanent Octahedra Distortion in
21 MAPbBr₃ Hybrid Perovskite. *ACS Energy Lett.* **2017**, *2* (4), 863-868.
- 22 (26) Kim, Y.-J.; Dang, T.-V.; Choi, H.-J.; Park, B.-J.; Eom, J.-H.; Song, H.-A.; Seol, D.; Kim,
23 Y.; Shin, S.-H.; Nah, J.; Yoon, S.-G., Piezoelectric Properties of CH₃NH₃PbI₃ Perovskite

- 1 Thin Films and Their Applications in Piezoelectric Generators. *J. Mater. Chem. A* **2016**, *4*
2 (3), 756-763.
- 3 (27) Jella, V.; Ippili, S.; Eom, J.-H.; Pammi, S. V. N.; Jung, J.-S.; Tran, V.-D.; Nguyen, V. H.;
4 Kirakosyan, A.; Yun, S.; Kim, D.; Sihm, M. R.; Choi, J.; Kim, Y.-J.; Kim, H.-J.; Yoon, S.-
5 G., A Comprehensive Review of Flexible Piezoelectric Generators Based on Organic-
6 Inorganic Metal Halide Perovskites. *Nano Energy* **2019**, *57*, 74-93.
- 7 (28) Shahrokhi, S.; Gao, W.; Wang, Y.; Anandan, P. R.; Rahaman, M. Z.; Singh, S.; Wang, D.;
8 Cazorla, C.; Yuan, G.; Liu, J. M.; Wu, T., Emergence of Ferroelectricity in Halide
9 Perovskites. *Small Methods* **2020**, *4* (8), 2000149.
- 10 (29) Khan, A. A.; Rana, M. M.; Huang, G.; Mei, N.; Saritas, R.; Wen, B.; Zhang, S.; Voss, P.;
11 Rahman, E.-A.; Leonenko, Z.; Islam, S.; Ban, D., Maximizing Piezoelectricity by Self-
12 Assembled Highly Porous Perovskite-Polymer Composite Films to Enable the Internet of
13 Things. *J. Mater. Chem. A* **2020**, *8* (27), 13619-13629.
- 14 (30) Ippili, S.; Jella, V.; Kim, J.; Hong, S.; Yoon, S. G., Unveiling Predominant Air-Stable
15 Organotin Bromide Perovskite toward Mechanical Energy Harvesting. *ACS Appl. Mater.*
16 *Interfaces* **2020**, *12* (14), 16469-16480.
- 17 (31) Jella, V.; Ippili, S.; Yoon, S.-G., Halide (Cl/Br)-Incorporated Organic-Inorganic Metal
18 Trihalide Perovskite Films: Study and Investigation of Dielectric Properties and Mechanical
19 Energy Harvesting Performance. *ACS Appl. Electron. Mater.* **2020**, *2* (8), 2579-2590.
- 20 (32) Liao, W. Q.; Zhao, D.; Tang, Y. Y.; Zhang, Y.; Li, P. F.; Shi, P. P.; Chen, X. G.; You, Y.
21 M.; Xiong, R. G., A Molecular Perovskite Solid Solution with Piezoelectricity Stronger
22 Than Lead Zirconate Titanate. *Science* **2019**, *363* (6432), 1206-1210.

- 1 (33) You, Y. M.; Liao, W. Q.; Zhao, D.; Ye, H. Y.; Zhang, Y.; Zhou, Q.; Niu, X.; Wang, J.; Li,
2 P. F.; Fu, D. W.; Wang, Z.; Gao, S.; Yang, K.; Liu, J. M.; Li, J.; Yan, Y.; Xiong, R. G., An
3 Organic-Inorganic Perovskite Ferroelectric with Large Piezoelectric Response. *Science*
4 **2017**, 357 (6348), 306-309.
- 5 (34) Chen, X. G.; Song, X. J.; Zhang, Z. X.; Li, P. F.; Ge, J. Z.; Tang, Y. Y.; Gao, J. X.; Zhang,
6 W. Y.; Fu, D. W.; You, Y. M.; Xiong, R. G., Two-Dimensional Layered Perovskite
7 Ferroelectric with Giant Piezoelectric Voltage Coefficient. *J. Am. Chem. Soc.* **2020**, 142 (2),
8 1077-1082.
- 9 (35) Deswal, S.; Singh, S. K.; Pandey, R.; Nasa, P.; Kabra, D.; Praveenkumar, B.; Ogale, S.;
10 Boomishankar, R., Neutral 1D Perovskite-Type ABX₃ Ferroelectrics with High Mechanical
11 Energy Harvesting Performance. *Chem. Mater.* **2020**, 32 (19), 8333-8341.
- 12 (36) Zhang, Z. X.; Zhang, H. Y.; Zhang, W.; Chen, X. G.; Wang, H.; Xiong, R. G.,
13 Organometallic-Based Hybrid Perovskite Piezoelectrics with a Narrow Band Gap. *J. Am.*
14 *Chem. Soc.* **2020**, 142 (41), 17787-17794.
- 15 (37) Zhang, Y.; Song, X.-J.; Zhang, Z.-X.; Fu, D.-W.; Xiong, R.-G., Piezoelectric Energy
16 Harvesting Based on Multiaxial Ferroelectrics by Precise Molecular Design. *Matter* **2020**, 2
17 (2), 1-14.
- 18 (38) Vijayakanth, T.; Ram, F.; Praveenkumar, B.; Shanmuganathan, K.; Boomishankar, R.,
19 Piezoelectric Energy Harvesting from a Ferroelectric Hybrid Salt [Ph₃MeP]₄ [Ni(NCS)₆]
20 Embedded in a Polymer Matrix. *Angew. Chem. Int. Ed.* **2020**, 59 (26), 10368-10373.

- 1 (39) Morss, L. R.; Carnall, W. T.; Williams, C. W.; Fahey, J. A.; Fuger, J.; Meyer, G.; Irmeler,
2 M., Syntheses and X-ray Diffraction Studies of $[\text{N}(\text{CH}_3)_4]_2\text{BkCl}_6$ and $[\text{N}(\text{CH}_3)_4]_2\text{ZrCl}_6$;
3 Absorption Spectrum of Bk^{4+} in $[\text{N}(\text{CH}_3)_4]_2\text{BkCl}_6$. *J. Less-Common Met.* **1991**, *169* (1), 1-8.
- 4 (40) Karim, M. M. S.; Ganose, A. M.; Pieters, L.; Winnie Leung, W. W.; Wade, J.; Zhang, L.;
5 Scanlon, D. O.; Palgrave, R. G., Anion Distribution, Structural Distortion, and Symmetry-
6 Driven Optical Band Gap Bowing in Mixed Halide Cs_2SnX_6 Vacancy Ordered Double
7 Perovskites. *Chem. Mater.* **2019**, *31* (22), 9430-9444.
- 8 (41) Maughan, A. E.; Ganose, A. M.; Almaker, M. A.; Scanlon, D. O.; Neilson, J. R., Tolerance
9 Factor and Cooperative Tilting Effects in Vacancy-Ordered Double Perovskite Halides.
10 *Chem. Mater.* **2018**, *30* (11), 3909-3919.
- 11 (42) Fedorovskiy, A. E.; Drigo, N. A.; Nazeeruddin, M. K., The Role of Goldschmidt's
12 Tolerance Factor in the Formation of A_2BX_6 Double Halide Perovskites and its Optimal
13 Range. *Small Methods* **2019**, *0* (0), 1900426.
- 14 (43) Autillo, M.; Wilson, R. E., Phase Transitions in Tetramethylammonium
15 Hexachlorometalate Compounds $(\text{TMA})_2\text{MCl}_6$ ($\text{M} = \text{U}, \text{Np}, \text{Pt}, \text{Sn}, \text{Hf}, \text{Zr}$). *Eur. J. Inorg.*
16 *Chem.* **2017**, *2017* (41), 4834-4839.
- 17 (44) Tan, Z.; Li, J.; Zhang, C.; Li, Z.; Hu, Q.; Xiao, Z.; Kamiya, T.; Hosono, H.; Niu, G.;
18 Lifshitz, E.; Cheng, Y.; Tang, J., Highly Efficient Blue-Emitting Bi-Doped Cs_2SnCl_6
19 Perovskite Variant: Photoluminescence Induced by Impurity Doping. *Adv. Funct. Mater.*
20 **2018**, *28* (29), 1801131.
- 21 (45) Hua, X. N.; Liao, W. Q.; Tang, Y. Y.; Li, P. F.; Shi, P. P.; Zhao, D.; Xiong, R. G., A Room-
22 Temperature Hybrid Lead Iodide Perovskite Ferroelectric. *J. Am. Chem. Soc.* **2018**, *140*
23 (38), 12296-12302.

- 1 (46) Liao, W. Q.; Tang, Y. Y.; Li, P. F.; You, Y. M.; Xiong, R. G., Competitive Halogen Bond
2 in the Molecular Ferroelectric with Large Piezoelectric Response. *J. Am. Chem. Soc.* **2018**,
3 *140* (11), 3975-3980.
- 4 (47) Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G.,
5 The Halogen Bond. *Chem. Rev.* **2016**, *116* (4), 2478-601.
- 6 (48) Huang, G.; Wang, C.; Zhang, H.; Xu, S.; Xu, Q.; Cui, Y., Post-Healing of Defects: an
7 Alternative Way for Passivation of Carbon-Based Mesoscopic Perovskite Solar Cells via
8 Hydrophobic Ligand Coordination. *J. Mater. Chem. A* **2018**, *6* (6), 2449-2455.
- 9 (49) Fukunaga, M.; Noda, Y., New Technique for Measuring Ferroelectric and Antiferroelectric
10 Hysteresis Loops. *J. Phys. Soc. Jpn* **2008**, *77* (6), 064706.
- 11 (50) Hu, L.; Dalgleish, S.; Matsushita, M. M.; Yoshikawa, H.; Awaga, K., Storage of an Electric
12 Field for Photocurrent Generation in Ferroelectric-Functionalized Organic Devices. *Nat.*
13 *Commun.* **2014**, *5*, 3279.
- 14 (51) Trithaveesak, O.; Schubert, J.; Buchal, C., Ferroelectric Properties of Epitaxial BaTiO₃ Thin
15 Films and Heterostructures on Different Substrates. *J. Appl. Phys.* **2005**, *98* (11), 114101.
- 16 (52) Han, H.; Voisin, C.; Guillemet-Fritsch, S.; Dufour, P.; Tenailleau, C.; Turner, C.; Nino, J.
17 C., Origin of Colossal Permittivity in BaTiO₃ via Broadband Dielectric Spectroscopy. *J.*
18 *Appl. Phys.* **2013**, *113* (2), 024102.
- 19 (53) Liu, S.; Zheng, F.; Grinberg, I.; Rappe, A. M., Photoferroelectric and Photopiezoelectric
20 Properties of Organometal Halide Perovskites. *J. Phys. Chem. Lett.* **2016**, *7* (8), 1460-5.
- 21 (54) Shi, J.; Grinberg, I.; Wang, X.; Rappe, A. M., Atomic Sublattice Decomposition of
22 Piezoelectric Response in Tetragonal PbTiO₃, BaTiO₃, and KNbO₃. *Phys. Rev. B* **2014**, *89*
23 (9), 094105.

- 1 (55) Tholander, C.; Abrikosov, I. A.; Hultman, L.; Tasnádi, F., Volume Matching Condition to
- 2 Establish the Enhanced Piezoelectricity in Ternary (Sc,Y)_{0.5}(Al,Ga,In)_{0.5}N Alloys. *Phys.*
- 3 *Rev. B* **2013**, 87 (9), 094107.

Accepted Manuscript