Supplementary Information

Selectively Tuning Ionic Thermopower in All-Solid-State Flexible Polymer Composites for Thermal Sensing

Cheng Chi, Meng An, Xin Qi, Yang Li, Ruihan Zhang, Gongze Liu, Chongjia Lin, He Huang, Hao Dang, Baris Demir, Yan Wang, Weigang Ma*, Baoling Huang* and Xing Zhang

1Key Laboratory for Thermal Science and Power Engineering of Ministry of Education, Department of Engineering Mechanics, Tsinghua University, Beijing, 100084, China
2College of Mechanical & Electrical Engineering, Shaanxi University of Science and Technology, Xi’an, 710021, China
3Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR, China
4Department of Mechanical Engineering, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609, USA
5Centre for Theoretical and Computational Molecular Science, The Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland 4072, Australia

*Corresponding author: W. G. Ma, email: maweigang@tsinghua.edu.cn; B. L. Huang, email: mebhhuang@ust.hk
†The authors contribute equally.
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Supplementary Table 1. The parameters in potential functions.

**Bond Parameters**

| Bond   | $K_r$ (Kcal/(mol·Å$^2$)) | $r_{eq}$ (Å) |
|--------|---------------------------|--------------|
| C10-C11 | 268.0000                  | 1.5290       |
| C10-H10 | 340.0000                  | 1.0900       |
| C11-C11 | 268.0000                  | 1.5290       |
| C11-C12 | 268.0000                  | 1.5290       |
| C11-C13 | 268.0000                  | 1.5290       |
| C11-F11 | 367.0000                  | 1.3600       |
| C12-H12 | 340.0000                  | 1.0900       |
| C13-C14 | 268.0000                  | 1.5290       |
| C13-C15 | 268.0000                  | 1.5290       |
| C13-F13 | 367.0000                  | 1.3600       |
| C14-C16 | 268.0000                  | 1.5290       |
| C14-F14 | 367.0000                  | 1.3600       |
| C15-C16 | 268.0000                  | 1.5290       |
| C15-F15 | 367.0000                  | 1.3600       |
| C16-F16 | 367.0000                  | 1.3600       |
| C16-H16 | 340.0000                  | 1.0900       |
| C20-F20 | 441.92                    | 1.323        |
| C20-S20 | 233.03                    | 1.818        |
| C40-O40 | 570.00                    | 1.2290       |
| C40-O41 | 214.00                    | 1.3270       |
| Bond          | $K_\theta$ (Kcal/(mol radian$^2$)) | $\theta_{eq}$ (degree) |
|--------------|-----------------------------------|------------------------|
| C10-C11-C12  | 58.350                            | 112.700                |
| C10-C11-F11  | 50.000                            | 109.500                |
| C11-C10-H10  | 37.500                            | 110.700                |
| C11-C11-C12  | 58.350                            | 112.700                |
| C11-C11-C13  | 58.350                            | 112.700                |
| C11-C11-F11  | 50.000                            | 109.500                |
| C11-C12-C11  | 58.350                            | 112.700                |
| C11-C12-H12  | 37.500                            | 110.700                |
| C11-C13-C14  | 58.350                            | 112.700                |
| C11-C13-C15  | 58.350                            | 112.700                |
| C11-C13-F13  | 50.000                            | 109.500                |
| C12-C11-C12  | 58.350                            | 112.700                |
| Bond          | Distance (Å) | Angle (°) |
|--------------|-------------|----------|
| C12-C11-F11  | 50.000      |          |
| C13-C11-F11  | 50.000      |          |
| C13-C14-F14  | 50.000      |          |
| C13-C15-C13  | 58.350      | 112.700  |
| C13-C15-C16  | 58.350      | 112.700  |
| C13-C15-F15  | 50.000      | 109.500  |
| C14-C13-C15  | 58.350      | 112.700  |
| C14-C13-F13  | 50.000      | 109.500  |
| C14-C16-C15  | 58.350      | 112.700  |
| C14-C16-F16  | 50.000      | 109.500  |
| C14-C16-H16  | 37.500      | 110.700  |
| C15-C13-C15  | 58.350      | 112.700  |
| C15-C13-F13  | 50.000      | 109.500  |
| C15-C16-F16  | 50.000      | 109.500  |
| C15-C16-H16  | 37.500      | 110.700  |
| C16-C14-F14  | 50.000      | 109.500  |
| C16-C15-F15  | 50.000      | 109.500  |
| C20-S20-N20  | 91.30       | 103.5    |
| C20-S20-O20  | 103.97      | 102.6    |
| C40-O41-C41  | 83.00       | 116.90   |
| C40-O41-C42  | 83.00       | 116.90   |
| C41-C42-H42  | 37.50       | 110.70   |
| C41-C42-O41  | 50.00       | 109.50   |
| Bond              | Angle    | Torsion |
|-------------------|----------|---------|
| C41-C43-H43       | 37.50    | 110.70  |
| C42-C41-C43       | 58.35    | 112.70  |
| C42-C41-H41       | 37.50    | 110.70  |
| C42-C41-O41       | 50.00    | 109.50  |
| C43-C41-H41       | 37.50    | 110.70  |
| C43-C41-O41       | 50.00    | 109.50  |
| F11-C11-F11       | 77.00    | 109.100 |
| F14-C14-F14       | 77.00    | 109.100 |
| F15-C15-F15       | 77.00    | 109.100 |
| F16-C16-H16       | 40.00    | 107.000 |
| F20-C20-F20       | 93.33    | 107.1   |
| F20-C20-S20       | 82.93    | 111.7   |
| H10-C10-H10       | 33.00    | 107.800 |
| H12-C12-H12       | 33.00    | 107.800 |
| H41-C41-O41       | 35.00    | 109.50  |
| H42-C42-H42       | 33.00    | 107.80  |
| H42-C42-O41       | 35.00    | 109.50  |
| H43-C43-H43       | 33.00    | 107.80  |
| N20-S20-O20       | 94.29    | 113.60  |
| O20-S20-O20       | 115.80   | 118.5   |
| O40-C40-O41       | 83.00    | 123.40  |
| O41-C40-O41       | 81.00    | 111.40  |
| S20-N20-S20       | 80.19    | 125.6   |
### VDW Parameter

| Atom type | ε (Kcal/mol) | σ (Å) |
|-----------|--------------|-------|
| C10       | 0.0660       | 3.5000 |
| C11       | 0.0660       | 3.5000 |
| C12       | 0.0660       | 3.5000 |
| C13       | 0.0660       | 3.5000 |
| C14       | 0.0660       | 3.5000 |
| C15       | 0.0660       | 3.5000 |
| C16       | 0.0660       | 3.5000 |
| C20       | 0.0660       | 3.5000 |
| C40       | 0.1050       | 3.7500 |
| C41       | 0.0660       | 3.5000 |
| C42       | 0.0660       | 3.5000 |
| C43       | 0.0660       | 3.5000 |
| F11       | 0.0600       | 2.9000 |
| F13       | 0.0600       | 2.9000 |
| F14       | 0.0600       | 2.9000 |
| F15       | 0.0600       | 2.9000 |
| F16       | 0.0600       | 2.9000 |
| F20       | 0.0530       | 2.9500 |
| H10       | 0.0300       | 2.5000 |
| H12       | 0.0300       | 2.5000 |
| H16       | 0.0300       | 2.5000 |
|     |     |     |
|-----|-----|-----|
| H41 | 0.0150 | 2.4200 |
| H42 | 0.0150 | 2.4200 |
| H43 | 0.0150 | 2.4200 |
| N20 | 0.1700 | 3.2500 |
| NA30| 0.0005 | 4.0700 |
| O20 | 0.2100 | 2.9600 |
| O40 | 0.2100 | 2.9600 |
| O41 | 0.1700 | 3.0000 |
| S20 | 0.2500 | 3.5500 |
Supplementary methods

Materials

Polyvinylidenefluoride-hexafluoropropylene pellet (PVDF-HFP, average M_w, 455,000 g mol^{-1}), sodium bis(trifluoromethylsulfonyl)imide (NaTFSI), propylene carbonate (PC, anhydrous, 99.7%), and N-Methyl-2-pyrrolidone (NMP, HPLC, ≥99%) were purchased from Sigma-Aldrich. Tris(pentafluorophenyl)borane (TPFPB, min. 97%) was purchased from Strem Chemicals, Inc. All the materials were stored in the glovebox without any additional treatment.

Preparation of PhNPs and T-PhNPs

PVDF-HFP pellets were firstly dried in an oven at 100°C for 24 h and were dissolved in NMP at a concentration of 0.1 g mL^{-1} with rapid magnetic stirring for about 8 h at 60°C. Next, 1M NaTFSI/PC solution with different mass ratios from 30 to 86 wt. % was added to the PVDF-HFP solution to form a homogeneous mixture in an argon atmosphere. The resulting mixture was then cast on a glass petri-dish and dried in a vacuum oven (10^{-3} Torr) at 60°C for over 1~10 h to obtain the free-standing PhNP films. For T-PhNPs, different amount of TPFPB was added to PhNP-86 mixtures at 60°C and then followed the same procedures to obtain free-standing solid-state T-PhNP films. All the films were stored in a glove box (O_2 < 0.1 ppm, and H_2O < 0.1 ppm) for future use. Here, the weight ratio means the liquid NaTFSI/PC is to the overall weight of the PVDF-HFP/NaTFSI/PC composites as illustrated by Eq. (1)

\[
W_{(NaTFSI/PC)} = \frac{m_{(NaTFSI/PC)}}{m_{(NaTFSI/PC)} + m_{PVDF-HFP}} \tag{1}
\]

where \(m_{(NaTFSI/PC)}\) and \(m_{PVDF-HFP}\) represented the mass of NaTFSI/PC and PVDF-HFP, respectively.

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**Fabrication of i-TE Device**

The as-fabricated $p$-type PhNP and $n$-type T-PhNP films were cut into identical thin-rectangular shapes with a dimension of 6×1.5 mm$^2$. The 13 pairs of the developed thermocouple films were carefully transferred to the corresponding electrodes. Next was to make sure the $p$-type and $n$-type films were electrically connected in series with the bridge gap between the hot side and cool side larger than 2.0 mm. Then, the in-plane all-solid-state i-TE generator module prototype can be ready for further test.

**Characterization**

A scanning electron microscope (SEM, JEOL-7100F) was used to characterize the morphology of the materials and element distribution. The samples were sputter-coated with approximately 10 nm of gold before the analysis. FTIR characterization was conducted using Bruker (Vertex 70 Hyperion 1000) within the range of 400-950 cm$^{-1}$ and the resolution of the spectra was 4 cm$^{-1}$. Raman characterization was conducted using InVia (Renishaw) within the range of 100-2500 cm$^{-1}$ and a laser source of 633 nm. X-ray photoelectron spectroscopy measurement was conducted using PHI 5600.

**Ionic conductivity measurement**

The ionic conductivity of the i-TE materials PVDF-HFP/NaTFSI/PC was determined by the electrochemical impedance spectroscopy (EIS) measurement in a frequency range from 100 kHz to 0.1 Hz using two stainless steel (SS) block electrodes (SS//CPE//SS). The ion conductivity was calculated according to *Eq. 2*:
\[ \sigma = \frac{l}{R_b A} \]  

(2)

where \( l \) and \( A \) are the thickness and contact area of the materials, respectively. The bulk electrolyte resistance value \( R_b \) was determined from the intercept of the semi-circular curve with the real axis at the low-frequency region. This method was widely used in the literature and calibrated in our previous work.

**Thermal conductivity measurement**

The thermal conductivity of the \( i \)-TE materials PVDF-HFP/NaTFSI/PC was determined by Hot disk thermal constant analyzer (TPS 2500S, Sweden) with a Kapton-insulated sensor 7854 at room temperature as shown in Supplementary Fig. 5. The transient plane source (TPS) method utilizes the Kapton-insulated sensors as the temperature sensor and heat source. The diameter of PVDF-HFP films should be larger than 2.1 centimeters and thickness should be limited from 10 to 500 microns.

All the measurements including thermopower, ionic conductivity and thermal conductivity are performed using at least 5 separate samples and the error bars are calculated using standard derivation.

**Supplementary discussion**

The potential energy of the systems \( U \) in our work was evaluated as a sum of individual energies (Eq. 3) for harmonic bond stretching and angle bending terms, a cosine series for torsional energetics, Coulomb, and 12-6 Lennard-Jones terms for the nonbonded interactions (Eq. 3-7).

\[ U = E_{bonds} + E_{angles} + E_{torsion} + E_{nonbond} \]  

(3)
\[ E_{\text{bonds}} = \sum_{\text{bonds}} k_b (r - r_{eq})^2 \] (4)

\[ E_{\text{angles}} = \sum_{\text{angles}} k_\theta (\theta - \theta_{eq})^2 \] (5)

\[ E_{\text{torsion}} = \sum_i \left[ \frac{1}{2} V_{1,i}(1 + \cos \phi) + \frac{1}{2} V_{2,i}(1 - \cos 2\phi) + \frac{1}{2} V_{3,i}(1 + \cos 3\phi) + \frac{1}{2} V_{4,i}(1 - \cos 4\phi) \right] \] (6)

\[ E_{\text{nonbond}} = \sum_i \sum_{j>i} \left\{ \frac{q_i q_j e^2}{r_{ij}} + 4 \epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right] \right\} \] (7)

where the parameters are the force constant \( k \), the \( r_{eq}, \theta_{eq} \), equilibrium bond and angle values, Fourier coefficient \( V \), partial atomic charges, \( q \), and Lennard-Jones radii and well-depths, \( \sigma \) and \( \epsilon \). The \( \sigma \) and \( \epsilon \) used in Eq. 6 for an interaction of atom \( i \) and atom \( j \) is \( \sigma_{ij} = \sigma_i + \sigma_j \) and \( \epsilon_{ij} = \sqrt{\epsilon_i \cdot \epsilon_j} \), respectively. In our systems, all the atomic types in empirical potential are shown in Supplementary Fig. 19.

**Preparation of ionic thermoelectric material samples in MD simulations**

The initial structures of PVDF-HFP chains, NaTFSI and PC molecules were generated using the freely available AVOGADRO software package\(^1\). These structures were then geometrically optimized via the use of the Generalized Amber Force field (GAFF)\(^2\). The structures were considered to be optimized when the energy difference between two successive interactions dropped below a threshold value (10\(^{-8}\) kJmol\(^{-1}\)). We used LigParGen web-based service\(^3\) that can provide the OPLS force-field parameters and partial atomic charges for the PVDF-HFP, NaTFSI, and PC molecules. We generated a solid-state ionic thermoelectric (i-TE) material sample by placing PVDF-HFP, NaTFSI and PC molecules together in a cubic simulation box with a dimension of 25.0 nm using PACKMOL\(^4\). We adjusted the number of PVDF-HFP, NaTFSI, and PC molecules so that the size of each system was similar. Each sample was equilibrated via the
use of NPT-MD simulations at 294 K and 1 atm over a period of 1 ns. Each ionic thermoelectric material sample was generated separately in the simulation box where all PVDF and HFP monomers, NaTFSI, and PC molecules were present. Then, the thermoelectric material samples were equilibrated via the use of NPT-MD simulations at 294 K and 1 atm over a period of 1 ns. Following this, a further 1 ns simulation was performed in the NVT-MD. We tracked a trajectory of 1000 frames that were generated every 1 ps. The whole trajectory was then used for calculating the radial distribution function and mean-squared displacement. The Newton’s equations of motion were time-integrated with a time-step of 1 fs implemented by the Large-scale Atomic/Molecular Massively Parallel Simulation (LAMMPS) package developed by Sandia National Laboratories. The Visual Molecular Dynamics (VMD) was used to visualize the trajectories generated during simulations.

Calculation of ion diffusion and thermal conductivity

All-atom molecular dynamics (MD) simulations were used to predict thermal conductivity and ionic transport properties of the solid-state ionic thermoelectric (i-TE) material PVDF-HFP/NaTFSI/PC (PhNP). Periodic boundary conditions in all three dimensions were implemented. The Nosé-Hoover thermostat and barostat were implemented in all the simulations to control the temperature and pressure, respectively. The cut-off distance for long-range energy calculations was set to be 12 Å. The contribution of long-range interactions was calculated via the particle-particle-particle-mesh (PPPM) solver. We predict the diffusion coefficient using results from NVT-MD simulations. To achieve this, we first calculated the three-dimensional mean-squared displacement (MSD),

$$\text{MSD} = \frac{1}{N} \sum_{i=1}^{N} \langle (\vec{r}_{i}(t) - \vec{r}_{i}(0))^2 \rangle$$

(8)
where \( \vec{r}_i(t) \) and \( \vec{r}_i(0) \) are the position of atom \( i \) at time \( t \) and time \( 0 \), respectively. The MSD was calculated for all molecules making up the system and for each of the ions separately to give MSD. From these values, the diffusion coefficients for each ion can be determined:

\[
D = \sum_{t \to \infty} \frac{1}{6t} MSD
\]  
(9)

Provided the limiting diffusive behavior of the ions is observed by the end of the simulations. The NVT-MD simulations for 5 ns at 300 K for three systems. To obtain an indication of the statistical accuracy of the MSD, we repeated these simulations three times for each sample. The initial velocities of atoms in each run were randomly distributed. For thermal transport properties, non-equilibrium molecular dynamics (NEMD) simulations were performed to calculate the thermal conductivity of ionic thermoelectric materials, which has been widely employed to study the thermal conductivity of amorphous organic materials. The heat source and heat sink were set as 320 K and 280 K, respectively, using Langevin thermostats, as shown in Supplementary Fig. 21a. A layer of atoms at each end of the simulation cell was fixed in space to prevent the heat flux across the periodic boundaries. Besides, the translational drift of the sample is blocked by the fixed atoms, which helps to extract the temperature profile. The system runs in the NVE ensemble for 1.5 ns to calculate thermal conductivity. A typical temperature profile at the steady-state is shown in Supplementary Fig. 21b. The heat flux \( (J) \) is calculated by averaging the energy input and output rates from the heat source and sink per unit across the sectional area in Supplementary Fig. 21c. The thermal conductivity \( (\kappa) \) of the system was calculated\(^8\),

\[
\kappa = -J/(A \cdot \nabla T)
\]  
(10)

where \( \nabla T \) is the temperature gradient across the sample. The temperature gradient was obtained by linear fitting to the local temperature, excluding the temperature jumps at the two ends. The
thermal conductivity is averaged for six independent simulations with different initial velocities. The error bars are the standard derivation of these data.

**Calculation of the entropy of cation and anion in i-TE systems**

The entropy is predicted by the MD simulations according to

\[
S = \frac{K_B}{2} \ln \det \left( \frac{K_B T e^2}{\hbar^2} M \delta + I \right)
\]

where \( K_B \) refers to the Boltzmann constant, \( \hbar \) is the reduced Planck constant, \( e \) is the Euler’s number and \( T \) corresponds to the temperature. \( M \) and \( I \) are the mass matrix and the unity matrix, respectively. \( \delta \) is the covariance matrix of the coordinate fluctuations, with \( \delta_{ij} = \langle (x_i - \langle x_i \rangle)(x_j - \langle x_j \rangle) \rangle \)\(^9,10\).
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