Supplementary Information

Thermoelectric Polymer Films with Significantly High Seebeck Coefficient and

Thermoelectric Power Factor through Surface Energy Filtering

Xin Guan,^a Erol Yildirim,^{bc} Zeng Fan,^a Wanheng Lu,^d Bichen Li,^a Kaiyang Zeng,^d Shuo-

Wang Yang^b and Jianyong Ouyang*a

^a Department of Materials Science and Engineering, National University of Singapore, Singapore, 117574. E-mail: mseoj@nus.edu.sg

^b Institute of High Performance Computing, 1 Fusionopolis Way, #16-16 Connexis, Agency for Science, Technology and Research, Singapore, 138632

^c Department of Chemistry, Middle East Technical University, 06800, Ankara, Turkey

^d Department of Mechanical Engineering, National University of Singapore, Singapore, 117576



Fig. S1 TE performance of treated PEDOT:PSS films coated with Rhodamine 101 of different concentrations. (A) Seebeck coefficient. (B) Conductivity. (C) Power factor. The PEDOT:PSS films were treated with 5 vol% DMSO or 0.1 M MAI/DMF prior to the spin



coating of Rhodamine 101. The values at 0 wt% are for PEDOT:PSS films prior to the Rhodamine 101 coating.

Fig. S2 The air stability of (A) the Seebeck coefficient and (B) conductivity of sRA-PEDOT:PSS and sRBA-PEDOT:PSS films in ambient conditions. (C) Dependence of the Seebeck coefficient of sRA-PEDOT:PSS on the thickness of A-PEDOT:PSS films.

Computational Methods

Molecular dynamics simulations were performed to elucidate the effect of Rhodamine 101 at the interface on the structure of PEDOT. Structure and atomic charges for PEDOT monomer are modelled in such a way that each monomer has a +0.334-hole charge.¹ CHELPG method was used to calculate these atomic charges.² A unit cell with four monomers was constructed in the π -stacked configuration. 5×4×4 supercell for PEDOT were modelled to study the effect of Rhodamine 101 (Fig. S3A). We built an amorphous cell with 48 Rhodamine 101 molecules at the similar cell dimensions by the Monte Carlo sampling of the torsional angle distribution

of the Rhodamine 101 backbone, avoiding close contacts between atoms within the cell. These two cells were then merged to model interface.

COMPASS (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies) force-field were employed in calculations as they had been validated extensively for phase properties of polymers at solid interfaces.³ In the molecular mechanics calculations, a cut-off distance of 12.5 Å was used for the van der Waals interactions and the electrostatic energy was calculated using the Ewald summation method with accelerated convergence. 1 ns MD simulations with 1fs steps were performed at NVT ensemble with Nose thermostat at 300 K to equilibrate PEDOT-Rhodamine 101 interface following 5000 initial molecular mechanics minimization steps.

Rhodamine 101 molecules are self-organized where all molecules have dipole moment in the same direction to induce regular electric field on PEDOT chains in the first type of calculations. Rhodamine 101 has strong directional intrinsic dipole moment and polarizability in zwitterion form. Calculations showed that negative charge is highly localized at the COO⁻ group and positive charge is distributed around two amino groups in heterocyclic aromatic rings with 6.5 Å average distance. Rhodamine 101 was modelled as a single dipole moment between positive and negative sites in the second type of interactions. This represents the presence of direct molecular interaction between Rhodamine 101 and PEDOT chains at the interface. Our results indicate that Rhodamine 101 and PEDOT chains has strong face-toface interactions and negatively charged group prefers to interact with hydrogen atoms of ethylene and positively charged group interact with the oxygen atoms in PEDOT.

Lowest energy structures for PEDOT₆-Rhodamine 101 (zwitterion) interaction and PEDOT₆-Rhodamine 101^+ (cation) interaction are given in Fig. S3B. The interaction energies are very strong due to the size and surface area of the face to face interactions calculated as 16.5 eV. Lowest energy positions of Rhodamine 101 zwitterion represented by two point charges with 6.5 Å distance (Fig. S3B(b)) and protonated Rhodamine 101^+ represented by a

positive point charge on PEDOT chain are provided in Fig. S3B(c)-(d). Positive charge is on the oxygen atom, while negative charge is on the hydrogen atoms of ethylene group in PEDOT that was also predicted by DFT calculations given in Fig. S3B(a). Positive charge is on the oxygen atom of PEDOT for Rhodamine 101⁺ in close distances of PEDOT and Rhodamine 101, however it is determined to have lower energy for the cationic charge placed in middle of monomers (C-C bond) for higher distances (9 Å and 12 Å).

Proton transfer from A-PEDOT:PSS was validated by the DFT calculations that show benzoid to quinoid transition by the end group protonic acid doping characterized by the decreased C-C bond length between PEDOT monomers.⁴ In addition, the DFT calculations demonstrated the low barrier energy for the dedoping based on proton transfer mechanism (Fig. S3C).



Fig. S3 Computational process. (A) Modelling steps for PEDOT including (a) calculation of monomer atomic charges and structure followed by (b) construction of unit cell, (c) building a supercell, (d) construction of Rhodamine 101 interface. (B) Geometry optimized lowest energy structures for (a) PEDOT₆-Rhodamine 101 zwitterion. Lowest energy positions determined for (b) Rhodamine 101 zwitterion represented as two-point charges. Protonated Rhodamine 101⁺ represented as a single point charge (c) at 6 Å distance (d) for higher distances on a PEDOT chain. (cation: blue, anion: pink in colour). (C) Backbone monomer (C-C bond) distances for (a) neutral PEDOT₆, (b) end group protonated PEDOT₆-H⁺. (c) Reactant, transition state and product for proton transfer from end group protonated PEDOT PEDOT₆-H⁺ to Rhodamine 101 zwitterion. (d) ESP and dipole moment direction for Rhodamine 101.

Dipole moment: 15.87 Debye (21.68 in water). Dipole vector directions: x=0.0 y=-12.98 z=9.13, Polarizability: xx=621.737 xy=0.004 yy=465.889 xz=-0.004 yz=-5.615 zz=277.053.



Fig. S4 Electrostatic potential surface (ESP) for (A) PEDOT₃, (B) PEDOT₆, (C) PEDOT₉. (red: electron rich, blue: electron deficient site) (D) Band gap for PEDOT₃, PEDOT₆, and PEDOT₉. (E) Band gap for PEDOT₆, PEDOT₆⁺² biradical polaron and PEDOT₆⁺² bipolaron.



Fig. S5 (A) Directions of continuous electric field applied to pristine $PEDOT_6$ and $PEDOT_6^{+2}$ bipolaron. (B) Rhodamine 101 zwitterion is defined as two-point charges with fixed distance at different intermolecular distances from PEDOT chain.



Fig. S6 (A) ESP for (a) PEDOT₆, (b) PEDOT₆ under the electric field at X-direction, (c) PEDOT₆ under the electric field at Y-direction. (B) ESP for (a) PEDOT₆⁺² bipolaron (b) PEDOT₆⁺² bipolaron under the electric field at X-direction and Y-direction, (c) PEDOT₆⁺² bipolaron under the effect of dipole moment at X-direction and Y-direction. (C) Geometry optimized structures for PEDOT₆ under the effect of (a)-(c) Rhodamine 101⁺ (protonated Rhodamine 101 as point charge) and (d)-(f) Rhodamine 101 zwitterion for (a, d) 6 Å, (b, e) 9 Å, and (c, f) 12 Å interaction distance.



Fig. S7 ESP and geometry optimized structures for PEDOT₉. (A) (a) Electrostatic potential surface for pristine PEDOT₉. (red: electron rich, blue: electron deficient site.) (b)-(c) Modelling details for one of the configurations where the distance between PEDOT and ions were kept at 6 Å and the distance between positive and negative ion is kept 6.5 Å. PEDOT₉ geometry is optimized and the geometry kept constant for other calculations. (d)-(i) Effect of two dipole moment which represents two Rhodamine 101 zwitterion molecules at different positions on the electrostatic potential surface of PEDOT₉. (B) PEDOT₉ under the effect of two Rhodamine 101 zwitterion represented as two pairs of charge aligned in x and y axis which show decreased planarity and aromaticity.



Fig. S8 (A) Initial structure and (B) equilibrium structure for PEDOT and Rhodamine 101 zwitterion interface constructed by using 5x4x4 supercell of PEDOT (320 PEDOT monomers) and amorphous cell with 48 Rhodamine 101 molecules. Chains with decreased crystallinity are shown by yellow in colour. (C) Concentration profile of atoms for equilibrated pristine PEDOT and PEDOT with Rhodamine 101 interface along the cell.

Initial structure and equilibrium structure for PEDOT and Rhodamine 101 zwitterion interface are shown in Figs. S8A and S8B. Concentration profile of pristine PEDOT chains and PEDOT chains at the Rhodamine 101 interface is given in Fig. S8C. Although pristine PEDOT has regular and sharp interlayer distances, PEDOT at the Rhodamine 101 has irregular interlayer distance distribution along the cell, especially for the first two layers at the interfaces as indicated by yellow colour. This suggests that the crystal structure at the interface is deteriorated by the strong dipole moment imposed by Rhodamine 101.

Table S1. TE properties of PEDOT:PSS films with different treatments. PEDOT:PSS treated with 5 vol% DMSO (D-PEDOT:PSS) and 0.1 M MAI/DMF solution (M-PEDOT:PSS) and optimal TE properties of D-PEDOT:PSS coated with Rhodamine 101 (RD-PEDOT:PSS) and M-PEDOT:PSS coated with Rhodamine 101 (RM-PEDOT:PSS).

Sample	S (µV K ⁻¹)	σ (S cm ⁻¹)	PF (μW m ⁻¹ K ⁻²)
D-PEDOT:PSS	21.5	983	45.4
RD-PEDOT:PSS	43.2	680	126.9
M-PEDOT:PSS	23.2	1655	89.1
RM-PEDOT:PSS	37.9	1219	175

Table S2. Summary of the representative TE properties of PEDOT:PSS solid films by different methods in literature.

Method	S (μV K ⁻¹)	σ (S cm ⁻¹)	PF (μW m ⁻¹ K ⁻²)	к (W m ⁻¹ K ⁻¹)	<i>ZT</i> at rt ^e	Ref
Addition of DMSO+PEO ^a	~38.4	1061	157.35	-	-	[5]
Electrochemical dedoping	~100	~20	23.5		0.041	[6]
Chemical dedoping by AF ^b	436.3	0.036	0.69	0.32	0.0011	[7]
Treated with TSA ^c and then HZ ^d and DMSO	~50	~1300	318.4	0.3	0.31	[8]
Treated with H ₂ SO ₄ and then NaOH	39.2	2170	334	-	-	[9]
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^{*a*} Poly(ethylene oxide)

^b Ammonium formate

^{*c*} *P*-toluenesulfonic acid monohydrate

^d Hydrazine

^e rt refers to room temperature

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