Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information for

Synergistic enhancement of thermoelectric and mechanical performances of ionic liquid LiTFSI modulated PEDOT flexible films

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1. Bending tests set-up

The bending test of free-standing hybrid film was conducted by the lab-made platform (Figure S1). The LabVIEW programming exactly controlled the translation of the two sides of conductive fixtures. The rate of movement was 1mm/s in this experiment. In the process of bending experiments, as-prepared film was well fixed in the fixtures and connected with nanovoltmeter that record the change of film electrical resistances.

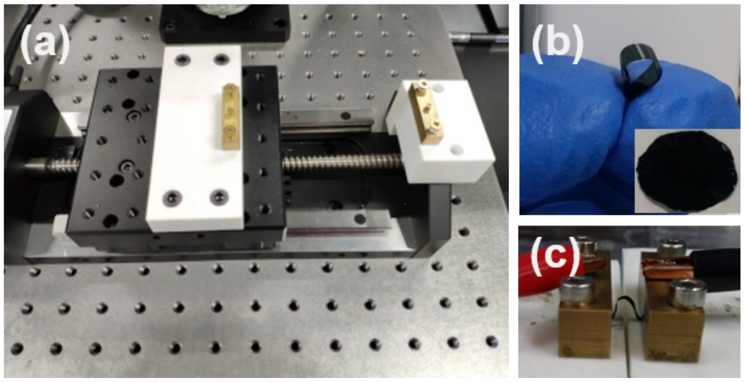

Figure S1. Bending tests set-up. (a) The lab-made translation platform; (b) As-prepared free-standing hybrid films; (c) The set-up connected with nanovoltmeter for monitoring the electrical properties of films in the bending tests.

2. 3ω method used in Linseis TFA analyzer

An AC current $I = I_0 cos(\omega t)$ is applied to the heating stripes and cause a temperature enhancement of the membrane in the form of $\Delta T = \Delta T_0 cos(2\omega t + \varphi)$ and therefore an oscillation in the resistance of the stripe $R = R_0(1 + \beta \Delta T)$ at angular frequency 2ω. By measuring the voltage drop across the heater, one gets an amplitude modulated signal which has a small component at the third harmonic frequency 3ω. By solving the 1-D heat diffusion equation in the membrane area[1],

$$|V_{3\omega}| = \frac{\beta \cdot {R_0}^2 \cdot {I_0}^3}{4 \cdot K_p \cdot \sqrt{1 + \omega^2 (4\tau^2 + \frac{w^4}{24D^2} + \frac{\tau w^2}{3D})}} . \qquad (1)$$

When using low frequencies, the ω term becomes negligible and $V_{3\omega}$ becomes constant that $|V_{3\omega}| = \frac{\beta \cdot {R_0}^2 \cdot {I_0}^3}{4 \cdot K_p}$ (as shown in the Figure S5). Since the conductance depends on k and the emissivity e, it is necessary to measure at least two samples with differing geometries (w1, w2) to determine its thermal conductivity and emissivity using

$$\lambda_t = \frac{G_m(w_1) tanh(\mu \frac{w_1}{2})}{2l\mu} = \frac{G_m(w_2) tanh(\mu \frac{w_2}{2})}{2l\mu} . \qquad (2)$$

The thermal conductivity of test film can be calculated from a differential measurement equation $\lambda_s = \frac{\lambda t - \lambda_m t_m}{t_s}$ while $\lambda_m t_m$ is the empty measurement setup value and t_s is the thickness of the testing sample.

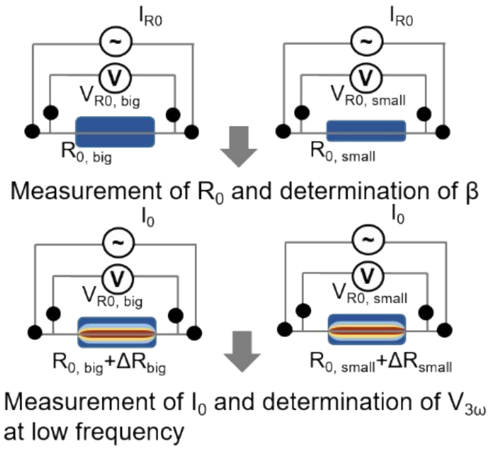

Figure S2. 3ω method for film thermal conductivity measurements used in Linseis TFA analyzer.

3. Cycling thermoelectric performances and thermal conductivity (κ‖) testing

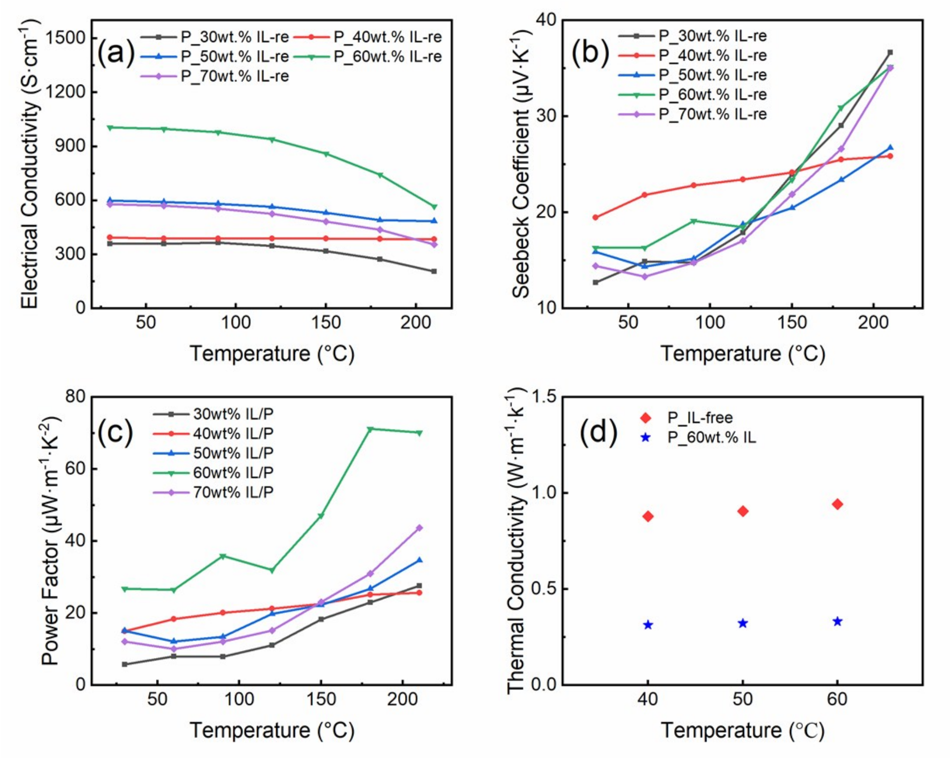

Figure S3. The electrical conductivity (a), Seebeck coefficients (b) and power factor (c) of different doped IL mass concentration with different temperature after the first heating testing process; (d) In-plane thermal conductivity ($\kappa_{//}$) of IL-free PEDOT:PSS and 60wt.% IL hybrid PEDOT:PSS by using Linseis 3ω method.

4. Electrical robustness over bending

In the heating process, the electrical resistivity of hybrid film with 60 wt.% IL was almost not changed before and after the bending tests.

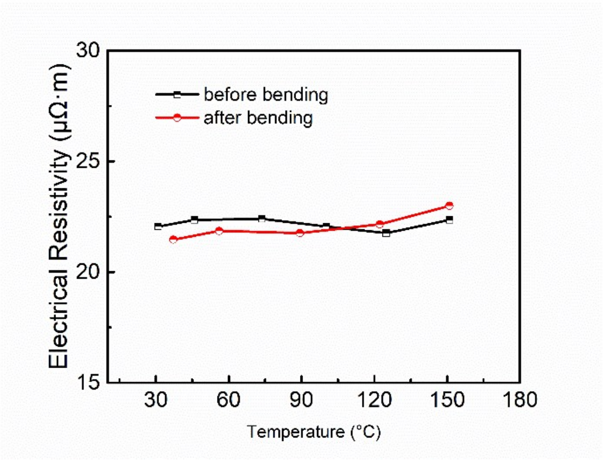

Figure S4. Electrical resistivity of PEDOT/ 60 wt.% IL film with different temperature before and after bending tests.

5. Tensile tests details

The tensile tests of free-standing films were performed on a small sized tensile machine with maximum load 100N. The SEM images of fracture surfaces of testing samples show layered stacked structures. The residual elongated sections in the fracture were obvious that this stacked structure had huge resistances to the film cracking process.

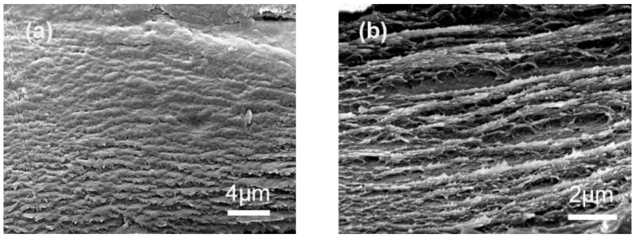

Figure S5. Cross section SEM images of (a) PEDOT/30 wt.% IL, (b) PEDOT/60 wt.% IL hybrid films.

6. DSC test images

By heating from room temperature into 300°C, the main change of hybrid films was the loss of combined water near 100°C. The structural integrities of these different films were maintained during heating process.

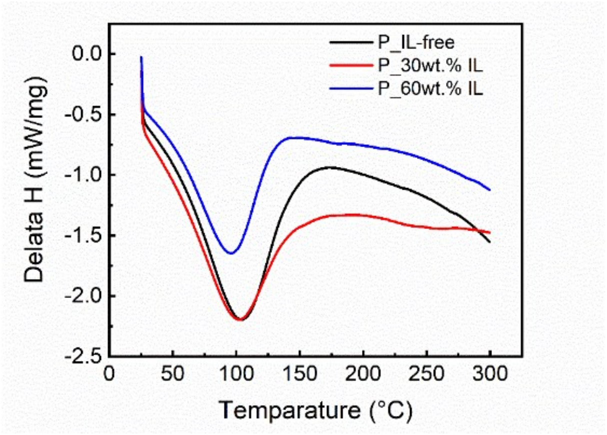

Figure S6. DSC test images of pristine PEDOT, PEDOT/ 30 wt.% IL, PEDOT/ 60 wt.% IL free-standing films.

7. GIWAXS images

Rigaku Smartlab 9KW performed GIWAXS tests of the corresponding thin films with different ionic liquids mass. As the mass concentration of ionic liquids increased, the diffraction rings got more distinct. Striking contrasts in these GIWASX images also indicated the enhanced crystallinities of PEDOT films with the ordering effects of ionic liquids.

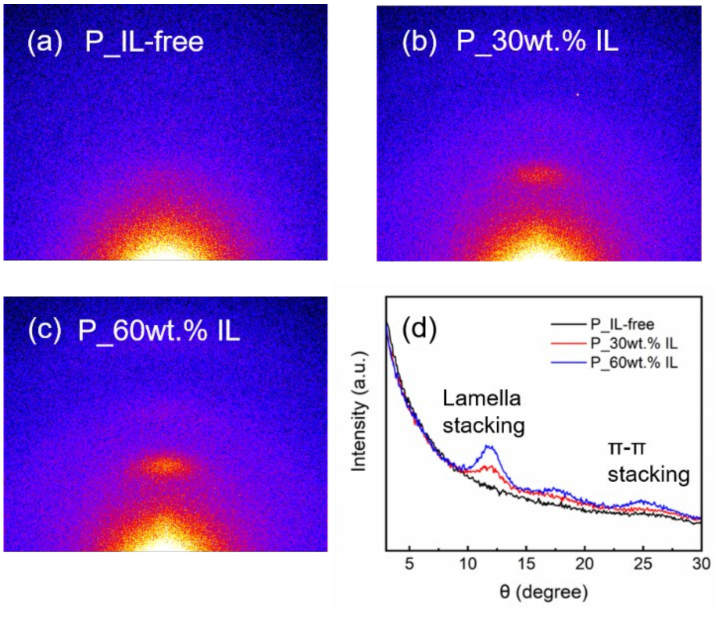

Figure S7. GIWAXS images of (a) pristine PEDOT, (b) 30wt% IL/PEDOT, (c) 60wt% IL/PEDOT hybrid thin films; (d) Intensity-θ curves during GIWAXS testing.

Reference

1. Linseis, V.; Volklein, F.; Reith, H.; Nielsch, K.; Woias, P., Advanced platform for the in-plane ZT

measurement of thin films. *Rev. Sci. Instrum.* **2018,** *89* (1), 015110.