Electronic Supplementary Information (ESI)

Water-dispersible conducting polyazulene and its application for thermoelectrics

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Synthesis of polyazulene:polystyrenesulfonate (PAZ:PSS)

The PAZ/PSS aqueous solution was synthesized via *in-situ* polymerization. Firstly, azulene (1.0 mmol), PSS (3.0 mmol, MW: 70 kD) solution and water (20 ml) were mixed and stirred rigorously at room temperature. After 30 minutes, $K_2S_2O_8$ (2.0 mmol) and a catalytic amount of $Fe_2(SO_4)_3$ (0.01 mmol) were added into the mixture. The resulted mixture was stirred rigorously for another 6 hours. The aqueous solution was washed by basic resins and acidic resins accordingly to remove the inorganic salts, followed by passing a PVDF membrane to give a purified PAZ/PSS solution.

Fabrication of PAZ:PSS film

UV-Vis-NIR absorption spectra of PAZ:PSS film were prepared by spin coating PAZ:PSS solution prepared above on quartz substrates. For other characterizations, PAZ:PSS water-dispersion was drop-casted on glass substrates and left overnight to form PAZ:PSS thin films.

Characterization of AFM, UV-Vis-NIR absorption spectra, Cyclic voltammograms

Atomic Force Microscopy (AFM) images were obtained on a Bruker Dimension Icon Atomic Force Microscope using the tapping mode. The absorption spectra were recorded on a Shimadzu UV3101PC UV-vis-NIR spectrophotometer. Cyclic voltammograms were obtained by spin coating the polymer film (10 mg/mL in chloroform) on an indium tin oxide (ITO) – coated glass substrate in 0.1M $LiClO_4$ / acetonitrile at a scan rate of 100 mVs^{-1}, using an Autolab PGSTAT30 electrochemical workstation.
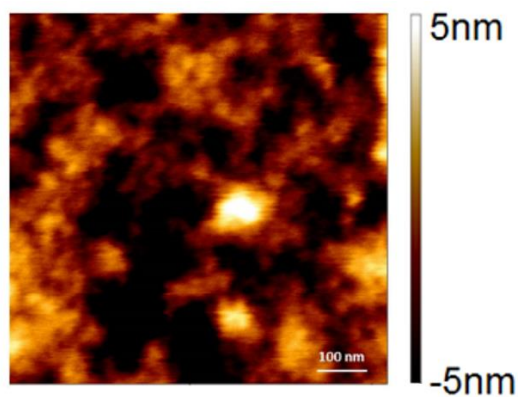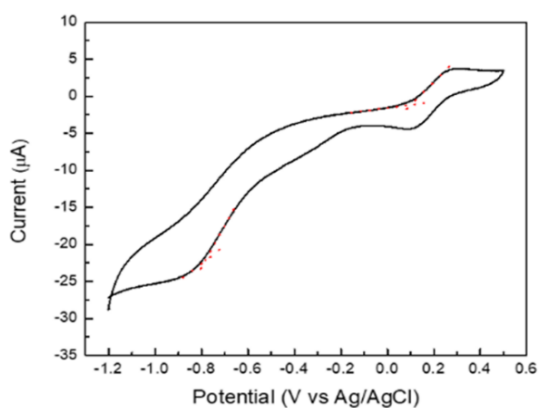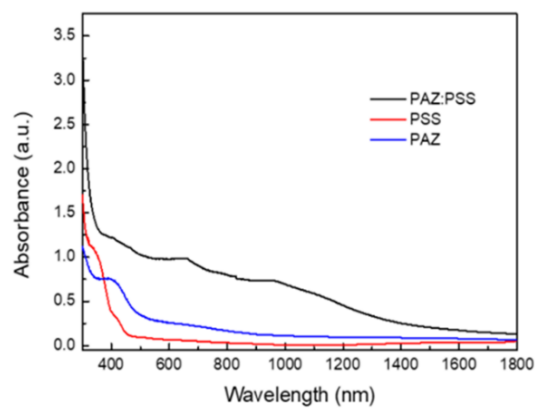
Fig. S1. AFM height image of drop-cast PAZ:PSS film.

(a)

(b)

Fig. S2. (a) Cyclic voltammetry curves of a PAZ:PSS film in 0.1 M LiClO4/acetonitrile solution using Ag/AgCl as the reference electrode and Pt as the counter electrode, and (b) UV-vis-NIR spectra of the spin-coated PAZ, PSS and PAZ:PSS films on glass substrates.
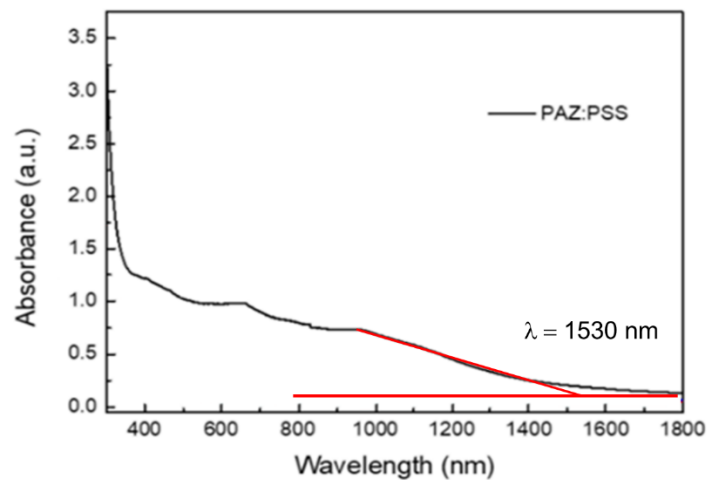
Estimation of optical bandgap

Fig. S3. UV-vis-NIR spectrum of PAZ:PSS, showing how to find out the absorption onset wavelength.

Based on UV-vis-NIR spectrum, the optical band gap can be approximately estimated according to equation 1 shown below. Bandgap E_g represents the optical bandgap expressed in eV and λ denotes the absorption onset wavelength expressed in nm, obtained from the offset wavelength derived from the low energy absorption band as shown in Fig. S3. The absorption onset wavelength λ is around 1530 nm, and thus the calculated bandgap E_g is 0.81 eV.

$$E_g(\text{eV}) = h \times f = h \times \frac{c}{\lambda} \approx \frac{1240}{\lambda\,(\text{nm})} \qquad \text{Eq. 1}$$

Four-point-probe DC conductivity measurement

To eliminate the contact resistance effect, we used the four-point probe DC conductivity measurement which was carried out with a sheet resistance meter (Mitsubishi, Hiresta). The spacing between the probes is 1.25 mm. Since the spacing between the probes is much larger than film thickness (12 μm) and much smaller than thin film area (25 mm × 25 mm), the resistivity can be obtained from the relationship, $\rho = \frac{\pi t}{ln2}\left(\frac{V}{I}\right)$, where ρ is the resistivity, t is the thickness of the film, V is the voltage measured across two inner probes and I is the injected current between the two outer probes and $\pi/\ln 2$ is the geometry factor for equal probe spacing. The conductivity was obtained from the reciprocal of the resistivity. The measurement at various levels of humidity was carried out in an acrylic enclosure in which humidity is controlled by purging with clean dry air or injecting the vapour. The humidity level was monitored with a humidity meter (Fluke 971).

Quantifying Electronic and Ionic Conductivity Contributions

The electronic and ionic conductivity was quantified from the two-point probe *I-V* sweeps using electron blocking electrode or ion blocking electrode, as reported by Shetzline et al.[1] Using the electronically-conductive glassy carbon electrode, the conducting part contributed from ions was cut off and the solely electronic conductivity could be determined. On the other hand, the pure ionic conductivity was measured using the ionically-conductive Nafion membranes in Ag^+ and K^+ form and silver foil. As Nafion membrane is purely ionic conductor, it effectively blocks the electron flow. *I-V* sweep was carried out using a potentiostat (Metrohm Autolab) at a rate of 0.1 mVsec^{-1} with sweeping potential from -10 mV to +10 mV. Because two-point probe is used, a transfer length method was used to compensate the contact resistance between the film and selective electrodes, where the contact resistance was determined by measuring the resistance at three electrode spacings (6 mm, 10 mm and 15 mm) and extrapolating to zero. The geometry of the sample and electrodes are illustrated in Supplementary Fig. S3 and *I-V* curve which is used for calculating the resistance for each electrode spacing is shown in Supplementary Fig. S4. The conductivity was calculated from the linear slope of the resistance vs. electrode spacing as shown in Supplementary Fig. S5, using the relationship: slope = $1/\sigma A$, where σ is the conductivity and A is the cross-sectional area of the film (ie., 10 mm × 12 μm).
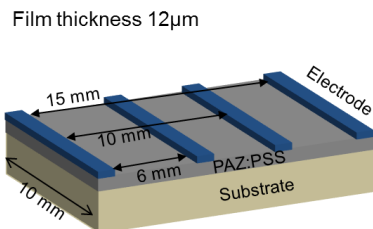

Fig. S4. The geometry of sample and electrodes that used in the *I-V* sweep for the resistance measurement.
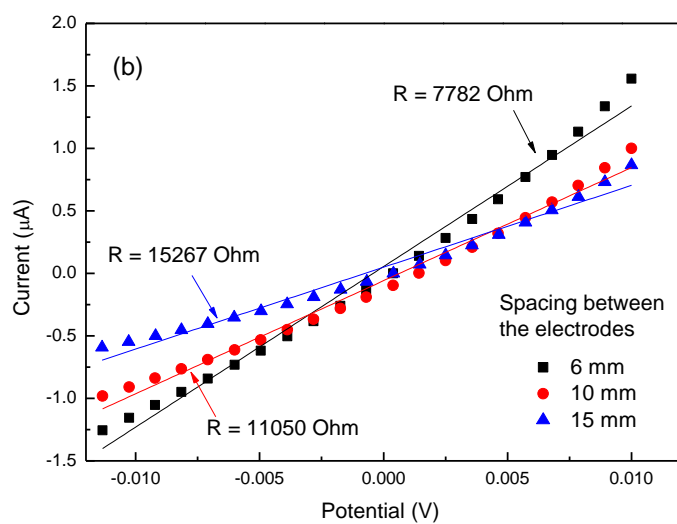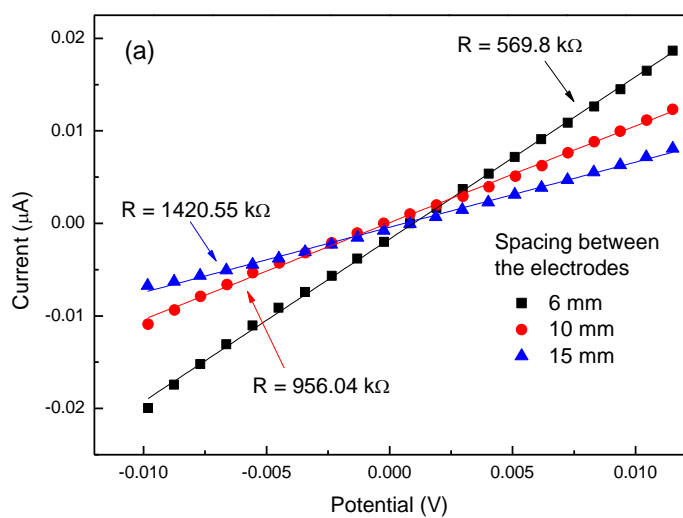
Fig. S5. *I-V* characteristics of the PAZ:PSS film at different electrode spacings, using (a) glassy carbon electrode and (b) Nafion membrane and silver foil electrode.
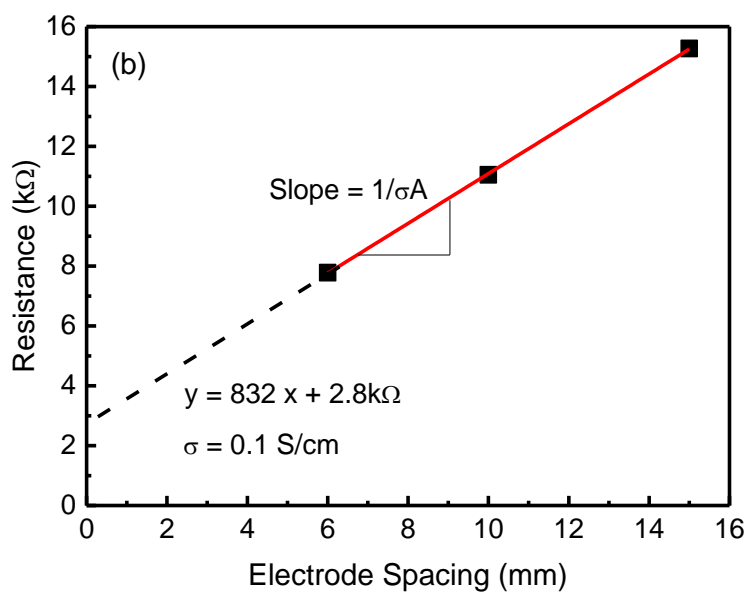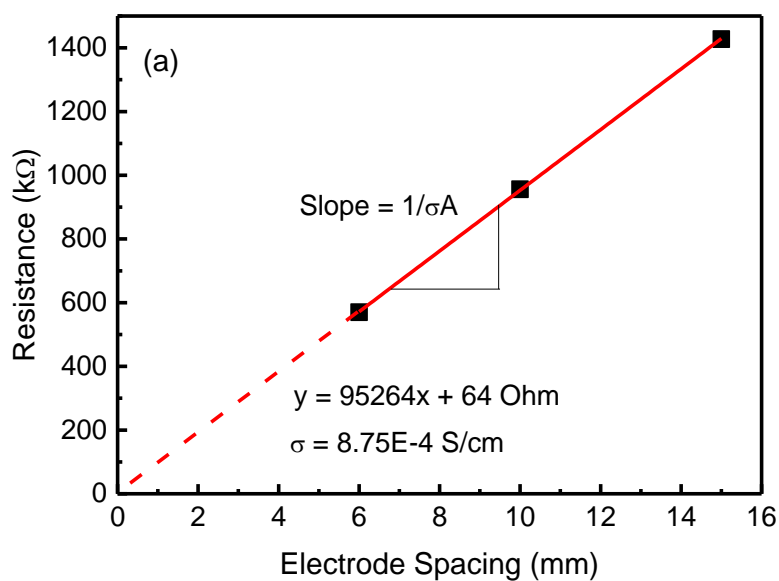
Fig. S6. The plot of resistance vs electrode spacing for the conductivity calculation: (a) electronic conductivity using glassy carbon electrode, and (b) ionic conductivity using Nafion membrane and silver foil. Measurement conditions: a relative humidity (RH) of 55% and at 25°C

Seebeck Coefficient Measurement

Seebeck coefficient was measured by a home built setup with a Keithley 4200 Semiconductor Characterization System. To measure the Seebeck coefficient, firstly the two Au electrodes (each of them is 1 mm wide and 20 mm long, and apart 3 mm) are deposited on the film as illustrated in Supplementary Fig. S6. We use long and narrow electrode design because such design gives the minimum error in the measurement.[2] The film outside the two electrodes is also removed for accurate Seebeck measurement. The two terminals from Keithley were connected to the electrodes to measure the thermovoltage while two K-type thermocouples were placed at the end of the electrodes to determine the temperature gradients. The thermocouples were connected to a data logger (Omron ZR-RX45) to collect temperature reading. The measurement was done in a home-made humidity-controlled chamber. The Seebeck coefficient was calculated from the slope of the linear plots between thermovoltage change and the temperature gradient between the two electrodes as shown in Supplementary Fig. S7.
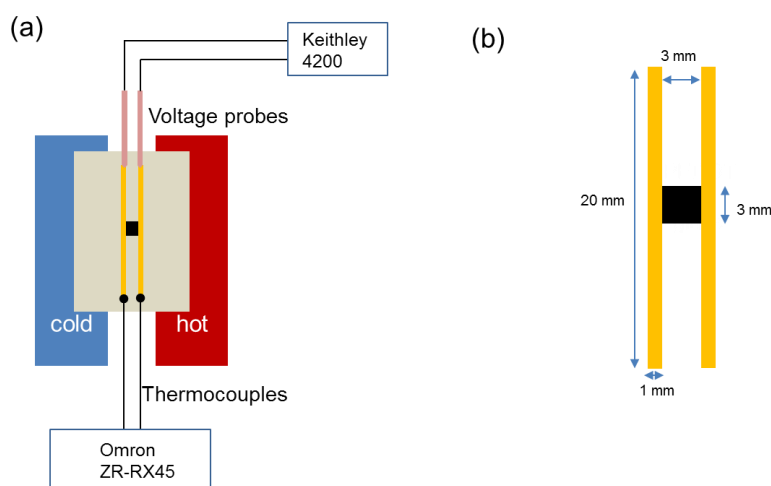

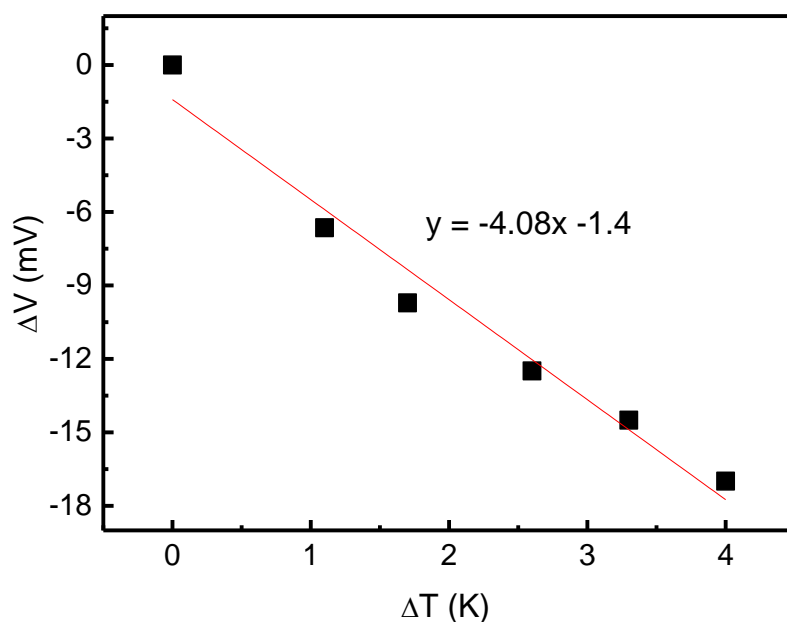**Fig. S7.** Illustration of the setup of Seebeck Coefficient measurement (a) and detailed electrode geometry (b)

Fig. S8. The plot of changes in thermovoltage (ΔV) at various temperature gradients between two electrodes (ΔT). The slope of the linear plot is determined as the Seebeck coefficient of the film.

Setup for Time-dependent V_{OC} and V_{OUT} measurement

The time-dependent V_{OC} and V_{OUT} were measured by a home-built setup with a Keithley 4200 Semiconductor Characterization System. Before the measurement, the two Au or Ag paste electrodes (each of them is 1mm wide and 20 mm long, and apart 3 mm) were deposited on the film as illustrated in Fig. 4a. A long and narrow electrode was used because such design gives the minimum error in the measurement. The film outside the two electrodes is also removed for the accurate voltage measurement. A hotplate with precision temperature controller (Präzitherm, PZ28-2) was used for heating. To measure the V_{OC}, the two terminals from Keithley were connected to the electrodes to measure the thermovoltage while two K-type thermocouples were placed at the end of the electrodes to determine the temperature gradients. The thermocouples were connected to a data logger (Omron ZR-RX45) to collect temperature reading.

To measure V_{OUT}, a load resistor is connected to the two electrodes and the voltage across the load resistor is measured by Keithley 4200, as shown in Fig. S8. The resistors were chosen in such a way that the resistance of the resistor is equal to the internal resistance of the device. All the measurements were done in a home-made humidity-controlled chamber.
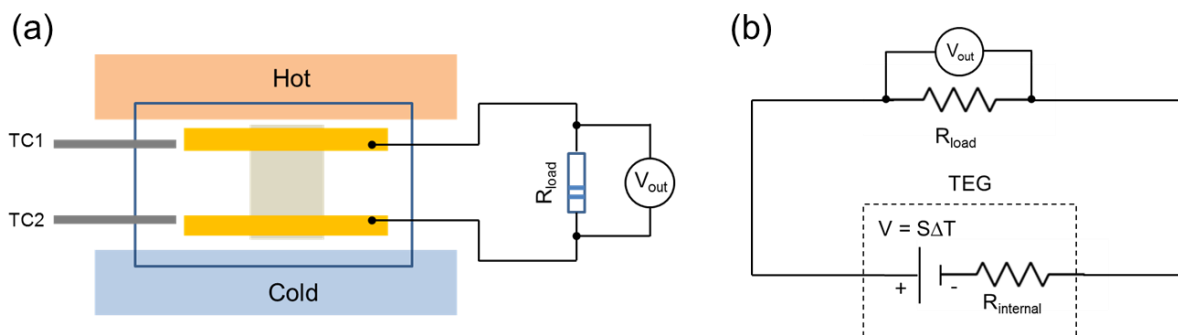
Fig. S9. The device structure of single leg TEG and the schematic of experimental setup for the measurement of V_{out} (a) and the equivalent circuit diagram of the setup (b).
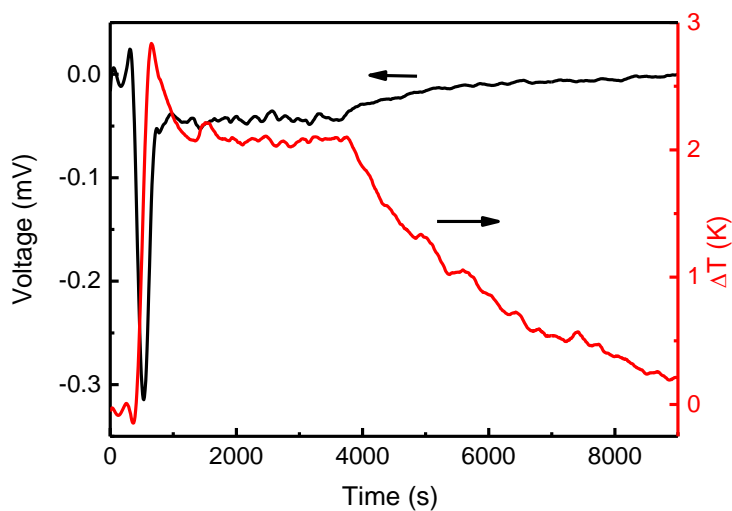

Fig. S10. Time-dependent V_{oc} measurement of as-cast PEDOT:PSS film (PH 1000 from Heraeus) using Au electrodes. Voc significantly changes over time even at constant heating. Voc increases to 0.3 mV at $\Delta T = 2$ K (at 500 s) but drastically decreases to 46 μV after next 400 s although ΔT maintains at 2 K.
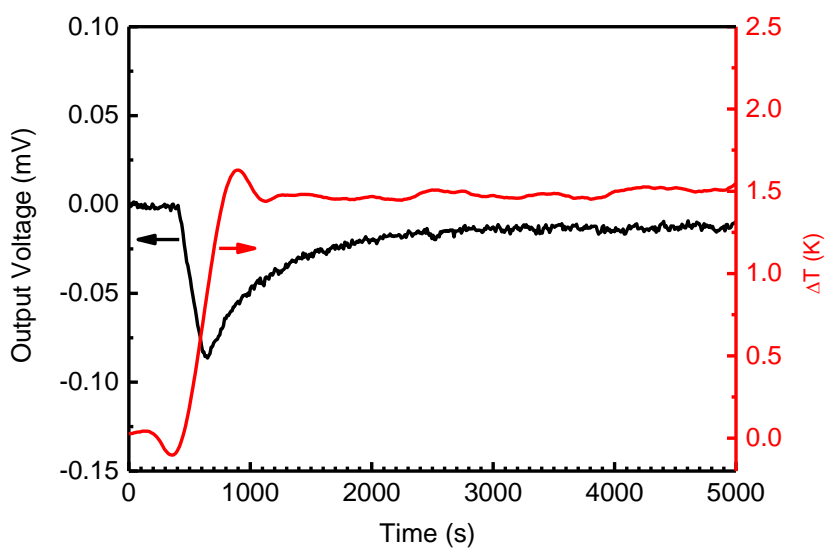
Fig. S11. Time-dependent V_{out} measurement of as-cast PEDOT:PSS film, using Au electrode. The profile shows that V_{out} decays exponentially over time even at the constant ΔT.
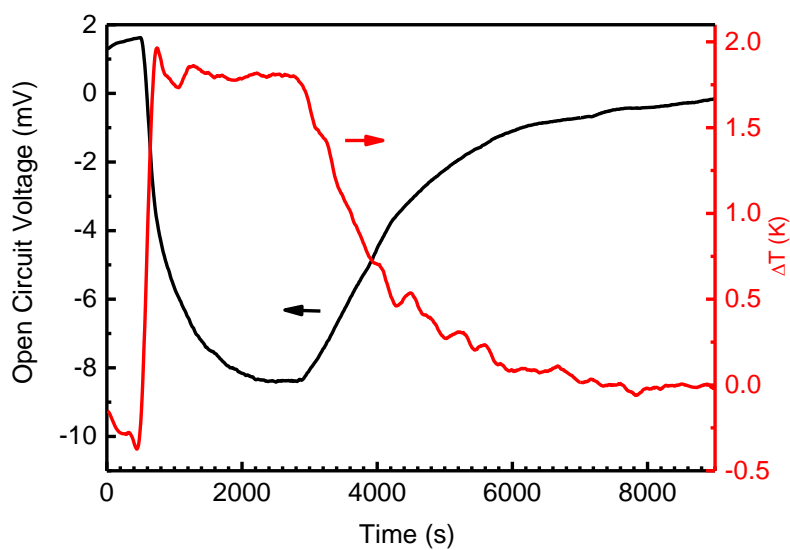

Fig. S12. Time-dependent V_{oc} measurement of PAZ:PSS film using Ag paste electrode.