

## *Electronic Supplementary Information (ESI)*

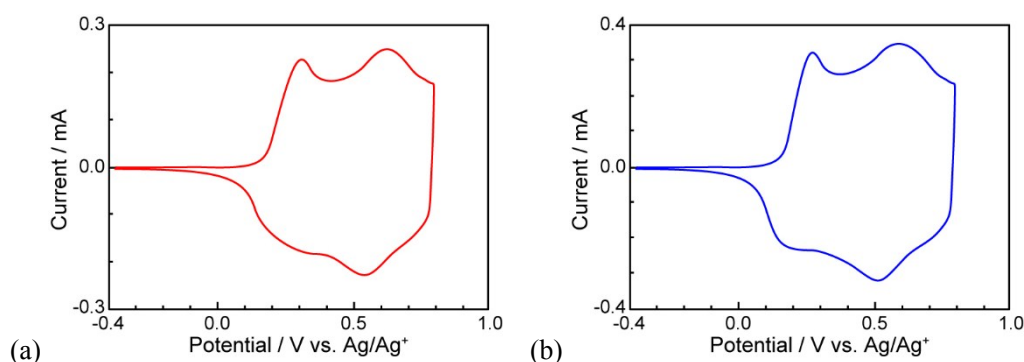
### Seebeck Coefficients of Regioregular Poly(3-hexylthiophene) Correlated with Doping Levels

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#### Experimental details of CV measurement and the estimation of doping levels of P3HT

##### (1) CV measurement

Regioregular P3HT (Lumtec, LT-S909,  $M_w > 45,000$ , regioregularity  $> 93\%$ ) was added in *o*-dichlorobenzene (*o*-DCB, Kanto Chemicals), and the solution was heated at 60 °C. The P3HT solution (50 mg/mL) was casted on Pt foil (Nilaco, PT-353211, thickness = 20  $\mu\text{m}$ ) by a doctor blade technique (gap = 25  $\mu\text{m}$ ) and dried in air. CV measurement of P3HT film was carried out in the acetonitrile solution containing 0.1 M TBAPF<sub>6</sub> or TEAClO<sub>4</sub>, using P3HT-covered Pt-foil, Pt-wire and Ag/Ag<sup>+</sup> as working, counter and reference electrodes, respectively, using an automatic polarization system (Hokuto Denko Corp., HSV-110). The results of CV measurements are shown in Figure S1.



**Fig. S1** Cyclic voltammograms of P3HT films deposited on Pt electrode  
in (a) TBAPF<sub>6</sub> and (b) TEAClO<sub>4</sub> solutions.

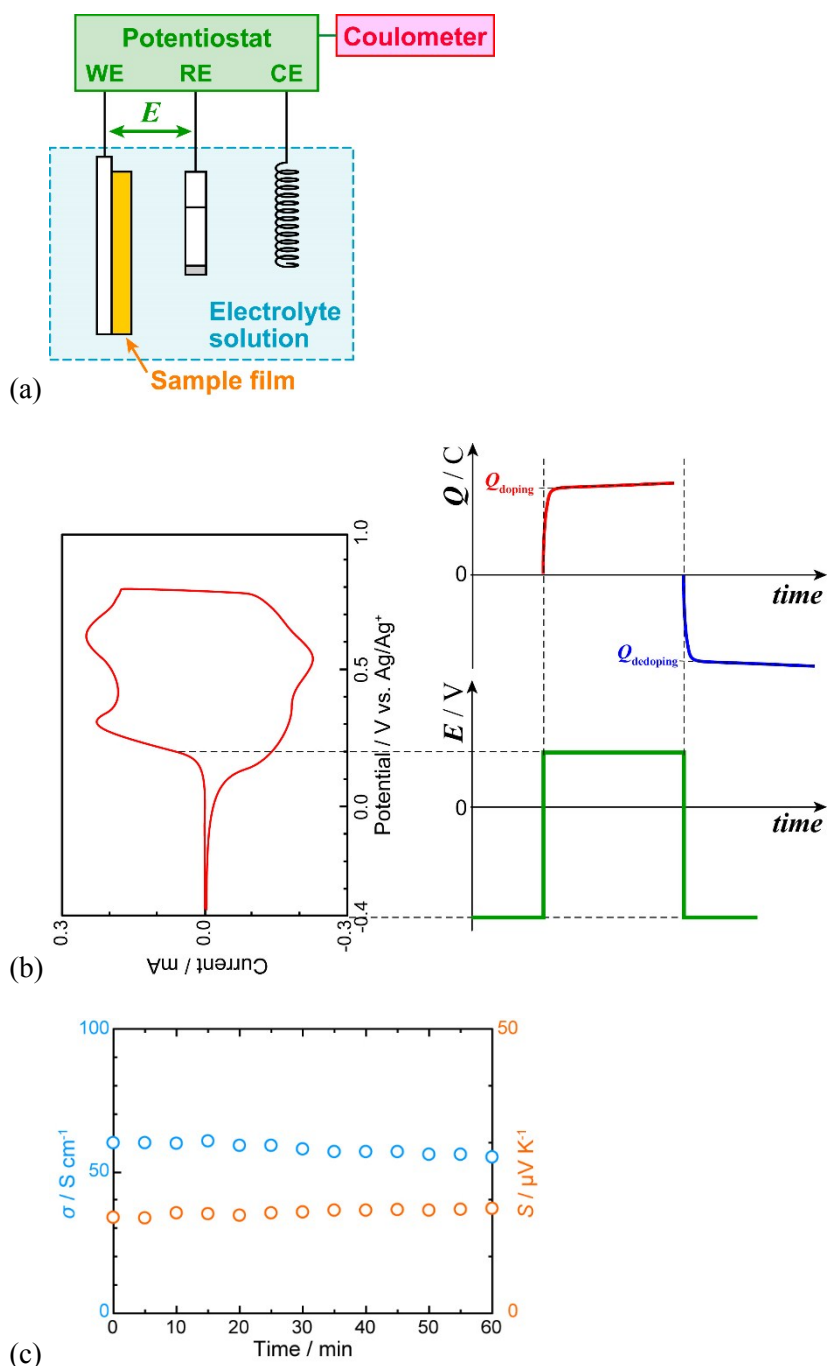
##### (2) Preparation of P3HT films for TE measurements

The P3HT films were prepared in a similar way to the CV measurements, except for the concentration (50  $\rightarrow$  150 mg/mL) and the gap used for the doctor blade technique (25  $\rightarrow$  75  $\mu\text{m}$ ) in order to obtain thicker and free-standing films for the measurements of TE properties.

##### (3) Estimation of doping levels of electrochemically-oxidized P3HT

The doping levels of P3HT were measured by the three-electrode system with P3HT-covered Pt-foil, prepared by the same method as described in (1), Pt wire and Ag/Ag<sup>+</sup> in the acetonitrile solution, using

a potentiostat/galvanostat (Hokuto Denko Corp., HAB-151) with an X-Y recorder (Riken Denshi Co., Ltd., F-57) and a coulometer (homemade) (Figure S2(a)). At first, the potential of the PHT film was set at -0.4 V, where P3HT is in a neutral state. Then, the P3HT film was oxidized at a certain potential ( $E_a$ ) by stepping the potential from -0.4 to  $E_a$ , and finally reduced at -0.4 V by stepping the potential back to -0.4V. The oxidation/reduction charges were recorded by the coulometer (Figure S2(b)). Stability of oxidized P3HT film in air was also examined by keeping the film in air for 1 hr (Figure S2(c)).



**Fig. 2S** (a) Set-up of PSC measurement, (b) estimation of oxidation/reduction charges, and (c) stability test of the oxidized P3HT film in air.

#### (4) Estimation of doping levels of chemically-oxidized P3HT

P3HT films prepared in the similar way to the CV measurement was dipped in an acetonitrile solution of NOPF<sub>6</sub> (0.4 mM). The rest potential ( $E_R$ ) of NOPF<sub>6</sub>-doped P3HT was measured in the three-electrode system using the potentiostat/galvanostat. The film was reduced at -0.4 V by stepping the potential from  $E_R$  to -0.4 V, and the reduction charge was recorded by the coulometer. To confirm the reliability of this measurement, the P3HT was oxidized at  $E_R$  and again reduced at -0.4 V, and the oxidation/reduction charges were recorded by the coulometer (Figure S3).

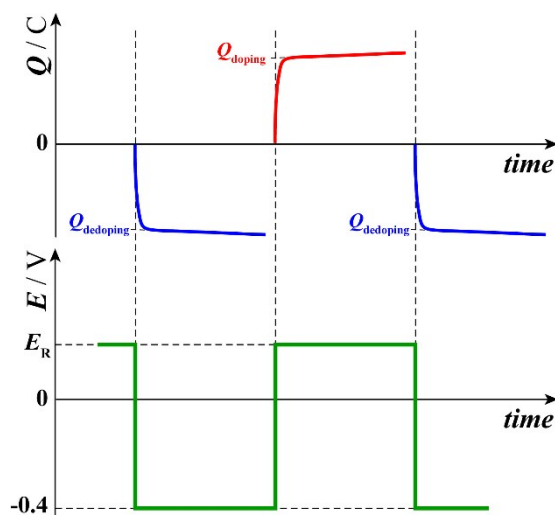


Fig. S3 Estimation of the amount of electric charges of chemically-oxidized P3HT films.

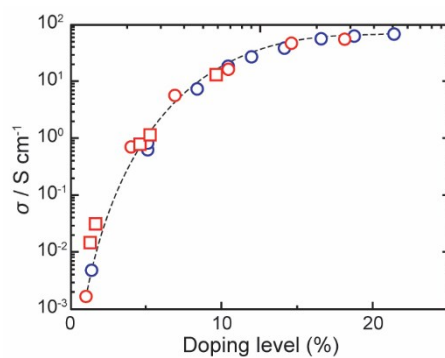
#### Measurements of electrical conductivity and Seebeck coefficient

Conductivities of the PEDOT:S-PHE films were measured using the four-probe method with a resistivity meter (Loresta-GP MCP-T610, Mitsubishi Chemical Corp.). A custom-made setup composed of thermocouples and Peltier devices was used to evaluate Seebeck coefficients, where it was calibrated in advance with the Seebeck coefficients of -18 and +22  $\mu\text{V K}^{-1}$  reported, respectively, for alumel and chromel alloys at room temperature.

For the measurements of thermoelectric properties, we need to peel off the polymer films from the working electrode, because we need to prepare polymer films on a working electrode. Thus, it is necessary to prepare the free-standing films in this measurement.

### Semi-log plot of electrical conductivities against doping levels.

Semi-log plot of electrical conductivities against doping levels is shown in Figure 4S.



**Fig. 4S** Semi-log plot of electrical conductivities against doping levels. (circles: electrochemically-oxidized P3HT with TBAPF<sub>6</sub> (red) and TEAClO<sub>4</sub> (blue). Red square: chemically-oxidized P3HT whose doping levels were estimated by PSC.)