Supporting Information for

Tailoring the Seebeck Coefficient of PEDOT:PSS by Controlling Ion Stoichiometry in Ionic Liquid Additives

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1. **Collapsed conductivity plot**

A variant of the conductivity plots shown in Figure 1b and 2b in the main text is shown below. Here, the x-axis is converted from volume % of additive in the film to volume % of I. L. pairs in the film. That is, the volume % of the additive that is solely 1:1 Im:TFSI, without considering other ions. For the 1:1 samples this does not change anything, but the points for the 4:1 samples will show lower volume % on this plot relative to Figure 2b, since the excess volume from the other ions is subtracted. As can be seen, when the volume from excess ions is removed, we find that the various additives plateau at a similar volume percent (~24%), confirming that the excess ions themselves do not contribute to the solvent annealing effect of the additive.

For the 4:1 samples, the volume of I.L. pairs added to the film was calculated by subtracting the volume of excess imidazolium from the total volume of the additive. In the case of 4:1 EMIm:TFSI, the weight of the excess 3 equivalents of solid EMIm:Cl added to the I.L. solution was converted to a volume of solid using the density (1.11g/cm^3). This was then subtracted from the total volume of additive to obtain the volume of EMIm:TFSI I.L. pairs added. For the 4:1 MIm:TFSI, the volume of the excess 3 equivalents of MIm (liquid) was subtracted from the total volume of additive to determine the volume of MIm:TFSI I.L. pairs added.

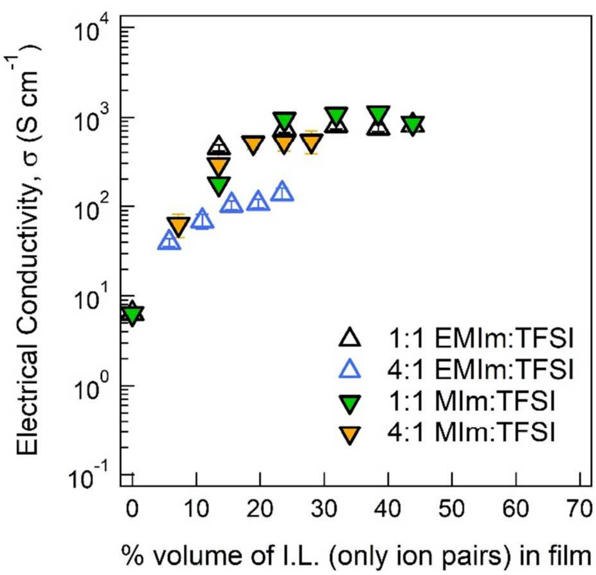

Figure S1. Modified conductivity plot, showing the conductivity all additives used in this study, plotted against the volume percentage of the additive I. L. ion pairs in the film.

2. **Control Experiments with DMSO and NaCl**

The procedure for blending these and other additives with PEDOT:PSS and preparing films is detailed in the Experimental Section of the main text. Plots of the conductivity and Seebeck coefficient for NaCl are shown below, overlaid on the plots from Figures 1 and 2 in the main text. A control showing *both* DMSO and NaCl in the dispersion, at the same concentrations that they were used individually, is also shown. A table showing the exact values and calculated error is also provided.

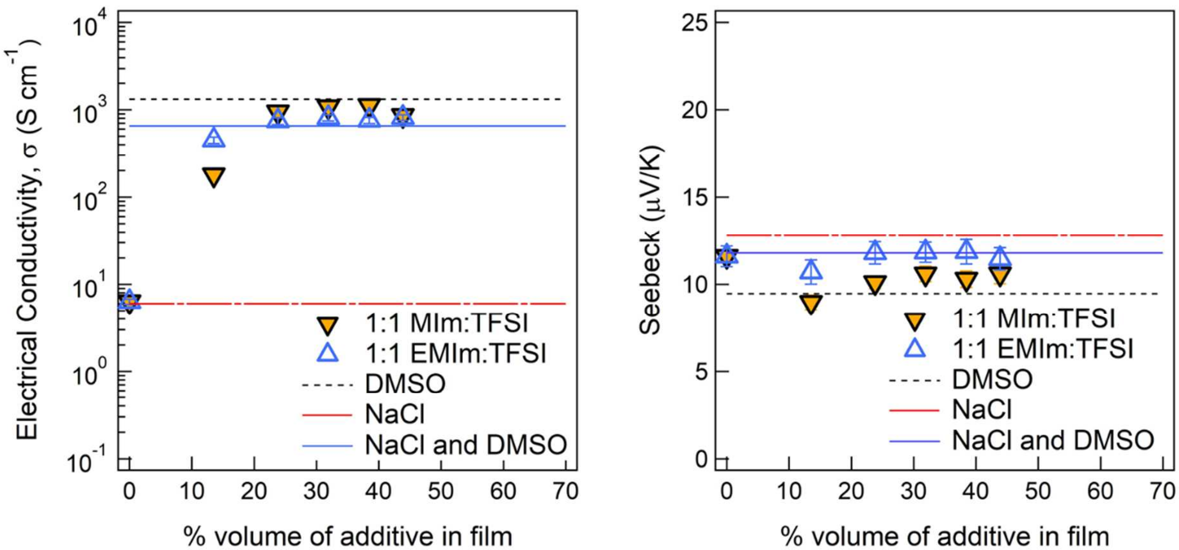

Figure S2. Conductivity and Seebeck coefficient plots corresponding to Figure 1 from the main text, overlaid with data from the NaCl control, as well as DMSO+NaCl for comparison.

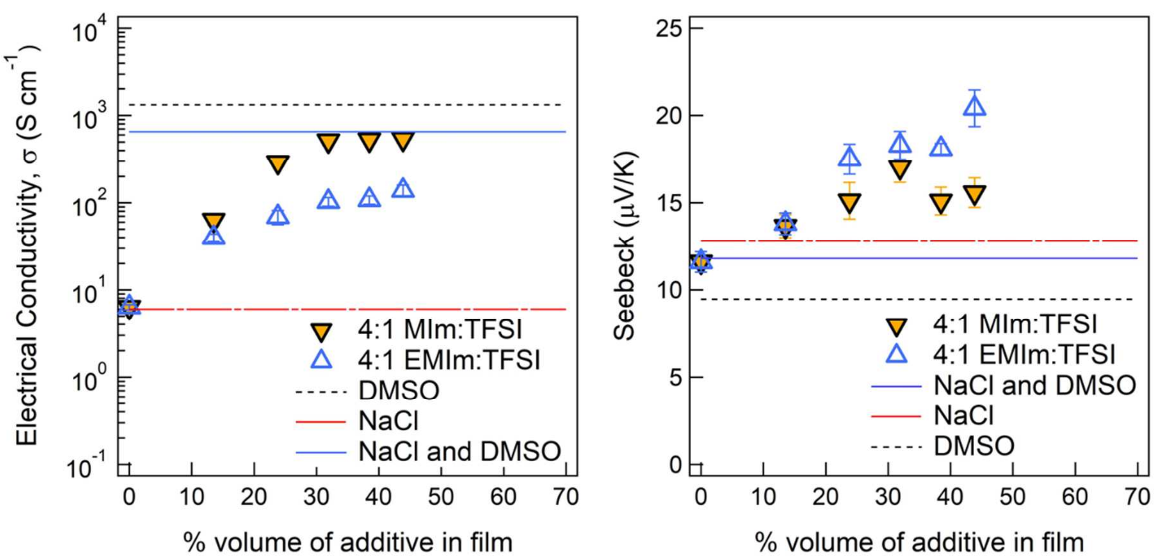

Figure S3. Conductivity and Seebeck coefficient plots corresponding to Figure 2 from the main text, overlaid with data from the NaCl control, as well as DMSO+NaCl for comparison.

	Conductivity (S/cm)	Error	Seebeck (μV/K)	Error
Pristine PEDOT:PSS	6.3	0.4	11.6	0.6
DMSO	1316.6	153	9.5	0.6
NaCl	6.0	0.5	12.8	0.7

NaCl+DMSO	655.3	49	11.8	0.7

Table S1. Conductivity and Seebeck coefficient values for pristine PEDOT:PSS and the various controls used in this study.

3. Thermoelectric measurement

A sample thermoelectric measurement for pristine PEDOT:PSS (Clevios Lot No. 9000819041) is plotted in Figure S4a, where the measured thermovoltage is plotted as a function of time for four temperature differences. Sufficient time is allowed so that initial voltage and temperature fluctuations for each temperature difference become negligible. The final value of thermovoltage for a given temperature difference is calculated as the average of the last 10% of the equilibrated value. This is plotted in Figure S4b as a function of the temperature difference between the electrodes and the slope of the fitted line through the points gives the Seebeck coefficient (the negative sign is absorbed in the temperature difference as it is measured in the opposite direction with respect to the voltage difference).

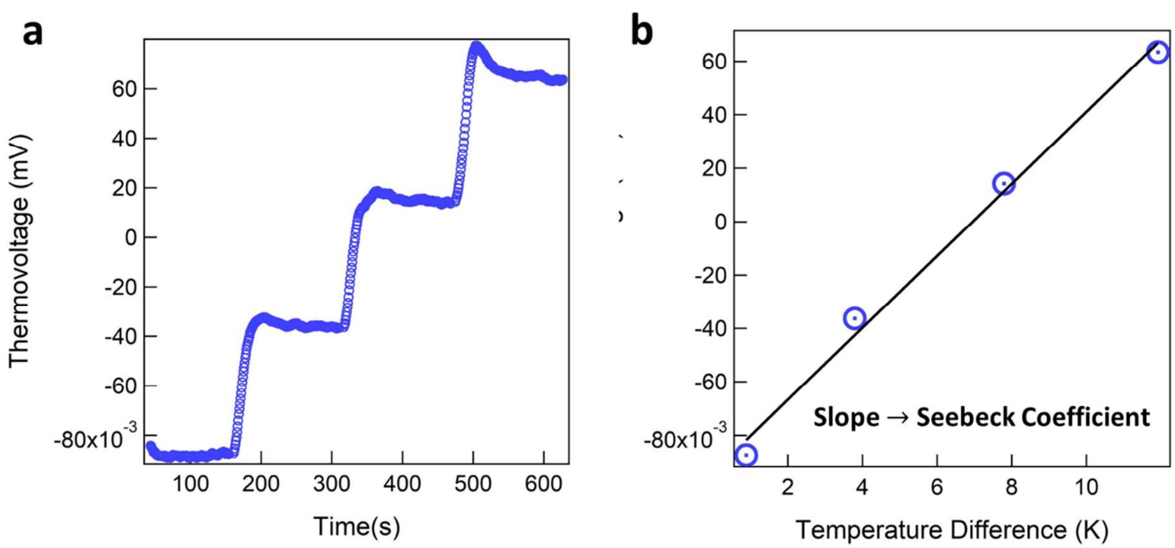

Figure S4. (a) Continuous measurement of thermovoltage as a function of time for four temperature differences. (b) Mean thermovoltage plotted as a function of the corresponding temperature difference. The slope of the fitted line is equal to the Seebeck coefficient.

4. **Electrical conductivity measurement**

A sample electrical conductivity measurement for pristine PEDOT:PSS is shown in Figure S5.

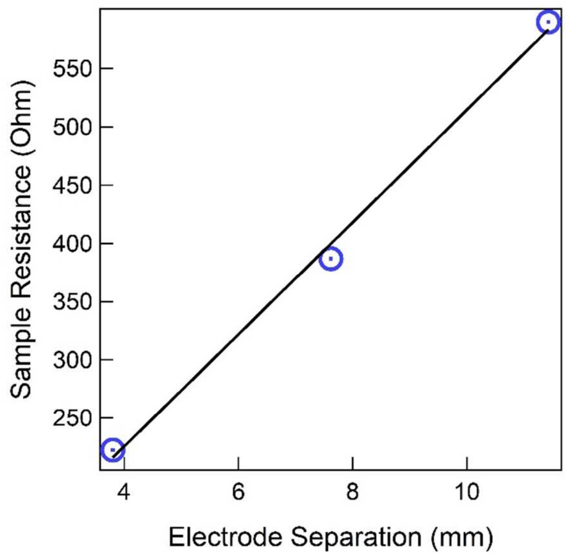

Figure S5. Measured resistance plotted as a function of electrode separation. The slope of the fitted line is related to the electrical conductivity as described in the Experimental Section of the manuscript.

5. **Expanded UV-Vis Spectrum**

Figure 3 is re-plotted below with an expanded energy axis.

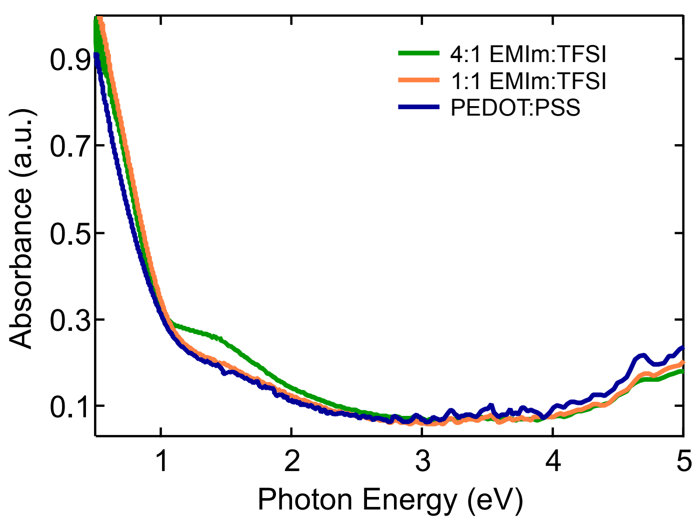

Figure S6. UV-Vis absorption spectra of PEDOT:PSS thin films shown in Figure 3 of the manuscript with an expanded energy range