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Supporting Information

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Novel Solution-Processable, Dedoped Semiconductors for Application in Thermoelectric Devices

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Experimental Section

Characterization

Four gold electrodes (2 mm × 2 mm) were evaporated onto a PEDOT:PSS film on a glass substrate for stable ohmic contacts. Then, the electrical conductivity (σ) was measured by the Van der Pauw method in a four-point contact configuration using a combination of a Keithley 2400 source-measure unit, a 2182 nanovoltmeter, and a 7001 switch system. S values were measured using a setup built in-house from a Peltier cooler and Peltier heater to apply temperature gradients that induce thermal voltage. The Peltier devices were controlled by a Keithley 2400 source-measure unit and a Keithley 2200-30-5 power supply. Two thermocouples (TCs) were placed on the hot and cold region gold electrodes, and were separated by 1 cm. The temperature difference between the TCs was fixed to 5 °C at room temperature. Thermoelectric efficiency values were calculated from the relationship $ZT = S^2{\cdot}\sigma T/\kappa$, where S is the Seebeck coefficient (also referred to as thermopower); σ and κ are the electrical and thermal conductivities, respectively; and T is the absolute temperature. Here, the product of electrical conductivity and the square of S is called 'power factor' ($S^2{\cdot}\sigma$). The average thickness of the films was measured on an AS500 alpha-step surface profiler (KLA-Tencor Co., USA). The PEDOT/PSS ratio and chemical composition on the film surface were determined by XPS (Thermo K-Alpha XPS, Thermo Fisher Scientific, West Palm Beach, FL, USA). The surface images of the nanofilms were obtained by using an atomic force microscope (AFM, Park Systems XE-100) in non-contact mode. The doping/de-doping states of the film as a function of the hydrazine concentration were studied by ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy (PerkinElmer Lambda 750) in the 300–1400 nm range. The film surface images were recorded on a Park Systems XE-100) atomic force microscope in non-contact mode. The carrier concentration and carrier mobility were measured on a HMS-3000 Hall measurement system (Ecopia, Repubilic of Korea). Thermal diffusivity (λ) was measured on a LFA 457 (Netzsch, Germany), and the specific heat capacity (C_p) was measured on a DSC 200 F3 differential scanning calorimeter (Netzsch, Germany). The thermal conductivity (κ) was calculated from the relationship $\kappa = \lambda \times C_p \times \rho$, where ρ is the density.[1]

RESULTS AND DISCUSSION

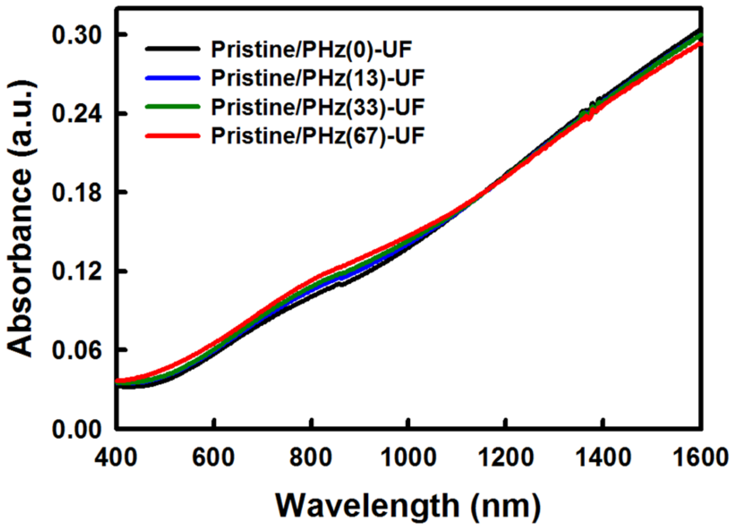
Table S1. Thermal conductivity, *ZT* values, and other parameters used for calculating the thermal conductivity of different PEDOT:PSS samples.

Sample	**ρ** [g/cm^3]	**C_p** [J/g·K]	**λ** [mm^2/s]	**κ** [W/m·K]	ZT
Pristine	1.327	1.415	0.176	0.330	0.049
PHz	1.385	1.415	0.195	0.382	0.013
Pristine/PHz(0)-UF	1.243	1.176	0.116	0.170	0.146
Pristine/PHz(33)-UF	1.241	1.201	0.117	0.174	0.191
Pristine/PHz(66)-UF	1.238	1.244	0.120	0.185	0.173

Table S2. Comparison of thermal conductivity measured by our laser flash method and literature values for commercial PEDOT:PSS (PH 1000).

Analysis method	Sample	Cross-plane (**κ**) [W/m·K]	In-plane (**κ**) [W/m·K]	Average (**κ**) [W/m·K]	reference
Laser flash	pellet	0.38	-	0.38	this work
3-omega technique	film	0.30	0.42	0.36	[2]

Unfortunately, this work is limited to the use of the 3-omega technique to analyse the κ values of nanofilms. We know that the laser flash method is based on the measurement of the thermal conductivity (κ) of the bulk material. Hence, previous studies to measure the thermal conductivity of the films used measurements over the 3-omega technique, which is a powerful tool for thermal conductivity analysis. However, the 3-omega technique is currently considered an informal guidance note in the industry. Additionally, accurate analytical methods of the thermal conductivity of films are still very limited. Thus, we chose to use the laser flash method as our official method. To clarify the accuracy of the laser flash method, we compared the thermal conductivity (0.38 W/m·K) measured by this method using the commercial PEDOT:PSS (PH 1000) with the known average thermal conductivity (0.36 W/m·K) measured by the previously published 3-omega technique.[2] Consequently, we confirmed that the average thermal conductivities measured by both these methods were almost identical.



Sample	Absorbance (a.u.) at a certain wavelength		
	600 nm	900 nm	1400 nm
Pristine/PHz(0)-UF	0.571	0.116	0.251
Pristine/PHz(17)-UF	0.595	0.120	0.249
Pristine/PHz(33)-UF	0.606	0.124	0.247
Pristine/PHz(67)-UF	0.651	0.130	0.246

Figure S1. UV-Vis-NIR absorption spectra and absorbance values at 600, 900, and 1600 nm in the UV-Vis-NIR spectra of Pristine/PHz-UF complex films as a function of PHz-UF content (wt%).

As the PHz-UF wt% increases, optical transitions in the visible region (~600 nm) gradually appear, while the bipolaronic optical transitions in the IR region are eliminated. This systematic change in the optical spectra depends on the chemical oxidation level[3] caused by blending with the de-doped PHz-UF material.

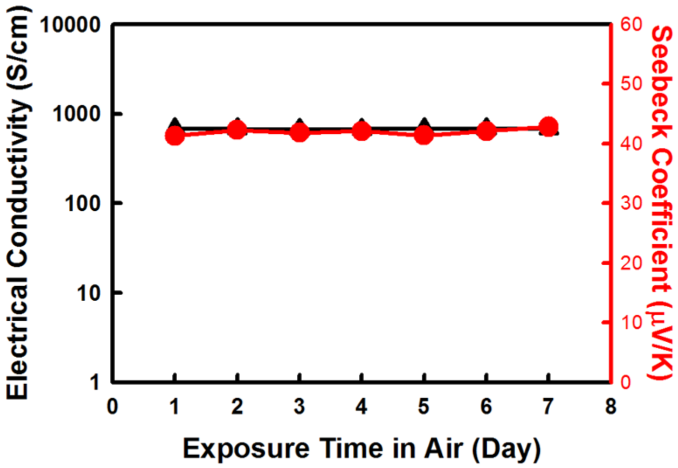


Figure S2. Effect of stability of electrical conductivity and Seebeck coefficient of the optimum Pristine/PHz-UF complex sample on TE performance as a function of exposure time in air.

References

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