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Supporting Information

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A New Polystyrene–Poly(vinylpyridinium) Ionic Copolymer Dopant for n-Type All-Polymer Thermoelectrics with High and Stable Conductivity Relative to the Seebeck Coefficient giving High Power Factor

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Jinfeng Han[1], Emma Tiernan[2], Taein Lee[1], Arlene Chiu[3], Patty McGuiggan[1], Nicholas Adams[1], Patrick E. Hopkins[2], Susanna M. Thon[3], John D. Tovar[1], Howard E. Katz[1,]*

[1]Department of Materials Science and Engineering and Department of Chemistry, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, United States

[2]Department of Mechanical and Aerospace Engineering, Department of Materials Science and Engineering (Courtesy) and Department of Physics (Courtesy), University of Virginia, 122 Engineer's Way, Charlottesville, VA 22904-4746, United States

[3]Department of Electrical and Computer Engineering, Johns Hopkins University, 3400 North Charles Street, Baltimore, Maryland 21218, United States

1. General procedures and experimental details.

Chemical reagents (Including solvent and PMMA) were purchased and used as received. All the synthesis procedures were performed under N_2.

^1H and ^{13}C NMR spectra were recorded on Bruker Advance (400 MHz) spectrometers. ^1H NMR chemical shifts were referenced to tetramethylsilane TMS (0 ppm). Gel permeation chromatography (GPC) was performed on a PL gel MIXED-B LS 300 x 7.5mm x 3 at 150 °C using trichlorobenzene (TCB) stabilized with 0.0125% BHT as eluent. The EPR measurements were performed on a Bruker-EMX EPR spectrometer at room temperature. Solutions of doped polymers were prepared by stirring at 120 ℃ for 3 min and then 50 μL solution was injected into EPR tubes. AFM images were taken in tapping mode using a Dimensional 3100 AFM (Bruker Nano, Santa Barbara, CA). The images were visualized using the Nanoscope software (Bruker). The absorption spectra were acquired on an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. GIXRD was performed on a Bruker D8 Advance A25 instrument.

OFET Film Fabrication and Characterization.

Organic field electric transistors (OFETs) with top-gate/bottom-contact (TGBC) configuration were fabricated using n^{++}-Si/SiO2 (300 nm) substrates with a channel length of 200 μm and a channel width of 8000 μm. The substrates were cleaned using ultrasonication in cleaning agent (Decon, labs, Inc), deionized water, acetone, and isopropanol. The cleaned substrates were dried under vacuum at 60 °C for 6 h and then transferred into a glovebox. The source and drain electrodes comprising a layer of Au (50 nm) were deposited through a shadow mask onto the silicon substrates by thermal evaporation. Thin films of polymers (2.5 mg/mL in orthodichlorobenzene (*o*-DCB)) and doped polymers were prepared by spin coating the solution on the substrates at 2000 rpm for 60 s and annealed at 150 °C for 30 min. Then, the solution of PMMA was spin-coated on the polymer films at 2000 rpm for 60 s and annealed at 110 °C for 30 min, resulting in a dielectric layer about 1050 nm thick. Gate electrodes comprising a layer of Au (50 nm) were then deposited through a shadow mask onto the dielectric layer by thermal evaporation. The OFET devices had a channel length (L) of 200 μm and a channel width (W) of 8000 μm. The evaluations of the OFETs were carried out in the ambient atmosphere on a probe stage using an Agilent B1500A as parameter analyzer. The mobility was calculated in the saturation regime according to the equation: $I_{DS} = (W/2L)\mu C_i(V_G - V_T)^2$, where I_{DS} is the drain current, μ is the mobility, and V_G and V_T are the gate voltage and threshold voltage, respectively.

Thermoelectric devices and properties measurements.

ITO electrodes with a channel length of 3 mm and a channel width of 7 mm patterned glass substrates were cleaned by sonication in cleaning agent, deionized water, acetone, and isopropanol. Polymer PFClTVT and PSpF were dissolved in *o*-DCB separately with the concentration of 2.5 and 10 mg mL^{-1}, respectively. N-DMBI was were dissolved in *o*-DCB with the concentration of 2.5 mg mL^{-1}. The polymers and the dopant solutions were heated at 100 °C for 24 h. Then the polymer was blended with dopant in the desired weight ratio. The mixed solution was heated at 120 ^{o}C and stirred for 2 min. The final solution was dropped on the glass substrates on which 2D wells are fabricated by laying a pattern of Novec polymer. After natural evaporation of solvent in a glove box over 24 h, square films form. The devices were annealed on a hot plate at 120 °C for 12 h in nitrogen. All the measurements were performed in ambient. Resistance was measured by using a four-probe method with an Agilent B1500A Semiconductor Parameter Analyzer with a channel length of 1000 μm and a channel width of 140 μm. 3-8 measurements of resistance were performed on each sample surface in different positions. Seebeck coefficient can be calculated by $S=\Delta V/\Delta T$ with a channel length of 2000 μm and a channel width of 8000 μm, where ΔV is the thermal voltage obtained between the two electrodes of the device subjected to a temperature gradient ΔT. 2-4 Devices were measured for Seebeck coefficient measurement. Six ΔT were imposed on the sample, so the slopes of ΔV versus ΔT give values of the Seebeck coefficient.

Statistics

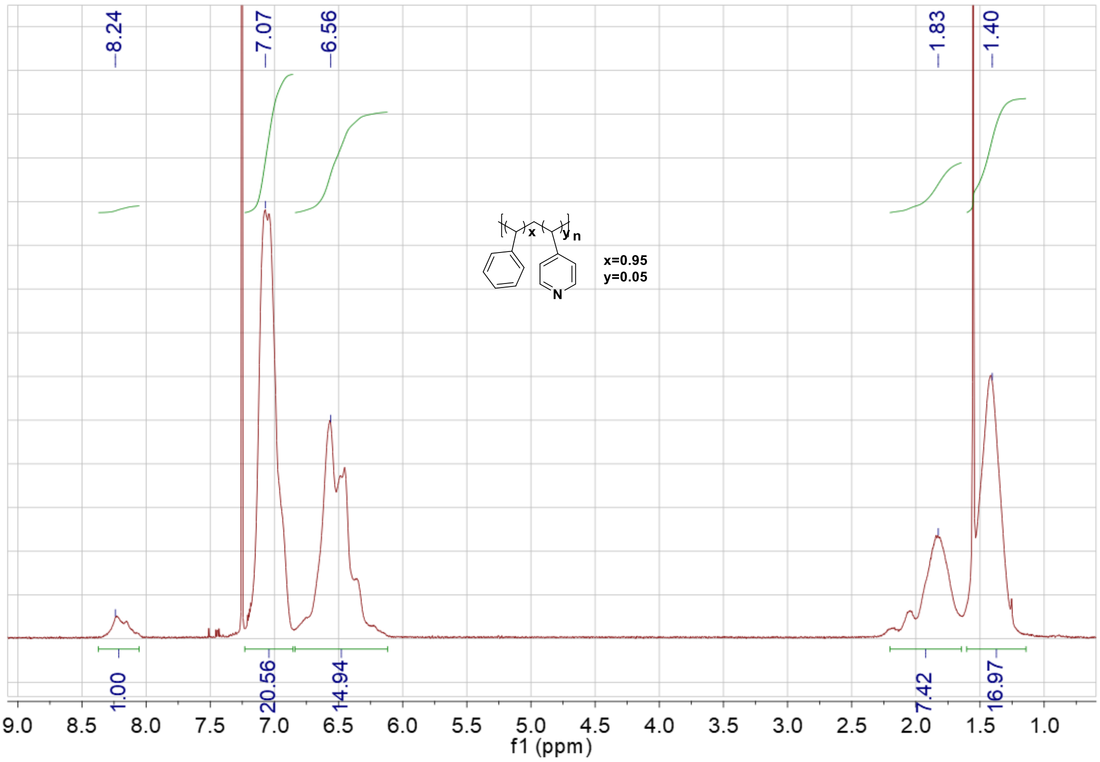
1. All the data in this work were processed by the software of OriginLab and without any normalization, except for the absorption spectra.
2. Data presentation: the data error bars were calculated and are shown as standard errors.
3. All the data were measured in different positions and repeated at different times with different devices. As noted above, for conductivity, at least 2 samples and 3-8 measurements at different positions on every sample; for Seebeck coefficient, at least 2 samples and 2-5 measurements at different positions on every sample.

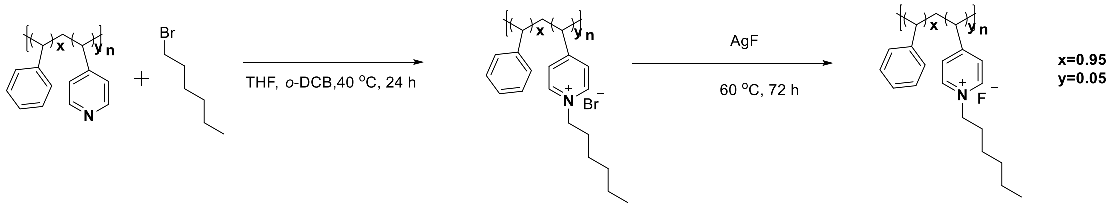
2. Synthesis of polymers.

PFClTVT was synthesized according to the previous work.[1]

PS-P

PS-P: Styrene (20 g, 22.08 mL, 192 mmol) and vinylpyridine (1 g, 1.04 mL, 9.6 mmol) was added to a dry Schlenk tube under N_2, then 2, 2-azobisisobutyronitrile (AIBN) (12 mg) and S, S-Dibenzyl trithiocarbonate (DBTTC) (6 mg) was added to the Schlenk tube under N_2. Then 16 mL *o*-DCB was added to the tube, and evacuation and refilling with N_2 was repeated 8 times under stirring. Then the solution was heated to 90℃ and stirred for 96 h. The polymer solution was dropped into 350 mL methanol and stirred for 1 h, then it was filtered and washed in a Soxhlet extractor with methanol for 2 days. White solid was obtained in the yield of 85%. GPC: M_n = 118.4 kDa, M_w = 334.1 kDa, *PDI* = 2.8.

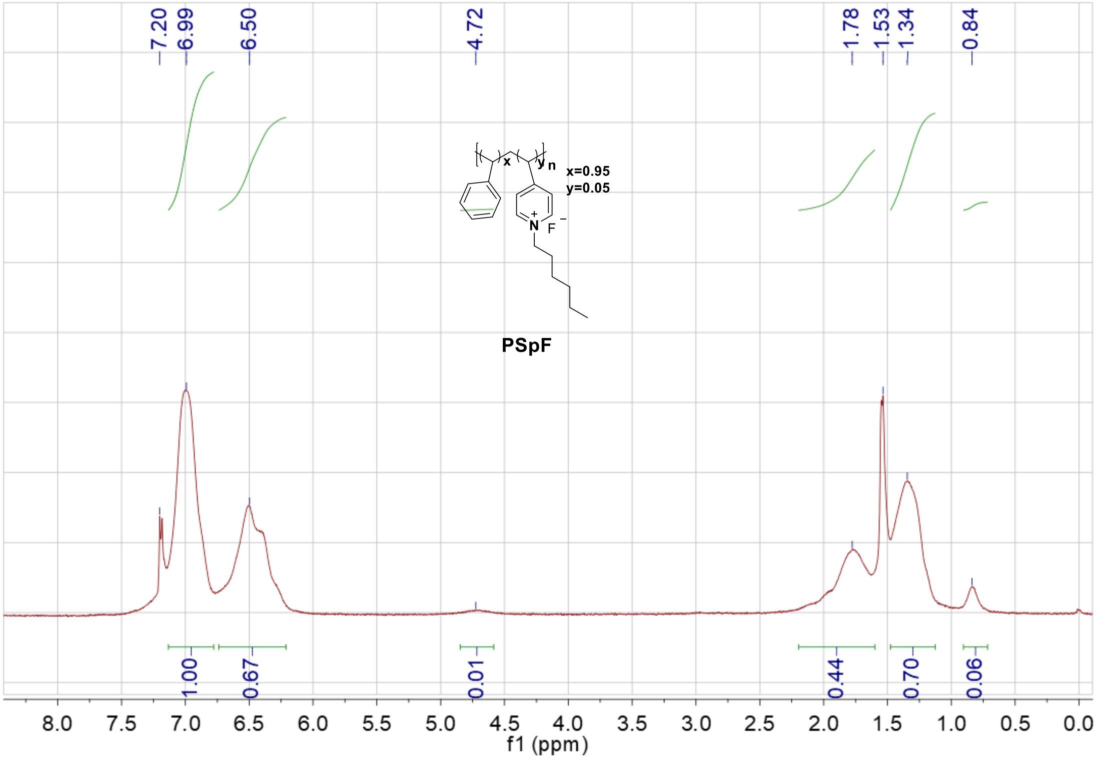




PS-P **PSpBr** **PSpF**

PSpBr: The polymer PS-P (3 g) and bromohexane (0.5 g) was added to a dry Schlenk bottle. Then 30 mL o-DCB and 10 mL THF was added and stirred for 0.5 h under N_2. Then the mixture was heated to 40℃ and reacted for 24 h. After reaction, the solution was cooled to room temperature and used in the next step without purification.

PSpF: Excess AgF (0.55 g) was added to the solution under N_2, and the mixture was heated to 60℃ and stirred for 72 h. After reaction, the solvent was removed with reduced pressure distillation. Then the solid was dissolved in chloroform and filtered. The filtrate was concentrated with rotary evaporation and dried in vacuum under 55 ℃ for 3 days. The faint yellow solid was obtained in the yield of 59%.



3. Characteristics of polymers and doped polymer films.

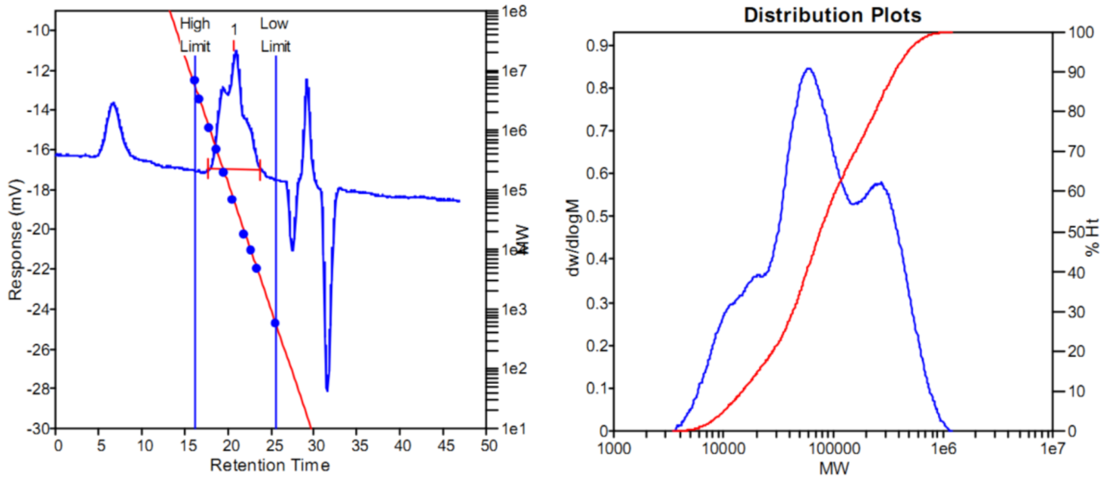


Figure S1. GPC spectra of PFClTVT.

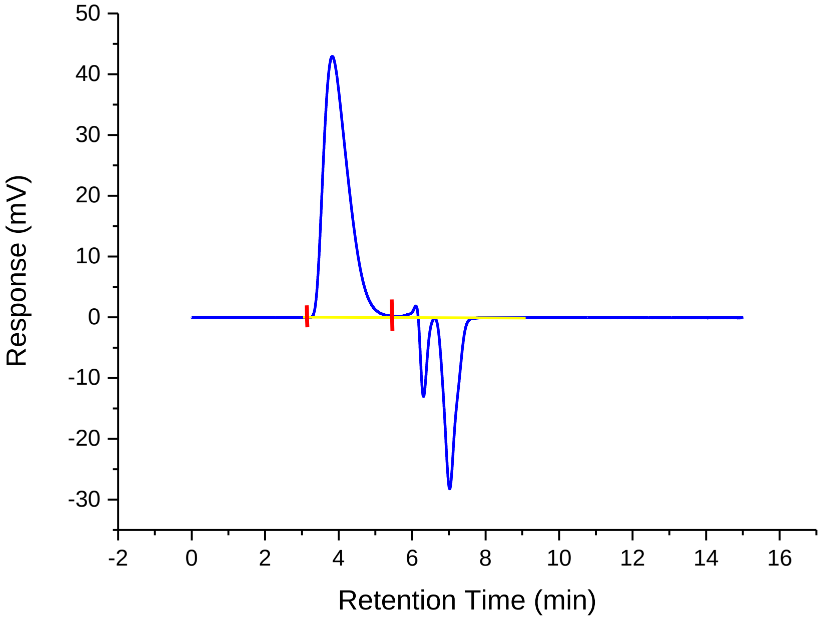


Figure S2. GPC spectra of PS-P.

Table S1. Characteristics of polymers. The molecular weight of PFClTVT was determined by GPC at 150 ℃ in 1,2,4-trichlorobenzene with polystyrene standards. The molecular weight of PS-P was determined by GPC at 30 ℃ in THF with polystyrene standards.

Polymer	M_n (kDa)	M_w (kDa)	*PDI*
PFClTVT	39.4	140.6	3.6
PS-P	118.4	334.1	2.8

Figure S3. Differential scanning calorimeter (DSC) traces of PS-P measured under N_2.

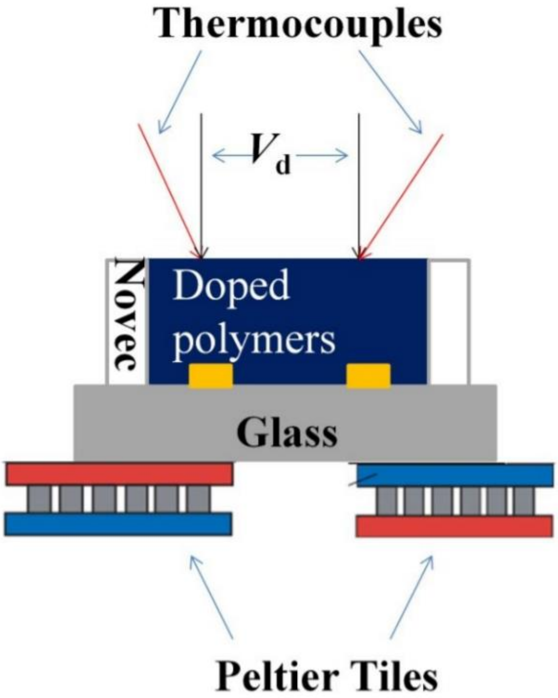


Figure S4. The sketch of the device cross-section used to estimate the Seebeck coefficient.[2]

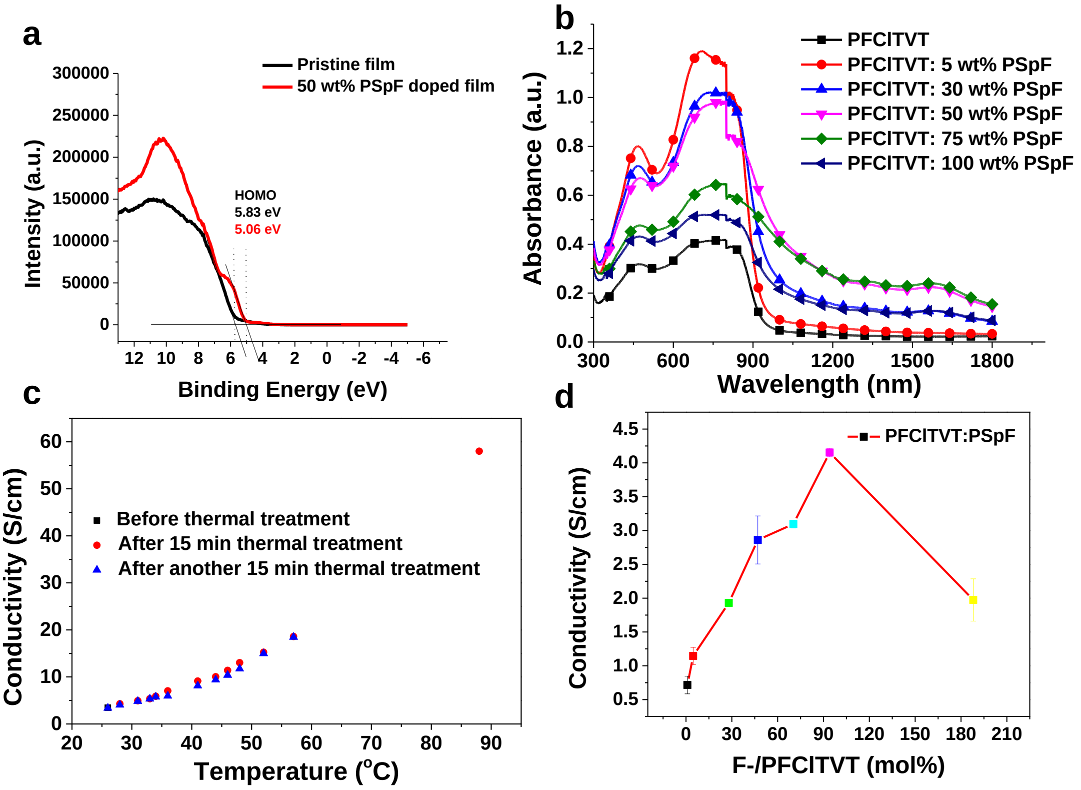


Figure S5. (a) UPS binding energy of the pristine and doped polymer films measured under -5 eV. (b) The normalized absorption of pristine and PSpF doped PFClTVT films. (c) Thermal air stability of electrical conductivity of 75 wt% PSpF doped PFClTVT films after thermal treatment at 120 °C for 2-circle 15 min in the open air. (d) The equivalent Figure 3a using F^-/PFClTVT mole ratio.

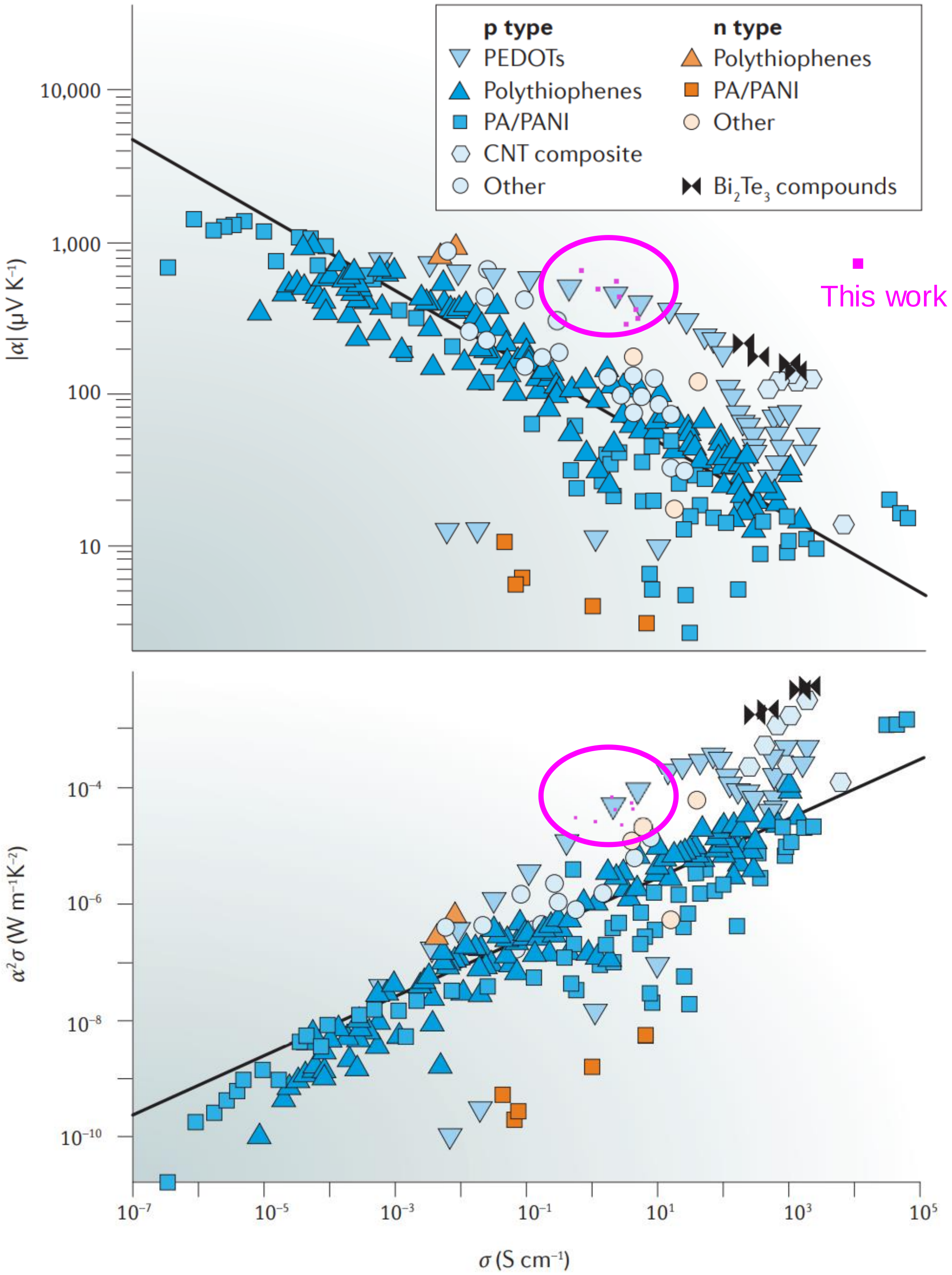


Figure S6. Seebeck coefficient (α; top) and power factor ($\alpha 2\sigma$; bottom) as functions of conductivity (σ) for a range of doped organic thermoelectric (OTE) polymers and composites summarized by Boris Russ et al.[3] with data from the present work superimposed. Reprinted by permission from Nature/Springer/Palgrave) B. Russ, A. Glaudell, J. J. Urban, M. L. Chabinyc, R. A. Segalman, *Nat. Rev. Mater.* **2016**, *1*, 16050. Copyright 2016.

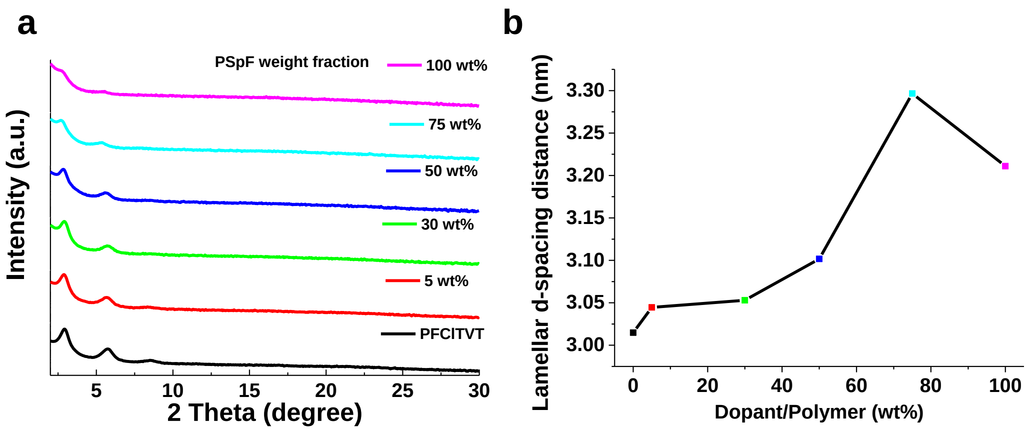


Figure S7. (a) Out-of-plane GIXRD diagrams of pristine and doped polymer films which are prepared similarly to the thermoelectric devices. (b) Lamellar *d*-spacing distances of polymers doped with various weight fractions of dopant.

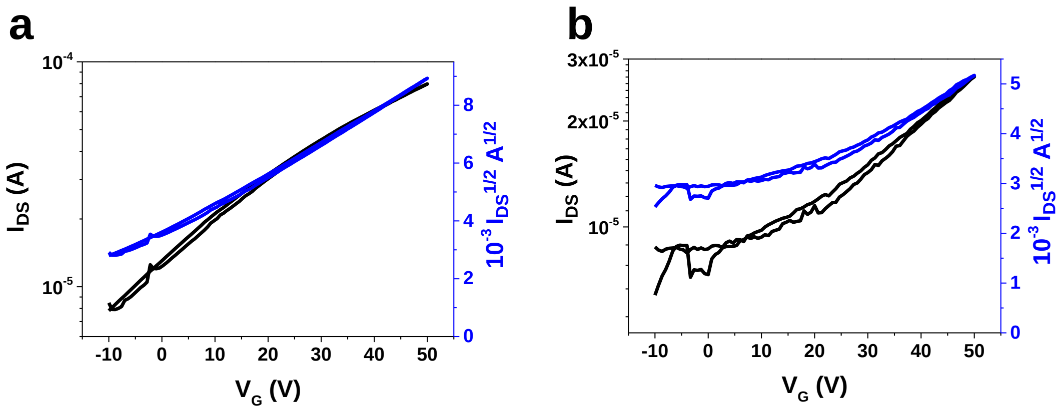


Figure S8. Transfer curves of OFETs of (a) 2 wt% and (b) 10 wt% PSpF doped polymer thin films.

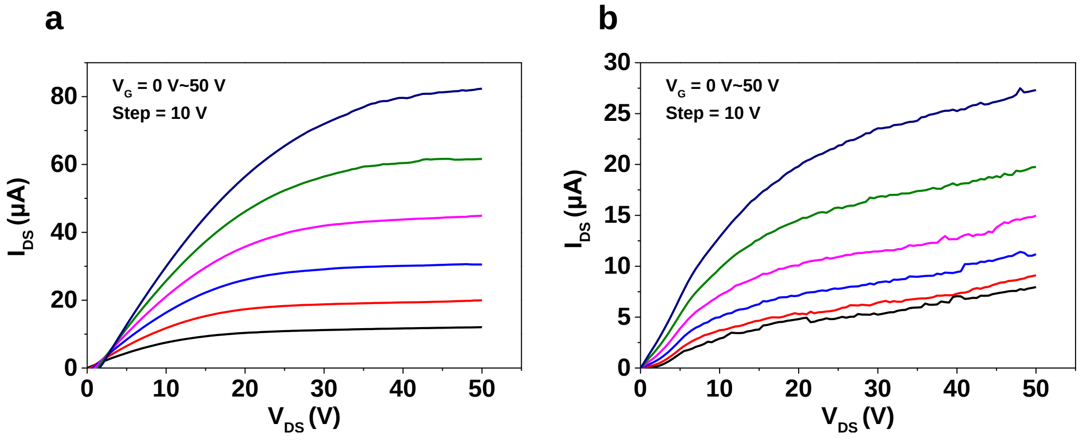


Figure S9. Output curves of OFETs of (a) 2 wt% and (b) 10 wt% PSpF doped polymer thin films.

Table S2. OFET device performance of the pristine and doped polymers.

Polymer films	**μ_e (cm^2 V^{-1} s^{-1})**	**V_T (V)**	**I_{on}/I_{off}**
PFClTVT	0.24±0.04	35-40	500-1000
1 wt% PSpF	0.81±0.05	-7--21	80-100
2 wt% PSpF	0.37±0.01	-25	10-15
10 wt% PSpF	0.13±0.05	-3--22	3-400

Table S3. EDS element analysis of pristine PFClTVT film in different spots.

Element	Spot 1 Atomic %	Spot 2 Atomic %	Spot 3 Atomic %	Spot 4 Atomic %	Spot 5 Atomic %	Spot 6 Atomic %
C K	52.54	52.46	61.49	70.23	53.08	53.06
O K	9.58	9.51	12.22	11.05	9.54	9.15
F K	0.14	0.18	0.5	0.32	0.17	0.17
Si K	35.77	35.68	23.26	13.59	35.26	35.37
S K	0.56	0.59	0.58	1.57	0.55	0.63
Cl K	0.56	0.66	0.83	1.59	0.53	0.63
Cr K	0.85	0.92	61.49	1.65	0.86	0.99

Table S4. EDS element analysis of 5 wt% PSpF doped PFClTVT film in different spots (Spot 6 is dust).

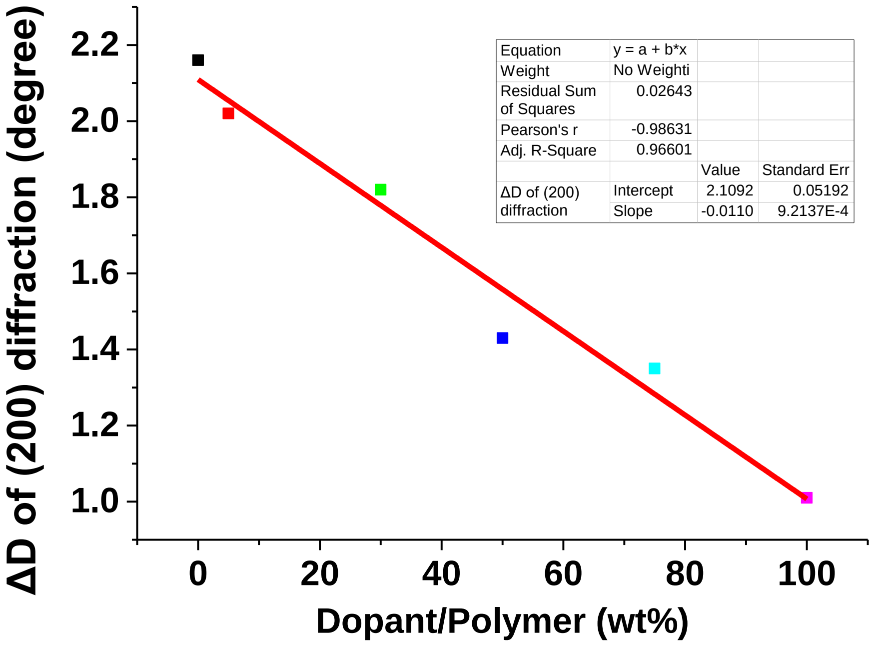
Element	Spot 1 Atomic %	Spot 2 Atomic %	Spot 3 Atomic %	Spot 4 Atomic %	Spot 5 Atomic %	Spot 7 Atomic %	Spot 8 Atomic %
C K	74.53	77.61	75.04	73.45	74.61	73.64	72.96
O K	10.61	7.89	7.27	6.08	8.27	5.9	6.22
F K	2	1.25	0.63	0.96	1.61	0.89	1.03
Br L	0.2	0.27	0.27	0.22	0.21	0.22	0.24
Si K	2.75	7.66	11.72	14.46	7.64	14.29	14.89
S K	2.37	2.01	1.92	1.79	2.34	1.88	1.73
Cl K	2.54	1.59	1.7	1.92	2.47	1.86	1.79
Ag L	3.53	0.19	0.24	0.11	1.3	0.13	0.1
Cr K	1.47	1.53	1.22	1.01	1.55	1.19	1.04

Table S5. EDS element analysis of 50 wt% PSpF doped PFClTVT film in different spots (Spot 3 is dust).

Element	Spot 1 Atomic %	Spot 2 Atomic %	Spot 4 Atomic %	Spot 5 Atomic %	Spot 6 Atomic %	Spot 7 Atomic %	Spot 8 Atomic %
C K	76.32	78.87	74.09	77.8	78.01	76.7	77.96
O K	10.5	5.27	13.48	6.39	7.95	9.3	5.48
F K	0.56	0.92	0.97	1	1.03	0.82	0.78
Br L	0.24	0.32	0.32	0.33	0.36	0.35	0.37
Si K	7.94	9.64	6.03	9.46	6.98	7.87	10.47
S K	1.21	1.55	1.24	1.62	1.61	1.36	1.62
Cl K	1.57	1.74	1.83	1.67	2.13	1.7	1.73
Ag L	0.18	0.3	0.26	0.32	0.39	0.24	0.31
Cr K	1.47	1.39	1.8	1.4	1.55	1.65	1.28

Table S6. EDS element analysis of pristine PSpF film in different spots (Spot 3 is dust).

Element	Spot 1 Atomic %	Spot 2 Atomic %	Spot 3 Atomic %	Spot 4 Atomic %	Spot 5 Atomic %
C K	90.19	89.23	90.51	37.65	86.53
O K	3.03	2.6	2.8	0	5.56
Br L	1.24	1.02	1.16	0.04	0.93
Si K	0.2	2.08	0.38	56.77	2.04
S K	0.21	0.24	0.28	0.05	0.19
Cl K	1.18	1.12	1.2	0.39	1
Ag L	1.68	1.36	1.37	0.52	1.24
Cr K	2.26	2.34	2.31	4.57	2.5



Equation	y = a + b*x		
Weight	No Weighti		
Residual Sum of Squares	0.02643		
Pearson's r	-0.98631		
Adj. R-Square	0.96601		
		Value	Standard Err
ΔD of (200) diffraction	Intercept	2.1092	0.05192
	Slope	-0.0110	9.2137E-4

Figure S10. Linewidth of the (200) peak of pristine and doped thin films.

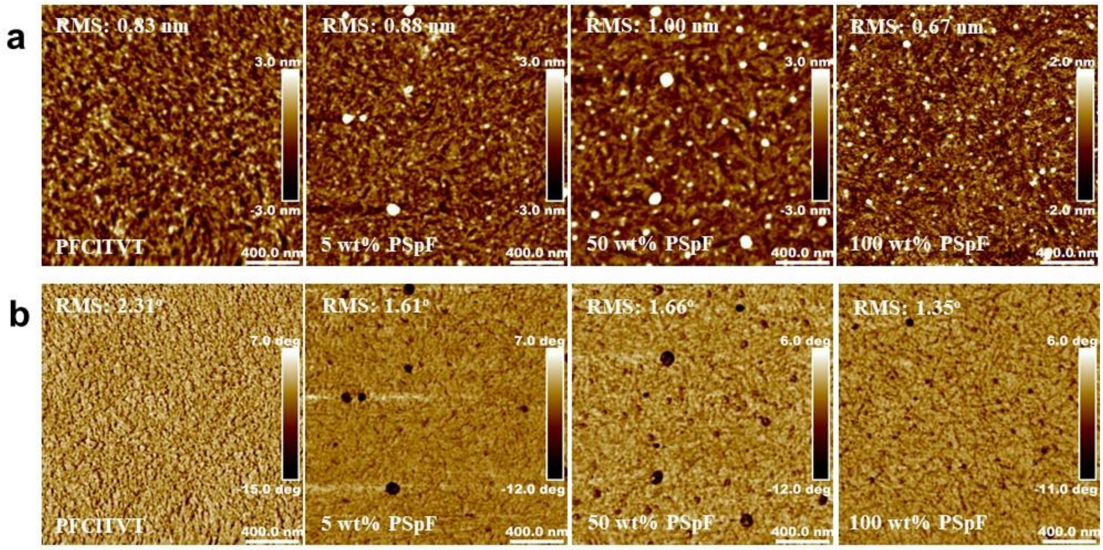


Figure S11. AFM (a) height images and (b) phase images of pristine and PSpF doped polymer thin films.

References

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[2] X. Zhao, D. Madan, Y. Cheng, J. Zhou, H. Li, S. M. Thon, A. E. Bragg, M. E. DeCoster, P. E. Hopkins, H. E. Katz, *Adv. Mater.* **2017**, *29*, 1606921.

[3] B. Russ, A. Glaudell, J. J. Urban, M. L. Chabinyc, R. A. Segalman, *Nat. Rev. Mater.* **2016**, *1*, 16050.