

## Supplementary Materials for

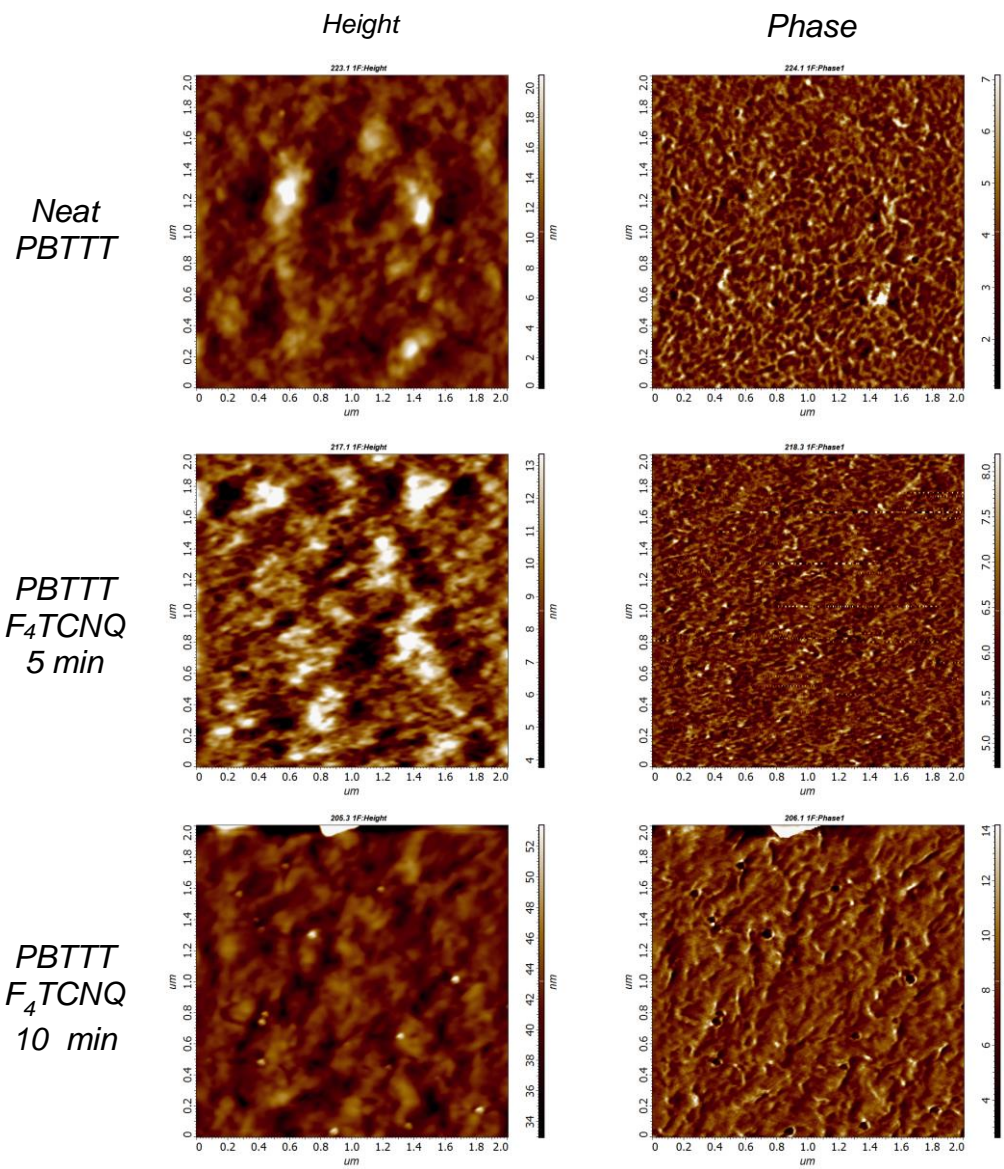
### **Morphology controls the thermoelectric power factor of a doped semiconducting polymer**

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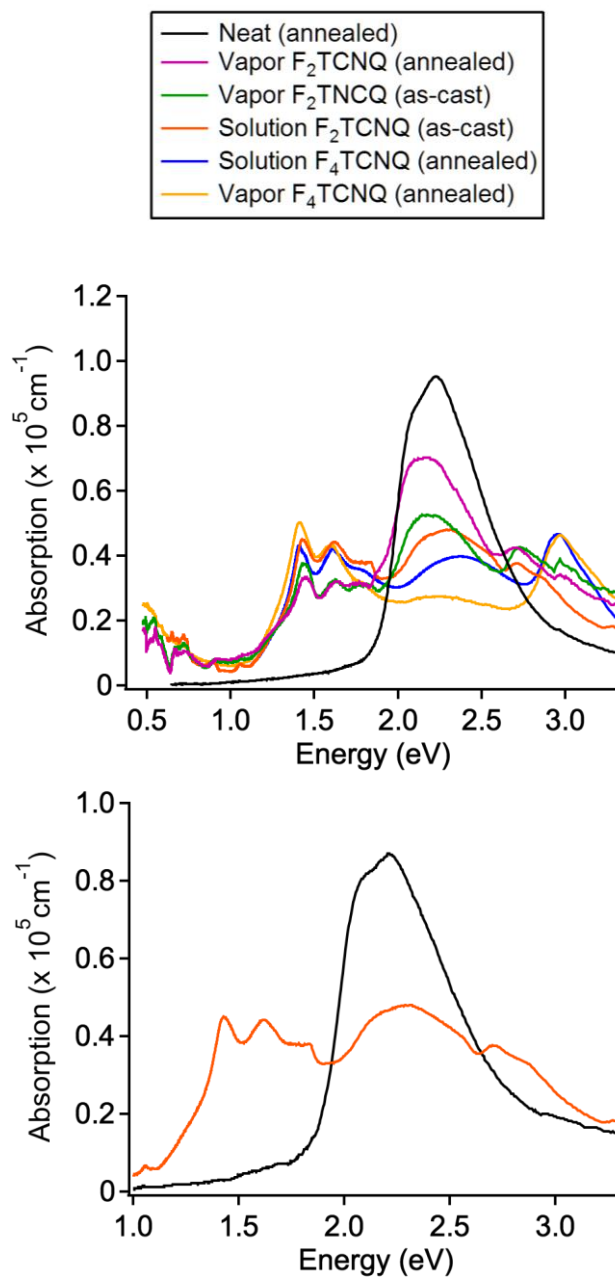
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#### **This PDF file includes:**

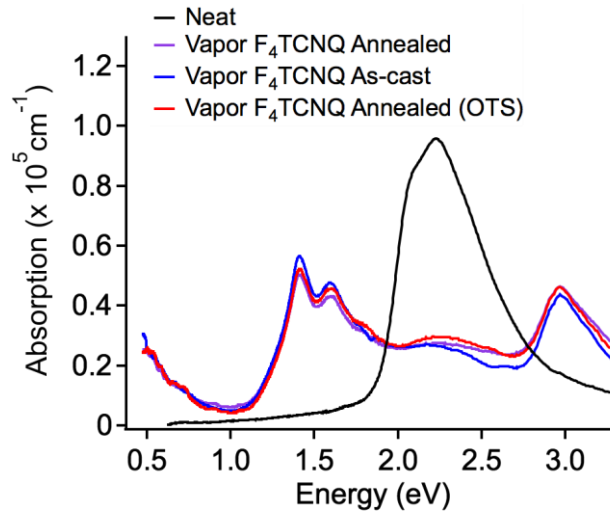
- fig. S1. AFM height and phase images of neat annealed PBTTT and F<sub>4</sub>TCNQ vapor-doped films at 5 and 10 min.
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- table S1. X-ray reflection peaks of annealed PBTTT thin films from GIWAXS.
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- table S3. Summary of OCLs for doped films.



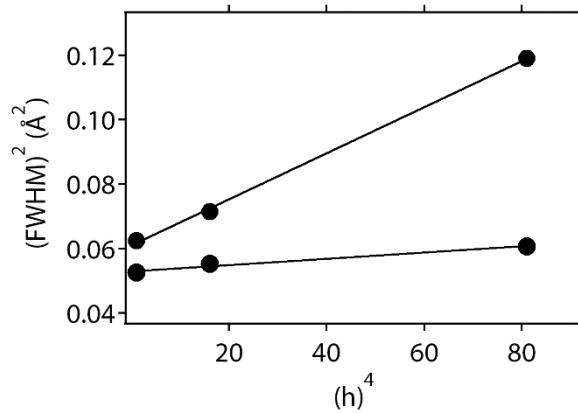
**fig. S1. AFM height and phase images of neat annealed PBTTT and F<sub>4</sub>TCNQ vapor-doped films at 5 and 10 min.**



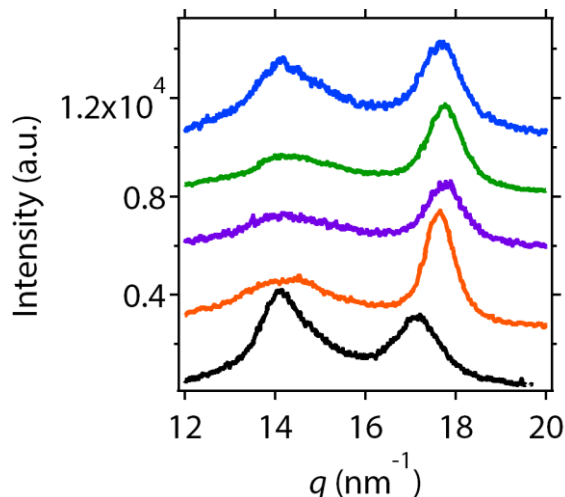
**fig. S2. Absorption spectra showing the NIR regime for doped PBTBT films and the thermal stability of F<sub>2</sub>TCNQ-doped films.** The curves near in the NIR regime are similar for all the doped films. Bottom graph: as-cast solution-doped PBTBT:F<sub>2</sub>TCNQ film (orange) and after thermally annealing at 150°C in N<sub>2</sub> environment for 10 min (black), which returns to the neutral PBTBT film absorption spectrum. The absorption is normalized by thickness.



**fig. S3. Additional UV-vis-NIR spectra of F<sub>4</sub>TCNQ vapor-doped films relative to a neat film.** As-cast and annealing yield nearly identical spectra. Vapor-doped PBTBT:F<sub>4</sub>TCNQ annealed film on an octyldecyltrichlorosilane (OTS) functionalized quartz substrate is consistent with films on bare quartz substrates. The absorption is normalized by thickness.



**fig. S4. Williamson-Hall plot for neat (black circle) and F<sub>4</sub>TCNQ vapor-doped film.** Full-width-half-max (FWHM) were determined using Lorentzian peak fits on (*h*00) scattering peaks obtained from high resolution specular scattering (Beamline 2-1, SSRL). The increase in slope in the above figure corresponds to increase in disorder along the alkyl stacking direction (*h*00).



**fig. S5. In-plane scattering profiles of as-cast neat and doped films.** Black = neat, orange = F<sub>4</sub>TCNQ solution doping, purple = F<sub>4</sub>TCNQ vapor doping, green = F<sub>2</sub>TCNQ solution doping, and blue = F<sub>2</sub>TCNQ vapor doping.

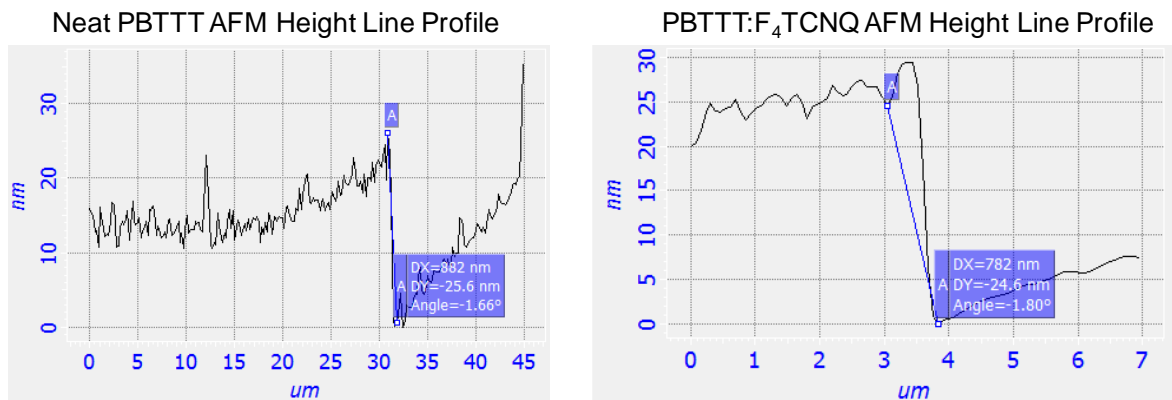


fig. S6. Thin-film thickness profile of neat and vapor-doped PBTTT:F<sub>4</sub>TCNQ film.

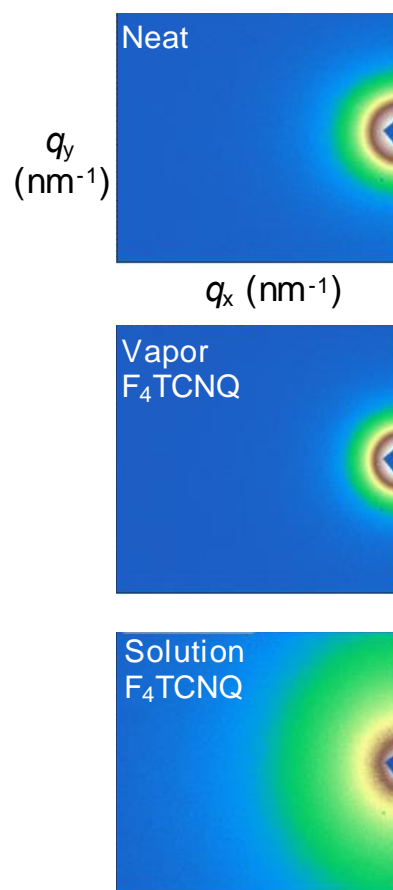
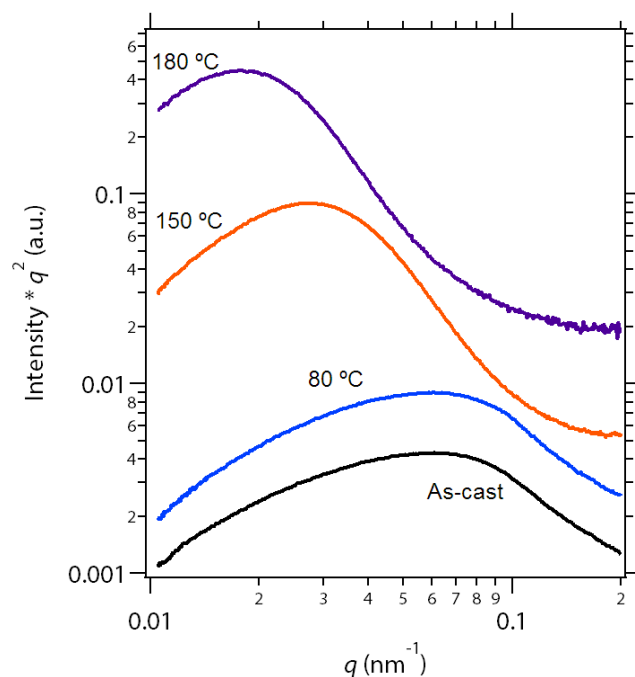
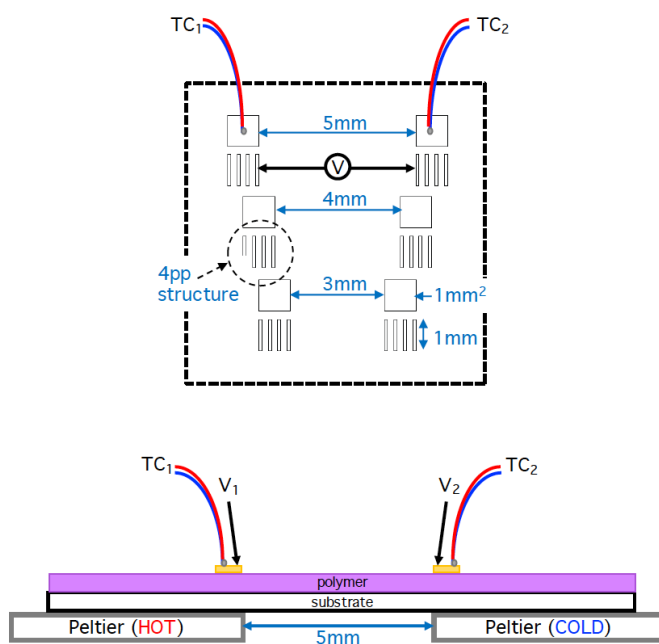


fig. S7. Representative 2D RSoXS images for neat PBTTT, F<sub>4</sub>TCNQ vapor-doped, and F<sub>4</sub>TCNQ solution-doped thin films (all thermally annealed).



**fig. S8. Lorentz-corrected scattering profiles of neat PBTTT for different annealing temperatures.** As-cast neat PBTTT thin film and annealed at elevated temperatures for 10 minutes. 150 °C and 180 °C are above the liquid crystalline transition temperature. The corresponding orientational correlation length (OCLs) are summarized in table S3.



**fig. S9. Schematic of the geometry of the contacts for electronic conductivity and Seebeck measurements on thin films of doped polymers.**

**table S1. X-ray reflection peaks of annealed PBTTT thin films from GIWAXS.**

PBTTT film Condition	Index	Peak Position ( $q$ ) ( $\text{nm}^{-1}$ )	domain spacing ( $d$ ) (nm)	FWHM ( $\text{nm}^{-1}$ )
Neat	(100)	2.95	2.12	
	(200)	5.89	1.07	0.312
	(300)	8.90	0.706	0.467
	(110)	17.1	0.367	0.8363
Solution F <sub>4</sub> TCNQ (10 wt%)	(100)	2.67	2.35	
	(200)	5.33	1.18	0.455
	(300)	8.09	0.777	0.626
	(110)	17.7	0.355	0.627
Vapor F <sub>4</sub> TCNQ	(100)	2.66	2.36	
	(200)	5.32	1.18	0.415
	(300)	8.08	0.777	0.678
	(110)	17.8	0.353	0.696
Vapor F <sub>2</sub> TCNQ	(100)	2.88	2.18	
	(200)	5.75	1.09	0.471
	(300)	8.58	0.732	0.817
	(110)	17.4	0.361	0.845

**table S2. X-ray reflection peaks of as-cast PBTTT thin films from GIWAXS.**

PBTTT film Condition	Index	Peak Position ( $q$ ) ( $\text{nm}^{-1}$ )	domain spacing ( $d$ ) (nm)	FWHM ( $\text{nm}^{-1}$ )
Neat	(100)	2.95	2.20	
	(200)	5.69	1.10	0.698
	(300)	8.59	0.731	1.34
	(110)	17.16	0.366	1.37
Solution F <sub>4</sub> TCNQ (10 wt%)	(100)	2.53	2.48	
	(200)	5.06	1.24	0.825
	(300)	7.78	0.808	1.32
	(110)	17.6	0.357	0.779
Vapor F <sub>4</sub> TCNQ	(100)	2.57	2.44	
	(200)	5.14	1.22	0.612
	(300)	7.89	0.96	1.17
	(110)	17.7	0.355	1.02
Solution F <sub>2</sub> TCNQ (10 wt%)	(100)	2.56	2.45	
	(200)	5.12	1.23	0.854
	(300)	7.82	0.803	1.47
	(110)	17.8	0.353	0.928
Vapor F <sub>2</sub> TCNQ	(100)	2.74	2.30	
	(200)	5.47	1.15	0.602
	(300)	8.30	0.757	0.855
	(110)	17.6	0.357	1.21



**table S3. Summary of OCLs for doped films.**

PBTTT film Condition	As-cast or Annealing Temperature	OCL (nm)
Neat	As-cast	70
	80 °C	70
	150°C	140
	180°C	180
Solution F <sub>4</sub> TCNQ (10 wt%)	As-cast	40
	150 °C	44
Vapor F <sub>4</sub> TCNQ (10 min)	As-cast	130
	180 °C	220
Solution F <sub>2</sub> TCNQ (10 wt%)	As-cast	130
	150 °C	100
Vapor F <sub>2</sub> TCNQ (10 min)	As-cast	60
	180 °C	210

Note: Thermal annealing step is done after casting a film from doped solution, while for vapor-doped samples are prepared by first thermal annealing a neat film.