Supporting Information

Backbone Effects on the Thermoelectric Properties of Ultra-small Bandgap Conjugated Polymers

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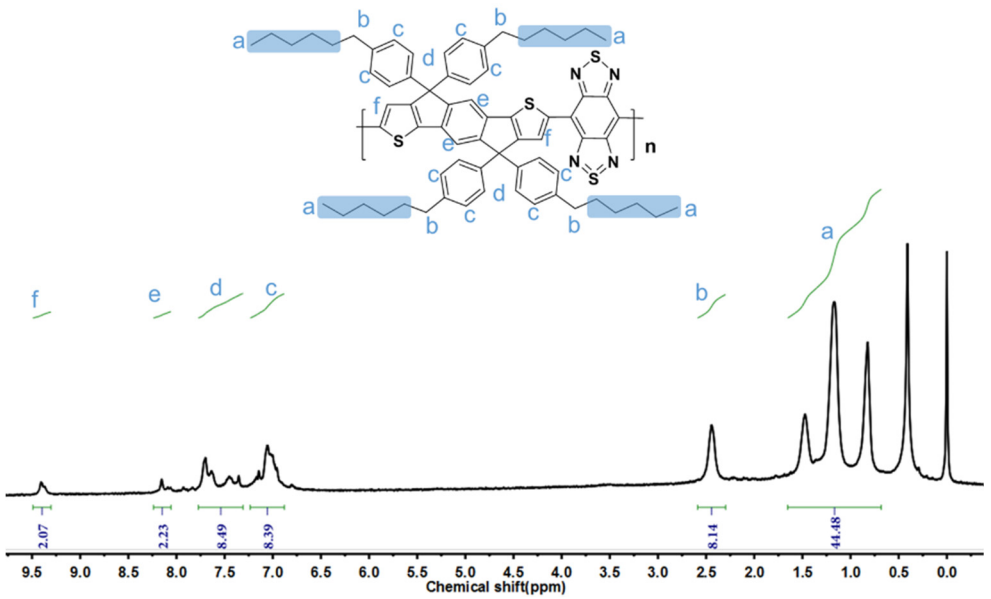
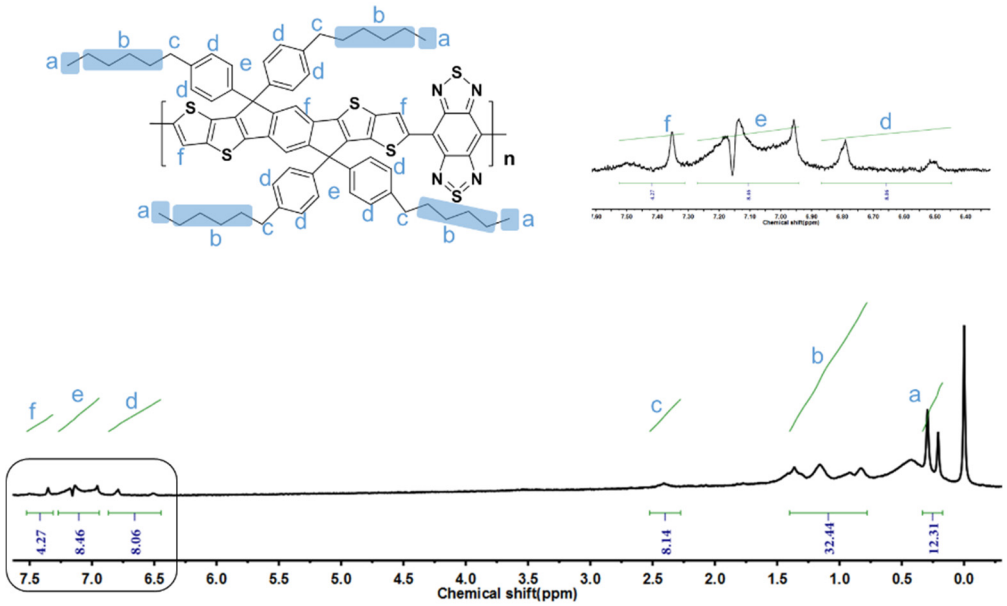


(a)



(b)

Figure S1. ^{1}H NMR spectra of (a) PIDT-BBT and (b) PIDTT-BBT.

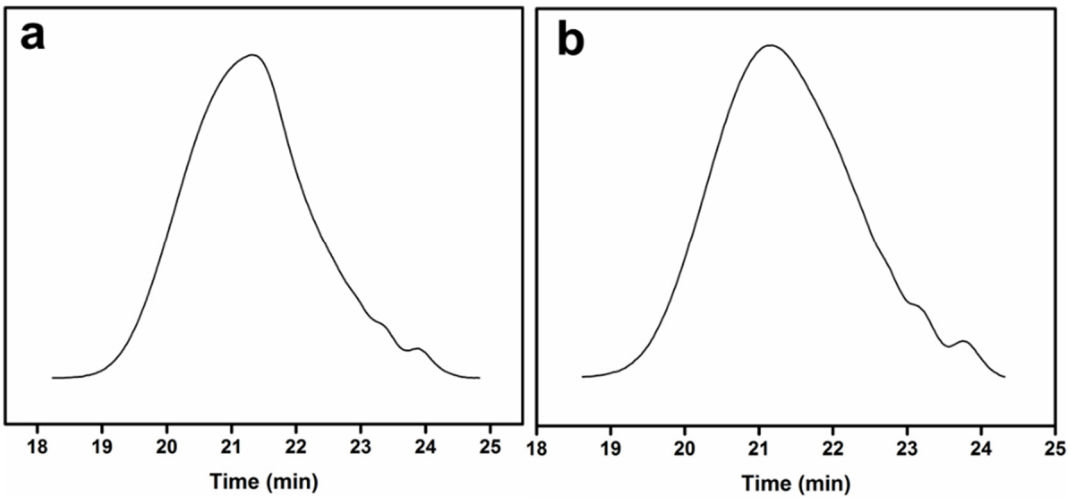


Figure S2. GPC curve of (a) PIDT-BBT and (b) PIDTT-BBT.

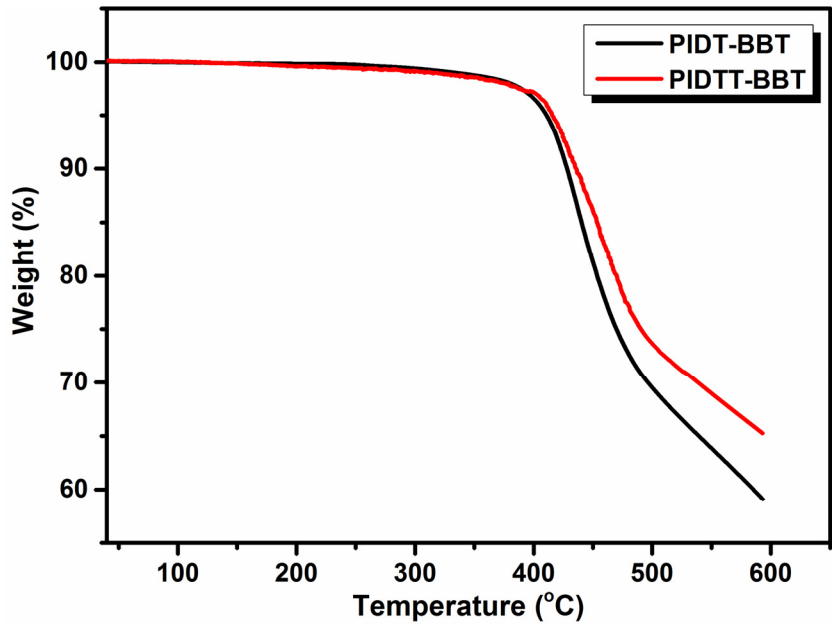


Figure S3. TGA curve of PIDT-BBT and PIDTT-BBT.

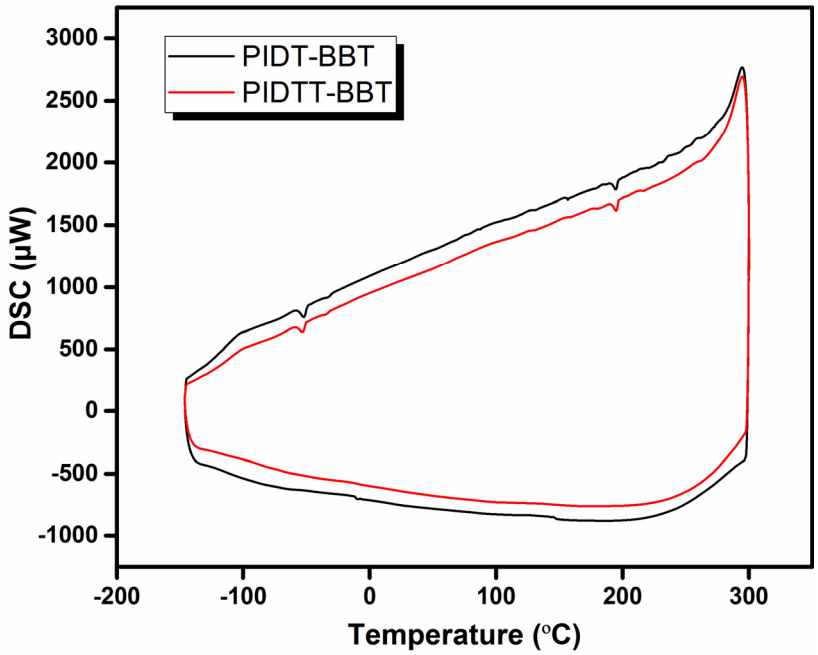


Figure S4. DSC spectra of PIDT-BBT and PIDTT-BBT.

Table S1. Molecular weights and thermal properties of PIDT-BBT and PIDTT-BBT.

Polymer	M_n (KDa)	M_w (KDa)	PDI	n	T_g (°C)	T_d (°C)
PIDT-BBT	16.85	44.32	2.63	15	146	410
PIDTT-BBT	16.76	39.91	2.38	14	138	415

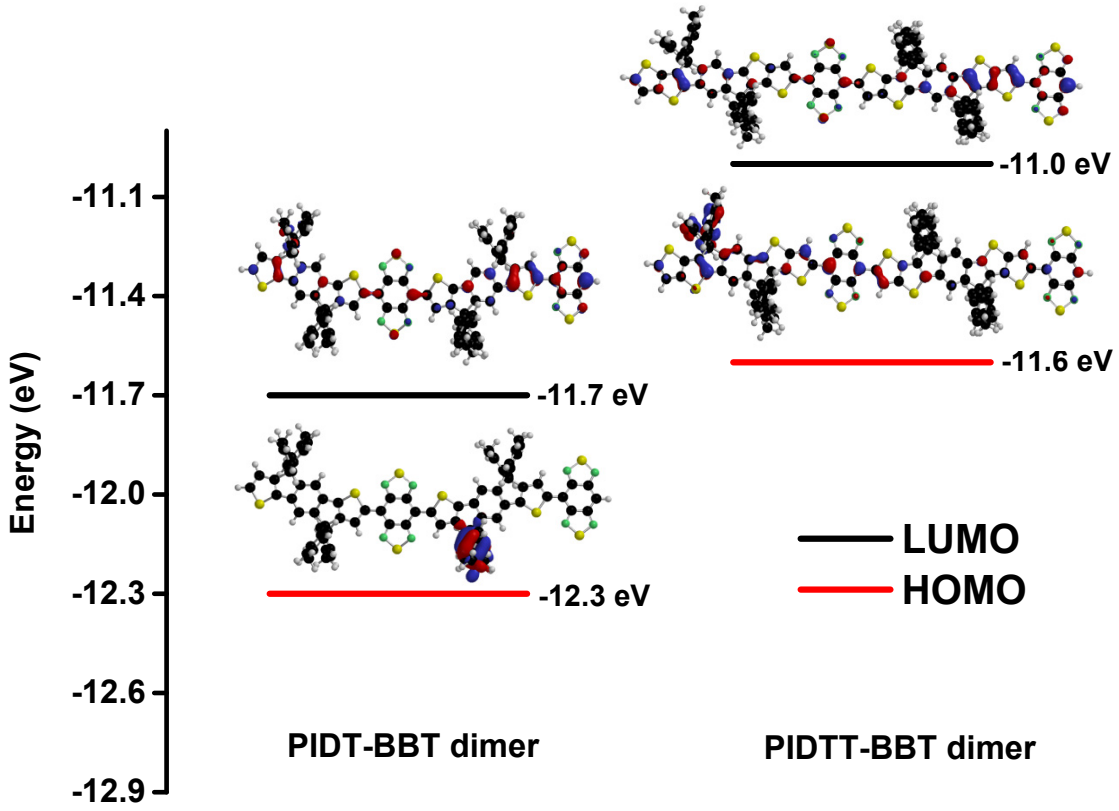


Figure S5. Calculated HOMO/LUMO molecular orbitals (B3LYP/6-31G* levels) for the dimers of PIDT-BBT and PIDTT-BBT.

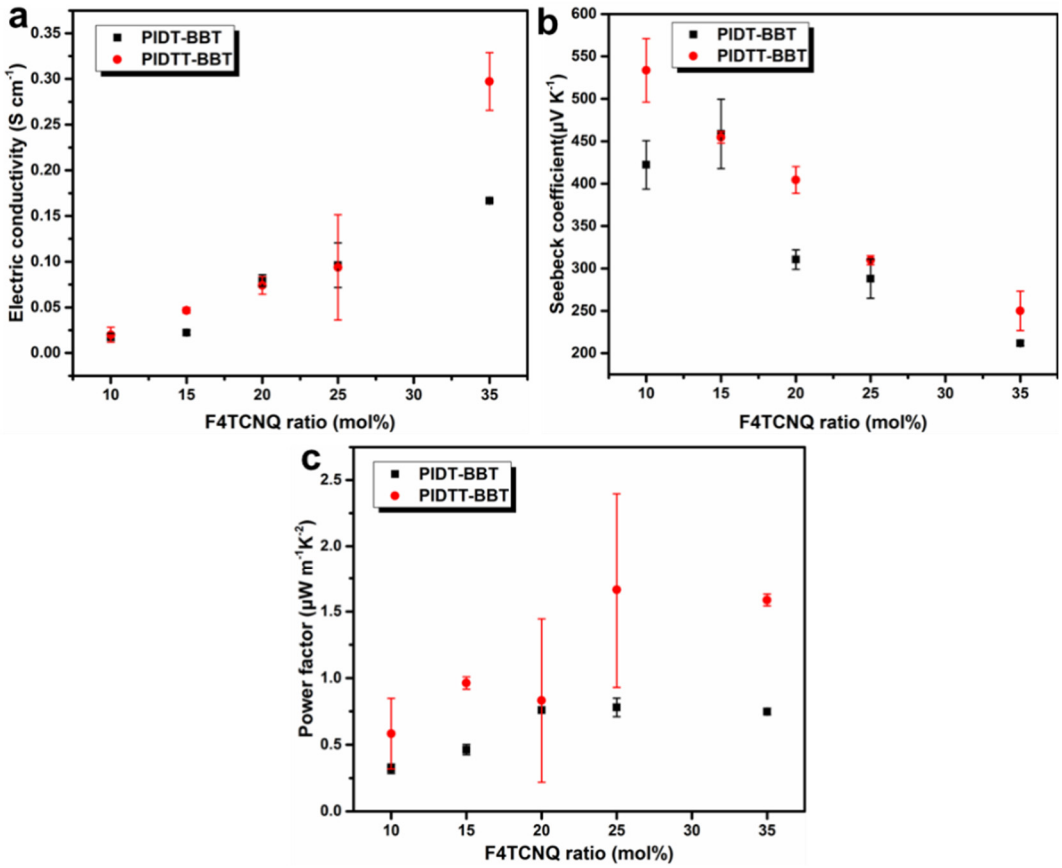


Figure S6. Thermoelectric performance of the polymers doped with different F4TCNQ molar ratios: (a) electrical conductivity σ, (b) Seebeck coefficient *S*, and (c) power factor *PF*.

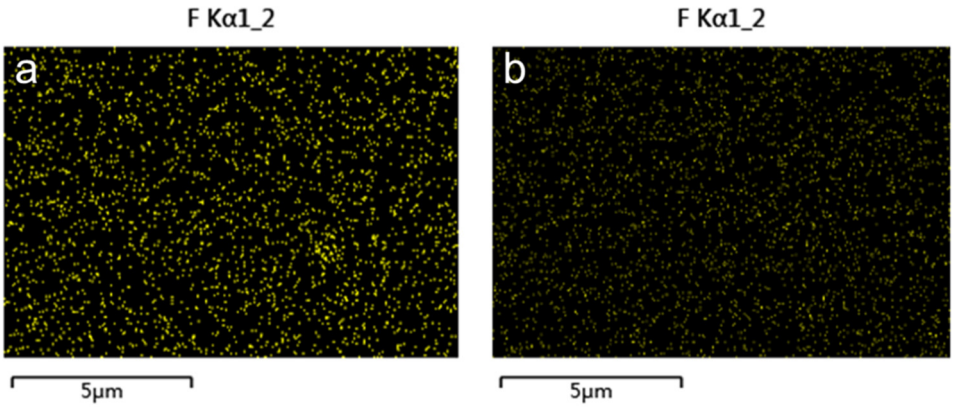


Figure S7. EDS of (a) PIDT-BBT and (b) PIDTT-BBT films doped with F4TCNQ (25 mol%).

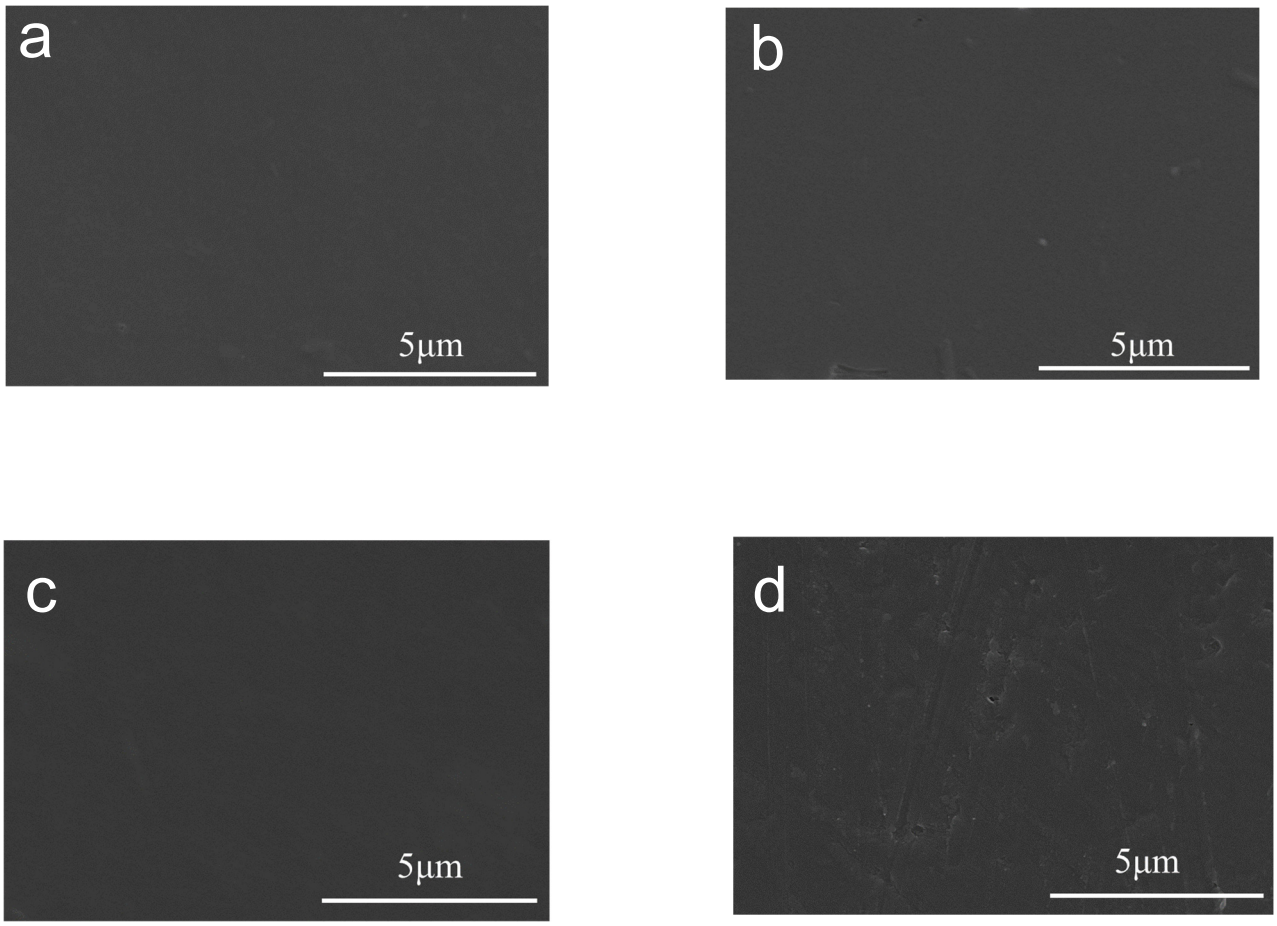


Figure S8. SEM images of PIDT-BBT (a) pristine films and (b) films doped with F4TCNQ, PIDTT-BBT (c) pristine films and (d) films doped with F4TCNQ.

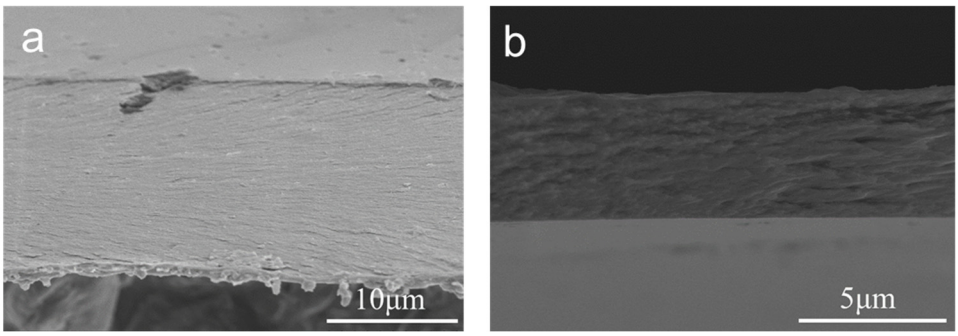


Figure S9. Cross-sectional SEM images of pristine (a) PIDT-BBT and (b) PIDTT-BBT films.

Details of the FET Fabrications and Testing: Solution-processed films of polymer are fabricated by dip coating method. SAM-modified substrate is immersed in the polymer solution (5 mg/mL) in a mixed solvent of dichloromethane and acetone (1:1 by volume), and subsequently pulling up at a constant speed of 10 μm/s as controlled by a LongerPump TJ-3A syringe pump controller. Vacuum-deposited films of the polymer solution are deposited on SAM-modified AlO_x using an vacuum coating system with a Turbomolecular pump (OPV450, SKY Technology Development Co., Ltd., CAS) at a pressure of 2.0×10^{-6} torr or lower, with a deposition rate of ca. 1 Å/s to a thickness of 40 nm as measured by a quartz crystal sensor. OTFTs of BTBT-C12 are completed by depositing a layer of gold through a shadow mask onto the dip-coated or vacuum-deposited films to form top-contact source and drain electrodes. The field effect mobilities of these OTFTs in the saturation regime are measured under ambient conditions and extracted from transfer *I-V* curves using the equation $I_{DS} = (\mu W C_i/2L)(V_{GS}–V_T)^2$, where I_{DS} is the drain current; μ is field effect mobility; C_i is the capacitance per unit area for the SAM-modified AlO_x dielectrics; W is the channel width; L is the channel length; V_{GS} and V_T are the gate and threshold voltages, respectively. The current-voltage measurement of thin-film transistors is conducted using a probe station (PS-100, Lakeshore) and a Keithley 4200A Semiconductor Characterization System in air under ambient conditions.