Electronic Supplementary Information

Thermoelectrics of two-dimensional conjugated benzodithiophene-based polymers: density-of-states enhancement and semi-metallic behavior

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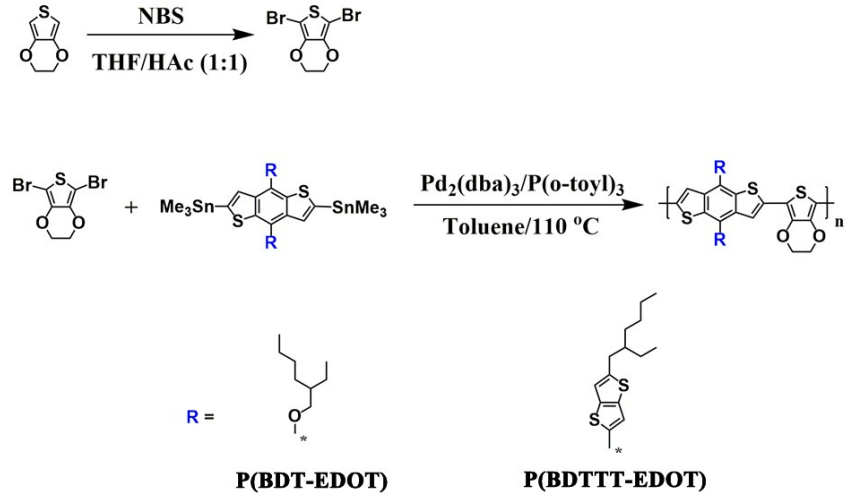

Fig. S1 Synthetic route of P(BDT-EDOT) and P(BDTTT-EDOT).

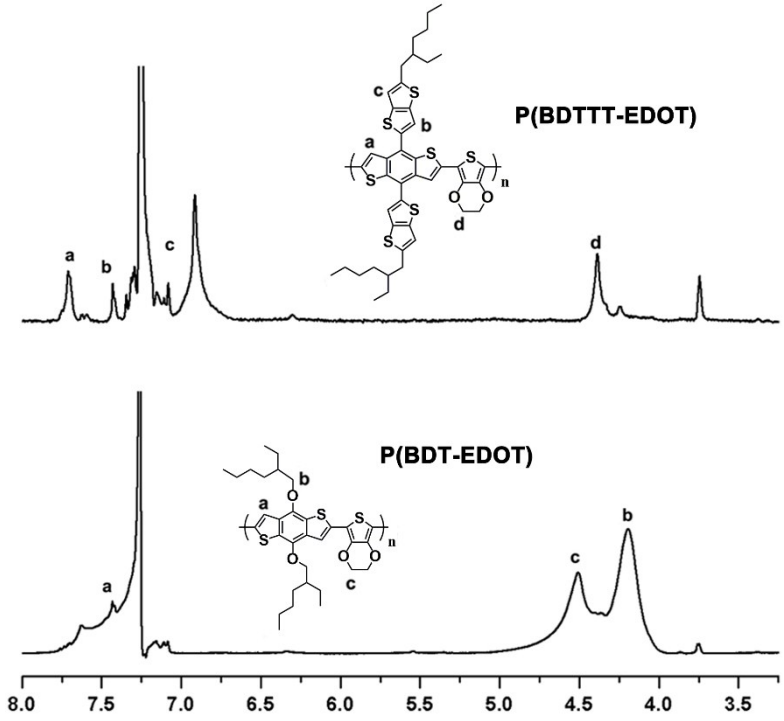

Fig. S2 ^{1}H NMR spectra of P(BDT-EDOT) and P(BDTTT-EDOT).

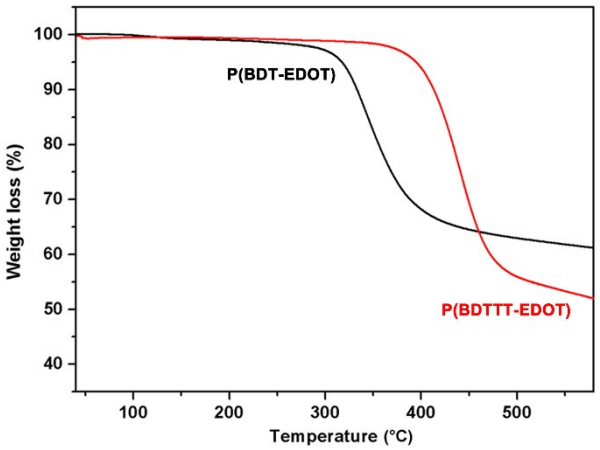

Fig. S3 TGA curves of P(BDT-EDOT) and P(BDTTT-EDOT).

Table S1 Molecular weights, and thermal properties of the polymers.

Polymer	M_n (kg mol^{-1})	M_w (kg mol^{-1})	PDI	T_d (℃)
P(BDT-EDOT)	9	18	2.00	317
P(BDTTT-EDOT)	12	26	2.17	395

HOMO and LUMO energy levels

From the electrochemical cyclic voltammetry (Fig. 1b), the onset oxidation and reduction potentials (E_{ox} and E_{red}) of P(BDT-EDOT) and P(BDTTT-EDOT) were estimated to be 0.27/-2.13 V and 0.46/-1.89 V, respectively. The HOMO energy level can be calculated from E_{ox} by E_{HOMO} = -(E_{ox} + 4.4) eV, while the LUMO energy level can be calculated from E_{red} by E_{LUMO} = -(E_{red} + 4.4) eV.[1] Thus, the E_{HOMO} and E_{LUMO} levels of P(BDT-EDOT) and P(BDTTT-EDOT) were calculated to be -4.67/-2.27 eV and -4.86/-2.51 eV, respectively. Moreover, the electrochemical band gap (E_g^{ec}) was deduced from the difference between E_{ox} and E_{red} of the polymer.[2]

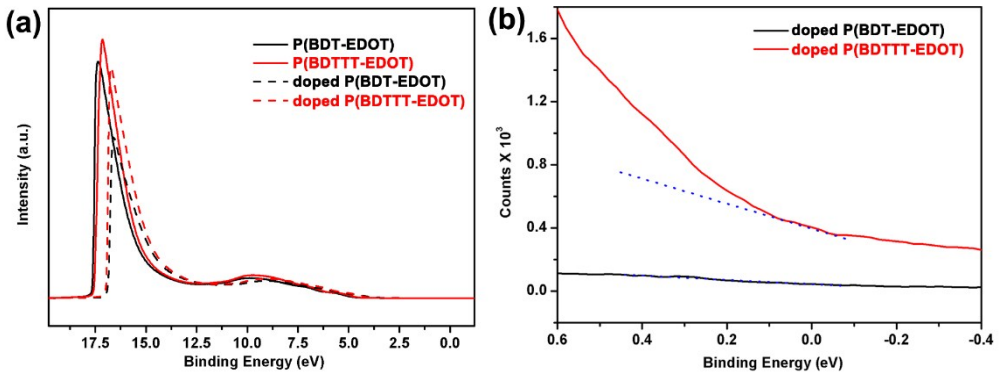

Fig. S4 (a) UPS valence band spectra (He I radiation) of P(BDT-EDOT) and P(BDTTT-EDOT) in pristine condition and doped condition. (b) Magnified view of the low-binding-energy region shows the DOVS of doped P(BDT-EDOT) and P(BDTTT-EDOT).

Mott parameters calculations

The temperature-dependent electrical conductivity described by the Mott's VRH mechanism is

$$\sigma = \sigma_0' \, exp\left[- \left(T_0/T\right)^m \right] \qquad (1)$$

where σ_0' is a constant, T_0 is the characteristic temperature that generally depends on the carrier hopping barriers, and $m = 1/(1+d)$, where d is the dimensionality.[3] In Equation (1), m is 1/2 for one-dimensional transport and 1/4 for three-dimensional transport.

The values of T_0 have been estimated from the slopes of ln(σ) versus $T^{-1/2}$ according to Equation (1).[4] T_0 can also be correlated to other Mott parameters by the following expressions

$$T_0 = \frac{B_0 \alpha^3}{k_B N(E_f)} \quad (2)$$

$$R = \left\{ \frac{9}{8\pi\alpha k_B T N(E_f)} \right\}^{1/4} \quad (3)$$

$$W = \frac{3}{4\pi R^3 N(E_f)} \quad (4)$$

where B_0 is the dimensionless constant and is assumed to be ~1.66, k_B is Boltzmann's constant, $N(E_f)$ is the density of states at the Fermi level, α is the coefficient of exponential decay of the localized states involved in the hopping process, R is the average hopping distance and W is the average hopping energy.[5-7] In these calculations, $\alpha^{-1}(r_p)$ represents the electron wavefunction localization length, which is equal to the width of the monomer unit, i.e. P(BDT-EDOT) ~10.95 Å, P(BDTTT-EDOT) ~10.96 Å, as the electrons are always at least delocalized to the extent of the π-orbitals on the monomer units.[8]

Table S2 Seebeck coefficients of doped polymer films measured at 300 K and 350 K.

Polymer	300 K			350 K		
	S_1[a)]	S_2[a)]	S_3[a)]	S_1[a)]	S_2[a)]	S_3[a)]
P(BDT-EDOT)	70.43	78.72	53.65	117.10	83.69	60.91
P(BDTTT-EDOT)	129.44	104.09	113.21	840.69	980.97	825.54

a) μV K^{-1}

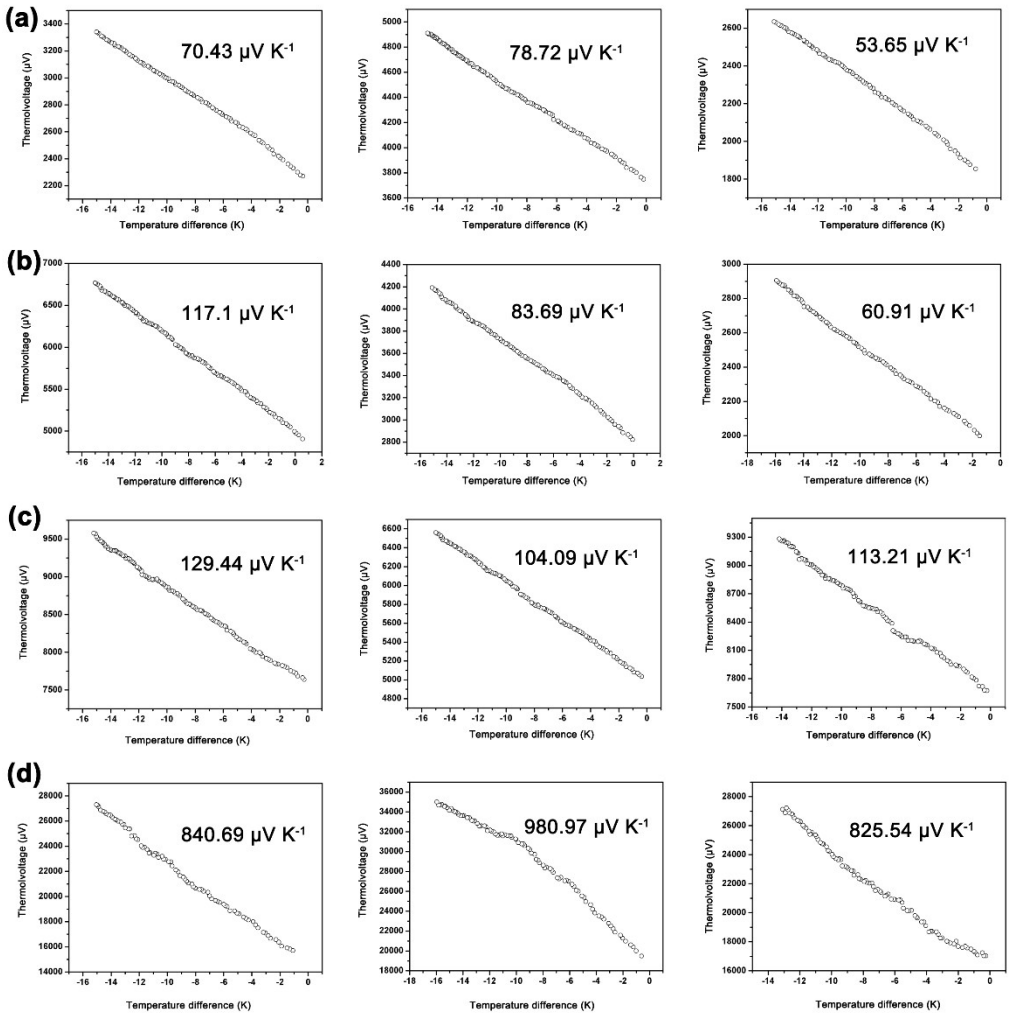

Fig. S5 Thermal voltage as a function of temperature gradient for the doped P(BDT-EDOT) films at 300 K (a) and 350 K (b); doped P(BDTTT-EDOT) films at 300 K (c) and 350 K (d).

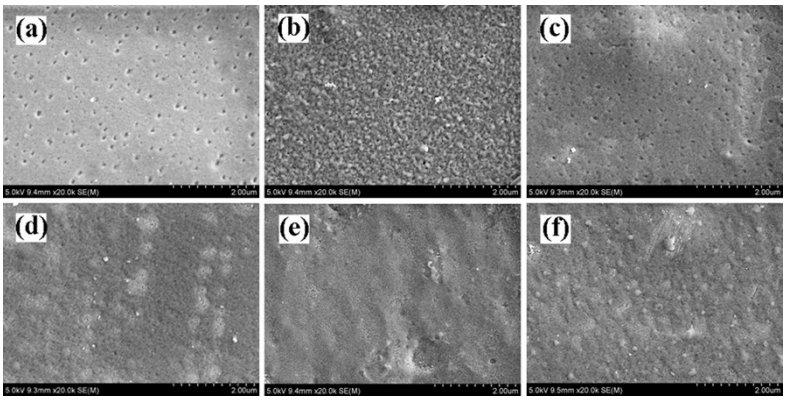

Fig. S6 SEM images of the polymer films. P(BDT-EDOT) film before (a) and after (b) doping, (c) doped P(BDT-EDOT) film was heated at 350 K; P(BDTTT-EDOT) film before (d) and after (e) doping, (f) doped P(BDTTT-EDOT) film was heated at 350 K.

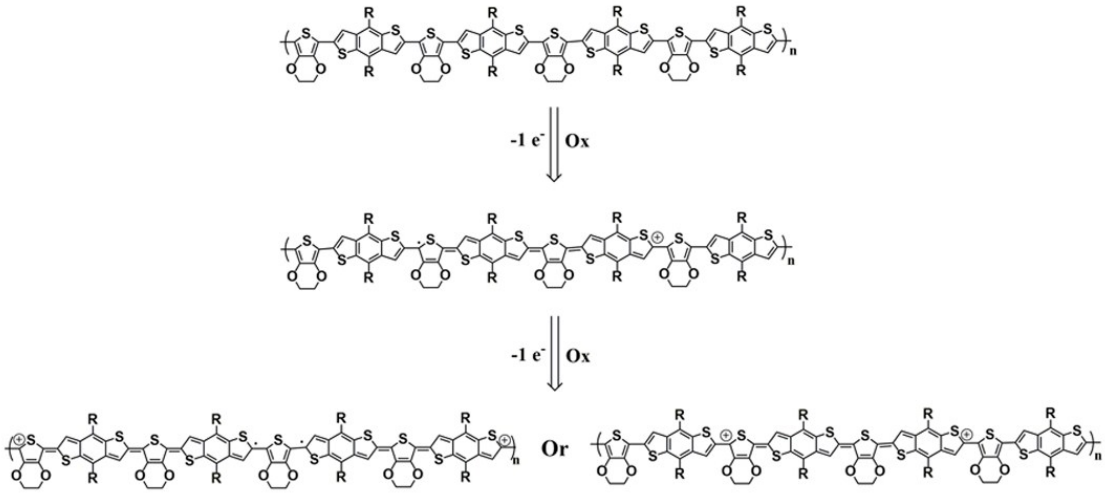

Fig. S7 Schematic of the oxidative doping process for the BDT-based conjugated polymer.

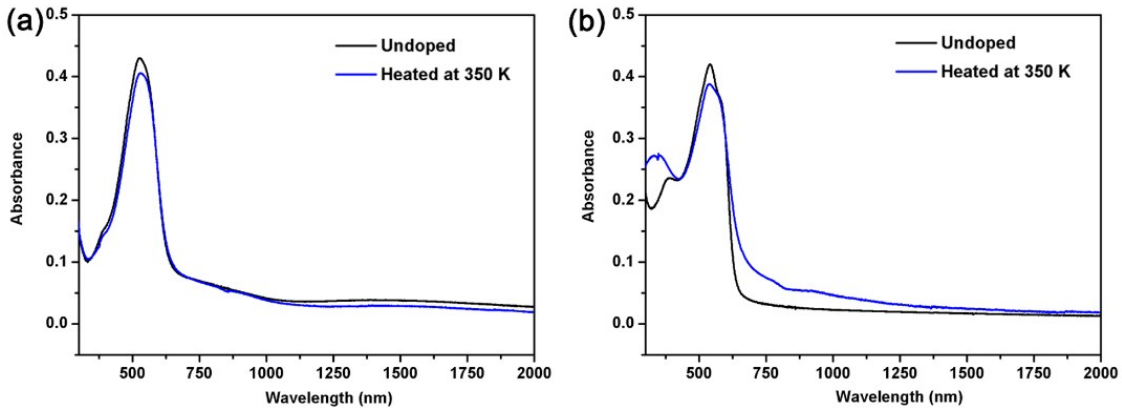

Fig. S8 UV-vis/NIR absorption spectra of pristine P(BDT-EDOT) (a) and P(BDTTT-EDOT) (b) films before and after heat treatment.

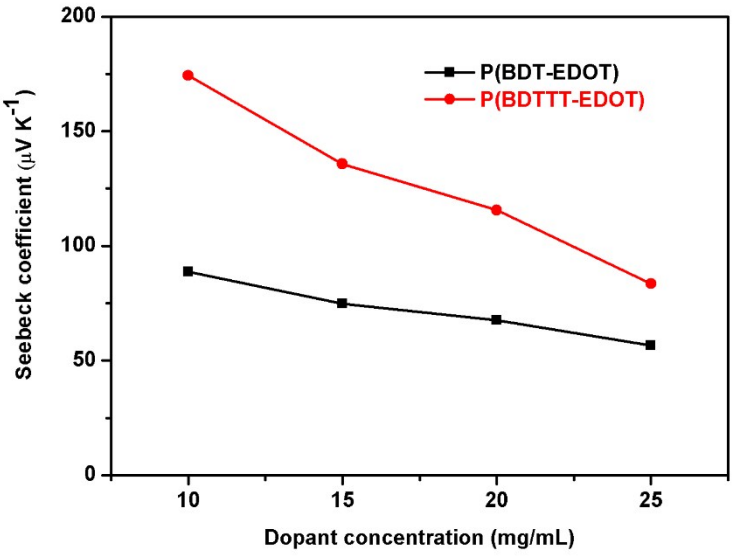

Fig. S9 Seebeck coefficient of P(BDT-EDOT) and P(BDTTT-EDOT) films as a function of the dopant concentration.

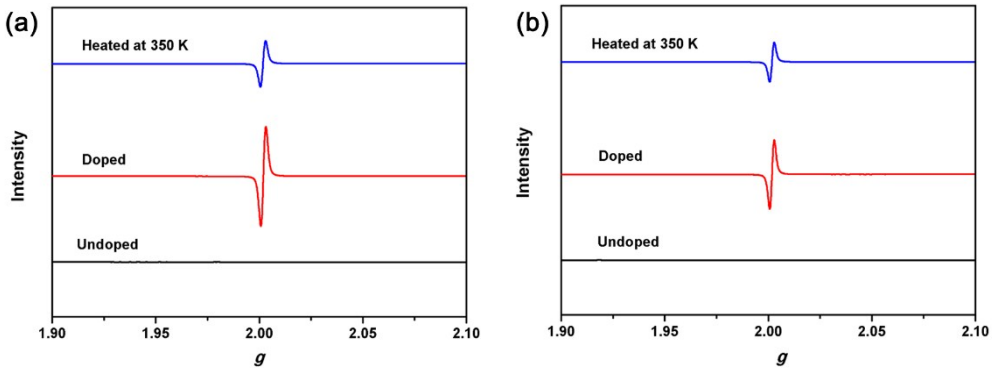

Fig. S10 Electron paramagnetic resonance spectra of P(BDT-EDOT) (a) and P(BDTTT-EDOT) (b) films after doping and heat treatment.

Spin signals at g = 2.001 – 2.003 were observed for the doped polymers, indicating the formation of polarons. However, it is inappropriate to deny the existence of bipolarons or polaron pairs, which show no appreciable spin signals. These charge carriers usually coexist at a certain doping level and are often indistinguishable, which makes unveiling the conduction mechanism very difficult.

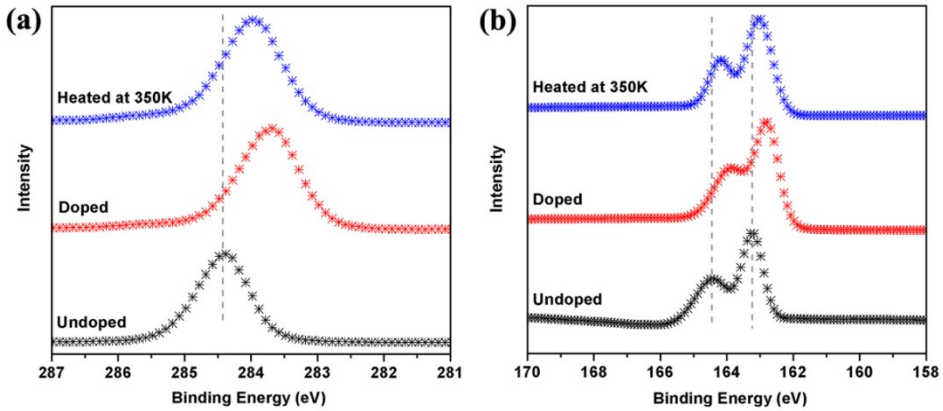

Fig. S11 XPS C 1s (a) and S 2p (b) core level spectra of P(BDT-EDOT).

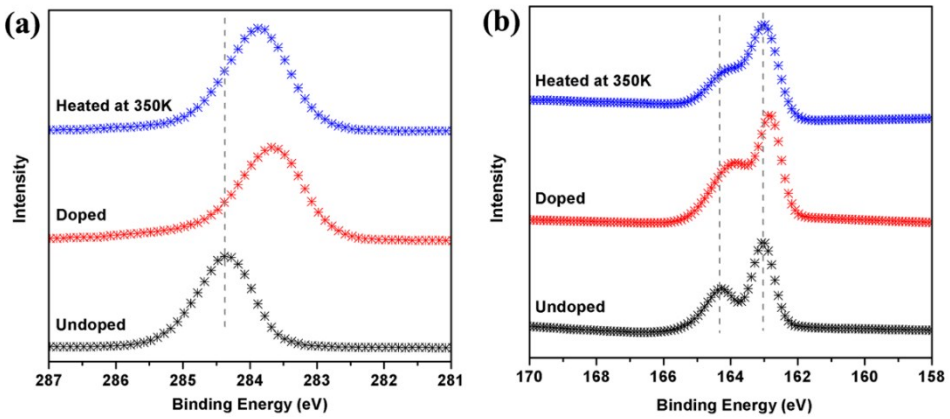

Fig. S12 XPS C 1s (a) and S 2p (b) core level spectra of P(BDTTT-EDOT).

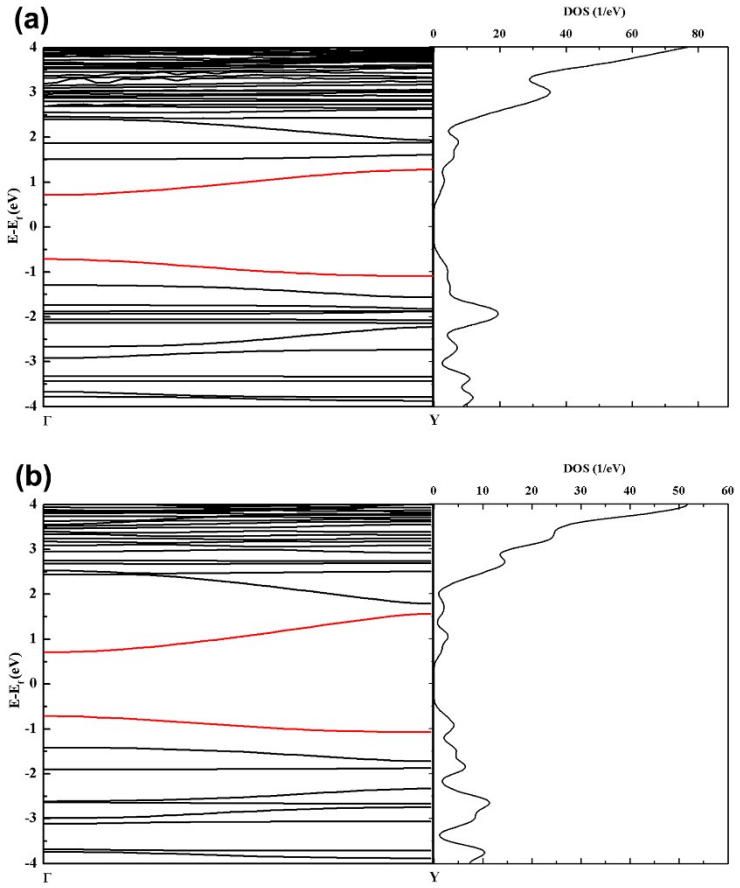

Fig. S13 Band structures and density of states of P(BDT-EDOT) (a) and P(BDTTT-EDOT) (b).

References

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