Supporting information for:

Balance of electrical conductivity and Seebeck coefficient by controlled interfacial doping towards high performance benzothienobenzothiophene-based organic thermoelectric materials

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Measurement of the thicknesses of composite films

The measurement of the thicknesses of composite films was characterized by microfigure measuring instrument (Surfcorder ET4000M, Kosaka Laboratory Ltd., Japan). Firstly, using ethanol to wipe off part of the composite films for making clear steps between the glass substrate and the rest of composite films. Then, the probe of microfigure measuring instrument scan the surface which ranges from the glass substrate to the rest of composite films. Finally, three thickness data of composite films can be obtained by the analysis software accurately. Repeat the mentioned operation above and obtain nine values totally. The final results of thickness were obtained by averaging nine thickness values. All data were collected in ambient air.

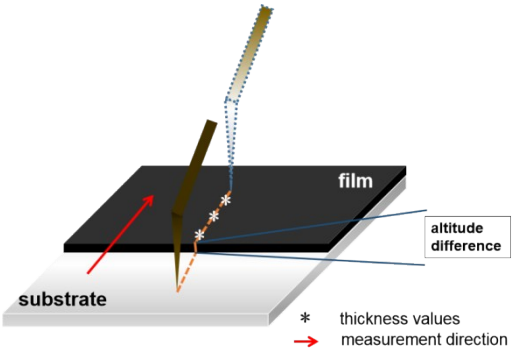

Fig. S1 The schematic diagram of measurement of the thicknesses of composite films.

Table S1 Summary of the thicknesses of different composite films.

Materials	Thickness (μm)									Average thickness (μm)	Standard deviation (μm)
the pristine SWCNT	1.524	1.307	1.477	1.369	1.236	1.295	1.206	1.198	1.274	1.321	0.115
SWCNT/C_8BTBT	1.111	1.366	1.568	1.466	1.427	1.512	1.574	1.476	1.298	1.422	0.147
SWCNT/C_8BTBT-TCNQ-40nm	1.454	1.238	1.565	1.429	1.468	1.508	1.361	1.556	1.376	1.439	0.104
SWCNT/C_8BTBT-TCNQ-10:1	1.204	1.518	1.224	1.247	1.163	1.341	1.224	1.194	1.230	1.260	0.108
SWCNT/C_8BTBT-F_4TCNQ-40nm	1.404	1.404	1.508	1.305	1.537	1.213	1.392	1.199	1.578	1.393	0.135
SWCNT/C_8BTBT-F_4TCNQ-10:1	1.310	1.224	1.153	1.397	1.264	1.175	1.120	1.150	1.026	1.202	0.110

Measurement of the morphologies of composite films

The surface morphologies of composite films were characterized by atomic force microscopy (AFM, Bruker Dimension ICON, the United States). The topographic images were obtained using a Nanoscope analysis from Digital Instruments. All AFM images were collected using tapping mode and in air under ambient conditions.

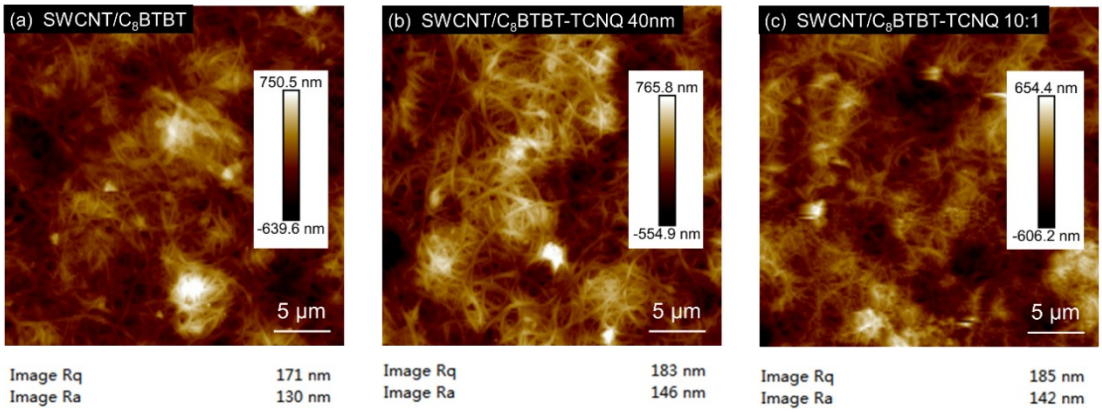

Fig. S2 The AFM height images and roughness analysis of (a) SWCNT/C_8BTBT, (b) SWCNT/C_8BTBT-TCNQ-40nm, (c) SWCNT/C_8BTBT-TCNQ-10:1 composite films.

The morphologies of composite films were characterized by Transmission electron microscope (TEM, JEM-2100 & Aztec Energy TEM SP X-MaxN 80T, Japan and the United Kingdom). Firstly, scrape the composite films from glass substrate (1cm × 1cm) and put it into a vial with 10 mL ethanol solution. Then the dispersion was sonicated for 15 h assuring efficient dispersion. Next, draw a small amount of dispersion by using a dropper to drop-cast on the copper grid until the solution evaporated completely. Finally, the TEM images of single bundle or single nanotube were obtained.

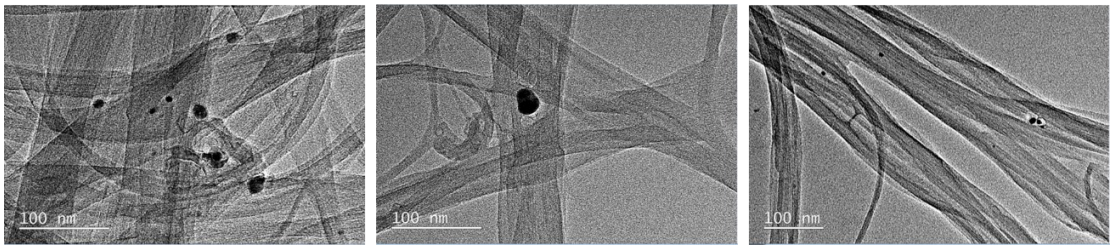

Fig. S3 The TEM images of SWCNT/C_8BTBT composite films.

The morphologies of composite films were characterized by scan electron microscopy (SEM, HitachiS-4700, Japan) and the elemental analysis for typical composite film were measured via line-based scanning mode of energy disperse spectroscopy (EDS, Oxford X-Max^N, the United Kingdom).

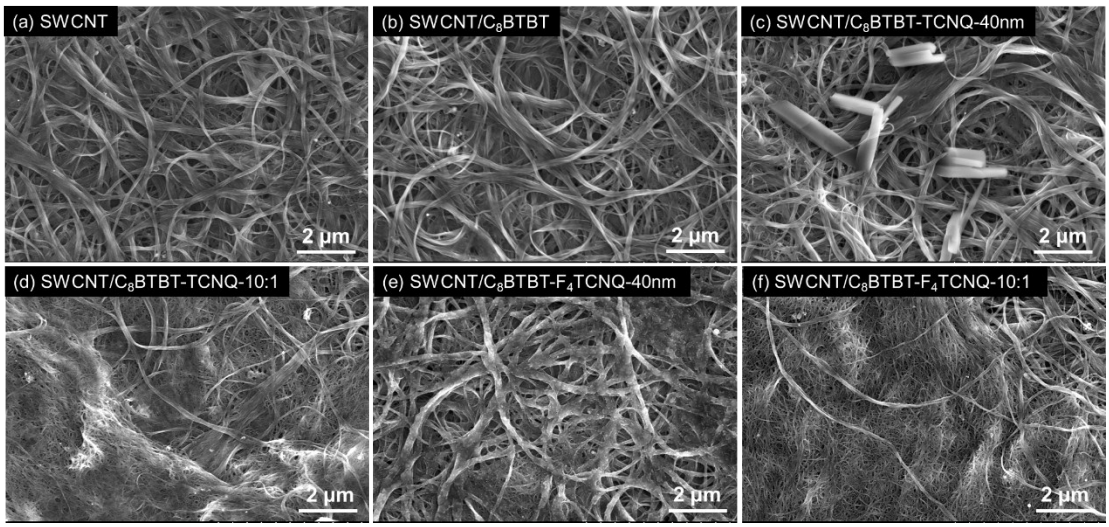

Fig. S4 The SEM images of (a) SWCNT, (b) SWCNT/C_8BTBT, (c) SWCNT/C_8BTBT-TCNQ-40nm, (d) SWCNT/C_8BTBT-TCNQ-10:1, (e) SWCNT/C_8BTBT-F_4TCNQ-40nm, (f) SWCNT/C_8BTBT-F_4TCNQ-10:1 composite films.

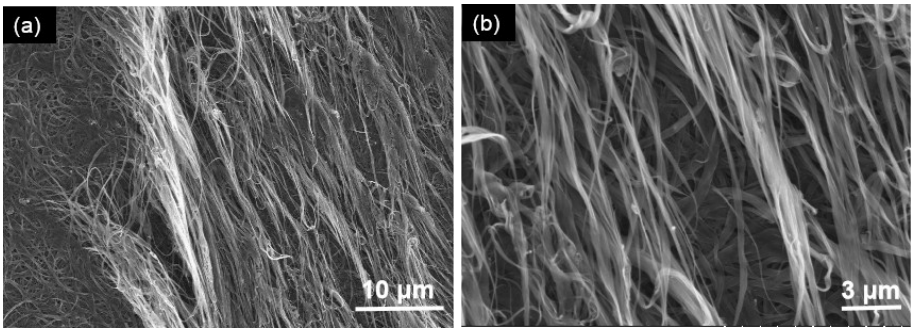

Fig. S5 The cross-sectional SEM images of SWCNT/C_8BTBT-TCNQ-40nm composite film with vapor-phase doped 40nm-thick TCNQ: (a) and enlarged image (b).

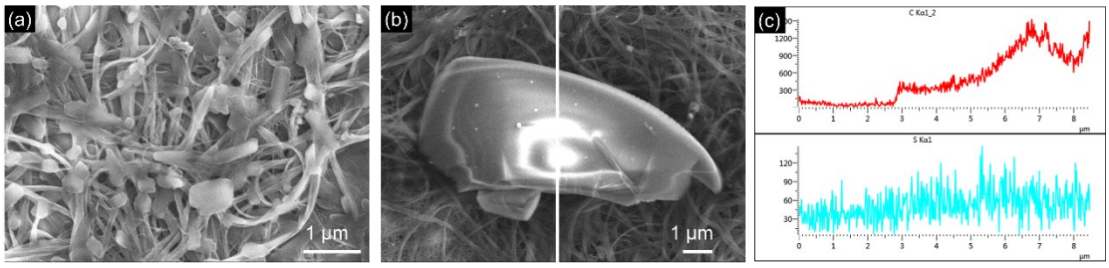

Fig. S6 The SEM image and EDS analysis of pristine SWCNT film with vapor-phase doped 40nm-thick TCNQ: (a) lamellar TCNQ crystals dispersed along the carbon nanotubes; (b) occasionally large TCNQ crystal with irregular shape; (c) EDS analysis of C element (red curve) and S element (blue curve) of image (b).

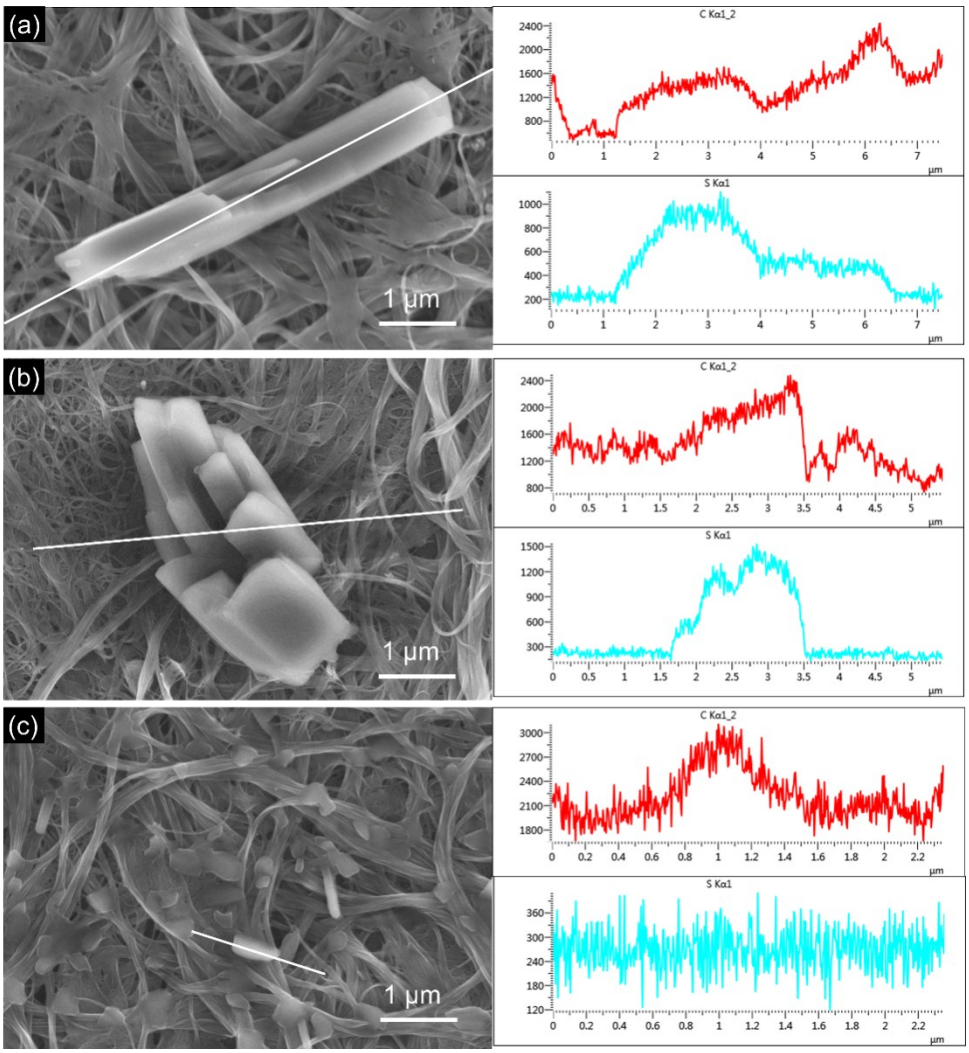

Fig. S7 The SEM image and EDS analysis of SWCNT/C_8BTBT-TCNQ-40nm composite film with vapor-phase doped 40nm-thick TCNQ: (a) and (b) images in the center of the composite film, (c) images on the periphery of the composite film.

Calculation of dopant addition

The molar dopant addition (mol%) of different composite films can be calculated according to the following formula:

$$\text{Molar dopant concentration (mol\%)} = \frac{\text{Molar amount of dopant}}{\text{Molar amount of } C_8\text{BTBT} + \text{Molar amount of dopant}} \times 100\%$$

The solid powder C_8BTBT were dissolved in anhydrous chlorobenzene with 1 mg/mL. The dopants, TCNQ and F_4CNQ were dissolved in anhydrous chlorobenzene with 1 mg/5 mL, respectively. The composite films of SWCNT/C_8BTBT/ F_nTCNQ were prepared by drop-casting of 120 μL mixed solution on the cleaned glass substrates (10 mm × 10 mm) under ambient conditions until the chlorobenzene evaporated completely. The molecular weight of C_8BTBT, TCNQ, and F_4TCNQ is 464.77 g/mol, 204.19 g/mol, 276.15 g/mol, respectively. The density of TCNQ and F_4TCNQ is 1.36g/cm^3 and 1.57g/cm^3, respectively. For SWCNT/C_8BTBT-TCNQ composite film with vapor-phase doped 40nm-thick TCNQ, its molar dopant concentration can be calculated as follows：

$$\text{Molar concentration of TCNQ}: \quad \frac{40nm \times 10mm \times 10mm \times 1.36g/cm^3}{204.19g/mol} = 2.67 \times 10^{-8} mol$$

$$\text{Molar concentration of } C_8\text{BTBT}: \quad \frac{1mg/ml \times 120\mu L}{464.77g/mol} = 2.58 \times 10^{-7} mol$$

$$\text{Molar TCNQ concentration (mol\%)}: \quad \frac{2.67 \times 10^{-8} mol}{2.58 \times 10^{-7} mol + 2.67 \times 10^{-8} mol} \times 100\% = 9.2\%$$

List relevant calculated data as follows (Table S2)：

Table S2 The relevant parameters of calculated amount of dopants addition.

	Molar amount of C_8BTBT (mol)	Molar amount of TCNQ (mol)	Molar amount of F_4TCNQ (mol)	Total molar amount of C_8BTBT and dopant (mol)	Molar dopant concentration (%)
SWCNT/C_8BTBT	2.58 × 10^{-7}	-	-	-	-
SWCNT/C_8BTBT -TCNQ-40nm		2.67 × 10^{-8}	-	2.85 × 10^{-7}	9.2
SWCNT/C_8BTBT -TCNQ-10:1		2.58 × 10^{-8}	-	2.84 × 10^{-7}	9.1
SWCNT/C_8BTBT -F_4TCNQ-40nm		-	2.27 × 10^{-8}	2.81 × 10^{-7}	8.2
SWCNT/C_8BTBT -F_4TCNQ-10:1		-	2.58 × 10^{-8}	2.84 × 10^{-7}	9.1

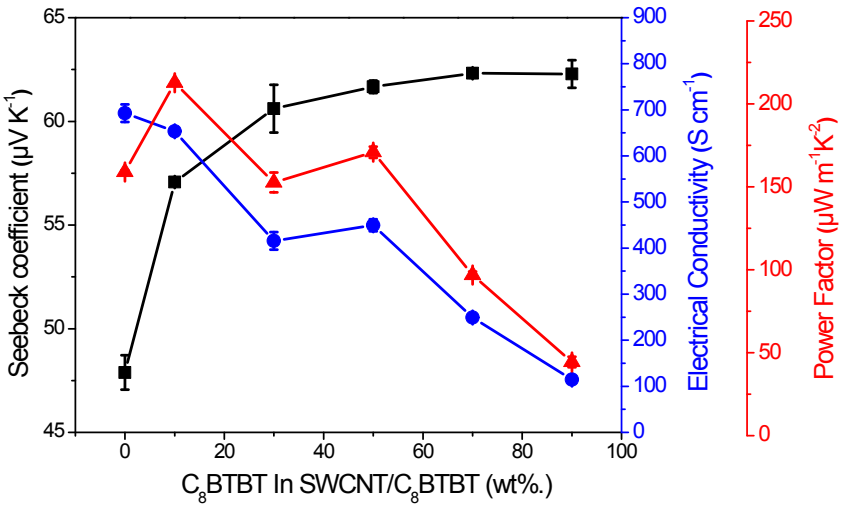

Fig. S8 The Seebeck coefficient, electrical conductivity, and power factor values of undoped composite films of SWCNT/C_8BTBT with different weight percentage of C_8BTBT.

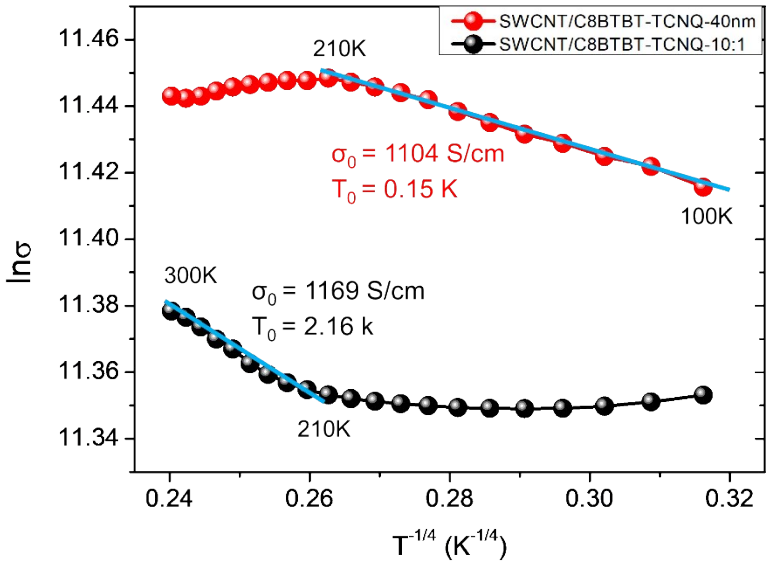

Fig. S9 Fitting the data with the equation $\sigma = \sigma_0 exp[-(T_0/T)^{1/4}]$ for SWCNT/C_8BTBT-TCNQ composite film with vapor-phase doped 40nm-thick TCNQ and SWCNT/C_8BTBT-TCNQ composite film with solution-phase doped TCNQ.

Thermoelectric properties of composite film based on other organic semiconductors

The electrical conductivity and Seebeck coefficient of the films were measured by a TE parameter test system (MRS-3, JiaYiTong Company, China). During the test, two probes were attached to the surface of the sample, and then the instrument provided a temperature difference by heating the copper sheets at both ends, thereby it caused voltage difference between the thermoelectric materials via Seebeck effect. The electrical conductivity was obtained by two-probe method. The power factor was calculated by the formula PF = S^2 σ, where S is Seebeck coefficient and σ is electrical conductivity.

Table S3. Thermoelectric properties of composite films doped by vapor-phase doping or solution-phase doping.

Composite films	Dopant addition (mol. %)	Seebeck coefficient (μV/K)	conductivity (S/cm)	Power factor (μV/K·m²)	$PF_{interfacial}$ / PF_{bulk}	Reported mobility of organic small molecules ($cm^2 V^{-1} s^{-1}$)
SWCNT/C_8BTBT -TCNQ-40nm	9.2	56.6 ± 1.1	885.4 ± 27.0	284.6 ± 6.1	4.9	31.3 [1]
SWCNT/C_8BTBT -TCNQ-10:1	9.1	26.12 ± 0.02	849.6 ± 15.2	58.1 ± 1.1		
SWCNT/TIPSPEN-TCNQ-40nm	12.1	38.5 ± 0.5	1629.9 ± 3.4	241.4 ± 5.6	2.5	11 [2]
SWCNT/TIPSPEN -TCNQ-7:1	12.1	25.16 ± 0.04	1546.9 ± 46.5	97.9 ± 3.3		
SWCNT/TTF -TCNQ-40nm	4.3	43.8 ± 0.2	1094.0 ± 59.4	210.2 ± 9.8	1.6	1.2 [3]
SWCNT/TTF -TCNQ-22:1	4.3	31.9 ± 1.0	1274.8 ± 39.1	129.7 ± 9.5		

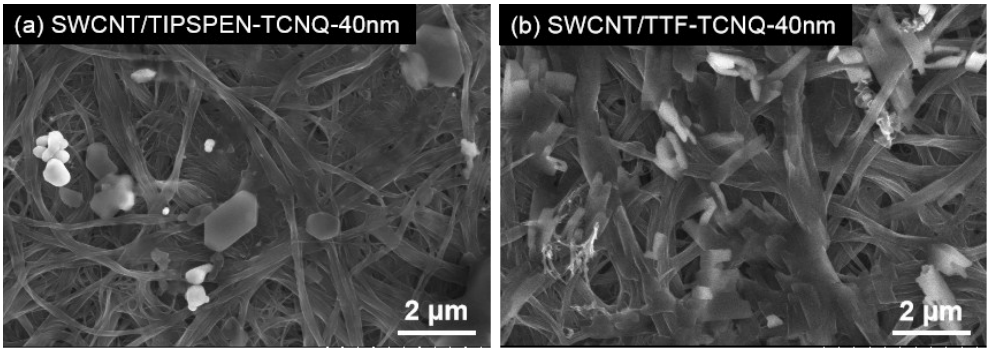

Fig. S10 The SEM images of (a) SWCNT/TIPSPEN-TCNQ-40nm composite film with vapor-phase doped 40nm-thick TCNQ. (b) SWCNT/TTF-TCNQ-40nm composite film with vapor-phase doped 40nm-thick TCNQ.

1 H. Minemawari, T. Yamada, H. Matsui, J. Tsutsumi, S. Haas,R. Chiba, R. Kumai and T. Hasegawa, Nature, 2011, 475, 364.

2 Y. Diao, B. C. Tee, G. Giri, J. Xu, D. H. Kim, H. A. Becerril, R. M. Stoltenberg, T. H. Lee, G. Xue, S. C. B. Mannsfeld and Z. Bao, Nat. Mater., 2013, 12, 665.

3 H. Jiang, X. Yang, Z. Cui, Y. Liu, H. Li, W. Hu, Y. Liuand D. Zhu , Appl. Phys. Lett., 2007, 91, 123505.

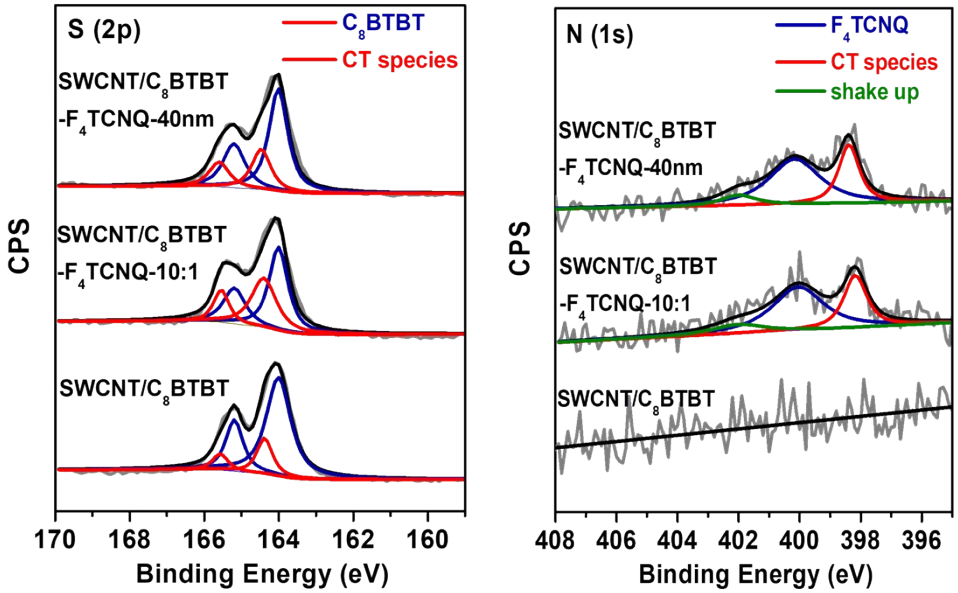

Fig S11 XPS spectra showing the S(2p) and N(1s) binding-energy peaks of composite films.

Table S4. The peak area ratioes of CT species and neutral molecules measured by XPS.

	Peak Area of CT Species		Peak Area of Neutral Molecules		Peak Area Ratio (CT Peak/Neutral Peak)	
	N(1s)	S(2p)	N(1s)	S(2p)	N(1s)	S(2p)
SWCNT/C_8BTBT	-	0.32	-	1.35	-	0.237
SWCNT/ C_8BTBT-TCNQ-40nm	0.11	0.34	1.51	1.18	0.07	0.288
SWCNT/ C_8BTBT-TCNQ-10:1	0.20	0.40	1.45	1.34	0.14	0.298
SWCNT/ C_8BTBT-F_4TCNQ-40nm	0.65	0.50	1.25	1.14	0.40	0.438
SWCNT/ C_8BTBT-F_4TCNQ-10:1	0.65	0.69	1.20	0.93	0.54	0.74

Thermostability of composite films

Thermal gravimetric analysis (TGA) was performed on a TGA-Q50 (USA) at a heating rate of 10 °C/min under a nitrogen flow of 40 mL/min.

The composite films exhibit satisfactory thermostability as shown in the TGA analysis. The SWCNT/C_8BTBT composite films manifested little mass loss (about 3 wt % loss) below 250 °C and displayed a large-scale degradation at higher temperatures above 300 °C. This long-term thermal stability upon heating will promote their applications in TE devices.

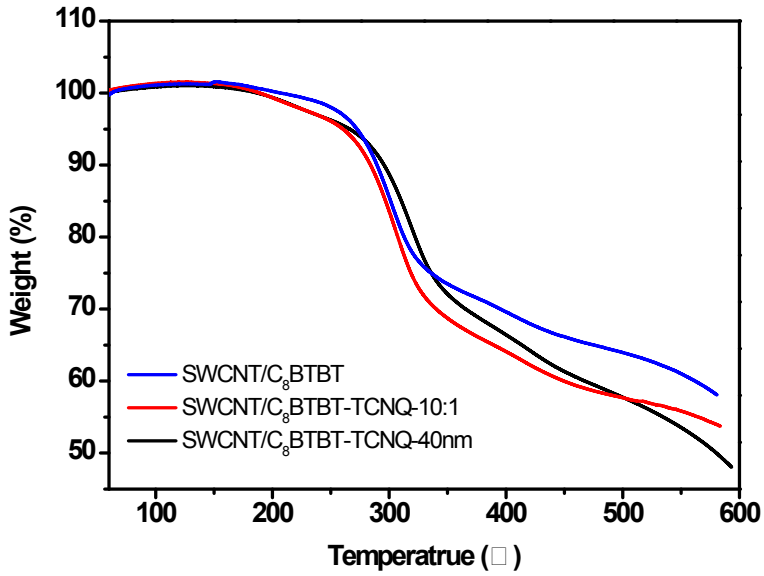

Fig S12 TGA curves of undoped SWCNT/C_8BTBT, solution-phase doped SWCNT/C_8BTBT-TCNQ-10:1 and vapor-phase doped SWCNT/C_8BTBT-TCNQ-40nm composite films under nitrogen atmosphere.