Supporting information for：

Charge transfer complexes doped single wall carbon nanotubes with reduced correlations between electrical conductivity and Seebeck coefficient for flexible thermoelectric generators

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The preparation process of charge transfer complexes (CTCs):

The solid powder TTF, TCNQ, F_4TCNQ were both dissolved in anhydrous chlorobenzene solution with the concentration of 1 mg/5 mL, respectively. The solutions of charge transfer complexes TTF-F_nTCNQ (n = 0, 4) was prepared by mixing solutions of TTF and F_nTCNQ (n = 0, 4) with molar ratio of 1:1, respectively. The colors of TTF-F_nTCNQ solutions would be changed as shown below.

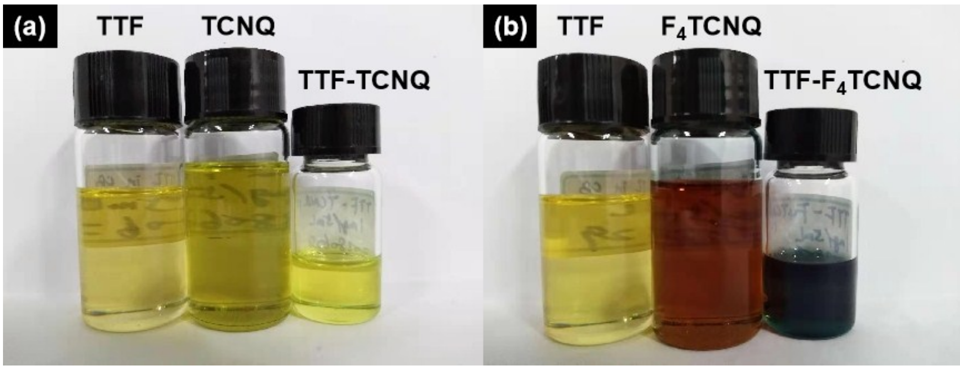

Fig. S1 The solutions of charge transfer complexes and their components in chlorobenzene.

Measurement of the thicknesses of thermoelectric films:

The thicknesses of composite films were collected by microfigure measuring instrument (Surfcorder ET4000M, Japan). Firstly, wipe off half of the composite films to build clear steps for thicknesses measurement. Next, the probe of microfigure measuring instrument scan the surface and ensuring across the two sides of the mentioned steps. Lastly, the final results were obtained by averaging nine thickness data of composite films.

Table S1 The thickness of different pristine SWCNT and doped SWCNT films.

Materials	Thickness (μm)									Average thickness (μm)	Standard deviation (μm)
the pristine SWCNT	1.465	1.625	1.629	1.751	1.737	1.413	1.735	1.555	1.760	1.630	0.129
SWCNT/ 0.1 wt% TCNQ	1.762	1.715	1.821	1.638	1.629	1.824	1.613	1.759	1.513	1.697	0.105
SWCNT/ 0.1 wt% F_4TCNQ	1.776	1.623	1.411	1.540	1.709	1.731	1.663	1.704	1.488	1.627	0.122
SWCNT/ 0.07 wt% TTF-TCNQ	1.490	1.490	1.667	1.582	1.752	1.693	1.681	1.473	1.472	1.589	0.110
SWCNT/ 0.07 wt% TTF-F_4TCNQ	1.737	1.571	1.541	1.770	1.457	1.756	1.684	1.666	1.568	1.639	0.109

Temperature dependency:

The temperature dependency below room temperature of electrical conductivity was measured by Keithley 4200-SCS and probe station (PS-100, Lakeshore) under vacuum. The temperature dependency above room temperature of electrical conductivity and Seebeck coefficient were measured by TE parameter test system (MRS-3).

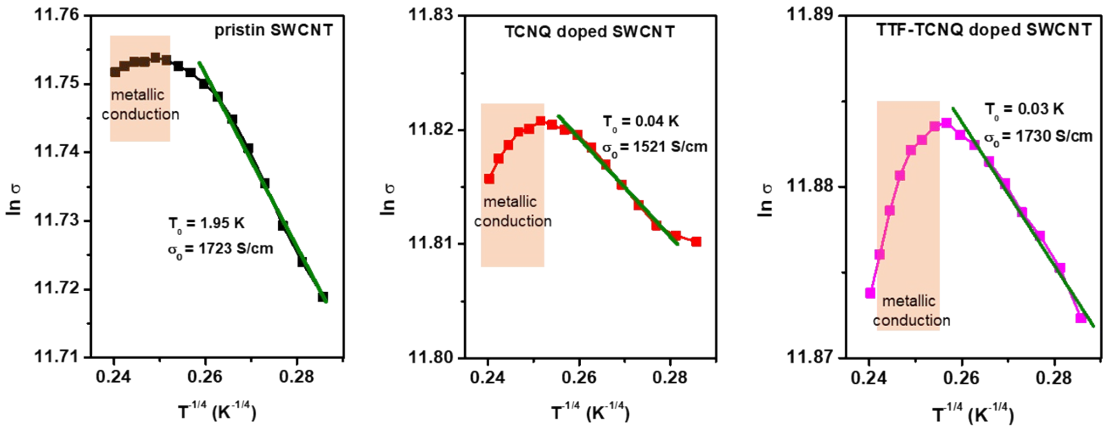

Fig. S2 Fitting the data with the equation $\sigma = \sigma_0 exp[-(T_0/T)^{1/4}]$ for the pristine SWCNT film, SWCNT doped with 0.1 wt% TCNQ and SWCNT doped with 0.07 wt% TTF-TCNQ.

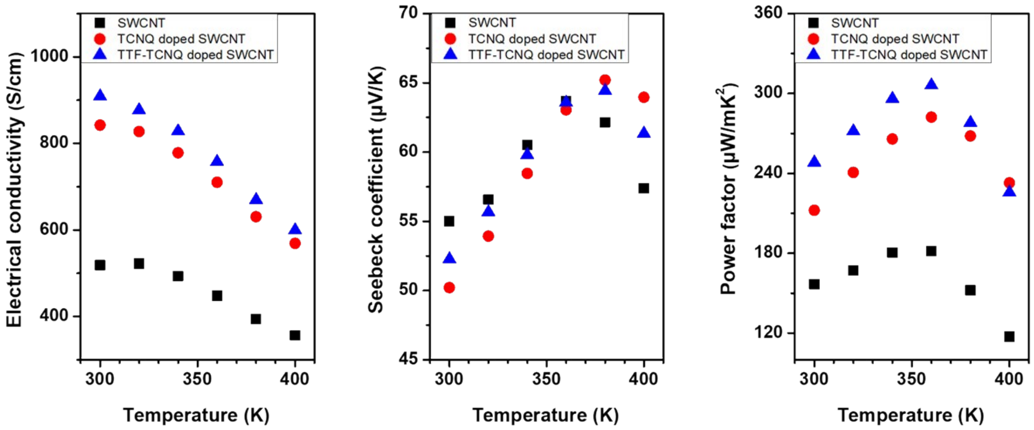

Fig. S3 Temperature dependency of electrical conductivity, Seebeck coefficient and power factor of pristine SWCNT, SWCNT doped with 0.1wt% TCNQ, and SWCNT doped with 0.07% TTF-TCNQ.

TGA measurements:

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 thermoelectric films exhibit satisfactory thermostability as shown in the TGA analysis. The pristine and doped SWCNT films manifested little mass loss (about 3 wt % loss) below 250 °C. This long-term thermal stability upon heating will promote their applications in TE devices.

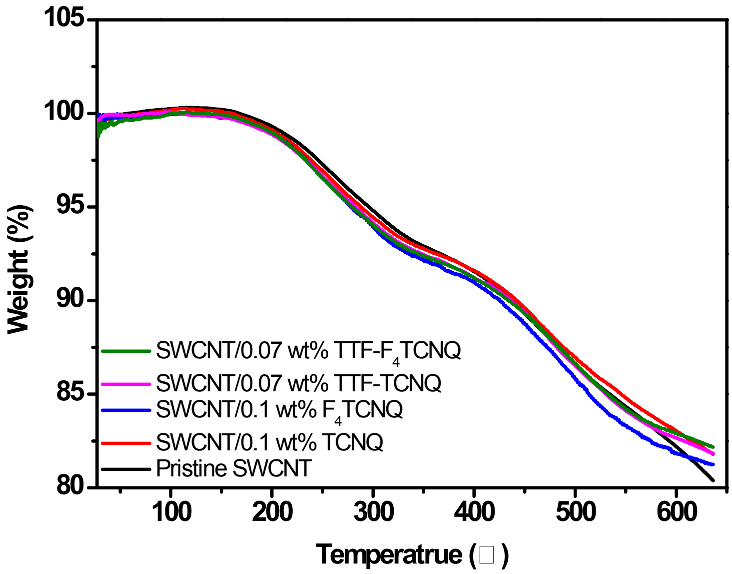

Fig. S4 TGA curves of doped SWCNT films and pristine SWCNT.

Table S2. Thermoelectric properties of 50 wt% SWCNT/50 wt% C_8BTBT composite films doped by TCNQ or TTF-TCNQ.

Composite films	Seebeck coefficient (μV/K)	Conductivity (S/cm)	Power Factor (μV/K·m²)	$PF_{TTF-TCNQ}/PF_{TCNQ}$
Doped with 0.1wt% TCNQ	63.4 ± 1.6	399.0 ± 20.4	154.6 ± 0.6	1.23
Doped with 0.1wt% TTF-TCNQ	66.8 ± 0.3	426.4 ± 13.1	190.2 ± 7.8	
Doped with 1wt% TCNQ	37.5 ± 0.8	669.0 ± 50.6	94.3 ± 11.0	1.50
Doped with 1wt% TTF-TCNQ	48.8 ± 0.7	595.9 ± 5.5	141.9± 10.7	

Table S3. Thermoelectric properties of 50 wt% SWCNT/50 wt% P3HT composite films doped by TCNQ or TTF-TCNQ.

Composite films	Seebeck coefficient (μV/K)	Conductivity (S/cm)	Power Factor (μV/K·m²)	$PF_{TTF-TCNQ}/PF_{TCNQ}$
Doped with 0.1wt% TCNQ	62.7 ± 0.6	78.9 ± 3.1	31.0 ± 0.6	1.16
Doped with 0.1wt% TTF-TCNQ	67.6 ± 2.3	78.7 ± 4.4	36.0 ± 0.5	
Doped with 1wt% TCNQ	32.0 ± 0.6	123.8 ± 4.1	12.7 ± 0.1	1.80
Doped with 1wt% TTF-TCNQ	44.9 ± 0.6	113.4 ± 2.1	22.8 ± 0.1	

Hall measurements:

The carrier concentration and carrier mobility were measured by a Hall effect measuring system (ET9007).

In order to investigate the correlation of doping on the electrical conductivity and Seebeck coefficient, the carrier concentrations and carrier mobilities of the doped SWCNT films with optimized doping concentrations were evaluated by Hall effect measurement (Table 1). In general, electrical conductivity is proportional to the carrier concentration, n, and the carrier mobility, μ, through the equation $\sigma = ne\mu$, where e is the electrical charge. With 0.1 wt% addition of traditional p-dopants FnTCNQ, the carrier concentrations of composite films were increased 2 ~ 3 times than the undoped SWCNT films, while the carrier mobilities of F_nTCNQ -doped composite films decreased about 33% ~ 42%. Therefore, the enhanced σ values of FnTCNQ-doped composite films mainly resulted from the largely increased carrier concentrations, which generally led to lower S values because S largely decreased with increase n. As for 0.07 wt% TTF-TCNQ doped composite films, the carrier concentration and carrier mobility became 50% and 10% higher than the pristine SWCNT films, respectively. Compared with the FnTCNQ-doped SWCNT films, SWCNT doped with the CTCs shown lower n and higher μ, leading to less reduced S and similar σ. The higher μ in the CTCs-doped SWCNT films were originated from the intrinsic higher mobility of TTF-TCNQ complexes, while the lower n was resulted from the strong intermolecular electron coupling between CTC molecules that consequently reduced their interaction with SWCNT bundles. Therefore, SWCNT doped with charge transfer complexes exhibited reduced correlations between electrical conductivity and Seebeck coefficient because of higher μ and lower n.

Table S4 Hall measurement of carrier concentrations (n) and carrier mobilities (μ) for the pristine and doped SWCNT films.

	SWCNT	SWCNT/ 0.1 wt% TCNQ	SWCNT/ 0.1 wt% F_4TCNQ	SWCNT/ 0.07 wt% TTF-TCNQ	SWCNT/ 0.07 wt% TTF-F_4TCNQ
n (cm^{-3})	2.27×10^{21}	6.82×10^{21}	4.23×10^{21}	3.43×10^{21}	3.59×10^{21}
μ ($cm^2\,V^{-1}\,s^{-1}$)	2.16	1.45	1.26	2.38	1.72

TEM measurements:

The film was scraped from a glass substrate (1 cm × 1 cm) and then placed in a vial with 10 mL absolute ethanol. Next, ultrasonic cleaning (SB-5200DTDN, Scientz, China) was used for 5 h at room temperature to ensure uniform dispersion of composite films. Finally, the amount of dispersion of composite films were drop-casting on the copper grid by using a pipette. The sample's preparation for TEM measurements is completed when absolute ethanol evaporates completely.

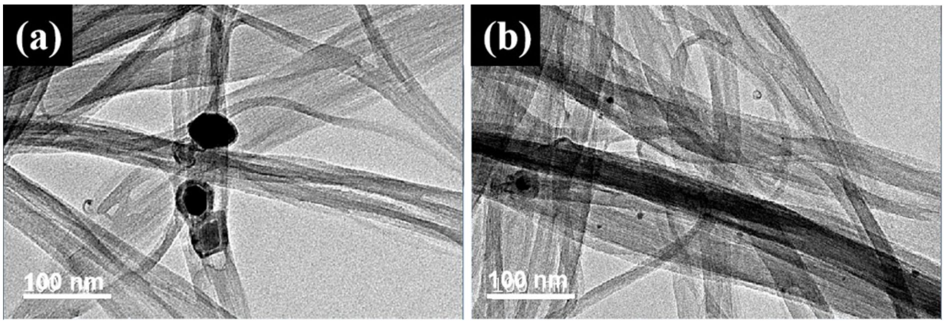

Fig. S5 The TEM images of (a) SWCNT/0.1 wt% F_4TCNQ and (b) SWCNT/0.07 wt% TTF-F_4TCNQ , respectively.

AFM analysis:

The surface morphologies and roughness of composite films (including pristine SWCNT, SWCNT/0.1 wt% TCNQ and SWCNT/0.07 wt% TTF-TCNQ) were measured by atomic force microscopy (AFM, Bruker Dimension ICON, the United States). All AFM images were collected by using tapping mode and in air under ambient conditions.

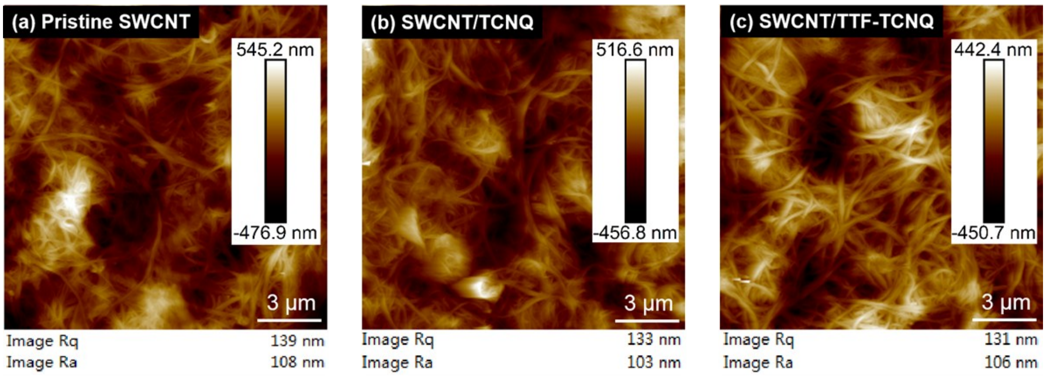

Fig. S6 The AFM images and roughness of (a) Pristine SWCNT, (b) SWCNT/0.1 wt% TCNQ and (c) SWCNT/0.07 wt% TTF-TCNQ , respectively.

XRD measurements:

X-ray diffraction (XRD) measurements were carried out using a SmartLab X-ray diffractometer with Cu Kα radiation.

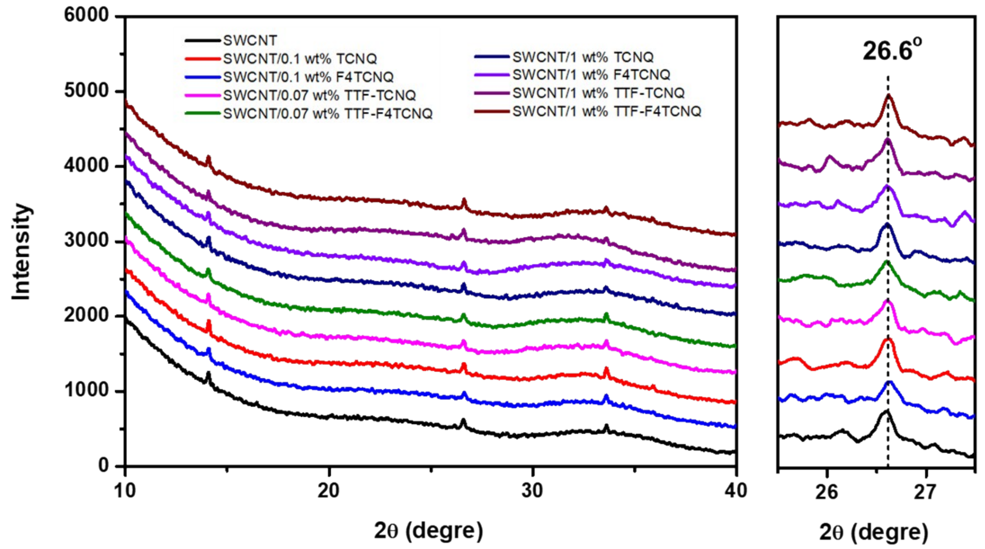

Fig. S7 X-ray diffractions of pristine SWCNT and doped SWCNT. On the right is an enlarged figure highlighting the peak of 2θ = 26.6 °C.

Table S5 Raman spectra data of the pristine SWCNT film and doped SWCNT films.

		SWCNT	SWCNT/ 0.1 wt% TCNQ	SWCNT/ 0.1 wt% F_4TCNQ	SWCNT/ 0.07 wt% TTF-TCNQ	SWCNT/ 0.07 wt% TTF-F_4TCNQ
I_D/I_G		0.0180	0.0151	0.0152	0.0145	0.0136
G' band	X	2682.58	2685.17	2686.03	2683.45	2685.17
	Y	0.22797	0.20872	0.14391	0.18916	0.20246

TEG measurements:

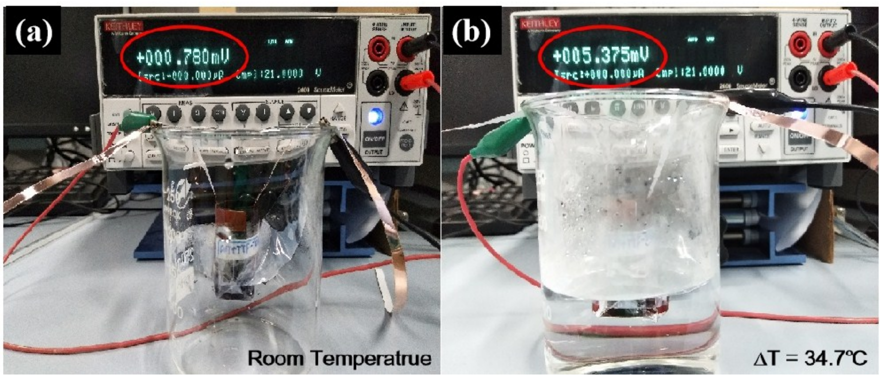

Fig. S8 The simple tested apparatus with Keithley 2400 Source Meter for monitoring the TEG composed of SWCNT/CTCs composite films to generate voltage from the temperature difference produced by hot water and ambient air.

The curves of the theoretical (V_T) and measured (V_M) output voltage dependence of temperature difference (ΔT) are shown in the supporting information (Fig. S9). The theoretical voltages (V_T) is calculated according to $V_T = NS\Delta T$, where N = 12, S = 55.2 for 0.07 wt% TTF-TCNQ doped films and 55.6 for 0.07 wt% TTF-F_4TCNQ doped films.

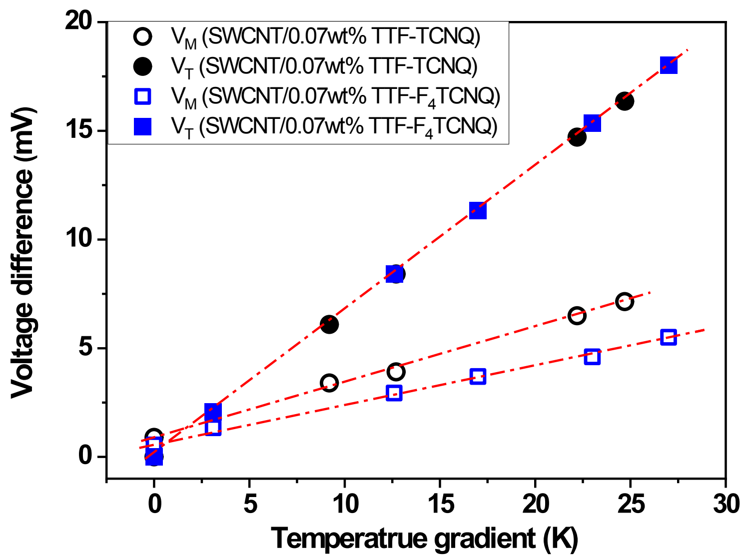

Fig. S9 Theoretical (V_T) and measured (V_M) output voltage dependence of temperature difference

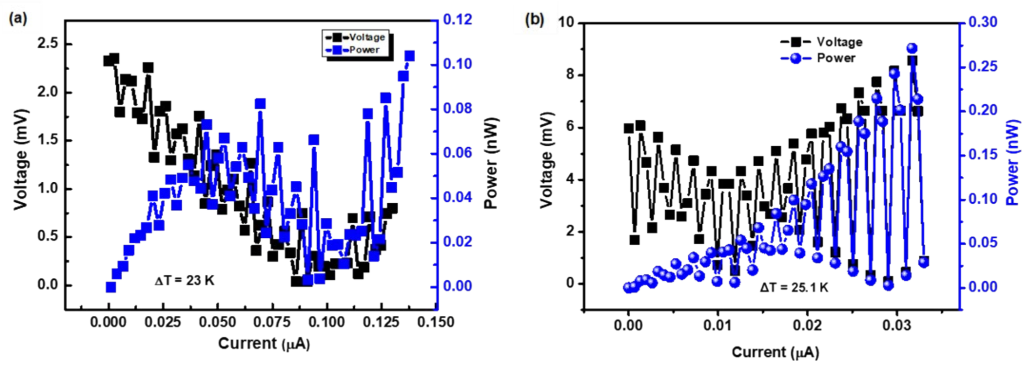

Fig. S10 Power output-current output and voltage output-current output curves for (a) SWCNT/0.1 wt% F_4TCNQ TE modules at a bias temperature 23 K; (a) SWCNT/0.1 wt% TCNQ TE modules at a bias temperature 25.1 K.