# **Electronic Supplementary Information**

# Enhanced thermoelectric performance of SWNT/organic small molecule (OSM) hybrid materials by tuning of the energy level of OSMs

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## **1. General Procedure**

#### 1.1 Spectroscopic, electronic, and thermal studies

<sup>1</sup>H and <sup>13</sup>C NMR spectra were taken in CDCl<sub>3</sub>, DMSO-*d*<sub>6</sub>, or THF-*d*<sub>8</sub> using Bruker Avance DPX-300 (Bruker Corporation), Agilent NMR system 400 MHz DD2MR400 (Agilent Technologies, Inc), or Varian NMR System 500 MHz (Varian, Inc.). High-resolution mass spectrometric data (JEOL, JMS-700) with fast atom bombardment (FAB) positive mode were obtained from the National Centre for Inter-University Research Facilities. UV-Vis absorption spectra were recorded on JASCO V-730 UV-visible spectrophotometer (JASCO, Inc.). The fluorescence spectra in both solution and solid states were obtained from JASCO FP-8300 Spectrofluorometer (JASCO, Inc.) at the excitation wavelength of 390, 395, 407, and 423 nm. LUMO levels were estimated from empirical HOMO levels and optical band gaps (Eg). Density functional theory (DFT) calculations were performed with Gaussian 09 at B3LYP/6-31G\* level. Thermal properties of new compounds were obtained using a thermal gravimetric analyser (TGA) and differential scanning calorimeter (DSC) with Q50 TGA and Q200 (TA Instruments). Raman spectra were obtained using Renishaw inVia microscope with a 514 nm excitation laser (Renishaw Plc.).

#### **1.2 Electrochemical properties**

The electrochemical properties of OSMs and SWNT were obtained by cyclic voltammetry (CV) (CH instruments, 650B electrochemical analyser). The electrochemical cell consists of three electrodes (reference electrode (Ag/Ag<sup>+</sup> 0.01 M), counter electrode (Pt), and working electrode (Pt)) in anhydrous tetrahydrofuran containing 0.1 mM OSM as a redox material and tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 0.1 M) as a supporting

electrolyte. All potentials were calibrated using a ferrocene/ferrocenium ( $Fc/Fc^+$ ) redox couple. For electrochemical measurements of SWNT, dispersed SWNT solution in tetrahydrofuran was casted onto ITO film, annealed for 2 h. ITO film and Ag wire were equipped as a working and reference electrode, respectively. The estimated HOMO level of SWNT from CV is nearly identical to a previous report.<sup>1</sup>

#### 1.3 Thermoelectric properties and Hall measurements

Seebeck coefficient measurements were conducted with a home-built system. The temperature gradient was controlled by two Peltier devices (one hot and one cold) and varied to 2, 4, 6, and 8°C. A homemade setup comprising thermoelectric measurement, measurement stage, and temperature control part was operated to measure Seebeck coefficient of SWNT and SWNT/OSMs hybrid films. The temperature gradients of the Peltier devices were controlled via Keithley 2604B as the power source and the source meter. Utilizing a Keithley 6485 picoammeter and a Keithley 2182A nanovoltmeter, the short-circuit current and the open-circuit voltage were evaluated. Thermoelectric data were acquired by Keithley 2700 multimeter system. SWNT/OSMs hybrid films were prepared with 2 cm x 2 cm rectangular shape and were pasted with 1.5 cm distance of Ag electro-conductive paste as a Ag electrode. The thermoelectric measurements were performed on more than three sets of TE films and three different locations on each film. Electrical resistivity measurements were conducted by four-point probe method (1 mm probe spacing) using Keithley 2400 source meter. Thicknesses of the hybrid films were measured from cross-sectional mini SEM image utilizing CUBE II Tabletop SEM (EmCrafts Co., Ltd.). The transport parameters including Hall coefficients were determined by Hall measurements (Ecopia, HMS 5500), averaging more than four results using a Van der Pauw method. Work functions of the SWNT and SWNT/OSMs films were obtained from photoelectron emission spectroscopy (Hitachi, High Tech AC-2).

#### 2. Reagents and Materials

Commercially available reagents and solvents were used without further purification unless otherwise noted. Commercially available single-walled carbon nanotube (80% purity, KH Chemicals Co., Ltd.) was used in our experiments to prepare SWNT/organic small molecules (OSMs) hybrid materials.



Scheme S1. Synthetic scheme of dCNBT, PBT, mBT, and dmBT

### 3. Synthesis and Characterization

Synthesis of 5,5''-(1,4-phenylene)bis[2,2'-bithiophene] (PBT).: To a mixture of 1,4-dibromobenzene (282 mg, 1.19 mmol) and tetrakis(triphenylphosphine) palladium(0) (177 mg, 0.15 mmol) was added 5-(tributylstannyl)-2,2'-bithiophene (1.6 g, 3.5 mmol) in 30 ml anhydrous toluene under nitrogen atmosphere. The reaction mixture was refluxed under nitrogen atmosphere for 40 h. The resulting mixture was diluted with dichloromethane and then filtered through Celite to remove palladium residue. Subsequent product isolation was conducted by silica gel column chromatography (gradient hexane/ethyl acetate, then tetrahydrofuran). The resulting solid was recrystallized from dichloromethane in excessive amount of hexane to give orange solid product (yield: 119 mg, 25%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  7.13 (2H, dd, *J*=5.0Hz, 3.7Hz), 7.36 (2H, d, *J*=3.6Hz), 7.38 (2H, d, *J*=6.3Hz), 7.56 (2H, d, *J*=5.4Hz), 7.58 (2H, d, *J*=3.9Hz), 7.73 (4H, s). HRMS (FAB<sup>+</sup>) [M = C<sub>22</sub>H<sub>14</sub>S<sub>4</sub>]<sup>+</sup>, calculated 405.9978, found 405.9982.

**Synthesis of 2,5-bis([2,2'-bithiophene]-5-yl)-1,4-benzenedicarbonitrile (dCNBT).** To a mixture of 2,5-dibromo-1,4-benzenedicarbonitrile (282 mg, 1.19 mmol) and tetrakis(triphenylphosphine)palladium(0) (177 mg,

0.15 mmol) was added 5-(tributylstannyl)-2,2'-bithiophene (1.6 g, 3.5 mmol) in 30 ml anhydrous toluene under nitrogen atmosphere. The reaction mixture was refluxed under nitrogen atmosphere for 20 h. The resulting mixture was diluted with dichloromethane and then filtered through celite to remove palladium residue. Subsequently, tin junk in concentrated mixture was removed through trimethylamine-neutralized silica gel. Solvents were concentrated *in vacuo* and the resulting solid was triturated with ether, filtered and dried. Further purification was conducted by silica gel column chromatography (gradient hexane/ether, then tetrahydrofuran). The resulting solid was recrystallized from ether in excessive amount of hexane to give orange solid product (yield: 155 mg, 63%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  7.13 (2H, dd, *J*=4.4Hz, 4.1Hz), 7.44 (2H, d, *J*=3.1Hz), 7.46 (2H, d, *J*=3.8Hz), 7.60 (2H, d, *J*=4.9Hz), 7.76 (2H, d, *J*=3.8Hz), 8.36 (2H, s). <sup>13</sup>C NMR (125 MHz, THF-*d*<sub>8</sub>)  $\delta$  113.208, 116.887, 124.644, 124.754, 125.792, 128.004, 129.652, 134.516, 135.131, 135.346, 136.014, 140.701. HRMS (FAB<sup>+</sup>) [M = C<sub>24</sub>H<sub>12</sub>N<sub>2</sub>S<sub>4</sub>]<sup>+</sup>, calculated 455.9883, found 455.9879.

Synthesis of 5,5''-(2-methoxy-1,4-phenylene)bis[2,2'-bithiophene] (mBT). To a mixture of 1,4-dibromo-2-methoxybenzene (372 mg, 1.4 mmol) and tetrakis(triphenylphosphine) palladium(0) (162 mg, 0.14 mmol) was added 5-(tributylstannyl)-2,2'-bithiophene (2.2g, 4.9 mmol) in 33 ml anhydrous toluene under nitrogen atmosphere. The reaction mixture was refluxed under nitrogen atmosphere for 46 h. The resulting mixture was diluted with dichloromethane and then filtered through celite to eliminate palladium residue. Subsequently, tin junk in concentrated reaction mixture was removed through triethylamine-neutralized silica gel. Further purification progressed by column chromatography (silica gel, gradient hexane/ether, then dichloromethane). The resulting solid was recrystallized from ether in excessive amount of hexane to give orange solid product (yield: 451 mg, 74%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  4.05 (3H, s), 7.11 (2H, dd, *J*=4.4Hz, 4.2Hz), 7.31 (2H, d, *J*=3.9Hz), 7.34 (2H, d, *J*=5.4Hz), 7.39 (2H, d, *J*=5.7Hz), 7.53 (2H, d, *J*=5.1Hz), 7.56(2H, d, *J*=5.1Hz), 7.64 (1H, d, *J*=1.5Hz), 7.65 (1H, d, *J*=1.5Hz), 7.83 (1H, d, *J*=8.4Hz). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ )  $\delta$  56.457, 109.087, 118.498, 121.841, 124.256, 124.705, 125.636, 125.798, 125.911, 126.169, 126.640, 128.213, 128.867, 128.948, 133.976, 136.623, 136.744, 137.010, 137.072, 137.341, 141.885, 155.667. HRMS (FAB<sup>+</sup>) [M = C<sub>23</sub>H<sub>16</sub>OS<sub>4</sub>]<sup>+</sup>, calculated 436.0084, found 436.0082.

Synthesis of 5,5''-(2,5-dimethoxy-1,4-phenylene)bis[2,2'-bithiophene] (dmBT). To a mixture of 1,4dibromo-2,5-dimethoxybenzene (152 mg, 0.5 mmol) and tetrakis(triphenylphosphine) palladium(0) (60 mg, 0.12 mmol) was added 5-(tributylstannyl)-2,2'-bithiophene (0.73 g, 1.6 mmol) in 13 ml anhydrous toluene under nitrogen atmosphere. The reaction mixture was refluxed under nitrogen atmosphere for 48h. The resulting mixture was diluted with dichloromethane and then filtered through celite to eliminate palladium residue. Subsequently, tin junk in concentrated mixture was removed through triethylamine-neutralized silica gel. Solvents were concentrated *in vacuo*, then concentrated solid was triturated with ether, filtered, and dried. Further purification progressed by silica gel column chromatography (gradient hexane/ether, then tetrahydrofuran). The resulting solid was recrystallized from ether in excessive amount of hexane to give dark orange solid product (yield: 86 mg, 77%). of <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  4.00 (6H, s), 7.12 (2H, dd, *J*= 3.9Hz, 3.9Hz), 7.35 (2H, d, *J*=3.9Hz), 7.37 (2H, d, *J*=3.3Hz), 7.50 (2H, s), 7.53 (2H, d, *J*=5.1Hz), 7.76 (2H, d, *J*=4.2Hz). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  56.480, 111.525, 122.762, 123.498, 123.692, 124.313, 126.098, 127.882, 137.494, 137.652, 137.908, 150.010. HRMS (FAB<sup>+</sup>) [M = C<sub>23</sub>H<sub>16</sub>OS<sub>4</sub>]<sup>+</sup>, calculated 436.0084, found 436.0082.

**Synthesis of 5-(tributylstannyl)-2,2'-bithiophene.** To 2,2'-bithiophene (600 mg, 3.6 mmol) in 24 ml dry THF under N<sub>2</sub> atmosphere at -78°C was added dropwise 1.0 eq of 1.6 M n-BuLi in hexanes with continuous stirring. To a stirred dark-green mixture was added 1.3 g (4.0 mmol) of tributyltin chloride dropwise at -78°C. The reaction mixture was slowly warmed to room temperature and stirred overnight. After quenching the reaction by dropping methanol, the organic layer was washed with saturated brine solution, extracted with  $CH_2Cl_2$  and dried over Na<sub>2</sub>SO<sub>4</sub>. Solvents were removed under reduced pressure and then tin byproduct in crude product was eliminated through triethylamine-neutralized silica gel chromatography to give yellowish-green liquid (yield: 1.36 g, 83%). The NMR spectrum coincides with a reported literature.<sup>2</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.93 (9H, t, *J*=7.2Hz), 1.11-1.16 (6H, m), 1.33-1.43 (6H, m), 1.55-1.65 (6H, m), 7.01-7.05 (1H, m), 7.08 (1H, d, *J*=3.3Hz), 7. 19-7.24 (2H, m), 7.31 (1H, d, *J*=3.3Hz).

Synthesis of 2,5-dibromophenol. 2,5-Dibromoaniline (3.0 g), sodium nitrite (1.0 g), urea (100 mg), and sodium sulfate (4.6 g) were used to conduct the synthesis according to a previously reported procedure.<sup>3</sup> After purification through silica gel chromatography, ivory solid product was obtained (yield: 1.9 g, 64%). <sup>1</sup>H NMR (300 MHz, DMSO- $d_6$ )  $\delta$  6.93 (1H, dd, *J*=8.4Hz, 1.9Hz), 7.10 (1H, d, *J*=1.9Hz), 7.43(1H, d, *J*=8.4Hz), 10.77(1H, s). <sup>13</sup>C NMR (75 MHz, DMSO- $d_6$ )  $\delta$  109.164, 119.316, 121.090, 123.620, 134.774, 155.732.

**Synthesis of 2,5-dibromoanisole.** A mixture of 2,5-dibromophenol (1.3 g, 5.1 mmol), K<sub>2</sub>CO<sub>3</sub>(1.1 g, 7.8 mmol), and methyl iodide (2.2 g, 964 μl) in 110 ml acetone was refluxed at 80 °C for 12 h. The resulting mixture was

concentrated, extracted with dichloromethane, washed with water, dried over sodium sulfate. After removal of volatiles, the resulting mixture was dried under vacuum to give white solid product (yield: 1.9 g, 95%). The product was then directly used for the next reaction without further purification. <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.88 (3H, s), 7.09 (1H, dd, *J*=3.9Hz, 8.4Hz), 7.30 (1H, d, *J*=2.0Hz), 7.52 (1H, d, *J*=8.4Hz). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  57.140, 110.362, 116.327, 121.659, 125.112, 134.623, 156.727.

Synthesis of 2,5-dibromo-1,4-benzenedicarboxaldehyde (dfdBr). Following a previously reported literature,<sup>4</sup> 2,5-dibromo-1,4-benzenedicarboxaldehyde was prepared using terephthalaldehyde (0.8 g, 6.0 mmol), concentrated sulfuric acid (10 ml), and *N*-bromosuccinimde (1.2 g, 6.9 mmol). After purification procedures, the resulting solid was triturated with methanol to give yellowish white solid (yield: 529 mg, 61%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) 8.08 (1H, s),  $\delta$  10.15 (1H, s) <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  124.477, 135.585, 137.792, 190.659, 190.674.

Synthesis of 2,5-dibromo-1,4-benzenedicarbonitrile (dCNdBr). A mixture of 2,5-dibromo-1,4benzenedicarboxaldehyde (605 mg, 2.1 mmol), hydroxylamine hydrochloride (870 mg, 12.5 mmol), sodium acetate (1.2 g, 14.6 mmol), and 20 ml formic acid was refluxed for 24 h under nitrogen atmosphere.<sup>5</sup> The resulting mixture was poured into water, precipitated and extracted with chloroform. The organic phase was washed with diluted NH<sub>4</sub>OH and water, dried over Na<sub>2</sub>SO<sub>4</sub>. Concentrated residue was triturated with methanol to give colorless solid (yield: 398 mg, 67%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.60 (2H, s). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ 115.750, 120.545, 124.560, 137.843.

### 4. Preparation of SWNT/organic small molecules (OSMs) hybrid films

SWNTs in anhydrous THF were firstly dispersed by tip sonicator (VCX 750, SONICS&MATERIALS, INC.) in ice bath for 3 h. SWNTs was then treated by bath sonication (Branson 5510) at 0°C for another 4 h to be further debundled. Placed into vials via micropipette, 3 ml SWNTs solution was mixed with **dCNBT**, **PBT**, **mBT**, and **dmBT** solutions dissolved in anhydrous THF at room temperature. Subsequent stirring was conducted on the shaker overnight. Thereafter, hybrid material films were fabricated by vacuum filtration method using nylon membrane filter (pore size: 0.20 µm, diameter: 47 mm). The resulting films underwent an annealing process for 2 h. SWNT/OSMs hybrid films on glass substrate were separately fabricated to measure solid-state photoluminescence (PL). Washed with isopropanol for 1 h, glass substrates were dried in vacuum oven. Then as-prepared SWNT/OSMs composite solutions were drop-casted on glass substrates, volatilized on a hot plate for 1 h to form solid-state hybrid films.

#### 5. Photophysical and thermal properties of OSMs

#### 5.1 Photophysical properties of OSMs

Absorption maximum of **dCNBT** appeared at 423 nm which is red-shifted compared to those of **PBT**, **mBT**, and **dmBT** (Fig. 2a). Photoluminescence (PL) spectra of the four OSMs in THF also showed similar trend as shown in Fig. 2b. Interestingly, structured two emission bands (Fig. 2b) of **PBT**, **mBT**, and **dmBT** are known to originate from typical vibronic coupling derived from an oligothiophene-based backbone.<sup>6</sup>

#### 5.2 Thermal properties of OSMs

Decomposition temperatures (T<sub>d</sub>) of **mBT** (297 °C), **dmBT** (303 °C), and **dCNBT** (326 °C) are higher than that of **PBT** (265 °C) (Fig. S4).<sup>7</sup>

### 6. Calculation of the adsorption amount of OSMs

We measured the physical adsorption amount of OSMs onto SWNT interface via quantitative UV analysis using JASCO V-730 UV-visible spectrophotometer (JASCO, Inc.).

wt % = 
$$\frac{m_{OSM}}{m_{OSM} + m_{SWNT}}$$

#### 6.1 General procedure to estimate the adsorption amount

Three solutions of different concentrations (5, 10, and 20  $\mu$ M) of each OSM in anhydrous tetrahydrofuran were prepared to obtain calibration curves of each OSM solution. An equal amount of SWNT (1 mg in 1 ml THF) was added into different amount of OSMs in THF to prepare 20, 40, 60, and 80 wt% of composite solution. Hybrid material films were fabricated by vacuum filtration method using nylon membrane filter (see section 4 for details). The corresponding absorbance of four unadsorbed OSMs at each concentration was recorded in UV spectrophotometer. Absorbance of unadsorbed OSM residues was automatically measured under Beer-Lambert law. The unadsorbed amount of each OSM can be deduced from their molecular weights and molar concentrations acquired from the calibration curve. Actual adsorption amount of OSMs on SWNT/OSMs hybrid films can be calculated by subtracting the unadsorbed mass from added mass of OSMs.

#### 6.2 Detailed method for calculating the adsorption amount

OSM ratio (wt%) =  $\frac{m_{OSM}}{m_{OSM} + m_{SWNT}}$ 

where  $m_{OSM}$  is the mass of an OSM (mg),  $m_{SWNT}$  is the mass of added SWNT (mg).

Initial OSM wt% (in a composite solution phase) is

 $\frac{m_{OSM,added}}{m_{OSM,added} + m_{SWNT,added}}$ 

In accordance with UV-quantitative analysis (vide infra), we can obtain the amount of unadsorbed OSM as follows:

 $m_{OSM,added} - m_{OSM,unadsorbed} = m_{OSM,adsorded}$ 

where  $m_{OSM,adsorded}$  corresponds to the mass of adsorbed OSM on the hybrid films (mg).

We assume that the amount of SWNT is nearly constant before and after the vacuum filtration (note that SWNT can hardly penetrate nylon membrane during film fabrication procedure). Therefore,

 $m_{SWNT,added} - m_{SWNT,unfiltered} \approx m_{SWNT,added}$ , since  $m_{SWNT,unfiltered} \approx 0$ 

In conclusion, the adsorbed OSM ratio on hybrid films (wt %) was estimated as follows:

 $\frac{m_{OSM,adsorbed}}{m_{OSM,adsorbed} + m_{SWNT,added}} \times 100 (\%)$ 

As a result, **dmBT** and **mBT** showed similarly higher adsorption amount of 62.4 and 62.8 wt% among the four OSMs (Table S1), followed by **dCNBT** (41.8 wt%) and **PBT** (36.0 wt%), upon 80 wt% mixing ratio ((OSM/(SWNT + OSM))). Figure S3 shows that **dmBT** and **mBT** are adsorbed better onto the SWNT surface compared to **dCNBT** and **PBT**.

# 7. Supplementary tables and figures



Fig. S1 Calculated energy levels and optimized orbital distributions of dCNBT, PBT, mBT, and dmBT



Fig. S2 a) UV-Vis absorption, (b) photoluminescence emission spectra of dCNBT, PBT, mBT, and dmBT in THF solution



Fig. S3 TGA curves of the four organic small molecules.  $T_d$  was obtained from the temperature at 5% weight loss under nitrogen.



Fig. S4 Adsorption patterns of the OSMs on the SWNT surfaces.

Compounds	$\lambda_{abs, max}^{a}$ [nm]	$\lambda_{em, max}^{a}$ [nm]	E <sup>b</sup> <sub>g</sub> [eV]	E <sup>c</sup> <sub>g</sub> [eV]	HOMO <sup>b</sup> [eV]	HOMO <sup>d</sup> [eV]	LUMO <sup>b</sup> [eV]	LUMO <sup>e</sup> [eV]	T <sub>m</sub> , T <sub>d</sub> <sup>f</sup> [°C]
dCNBT	423	505	2.90	2.58	-5.83	-5.70	-2.93	-3.12	257, 326
PBT	390	446, 470	3.18	2.84	-5.33	-5.30	-2.15	-2.46	-,265
mBT	395	456, 478	3.11	2.79	-5.22	-5.20	-2.11	-2.41	158, 297
dmBT	407	461, 487	3.09	2.71	-5.20	-5.12	-2.11	-2.41	202, 303

Table S1. Photophysical properties, electronic properties, and thermal properties of four OSMs.

<sup>*a*</sup> Measured in THF solution (each 10  $\mu$ M). <sup>*b*</sup> Obtained from the DFT calculations (B3LYP/6-31G). <sup>*c*</sup> Estimated values from the optical absorption edge in UV spectra <sup>*d*</sup> Experimental data measured by cyclic voltammetry from the onset of the oxidation potential. <sup>*e*</sup> Extrapolated from the HOMO and optical band gap. <sup>*f*</sup> Determined from the DSC and TGA curves.

Component in	Mixing wt% in	wt% of OSMs on the
hybrid film	composite solution	hybrid film
	20	12.1
ACNDT	40	20.5
UCINDI	60	26.4
	80	41.8*
	20	12.7
DDT	40	21.3
PRI	60	25.3
	80	36.0*
	20	15.2
mDT	40	25.6
IIID I	60	43.5
	80	62.8
	20	14.6
dmDT	40	23.6
unid I	60	41.1
	80	62.4

**Table S2.** Initial wt% of OSMs in composite solutions and the actual adsorbed amount of OSMs on SWNT/OSMs hybrid films. \*Further diluted by additional solvent due to the poor solubility.

Experimental frequency (cm <sup>-1</sup> )	Raman peak classification	Corresponding OSMs
366	Ring deformation	dCNBT
683-744	C-S stretching Out-of-plane bending	All
1040-1060	C-H in-plane bending C-C Stretching	All
1122	C-H in plane deformation	dCNBT
1188	C-C Stretching C-H in-plane bending	РВТ
1265-1453	C-C and C=C Stretching C-H in-plane bending	All
1500-1517	C=C Stretching C-H in-plane bending	All
2220	C≡N Stretching	dCNBT

Table S3. Vibrational normal modes for four OSMs in SWNT/OSM hybrid films (each 40wt% mixing ratio).

Name of materials	SWNT	SWNT/dCNBT	SWNT/PBT	SWNT/mBT	SWNT/dmBT
Work Function (eV)	4.75	4.78	4.78	4.77	4.77

**Table S4** Work functions of SWNT and its hybrid materials obtained from the photoelectron emissionspectroscopy. The OSM ratio of each hybrid films were set to  $23 \sim 27$  wt%.

Materials		S (µV K <sup>-1</sup> )	σ (S cm <sup>-1</sup> )	PF (W m <sup>-1</sup> K <sup>-2</sup> )
Pristine SWNT	,	$42.0\pm1.1$	$349.5\pm14.5$	$61.5\pm2.6$
	12.1	$48.9\pm1.2$	$233.3\pm18.0$	$55.8\pm4.3$
SWNT/dCNBT	20.5	$53.5\pm2.2$	$181.2\pm9.5$	$51.9\pm2.7$
(wt%)	26.4	$51.4\pm1.4$	$146.0\pm5.1$	$38.5 \pm 1.3$
	41.8	$52.4\pm3.3$	$88.1 \pm 3.4$	$22.4\pm0.9$
	12.7	$47.7\pm2.4$	$263.1\pm9.6$	$59.9\pm 6.1$
SWNT/PBT	21.3	$47.6\pm0.8$	$198.5\pm5.4$	$45.0 \pm 1.5$
(wt%)	25.3	$54.8 \pm 1.3$	$143.4\pm4.2$	$43.1\pm2.1$
	36.0	$53.2\pm1.4$	$122.3\pm4.0$	$34.6\pm1.8$
SWNT/ <b>mBT</b>	15.2	$52.8\pm3.1$	$260.3\pm8.3$	$72.7\pm2.3$
	25.6	$63.3\pm2.2$	$215.6\pm 6.0$	$86.4 \pm 2.4$
(wt%)	43.5	$62.3\pm3.6$	$178.8 \pm 10.0$	$69.4\pm3.9$
	62.8	$63.1\pm2.4$	$115.6 \pm 14.3$	$46.1\pm5.7$
	14.6	$68.4\pm3.5$	$309.9\pm31.6$	$144.9\pm14.8$
SWNT/dmBT	23.6	$76.6 \pm 1.9$	$289.3\pm39.0$	$161.0\pm22.9$
(wt%)	41.1	$63.4\pm2.6$	$237.9\pm25.4$	$95.7\pm10.2$
	62.4	$65.9\pm0.9$	$88.1{\pm}6.5$	$38.3\pm2.8$

 Table S5. Thermoelectric characteristics of the pristine SWNT films and the four hybrid films at room temperature.

Name of materials	Seebeck coefficient (µV K <sup>-1</sup> )	Electrical conductivity (S cm <sup>-1</sup> )	Power Factor (W m <sup>-1</sup> K <sup>-2</sup> )	Ref.
SWNT/PANI	38	1440	217	8
SWNT/PPy	26.5	300	21.7	9
SWNT/PEDOT:PSS	19	4000	140	10
SWNT/PVAc	78	71	42.8	11
SWNT/P3HT	40	510	105	12
SWNT/TCzPy	79.2	198.4	113.2	13
SWCNT/TDPAPy	70.4	97	42.8	13
SWCNT/Por-N	50.5	1005.3	256.1	14
SWCNT/Por-5F	53.3	982.4	279.3	14
SWNT/dmBT (This work)	78.5	272.7	183.9	

Table S6. A comparison of the thermoelectric performances for SWNT-filled hybrid materials at room temperature.



Fig. S5 A comparison of the thermoelectric performances for SWNT/Polymer and SWNT/OSMs composites in Table S6. (Ref 8-14)

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