Electronic Supplementary Material

Controlled Synthesis of Alkylthio-Substituted Poly(thienylene vinylene) and Its Carbon Nanotube Composites for Enhanced Thermoelectric Performance

Koya Nishiyama,[a,†] Yi-Tso Hsiao,[b,†] Wei-Ni Wu,[b] Jhih-Min Lin,[c] Shih-Huang Tung,[d] Cheng-Liang Liu,[b,d,e,*] and Tomoya Higashihara[a,*]

General Experimental Section

Materials. Tetrahydrofuran (THF, 99.5%, stabilizer free, Kanto Chemical Co., Inc.) was refluxed over sodium benzophenone under nitrogen for 2 h, then distilled just before use. All other reagents were purchased from BLD pharm Ltd., Sigma-Aldrich Japan K.K., Tokyo Chemical Industry (TCI) Co., Ltd., Kanto Chemical Co., Inc. or FUJIFILM Wako Pure Chemical Industries, Ltd., and used as received. Diethyl ((3,4-bis(2-ethylhexyl)-5-formylthiophen-2-yl)methyl)phosphonate (**3,4-EHT**) and poly[3,4-bis(2-ethylhexyl)thienylene vinylene] (P3,4EHTV) were synthesized according to the previous literature.[1] Tuball™ SWCNTs (purity ~ 80 %) were purchased from OCSiAl.

Characterizations. ^{1}H and ^{13}C nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra for the polymer characterization were recorded on a JEOL JNM-ECX400 (400 MHz) in deuterated chloroform-*d* ($CDCl_3$) at 25 °C calibrated to chloroform as a standard (δH 7.26). The number-average molecular weight (M_n), weight-average molecular weight (M_w), and molecular weight distribution (M_w/M_n) values were measured by size exclusion chromatography (SEC) using a JASCO GULLIVER HPLC system equipped with a pump (JASCO PU-4580), a column oven (JASCO CO-1565). The column set was as follows: a guard column (Shodex K-G 4A) and two consecutive columns (Shodex K-804L, Shodex K-805L) eluted with THF at 40 °C at a flow rate of 1.0 mL min^{-1}. Polystyrene standards were employed for a calibration for SEC. Thermal analysis was performed on a Seiko EXSTAR 6000 TG/DTA 6300 thermal analyzer at a heating rate of 10 °C/min for thermogravimetry analysis (TGA) and on a TA Instruments Q-100 connected to a cooling system at a heating rate of 10 °C/min for differential scanning calorimetry (DSC) measurement.

UV–vis–NIR absorption spectra were detected by a spectrophotometer (U-4100, Hitachi). Raman spectra were recorded with a UV spectrometer (LabRAM HR800, Horiba Jobin Yvon) equipped with Nd:YAG laser (incident laser wavelength: 532 nm). The film thicknesses were measured by KLA-Tencor D300 profilometer. The surface morphology was collected under tapping mode by using atomic force microscopy (AFM5100N, Hitachi). Scanning electron microscope (SEM) and transmission electron microscope (TEM) studies were scanned with a JEOL JSM-7600F, and JEOL JEM-2100F, respectively. 2D grazing-incidence wide-angle scattering (2D GIWAXS) measurements were carried out the National Synchrotron Radiation Research Center (NSRRC) of Taiwan on the beamline of TPS 25A. The coherence length (CL) is derived from the Scherrer equation: $\mathrm{CL} = \frac{2\pi}{\mathrm{FWHM}}$, where the full width at half maximum (FWHM) should be taken in q values. Hall effect measurements were performed by an Ecopia HMS-3000. X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) were performed on ULVAC-PHI 5000 VersaProbe Ⅲ. Work functions and the onsets of valence band were determined with He I gas discharge line (21.2 eV); for the measurements, the samples were biased at -5 V.

Synthesis of Monomer.

The monomers of P3,4EHTTV were synthesized *via* four-step reactions by modifying the procedure for P3,4EHTV (without S elements in the side chains) previously reported by our group (**Scheme S1**).[1, 2, 3] Notably, the chemical structures of the AB-type monomers for P3,4EHTTV were new. In the first step, 3-methoxythiophene was reacted with 2-ethylhexylthiol to replace the methoxy group with the 2-ethylhexylthio group at the 3-position, affording 3-(2-ethylhexylthio)thiophene (**1a**). In the second step, a formyl group was substituted at the 2-position of **1a** *via* the Vilsmeier–Haack reaction using N,N-dimethylformamide/phosphoryl chloride to afford 3-(2-ethylhexylthio)thiophene-2-carbaldehyde (**2a**). Starting from 3,4-dimethoxythiophene, 3,4-bis(octylthio)thiophene (**2b**) and 3,4-bis(2-ethylhexylthio)thiophene (**2c**) were synthesized using the same synthetic protocols of steps 1 and 2. The yield for each step was high (72%–92% for **1a**–**1c** and 80%–90% for **2a**–**2c**). In the third step, the bromomethylation reaction of 2a was attempted using hydrobromic acid/trioxane in sulfuric acid in the presence of catalytic tetradecyltrimethylammonium bromide; however, considerable side reactions occurred at the 4-position of the thiophene ring and 5-(bromomethyl)-3-(2-ethylhexylthio)thiophene-2-carbaldehyde was not obtained (**3a**). By contrast, 3,4-bis(3-alkylthio)thiophene-2-carbaldehyde (**3b**: R = octyl and **3c**: R = 2-ethylhexyl) was successfully prepared under the same conditions for **3a** in 47%–66% yields. In the final step, the bromide group was replaced with a phosphonate group by reacting **3b** or **3c** with triethyl phosphite. Although the reaction yield of **3b** was very low, **4c**, a new monomer, was successfully isolated in a 20% yield, which was comparable to the yield of the monomer **P3,4EHTV** (26%).[3] Note that **4c** possesses branched side chains which would be preferable for efficiently dispersing SWCNT and thereby improving the thermoelectric performance, as expected by our previous results employing **P3ATT** analogous.[4] The proton nuclear magnetic resonance (^{1}H NMR) spectra of the products are shown in Figs. **S1**–**S8** (**1a**, **1b**, **1c**, **2a**, **2b**, **2c**, **3b**, and **3c**) and **Fig. S9** (**4c**). **Fig. S9** shows a characteristic singlet signal for the formyl group of **4c** at 10.2 ppm. Additionally, a doublet signal assignable to the methylene units next to the phosphonate group was observed at 4.0–4.2 ppm with an intensity of ~1:2. Moreover, the ^{13}C NMR spectrum of **4c** showed the expected signals for 16 carbons. The elemental analysis of **4c** showed C:H:S = 56.54:8.90:17.29, which agreed well with the calculated values of C:H:S = 56.70:8.60:17.46. Thus, all the results indicate that the target monomer **4c** was successfully obtained without problems.

Synthesis of (2-ethylhexylthio)thiophene (1a). A solution of 3-methoxythiophene (BLD pharm, 98%, 6.47 g, 54.7 mmol), 2-ethylhexyl-1-thiol (TCI, >98%, 23.5 mL, 20.0 g, 137 mmol), and *p*-toluene sulfonic acid monohydrate (TCI, 98%, 1.04 g, 5.47 mmol) in toluene (FUJIFILM Wako, 40 mL) was heated to reflux for 48 h. After cooling to room temperature (r.t.), the mixture was taken up with CH_2Cl_2, and then a saturated aqueous solution of $NaHCO_3$ was added. The organic phase was dried over anhydrous magnesium sulfate ($MgSO_4$), rotary-evaporated and purified by silica gel chromatography using hexane as an eluent to afford **1a** as a colorless oil (10.6 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, *δ* ppm, 25 °C, **Figure S1**): δ 7.31 (q, *J* = 2.6 Hz, 1H), 7.09-7.07 (m, 1H), 7.04-7.01 (m, 1H), 2.88-2.80 (m, 2H), 1.59-1.20 (m, 10H), 0.94-0.69 (m, 7H).

Synthesis of 3,4-bis(octylthio)thiophene (1b). A solution of 3,4-dimethoxythiophene (BLD pharm, 97%, 5.00 g, 34.68 mmol), 1-octylthiol (TCI, >98%, 24.0 mL; 20.3 g, 139 mmol), and *p*-toluene sulfonic acid monohydrate (TCI, 98%, 0.561 g, 2.95 mmol) in toluene (FUJIFILM Wako, 50 mL) was heated to reflux for 48 h. After cooling to r.t., the mixture was taken up with CH_2Cl_2, and then a saturated aqueous solution of $NaHCO_3$ was added. The organic phase was dried over anhydrous $MgSO_4$, rotary-evaporated and purified by silica gel chromatography using hexane as an eluent to afford **1b** as a colorless oil (12.9g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, *δ* ppm, 25 °C, **Figure S2**): δ 7.08 (s, 2H), 2.88 (s, 4H), 1.67-1.26 (m, 28H), 0.87 (t, *J* = 6.9 Hz, 7H).

Synthesis of 3,4-bis((2-ethylhexylthio)thiophene (1c). A solution of 3,4-dimethoxythiophene (BLD pharm, 97%, 2.00 g, 13.9 mmol), 2-ethylhexyl-1-thiol (TCI, >98%, 11.8 mL; 10.1 g, 69.4 mmol), and *p*-toluene sulfonic acid monohydrate (TCI, 98%, 0.22 g, 1.16 mmol) in toluene

(FUJIFILM Wako, 20 mL) was heated to reflux for 48 h. After cooling to r.t., the mixture was taken up with CH_2Cl_2, and then a saturated aqueous solution of $NaHCO_3$ was added. The organic phase was dried over anhydrous $MgSO_4$, rotary-evaporated and purified by silica gel chromatography using hexane as an eluent to afford **1c** as a colorless oil (7.63g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, 25 °C, **Figure S3**): δ 7.06 (s, 2H), 2.87 (t, *J* = 5.9 Hz, 4H), 1.63-1.25 (m, 19H), 0.90-0.87 (m, 12H).

Synthesis of 3-(2-ethylhexylthio)thiophene-2-carbaldehyde (2a). 2a was prepared according to the general procedure for Vilsmeier-Haack formylation. **1a** (5.45 g, 23.9 mmol), *N,N*-dimethylformamide (DMF, FUJIFILM Wako, 3.72 ml, 3.49 g , 47.8 mmol), and phosphoryl chloride ($POCl_3$, Kanto, 100.5% ~ 98.5%, 3.57 ml, 5.86 g, 38.2 mmol) were dissolved in 1,2-dichloroethane (DCE, Kanto, >99%, 50 ml) and refluxed for 4 h. Then, the reaction mixture was poured into water (100 mL). The solution was extracted with chloroform, followed by washing with water and brine. The organic phase was dried over anhydrous $MgSO_4$ and rotary-evaporated. After purification by silica gel chromatography using hexane/CH_2Cl_2 (4:1) as an eluent to afford **2a** as a yellow oil (5.15 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, 25 °C, **Figure S4**): δ 10.10 (s, 1H), 7.70 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.12 (d, *J* = 5.0 Hz, 1H), 2.99 (t, *J* = 5.9 Hz, 2H), 1.62-1.21 (m, 11H), 0.92-0.87 (m, 7H).

Synthesis of 3,4-bis(octylthio)thiophene-2-carbaldehyde (2b). 1b (12.9 g, 32.2 mmol), DMF (FUJIFILM Wako, 5.01 ml, 4.71 g, 64.4 mmol), and $POCl_3$ (Kanto, 100.5% ~ 98.5%, 4.19 ml, 6.87 g, 51.5 mmol) was dissolved in DCE (Kanto, >99%, 60 ml) and refluxed for 4 h. Then, the reaction mixture was poured into water (100 mL). The solution was extracted with chloroform, followed by washing with water and brine. The organic phase was dried over anhydrous $MgSO_4$ and rotary-evaporated. After purification by silica gel chromatography using hexane/CH_2Cl_2 (5:4) as an eluent to afford **2b** as a yellow oil (11.6 g, 90%). ^1H NMR (400 MHz, $CDCl_3$, *δ* ppm, 25 °C, **Figure S5**): δ 10.21 (s, 1H), 7.32 (d, *J* = 0.9 Hz, 1H), 2.94-2.88 (m, 4H), 1.73-1.22 (m, 29H), 0.88-0.69 (m, 7H).

Synthesis of 3,4-bis(2-ethylhexylthio)thiophene-2-carbaldehyde (2c). 1c (7.63 g, 20.5 mmol), DMF (FUJIFILM Wako, 3.02 ml, 3.00 g , 41.0 mmol), and $POCl_3$ (Kanto, 100.5% ~ 98.5%, 3.10 ml, 5.03 g, 32.8 mmol) were dissolved in DCE (Kanto, >99%, 50 ml) and refluxed for 4 h. Then, the reaction mixture was poured into water (100 mL). The solution was extracted with chloroform, followed by washing with water and brine. The organic phase was dried over anhydrous $MgSO_4$ and rotary-evaporated. After purification by silica gel chromatography using hexane/CH_2Cl_2 (5:4) as an eluent to afford **2c** as a yellow oil (6.59g, 80%). ^1H NMR (400 MHz, $CDCl_3$, *δ* ppm, 25 °C, **Figure S6**): δ 10.24 (s, 1H), 7.32 (s, 1H), 2.93 (t, *J* = 5.5 Hz, 4H), 1.66-1.20 (m, 20H), 0.92-0.83 (m, 13H).

Synthesis of 5-(bromoethyl)-3,4-bis(octylthio)thiopehene-2-carbaldehyde (3b). 2b (7.50 g, 18.7 mmol) and hydrobromic acid (TCI, 47 wt% in water, 117 mL) were placed in a 300 mL three-necked flask with a condenser purged with N_2. After the mixture was cooled down to 0 °C, sulfuric acid (conc., Kanto, 44.1 mL), trioxane (TCI, >99%, 2.53 g, 28.1 mmol), and tetradecyltrimethylammonium bromide (TCI, >98%, 0.630 g, 1.87 mmol) were added and stirred at 80 °C for 5 h. Then, the reaction mixture was poured into water (200 mL). The solution was extracted with chloroform, followed by washing with water and brine. The organic phase was dried over anhydrous $MgSO_4$, rotary-evaporated, and purified by silica gel chromatography using hexane/CH_2Cl_2 (2/1) as an eluent to afford **3b** as a yellow oil (4.31 g, 47%). ^1H NMR (400 MHz, $CDCl_3$, δ ppm, 25 °C, **Figure S7**): δ 10.26 (s, 1H), 4.85 (s, 2H), 3.03-2.90 (m, 5H), 1.54-1.24 (m, 33H), 0.87 (t, J = 6.6 Hz, 8H).

Synthesis of 5-(bromoethyl)-3,4-bis(2-ethylhexylthio)thiopehene-2-carbaldehyde (3c). 2c (6.59 g, 16.5 mmol) and hydrobromic acid (TCI, 47 wt% in water, 104 mL) were placed in a 300 mL three-necked flask with a condenser purged with N_2. After the mixture was cooled down to 0 °C, sulfuric acid (conc., Kanto, 39 mL), trioxane (TCI, >99%, 2.22 g, 24.7 mmol), and tetradecyltrimethylammonium bromide (TCI, >98%, 0.555 g, 1.65 mmol) were added and stirred at 80 °C for 5 h. Then, the reaction mixture was poured into water (200 mL). The solution was extracted with chloroform, followed by washing with water and brine. The organic phase was dried over anhydrous $MgSO_4$, rotary-evaporated, and purified by silica gel chromatography using hexane/CH_2Cl_2 (2/1) as an eluent to afford **3c** as a yellow oil (5.26 g, 66%). ^1H NMR (400 MHz, $CDCl_3$, δ ppm, 25 °C, **Figure S8**): δ 10.27 (s, 1H), 4.85 (s, 2H), 3.04 (d, J = 5.5 Hz, 2H), 2.94 (dd, J = 5.9, 1.8 Hz, 2H), 1.57-1.20 (m, 23H), 0.91-0.84 (m, 15H).

Synthesis of diethyl ((3,4-bis(2-ethylhexylthio)-5-formylthiophene-2-yl) phosphonate (4c). 3c (5.26 g, 10.9 mmol), triethyl phosphite (TCI, >97%, 5.33 g, 32.1 mmol), and anhydrous CH_2Cl_2 (FUJIFILM Wako, 25 mL) were placed in a 100 mL one-necked flask purged with N_2. The solution was cooled to 0 °C, and ZnBr (TCI, >98%, 3.85 g, 17.1 mmol) was then added. The reaction mixture was warmed to r.t. and stirred for 6 h, followed by quenching with *sat.* sodium hydrogen carbonate ($NaHCO_3$) aq.. The resultant solution was extracted with EtOAc and washed with water and brine. The organic phase was dried over anhydrous $MgSO_4$. The crude product was purified by silica gel chromatography using hexane/EtOAc (6/4) as an eluent. The combined solution was stirred with activated carbon for 5 min to remove byproducts colored in red, followed by filtering through a filter paper (ADVANTEC 5C). The filtrate was evaporated and dried in vacuo to afford **4c** as a viscous reddish yellow oil (1.16 g, 20%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, 25 °C, **Figure 1**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 4.15-4.08 (m, 4H), 3.70 (d, J = 22.0 Hz, 2H), 3.03 (dd, J = 18.3, 12.8 Hz, 2H), 2.90-2.86 (m, 2H), 1.60-1.13 (m, 27H), 1.02-0.73 (m, 13H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 184.0, 146.9, 146.8, 146.6, 146.6, 142.5, 137.3, 137.2, 77.4, 77.1, 76.8, 62.8, 62.7, 41.6, 40.9, 39.7, 39.5, 32.4, 32.3, 29.8, 28.9, 28.8, 28.4, 25.6, 25.5, 23.0, 16.5, 16.5, 14.2, 14.1, 10.9, 10.8. Anal. Calcd. for $C_{26}H_{47}O_4PS_3$ (%): C, 56.70; H, 8.60; S, 17.46; Found (%): C, 56.54; H, 8.90; S, 17.29.

Synthesis of P3,4EHTTV using 2c as an initiator. The representative experiment for Run 2 is as follow: Anhydrous THF (6 mL), 15-crown-5 (>98%, Aldrich, 0.076 mL), and a THF solution of sodium hexamethyldisilazide (NaHMDS, TCI, 1.9 M, 0.20 mL) were placed in a 20 mL two-necked flask purged with N_2. The monomer **4c** (200 mg, 0.363 mmol) solution in THF (2 mL) was also prepared in another 5 mL two-necked flask. After stirring for 10 min at r.t., both of 20 mL and 5 mL two-necked flasks were cooled to −78 °C and stirred 10 min. Then, the monomer solution was added to the former 20 mL two-necked flask. After stirring for 1 min, a THF solution of **2c** (11.2 mg, 0.028 mmol) was added to start polymerization. The reaction mixture was warmed to −40 °C and stirred for 2 h. The polymerization mixture was quenched by 5M HCl aq.. The quenched solution was extracted with chloroform, washed with water, and analyzed by SEC directly before precipitation. The crude solution was poured into a large amount of methanol/water (200 mL/100 mL) to precipitate the polymer. After filtering and drying under vacuum, the crude P3,4EHTTV was obtained as a dark blue solid (135 mg, 94%). SEC: M_n = 7,200, M_w/M_n = 1.37.

Synthesis of P3,4EHTTV using as undecanal an initiator. The representative experiment for Run 8 is as follow: Anhydrous THF (10 mL), 15-crown-5 (>98%, Aldrich, 0.113 mL), and a THF solution of NaHMDS (TCI, 1.9 M, 0.30 mL) were placed in a 20 mL two-necked flask purged with N_2. The monomer **4c** (300 mg, 0.545 mmol) solution in THF (2 mL) was also prepared in another 5 mL two-necked flask. After stirring for 10 min at r.t., both of 20 mL and 5 mL two-necked flasks were cooled to −78 °C and stirred 10 min. Then, the monomer solution was added to the former 20 mL two-necked flask. After stirring for 1 min, a THF solution of undecanal (TCI, >97% 0.155 mg, 0.00908 mmol) was added to start polymerization. The reaction mixture was warmed to −40 °C and stirred for 1 h. It was further warmed to r.t. and stirred for 5 h. The polymerization mixture was quenched by 5M HCl aq. The crude solution was poured into a large amount of methanol/water (200 mL/100 mL) to precipitate the polymer. After filtering, it was purified by Soxhlet extraction with methanol, acetone, and recovered with chloroform (24 h for each). After evaporating chloroform, the polymer was freeze-dried from its benzene solution to afford P3,4EHTTV as a dark blue solid (145 mg, 67%). SEC: M_n =36,300, M_w/M_n =2.33. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, 25 °C, **Figure S10**): δ 7.63-7.55 (m, 2H), 3.04-2.78 (m, 4H), 1.54-1.26 (m, 23H), 1.06-0.69 (m, 15H).

Post-polymerization of 4c for P3,4EHTTV. Anhydrous THF (2 mL), 15-crown-5 (>98%, Aldrich, 0.019 mL), and a THF solution of NaHMDS (TCI, 1.9 M, 0.05 mL) were placed in a 20 mL two-necked flask purged with N_2. The monomer **4c** (0.05mg, 0.091 mmol) solution in THF (1 mL) was also prepared in another 5 mL two-necked flask. After stirring for 10 min at r.t., both of 20 mL and 5 mL two-necked flasks were cooled to −78 °C and stirred 10 min. Then, the monomer solution was added to the former 20 mL two-necked flask. After stirring for 1 min, a THF solution of **2c** (5.20 mg, 0.013 mmol) was added to start polymerization. The reaction mixture was warmed to −40 °C and stirred for 1 h. After sampling an aliquot of the solution and quenching with 5 M HCl aq. for SEC characterization (M_n (SEC) = 3,100, M_w/M_n = 1.28), the second monomer solution was added to the reaction mixture, which was prepared in another batch as described below. The solution was further stirred at -40 °C for additional 2 h, followed by quenching with 5 M HCl aq. (2 mL). The quenched solution was extracted with chloroform, washed with water, and analyzed by SEC directly before precipitation. The crude solution was poured into a large amount of methanol/water (200 mL/100 mL) to precipitate the polymer. After filtering and drying under vacuum, the crude P3,4EHTTV was obtained as a dark blue solid (74 mg, 68%). SEC: M_n = 11,400, M_w/M_n = 1.37.

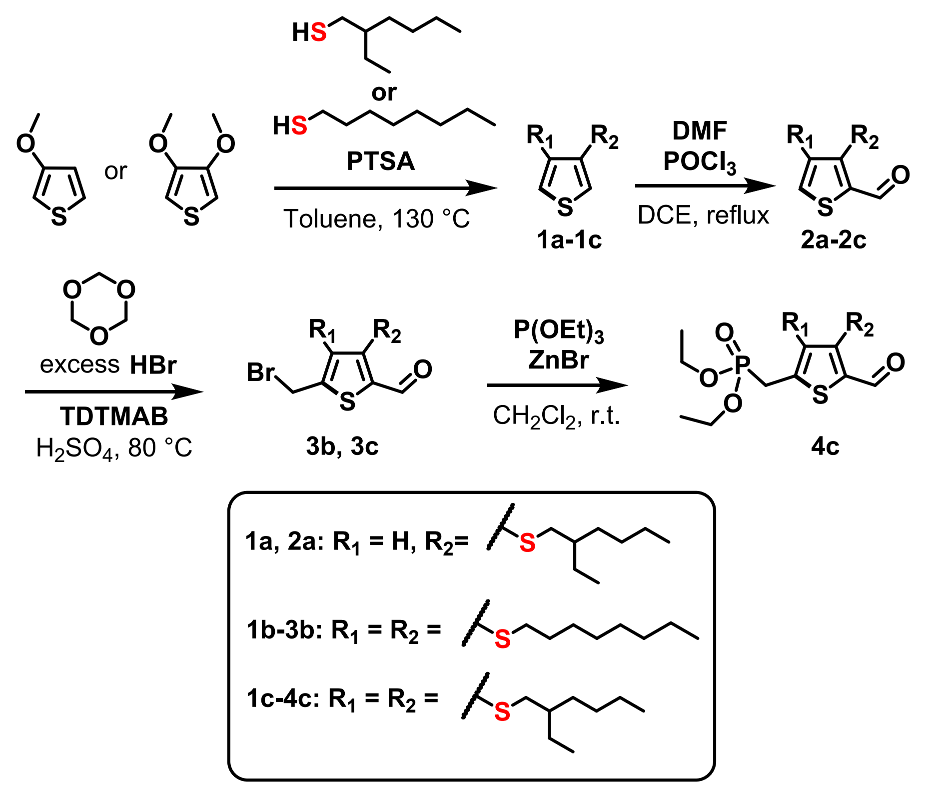
Preparation of THF solution of the second monomer: Anhydrous THF (2 mL), 15-crown-5 (>98%, Aldrich, 0.038 mL), and a THF solution of sodium NaHMDS (TCI, 1.9 M, 0.10 mL) were placed in a 10 mL two-necked flask purged with N_2 and cooled down to -78 °C. A monomer **4c** (100 mg, 0.182 mmol) solution in THF (1 mL) was also prepared in another 5 mL two-necked flask. After stirring for 10 min at r.t., both of 10 mL and 5 mL two-necked flasks were cooled to −78 °C and stirred 10 min to afford the second monomer solution.

Synthesis of P3,4EHTTV-*b*-P3,4EHTV. Anhydrous THF (2 mL), 15-crown-5 (>98%, Aldrich, 0.019 mL), and a THF solution of sodium NaHMDS (TCI, 1.9 M, 0.05 mL) were placed in a 20 mL two-necked flask purged with N_2. The monomer **4c** (0.05mg, 0.091 mmol) solution in THF (1 mL) was also prepared in another 5 mL two-necked flask. After stirring for 10 min at r.t., both of 20 mL and 5 mL two-necked flasks were cooled to −78 °C and stirred 10 min. Then, the monomer solution was added to the former 20 mL two-necked flask. After stirring for 1 min, a THF solution of **2c** (5.20 mg, 0.013 mmol) was added to start polymerization. The reaction mixture was warmed to −40 °C and stirred for 1 h. After sampling an aliquot of the solution and quenching with 5 M HCl aq. for SEC characterization (M_n (SEC) = 3,100, M_w/M_n = 1.26), a **3,4-EHT** solution was added to the reaction mixture, which was prepared in another batch as described below. The solution was further stirred at -40 °C for additional 2 h, followed by quenching with 5 M HCl aq. (2 mL). The quenched solution was extracted with chloroform, washed with water, and analyzed by SEC directly before precipitation. The crude solution was poured into a large amount of methanol/water (200 mL/100 mL) to precipitate the polymer. After filtering and drying under vacuum, the crude P3,4EHTTV-*b*-P3,4EHTV was obtained as a dark blue solid (46 mg, 69%). SEC: M_n = 5,000, M_w/M_n = 1.32.

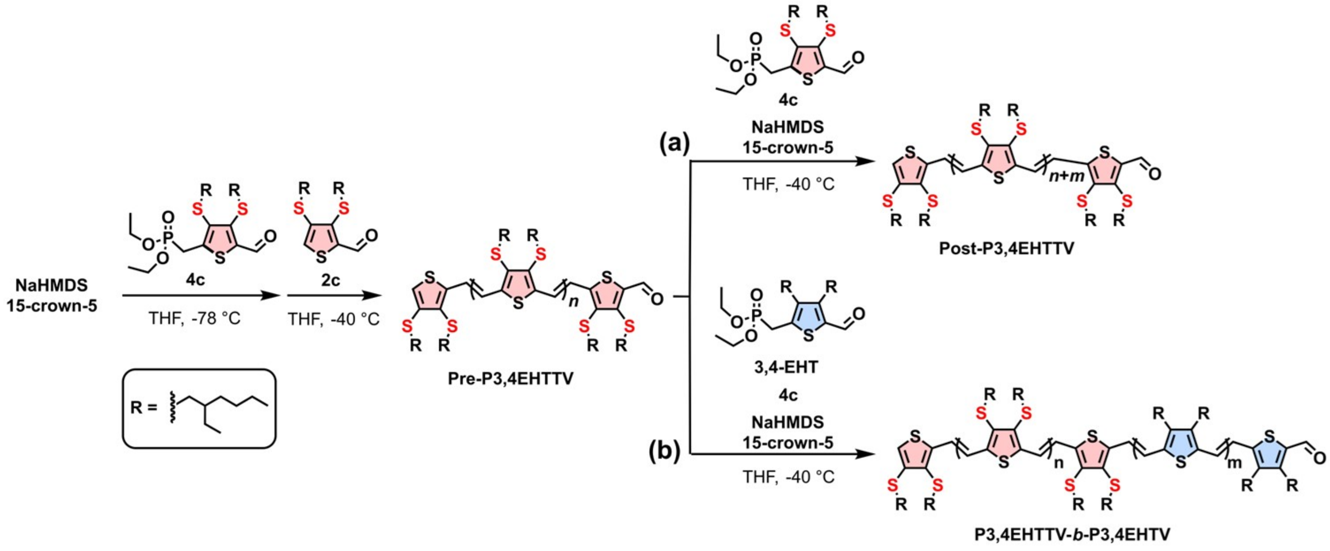
Preparation of THF solution of the Diethyl ((3,4-bis(2-ethylhexyl)-5-formylthiophen-2-yl)methyl)phosphonate (3,4-EHT): Anhydrous THF (2 mL), 15-crown-5 (>98%, Aldrich, 0.019 mL), and a THF solution of NaHMDS (TCI, 1.9 M, 0.05 mL) were placed in a 10 mL two-necked flask purged with N_2 and cooled down to -78 °C. A **3,4-EHT** (44 mg, 0.091 mmol) solution in THF (1 mL) was also prepared in another 5 mL two-necked flask. After stirring for 10 min at r.t., both of 10 mL and 5 mL two-necked flasks were cooled to −78 °C and stirred 10 min to afford the **3,4-EHT** solution.

Thermoelectric polymer/SWCNT nanocomposite thin film fabrication and measurement. The synthesized poly(thienylene vinylene)s were dissolved individually in chlorobenzene at the concentration of 1.5 mg mL^{-1}; each was then vigorously stirred by vortex and heated at 60 °C overnight to ensure complete solvation. After dissolution, an equal weight of SWCNTs was added into the polymer solution, with a total solid content of 3 mg mL^{-1}. The nanocomposite solution was homogeneously mixed with a ball mill (Restch MM440) at 25 Hz for 10 min. The prepared nanocomposite solution was spin-coated onto a glass substrate (15 × 15 mm^2), pre-cleaned by sonication in acetone, isopropanol, and deionized water, then heated at 60 °C to remove residual solvent with N_2.

The thicknesses of the as-cast nanocomposite films were around 300 nm. Before conducting the thermoelectric measurements, the nanocomposite thin films were annealed at 190 °C for 10 minutes under a nitrogen environment to adjust interfacial alignments between the polymers and SWCNTs. The silver paste was applied to both sides of the sample for contact probing. The S and σ of the thin film samples were collected in the in-plane direction by a commercially available thermoelectric measurement system (ZEM-3, Advance Riko) at the ambient temperature of 323 K under a low-pressure helium atmosphere. At least three samples for each thin films were collected to obtain the average thermoelectric properties.



Scheme S1. Synthetic routes for monomers.



Scheme S2. (a) Post-polymerization of **4c** and (b) synthesis of P3,4EHTTV-*b*-P3,4EHTV.

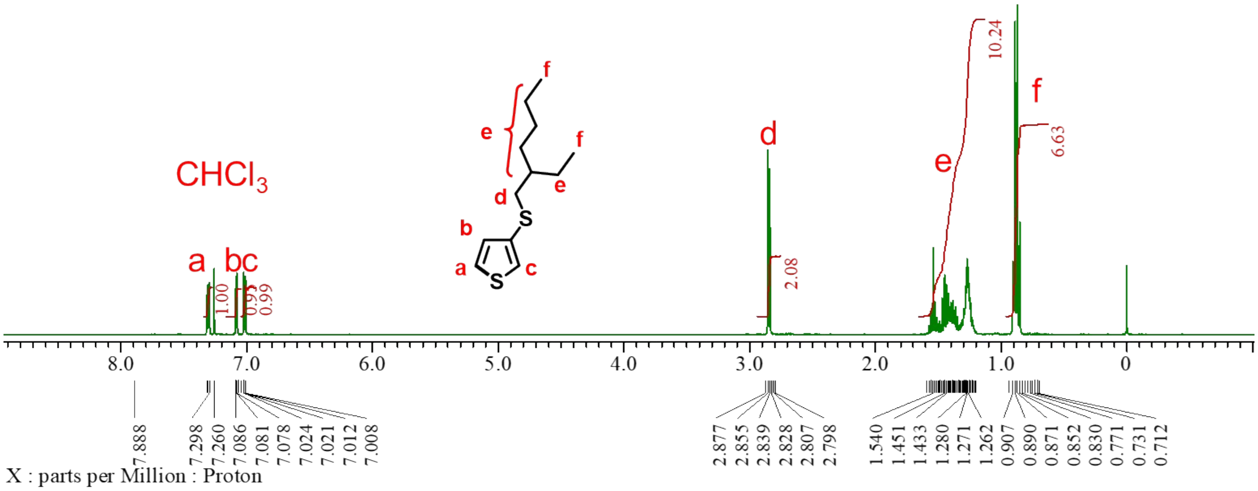


Fig. S1 ^{1}H NMR spectrum of **1a** measured in $CDCl_3$ (400 MHz).

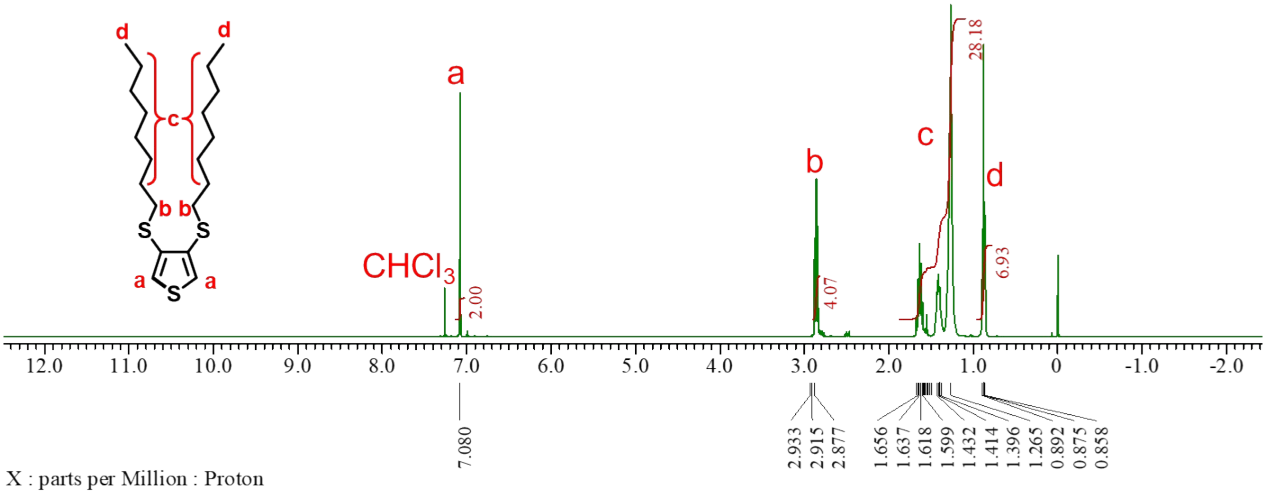


Fig. S2 ^{1}H NMR spectrum of **1b** measured in $CDCl_3$ (400 MHz).

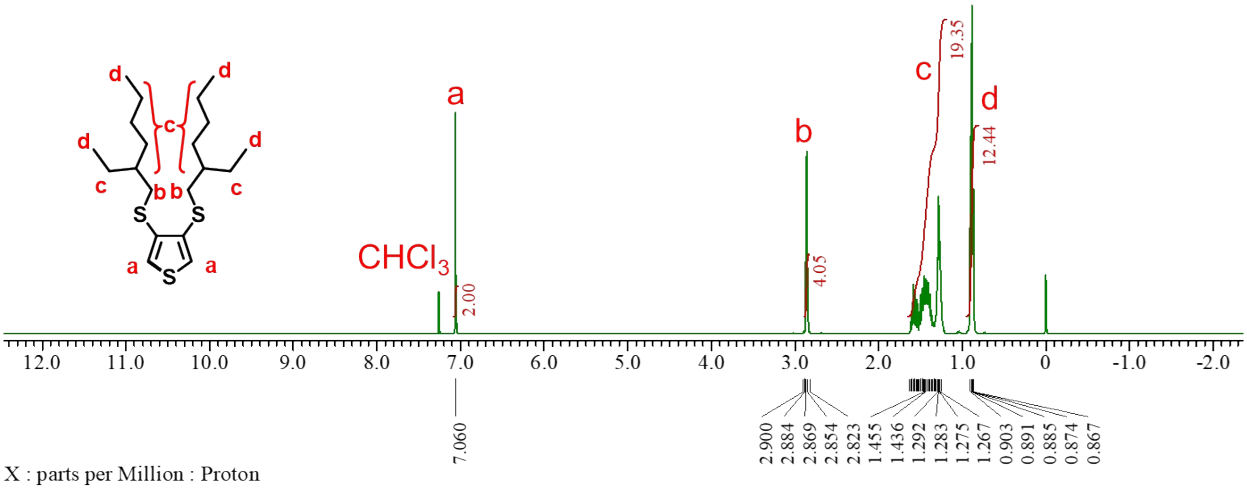


Fig. S3 ^{1}H NMR spectrum of **1c** measured in CDCl$_3$ (400 MHz).

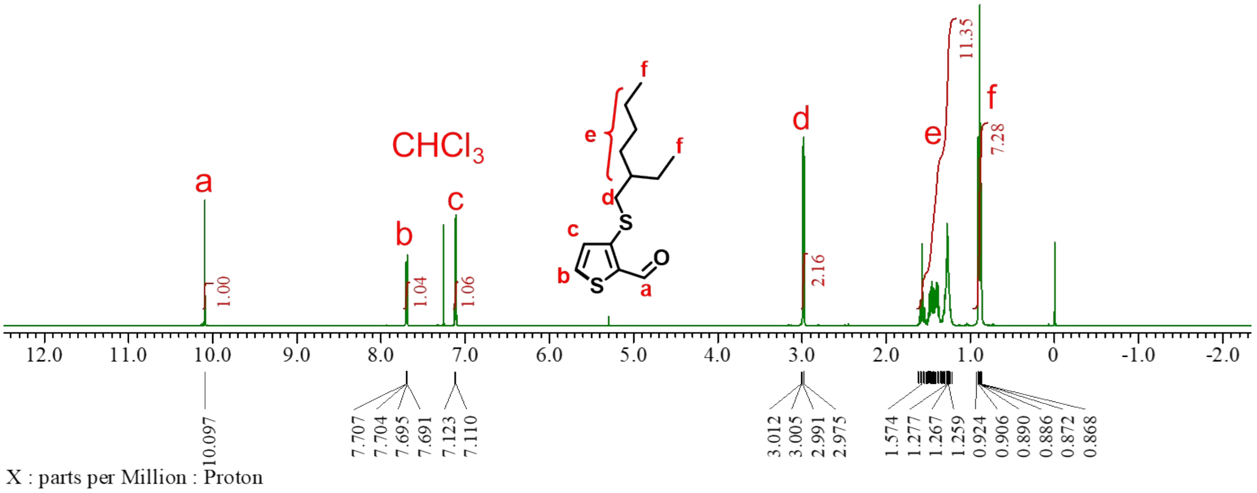


Fig. S4 ^{1}H NMR spectrum of **2a** measured in CDCl$_3$ (400 MHz).

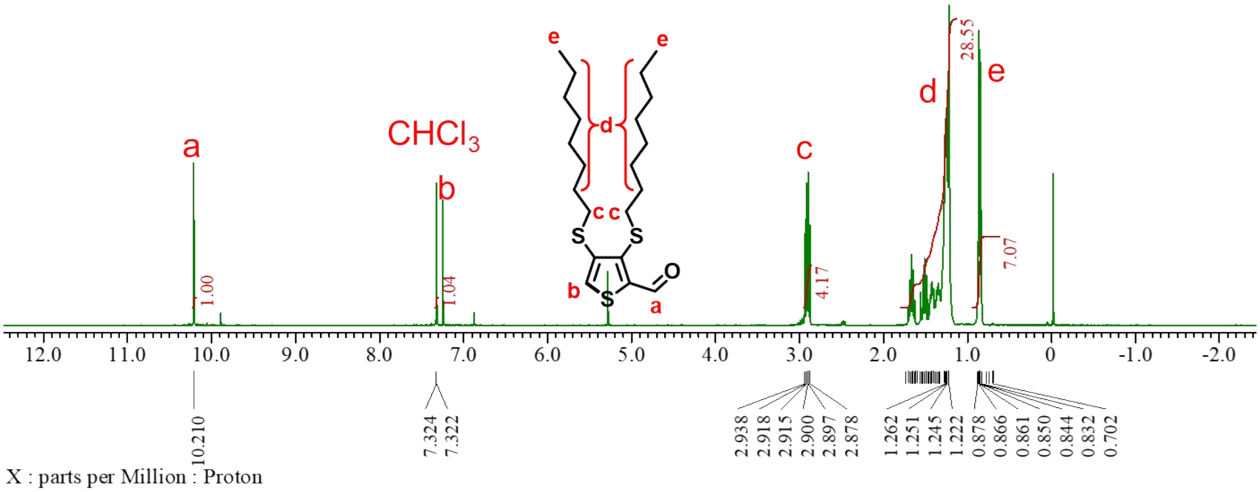


Fig. S5 ^{1}H NMR spectrum of **2b** measured in CDCl$_3$ (400 MHz).

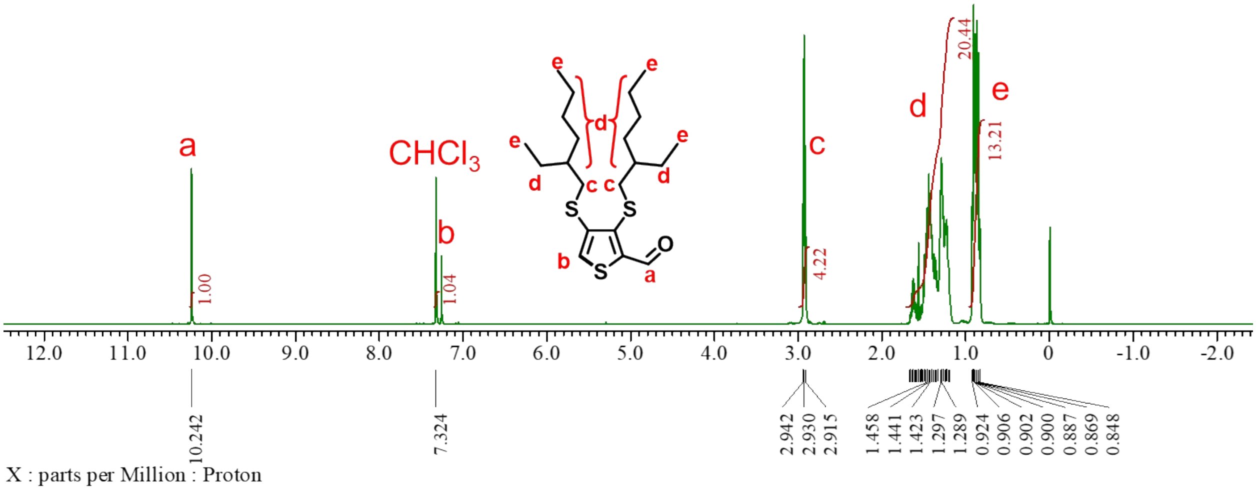


Fig. S6 ^{1}H NMR spectrum of **2c** measured in CDCl$_3$ (400 MHz).

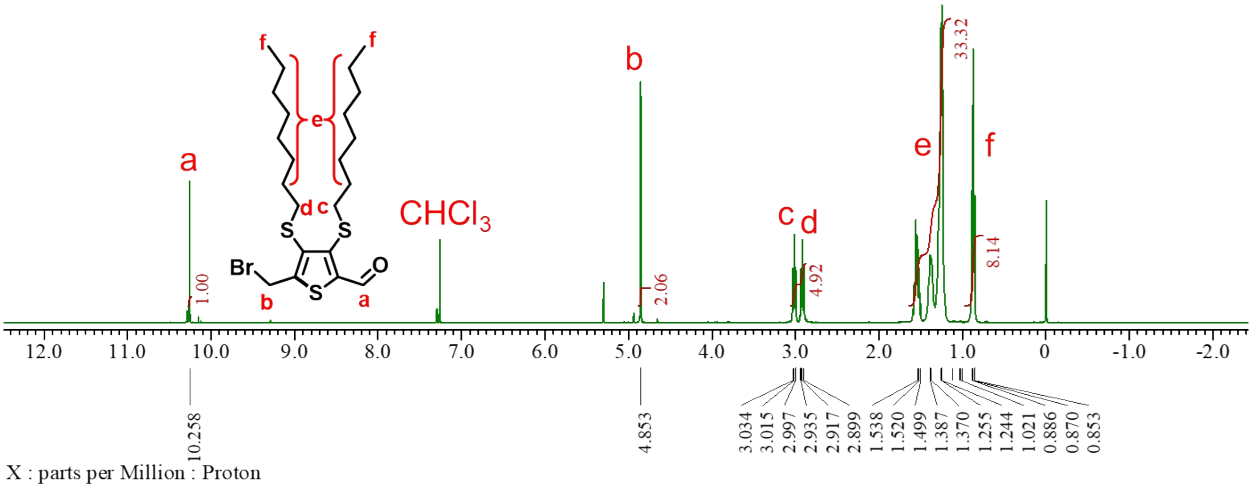


Fig. S7 ^{1}H NMR spectrum of **3b** measured in $CDCl_3$ (400 MHz).

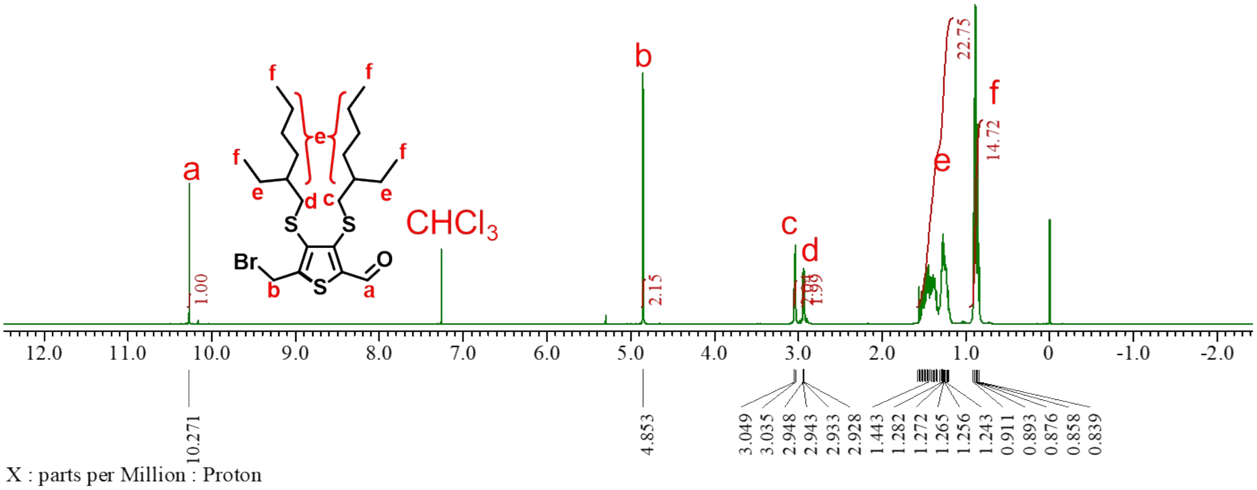


Fig. S8 ^{1}H NMR spectrum of **3c** measured in $CDCl_3$ (400 MHz).

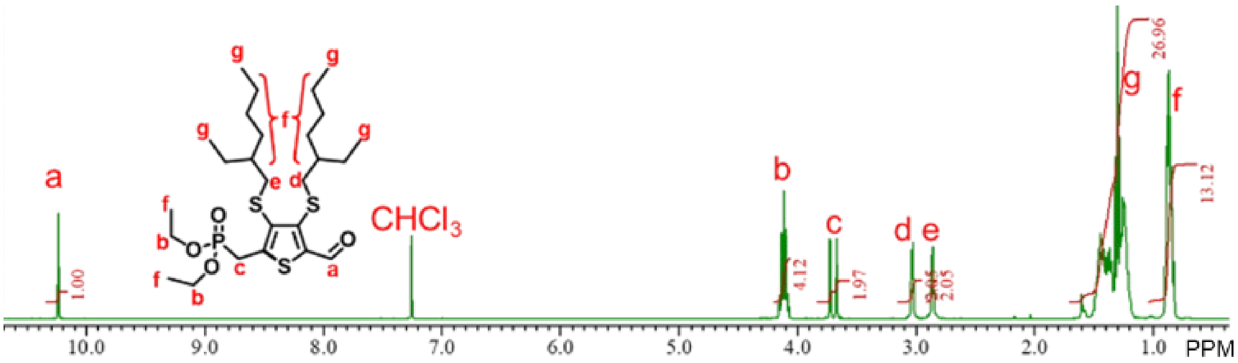


Fig. S9 ^{1}H NMR spectrum of **4c** measured in CDCl$_3$.

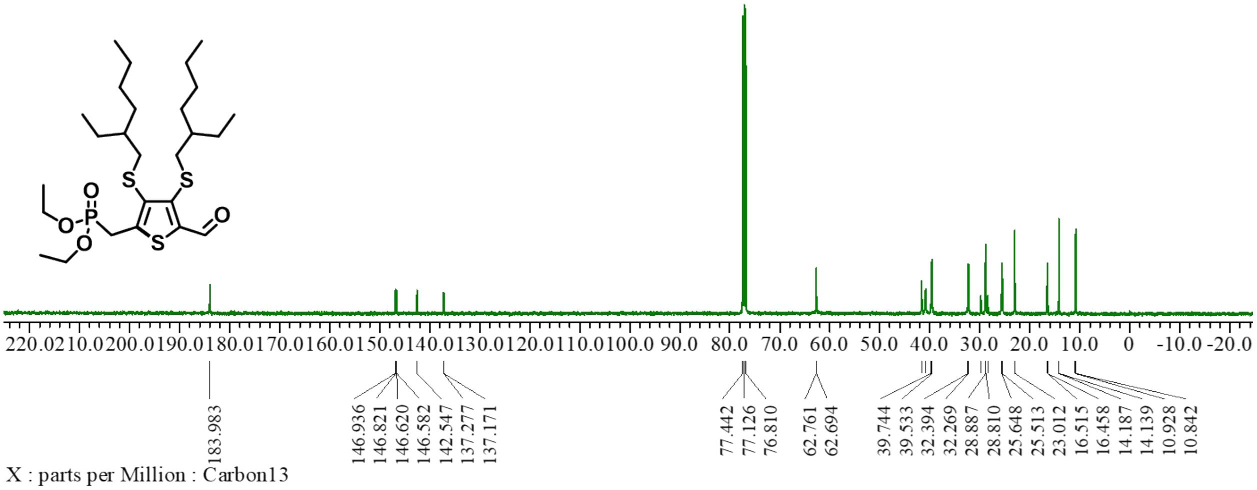


Fig. S10 ^{13}C NMR spectrum of **4c** measured in CDCl$_3$ (101 MHz).

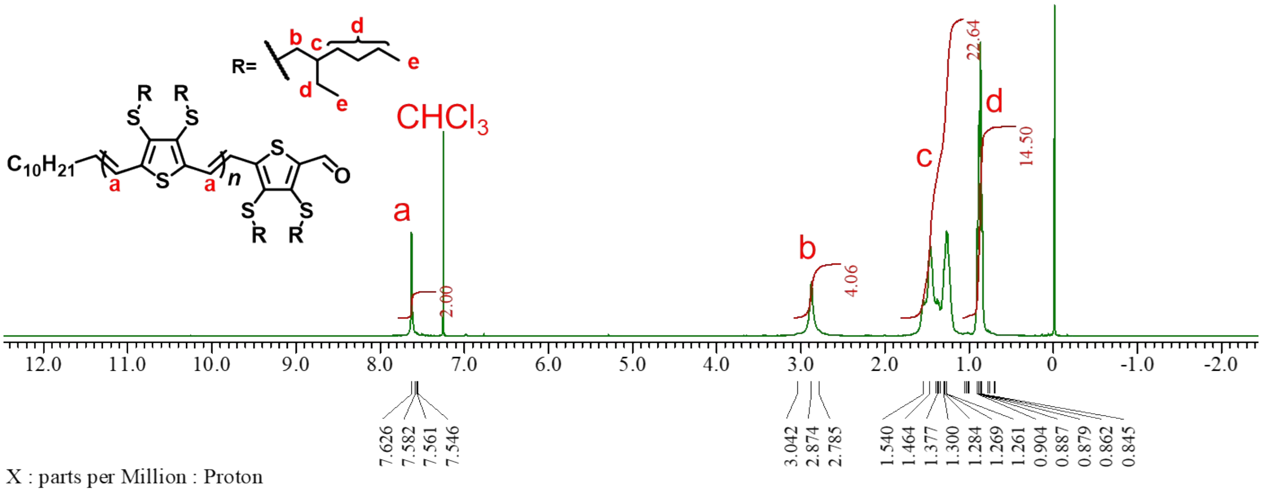


Fig. S11 ^{1}H NMR spectrum of P3,4EHTTV (Run 8) measured in $CDCl_3$ (400 MHz).

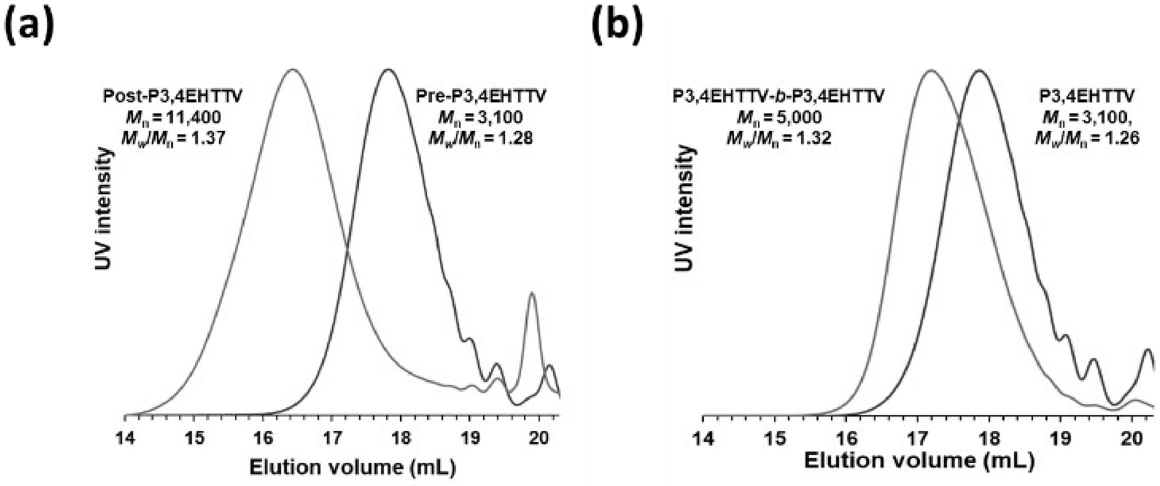
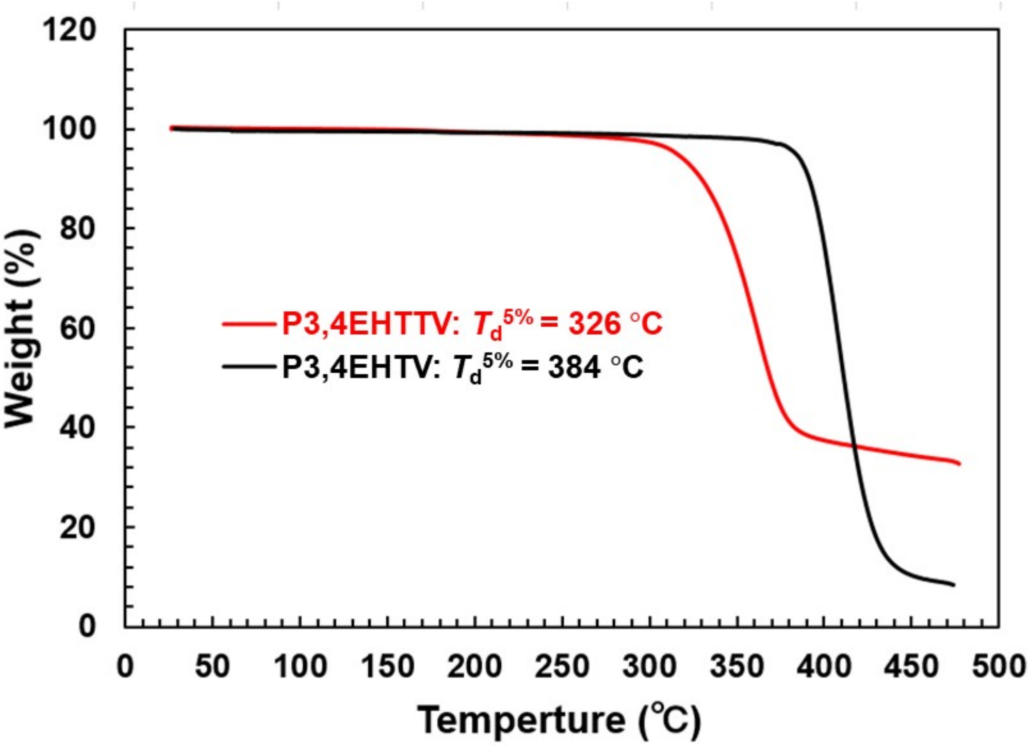
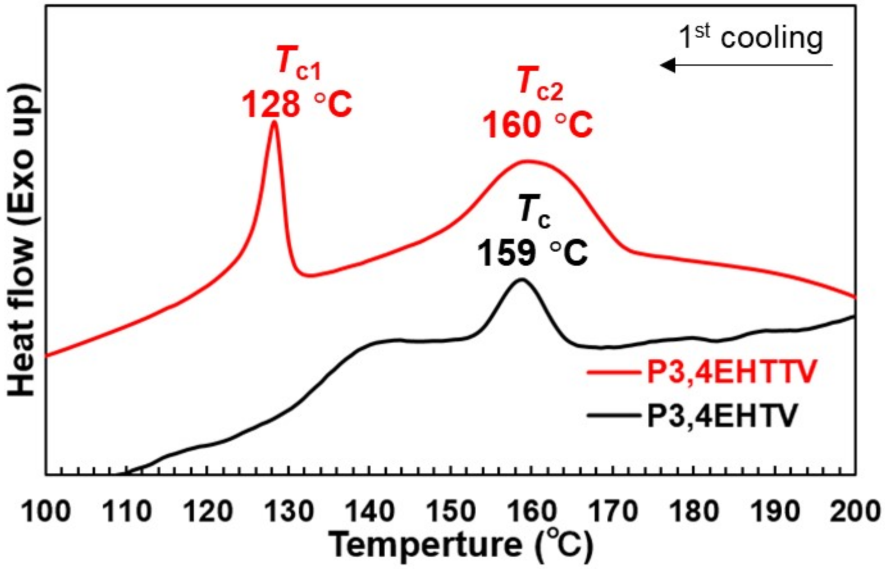


Fig. S12 SEC UV traces of studied polymers: (a) P3,4EHTTV before (pre-P3,4EHTTV, black) and after (post-P3,4EHTTV, red) the post-polymerization and (b) P3,4EHTTV-*b*-P3,4EHTV (red) and

(a)


120
100
80
60
40
20
0
Weight (%)
0
50
100
150
200
250
300
350
400
450
500
Temperture (°C)
P3,4EHTTV: $T_d^{5\%}$ = 326 °C
P3,4EHTV: $T_d^{5\%}$ = 384 °C

(B)


1st cooling
T_{c1}
128 °C
T_{c2}
160 °C
T_c
159 °C
Heat flow (Exo up)
P3,4EHTTV
P3,4EHTV
100
110
120
130
140
150
160
170
180
190
200
Temperture (°C)

(c)

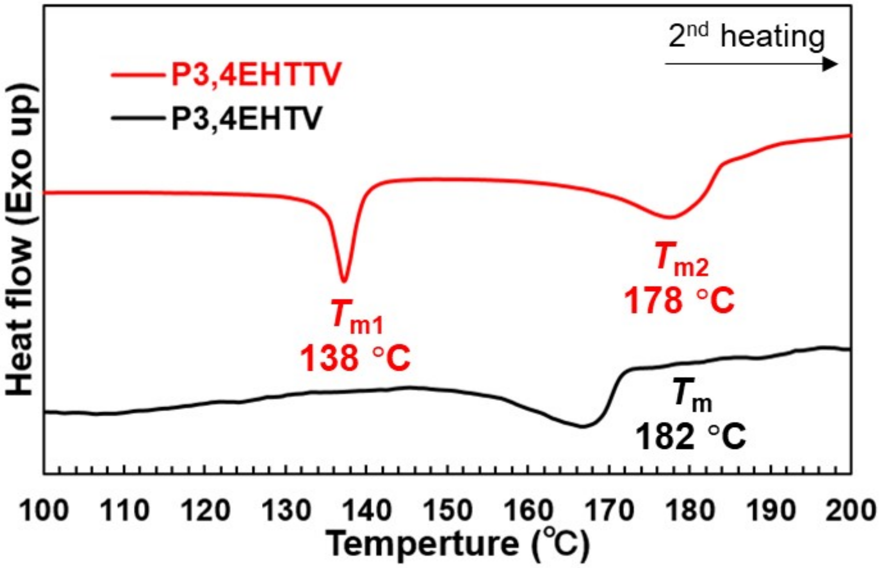


Fig. S13 (a) TGA thermograms (N_2 flow: 200 mL min^{-1}, heating scan: 10 °C min^{-1}), (b) DSC curves (N_2 flow: 20 mL min^{-1}, the 1st cooling scans, 10 °C min^{-1}), and (c) DSC curves (N_2 flow: 20 mL min^{-1}, the 2nd heating scans: 10 °C min^{-1}). Red and black lines indicate P3,4EHTTV and P3,4EHTV, respectively.

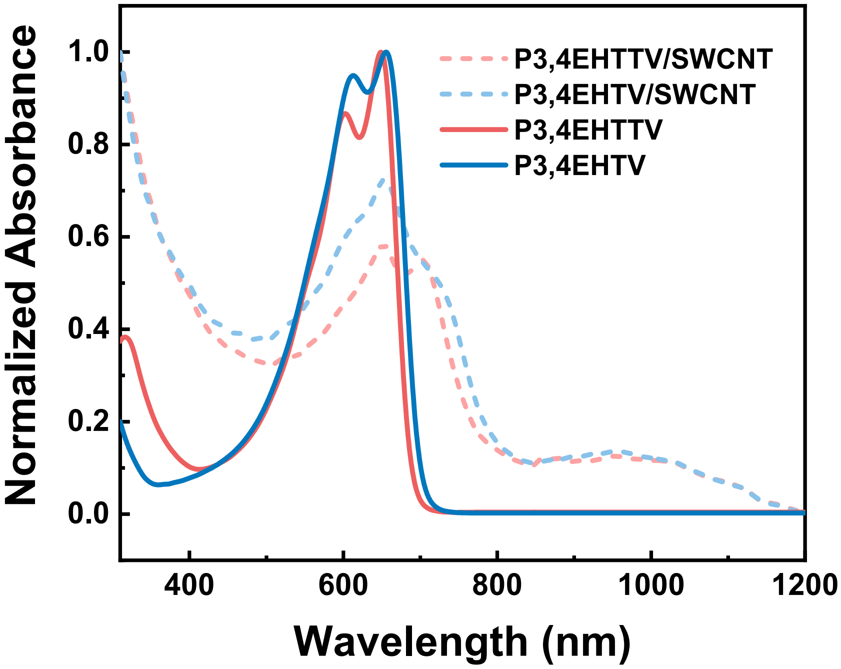


Fig. S14 The UV-vis-NIR spectrum of the PTV/SWCNT nanocomposites in chlorobenzene solutions.

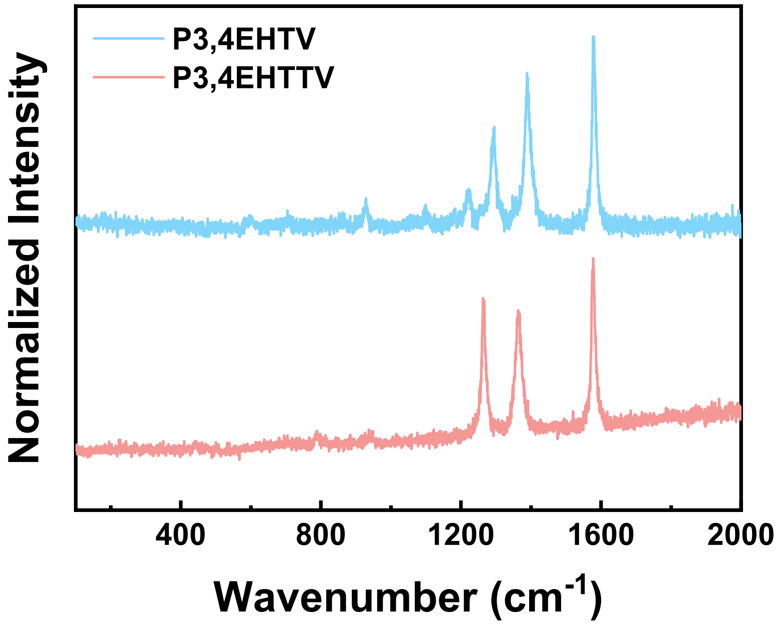


Fig. S15 The Raman spectrum of the pristine PTVs thin films.

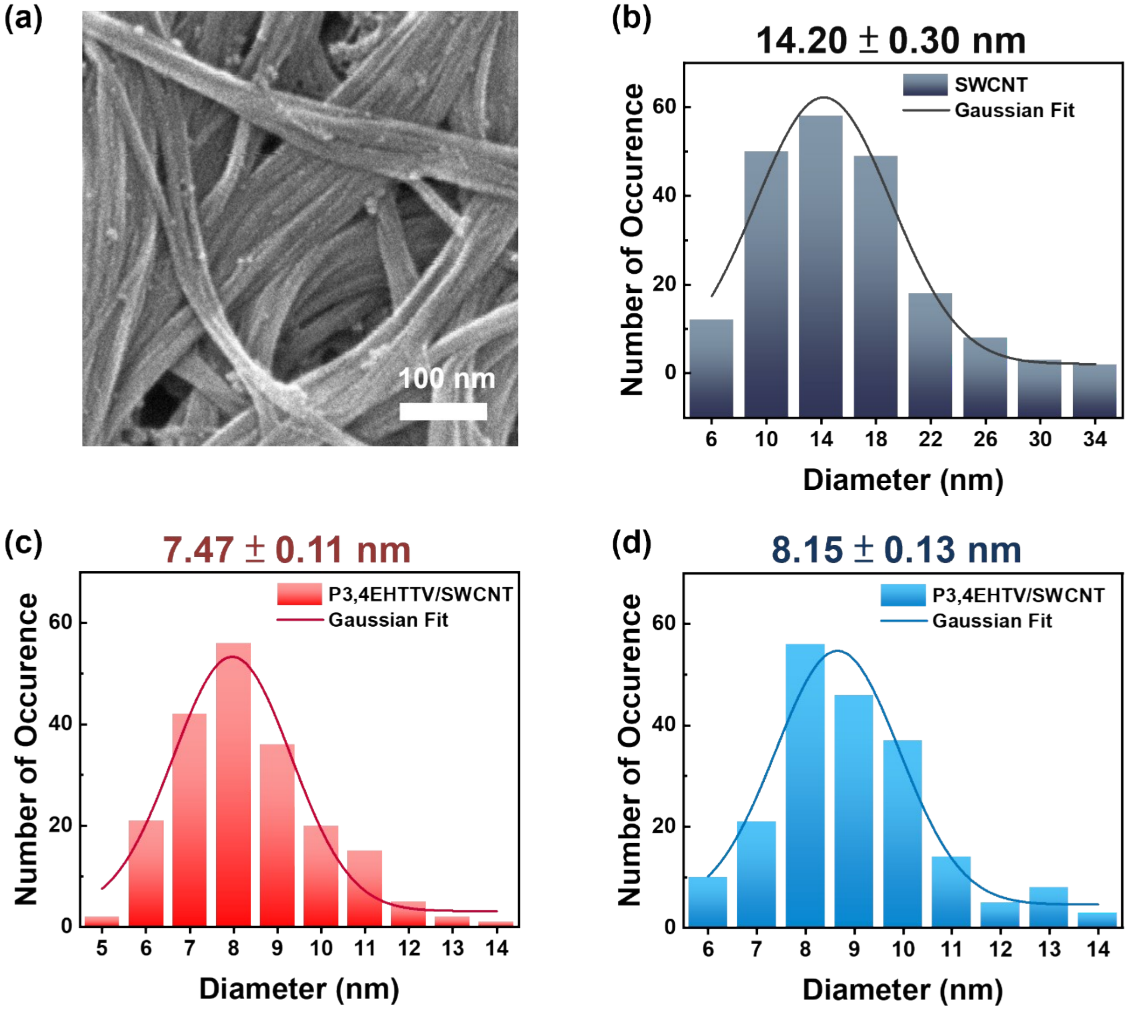


Fig. S16 (a) The SEM image of the pristine SWCNT thin films. The statistics of the Gaussian distribution of the 200 bundle sizes of (b) SWCNT, (c) P3,4EHTTV/SWCNT, and (d) P3,4EHTV/SWCNT.

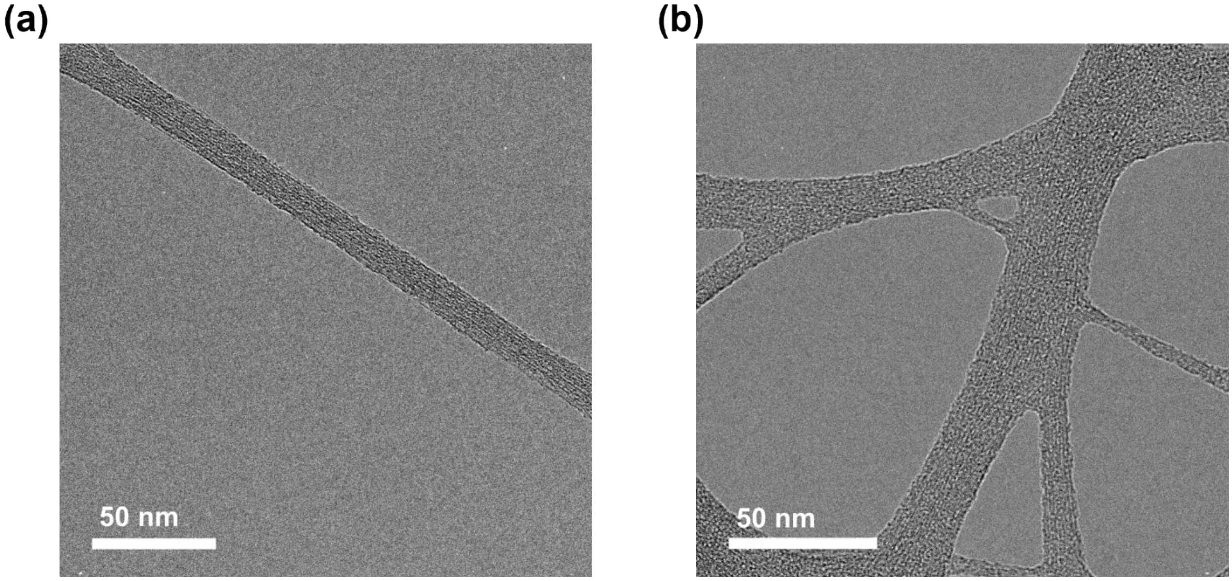


Fig. S17 The TEM images of the PTV/SWCNT thin films of (a) P3,4EHTTV/SWCNT under 100 kX amplification and (b) P3,4EHTV/SWCNT under 120 kX amplification.

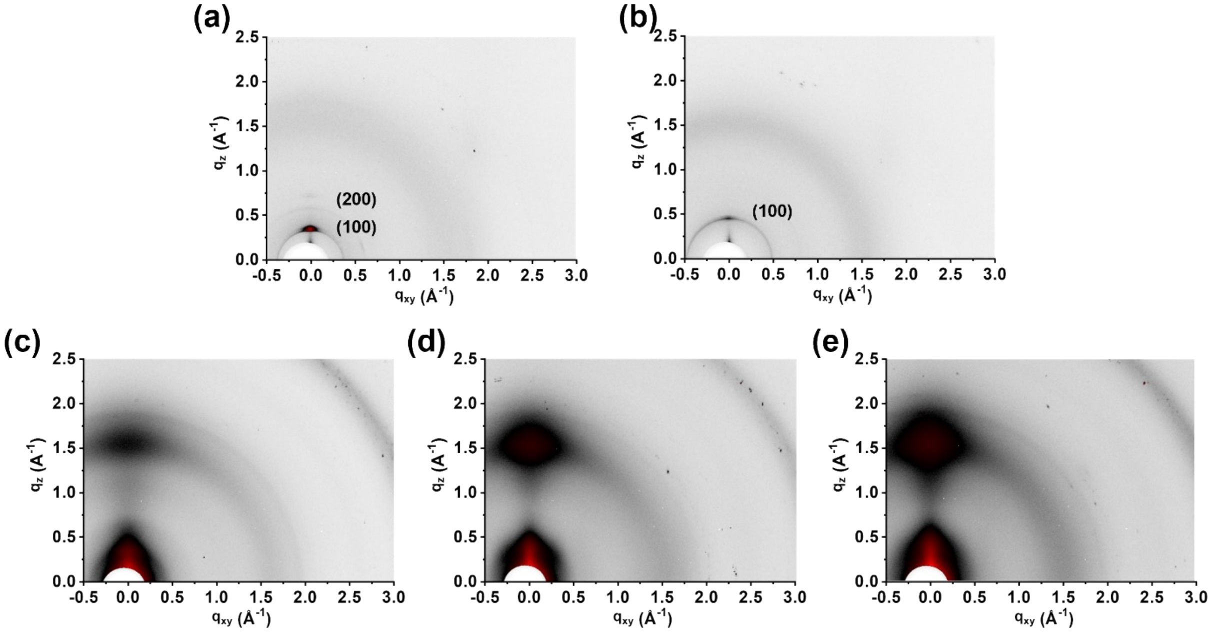


Fig. S18 The 2-D GIWAXS images of the pristine (a) P3,4EHTTV, (b) P3,4EHTV, (c) SWCNT, (d) P3,4EHTTV/SWCNT, and (e) P3,4EHTV/SWCNT.

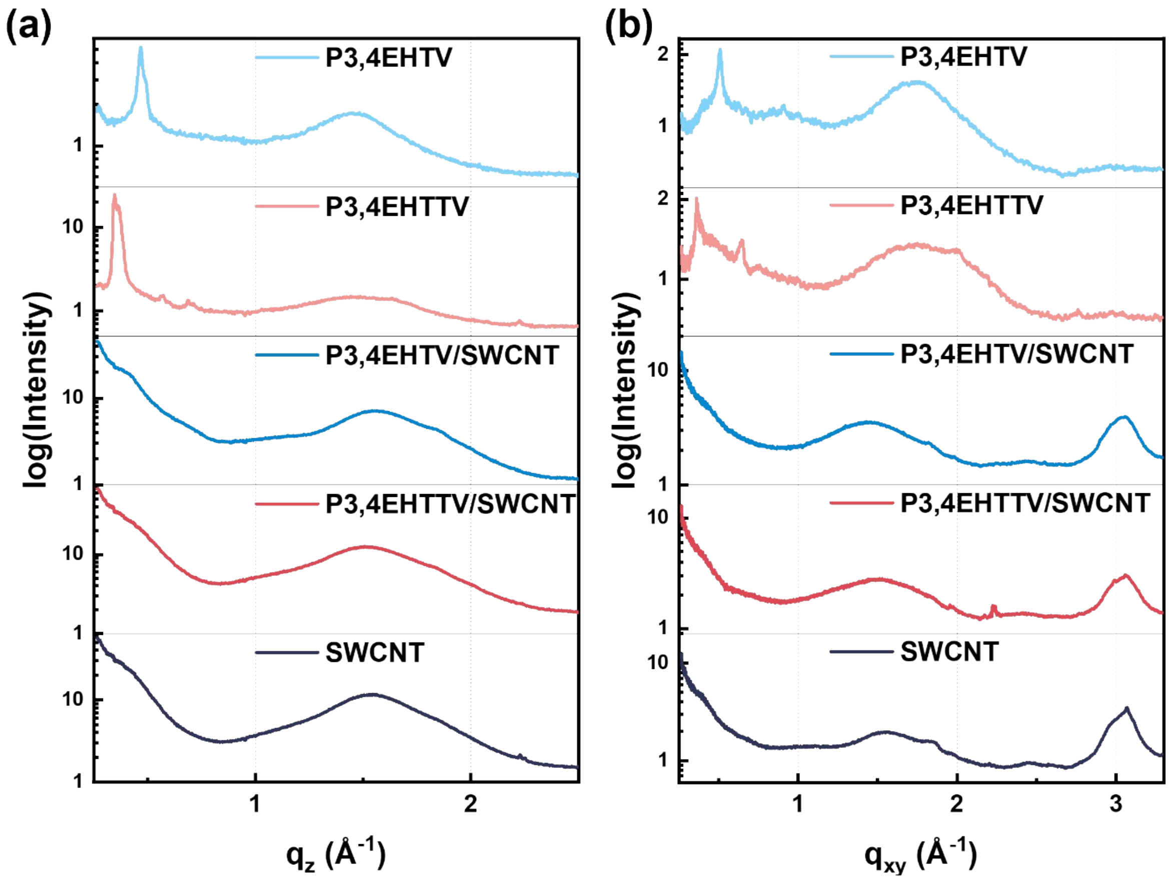


Fig. S19 The 1-D GIWAXS integration of the pristine PTVs, PTV/SWCNTs, and pure SWCNT (a) in the out-of-plane direction and (b) in the in-plane direction, respectively.

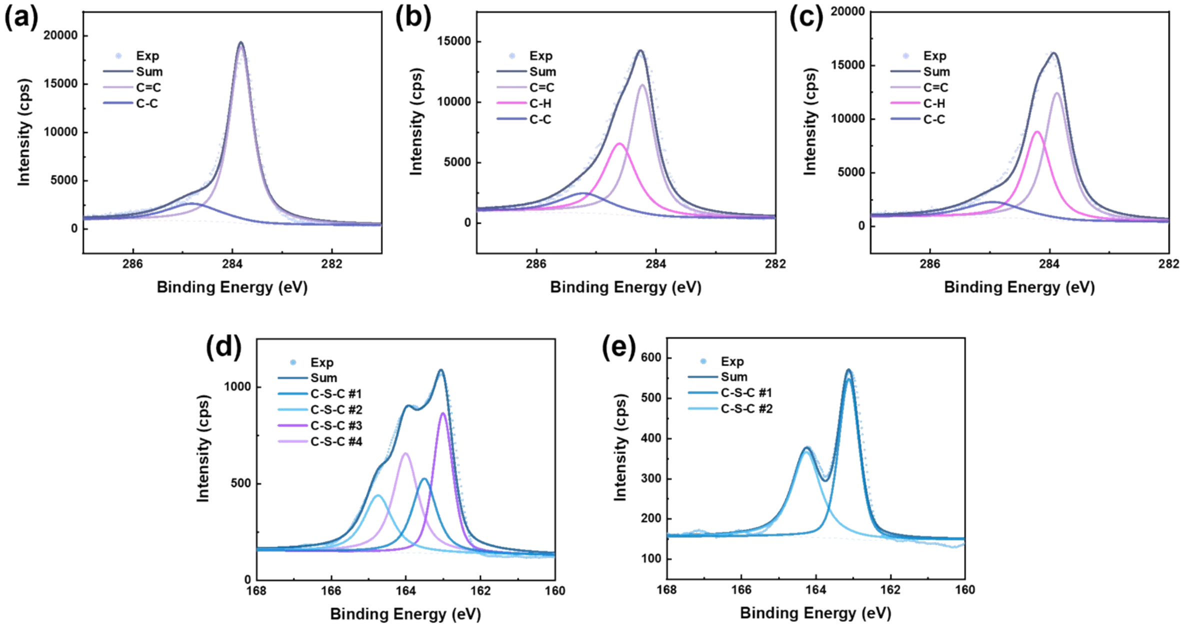


Fig. S20 The signal deconvolution of the XPS spectra of the C1s (first row) and the S2p (second row), generated from (a) the pristine SWCNT, (b, d) the P3,4EHTTV/SWCNT nanocomposite, and (c, e) the P3,4EHTV/SWCNT nanocomposite.

Here, the C–S–C bonds #1 and #2 are attributed to the sulfur atoms on the thienyl backbones, and the C–S–C bonds #3 and #4 bonds are attributed to the sulfur atoms on the alkylthio side chains of the P3,4EHTTV/SWCNT sample.

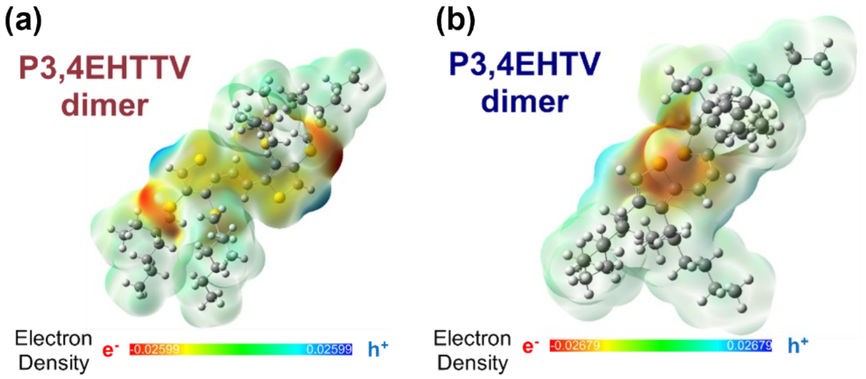


Fig. S21 DFT calculation using the self-consistent field (SCF) methods for (a) the P3,4EHTTV dimer, and (b) the P3,4EHTV dimer. Herein, the ethylhexylthio side chains are applied for stimulation of P3,4EHTTV dimer, and the ethylhexyl side chains are applied for stimulation of P3,4EHTV dimer.

Table S1 Thermoelectric properties of the PT/SWCNT nanocomposites summarized from reported research.

Nanocomposite	Casting method	Post-treatment	σ (S cm^{-1})	S (μV K^{-1})	PF (μW m^{-1} K^{-2})	Ref.
P3HT/SWCNT	Drop-casting	-	275	32	28	5
P3HT/SWCNT	Drop-casting	$FeCl_3$ doping	1130	29	95	5
P3HT/SWCNT	Bar-coating	-	141	56.1	44	6
P3HT/SWCNT	Bar-coating	$FeCl_3$ doping (immersion)	638	40.0	103	6
P3HT/SWCNT	Bar-coating	$FeCl_3$ doping (spin)	2760	31.1	267	6
rrP3HT/SWCNT	Drop-casting	-	383	32.7	41.7	7
rrP3HT/SWCNT	Bar-coating	-	524	40.3	86.6	7
P3HT/SWCNT	Drop-casting	$Fe(TFSI)_3$	579	29.1	49.0	8
rrP3HT/SWCNT	Mold	-	170	47	37	9
rrP3HT/SWCNT	Mold	I_2 doping	1722	29	148	9
raP3HT/SWCNT	Mold	I_2 doping	85	19	3	9
P3HT/SWCNT	Mold	-	131	38.7	19.6	10
P3HT/SWCNT	Drop-casting	$HClO_4$	118	44.3	23.2	11
P3HT/SWCNT	Drop-casting	-	219	54.5	65	12
PMEET/SWCNT	Drop-casting	-	699	41.6	121	12
PHEX/SWCNT	Drop-casting	Thermal cleavage of terminal groups	79	44.8	15.8	13
PTEG/SWCNT	Drop-casting	Thermal cleavage of terminal groups	118	38.8	28.8	13
P3HT/CNTF	Spin-coating	LiTFSI/TBP doping	130	91.9	110	14
P3HT/SWCNT	Drop-casting	-	506	62	194.5	15
P3HT/SWCNT	Spin-coating	-	397	68.1	172.2	4
P3EHT/SWCNT	Spin-coating	-	353	69.5	170.3	4
P3EHTT/SWCNT	Spin-coating	-	487	65.2	202.7	4
P3HDTT/SWCNT	Spin-coating	-	746	68.0	307.7	4

rrP3DDT/ sc-SWCNT	Rotary evaporation	-	2260	23	120	[16]
P3(TEG)T/ SWCNT	Drop-casting	-	1368	39.6	215	[17]
P3,4EHTV/ SWCNT	Spin-coating	-	513.8	53.5	158.4	This work
P3,4EHTTV/ SWCNT	Spin-coating	-	920.7	61.5	363.7	This work

Table S2 Molecular weight (M_n), polydispersity index (*PDI*), thermal decomposition temperature (T_d), melting temperature (T_m), onset absorption wavelength (λ_{onset}), energy level (E_g)[a], HOMO, and LUMO of the studied PTVs.

Polymer	M_n (kDa)	*PDI*	$T_d^{5\%}$ (°C)	T_m (°C)	λ_{onset}^{soln}(nm)	λ_{onset}^{film}(nm)	E_g^{film} (eV)
P3,4EHTV	21,800	1.54	384	182	740	786	1.58
P3,4EHTTV	36,300	2.33	326	T_{m1} = 138, T_{m2} =178	724	791	1.57

[a] $E_g = 1240/\lambda_{onset}$

Table S3 Maximum transition wavelength (λ) of the studied PTVs and PTV/SWCNT nanocomposites.

Pristine polymer	λ_{soln}^{0-1}(nm)	λ_{film}^{0-1}(nm)	λ_{soln}^{0-0}(nm)	λ_{film}^{0-0}(nm)	Nanocomposite	λ_{soln}^{0-1}(nm)	λ_{film}^{0-1}(nm)	λ_{soln}^{0-0}(nm)	λ_{film}^{0-0}(nm)
P3,4EHTV	613	628	656	669	P3,4EHTV/SWCNT	653	654	705	690
P3,4EHTTV	601	614	649	665	P3,4EHTTV/SWCNT	653	651	699	694

Table S4 Wavenumber of characteristic peaks of the studied pristine PTVs thin films.

Pristine polymer	Peak 1 (cm^{-1})	Peak 2 (cm^{-1})	Peak 3 (cm^{-1})
P3,4EHTV	1293.2	1388.4	1577.4
P3,4EHTTV	1262.9	1363.1	1577.4

Peak 1: The thiophene ring stretching with some contribution from in-plane C–H bending.[18, 19]

Peak 2: The peaks of stretching C_α–C_β bonds at α–β positions of the thiophene ring.[19, 20]

Peak 3: The peaks of the stretching vinyl C=C bonds at α–β positions with respect to the S atoms of the thiophene rings.[19, 21]

Table S5 Wavenumber of characteristic peaks of the studied SWCNT and PTV/SWCNT nanocomposite thin films.

Nanocomposite	G^+ band (cm^{-1})	G^+ band shift (cm^{-1})
SWCNT	1593.5	-
P3,4EHTV/SWCNT	1593.9	0.4
P3,4EHTTV/SWCNT	1594.9	1.5

Table S6 GIWAXS measurement of the (100) peak positions in the q_z values with the maximum intensities. The full width at half maximum (FWHM) are applied to calculate the coherence lengths (CL) in the out of plane direction of (100) plane of the studied pristine PTVs thin films.

Pristine polymer	q_z (Å^{-1})	FWHM(Å^{-1})	CL(nm)
P3,4EHTV	0.47	0.0415317	15.13
P3,4EHTTV	0.35	0.0304698	20.62

Table S7 Deconvolution of XPS analysis of C1s of the SWCNT and the polymer/SWCNT nanocomposites thin films.

Sample	Bond	Binding energy (eV)	Peak area	FWHM (eV)
SWCNT	C=C	283.82	14960	0.56
	C–C	284.80	3447	1.31
P3,4EHTV/SWCNT	C=C	283.87	8743	0.50
	C–H	284.20	6364	0.53
	C–C	284.94	2441	1.14
P3,4EHTTV/SWCNT	C=C	284.22	8000	0.50
	C–H	284.60	5580	0.65
	C–C	285.20	2313	1.00

Table S8 Deconvolution of XPS analysis of S2p of the polymer/SWCNT nanocomposites thin films. The C–S–C bonds #1 and #2 are attributed to the sulfur atoms on the thienyl backbones, and the C–S–C bonds #3 and #4 bonds are attributed to the sulfur atoms on the alkylthio side chains of the P3,4EHTTV/SWCNT sample.

Sample	Bond	Binding energy (eV)	Peak area	FWHM (eV)
P3,4EHTV/SWCNT	C–S–C #1	163.11	321	0.58
	C–S–C #2	164.25	283	0.91
P3,4EHTTV/SWCNT	C–S–C #1	163.50	425	0.72
	C–S–C #2	164.74	395	0.89
	C–S–C #3	163.00	571	0.55
	C–S–C #4	164.00	606	0.78

Table S9 Energy levels of the studied PTV/SWCNT nanocomposite thin films.

Nanocomposite	WF (eV)	E_F (eV)	HOMO (eV)	E_F – HOMO (eV)
P3,4EHTV/SWCNT	4.31	-4.31	-4.75	0.44
P3,4EHTTV/SWCNT	4.15	-4.15	-4.67	0.52

Table S10 Hall effect measurement of the studied SWCNT and polymer/SWCNT nanocomposite thin films.

Nanocomposite	bulk concentration (cm^{-3})	mobility (10^{-2} cm^2 V^{-1} s^{-1})
SWCNT	2.53×10^{22}	41.28 ± 1.54
P3,4EHTV/SWCNT	7.96×10^{23}	0.69 ± 0.40
P3,4EHTTV/SWCNT	3.10×10^{23}	0.85 ± 0.13

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