

Supporting Information

Pseudo *in-situ* construction of high-performance thermoelectric composites with the dioxothiopyrone-based D–A polymer coating on SWCNTs

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Experimental Section

1. Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 400 and 300 MHz NMR spectrometers. The molecular mass was confirmed using an APEX II fourier transform ion cyclotron resonance mass spectrometer (FT-ICR-MS). Molecular weight was determined with by gel permeation chromatography (GPC) (Waters1515) using tetrahydrofuran as eluent and polystyrene as standards at 35 °C. Thermogravimetric analysis (TGA) was performed on a PerkinElmer TGA 8000 instrument at a heating rate of 20 °C min⁻¹ under a nitrogen flow of 20 mL min⁻¹. Melting point was measured using melting point apparatus (WRS-1B). The cyclic voltammetry (CV) was obtained using an electrochemical work-station (CHI 660E) in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) at a scan rate of 100 mV s⁻¹. A platinum wire, Ag/AgCl, and a platinum plate were used as the counter electrode, reference electrode, and working electrode, respectively. Fc/Fc⁺ was used as an internal standard. FT-IR spectra were collected using a spectrophotometer (Perkin-Elmer System 2000 FTIR) by 64 scans in the wavenumber range of 4000–400 cm⁻¹. Raman spectra were recorded within the wavenumber range of 500–2000 cm⁻¹ through a Raman spectrometer (Renishaw inVia plus) with an excitation wavelength of 514 nm. The UV–vis spectra were obtained by UV–vis spectrophotometer (UV-1800). X-ray photoelectron spectra (XPS) was performed on the Thermo Scientific Nexsa using 72 W monochromatic Al K α radiation. The 400 μm X-ray spot was used for SAXPS analysis. The base pressure in the analysis chamber was about 3×10^{-9} mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing. The morphologies of the polymer and composite films were observed by scanning electron microscopy (SEM) (HITACHI S-4800) and transmission electron microscopy (TEM) (HT7700). The Seebeck coefficients and electrical conductivities of the composite films were

measured using an MRS-3RT thin-film thermoelectric test system (Wuhan Joule Yacht Science & Technology Co., Ltd, China).

2. Chemicals

All commercially available reagents and solvents were used directly without further treatment unless specified otherwise. The SWCNT (diameter: < 3 nm, purity: > 85.0 wt%) was provided by Shenzhen Nanotech Port Co. Ltd, China. The key starting materials such as 2,5-bis(tributylstannyl)thiophene, 2-bromo-3-dodecylthiophene, 4-bromobenzaldehyde and acetone were purchased from Shanghai Aladdin Reagent Co. Ltd. *n*-Butyllithium (*n*-BuLi), *m*-chloroperbenzoic acid, tri-*n*-butyltin chloride (*n*-Bu₃SnCl), and tetrakis(triphenylphosphine)palladium (Pd(PPh₃)₄), were obtained from Sigma-Aldrich Co. LLC. Sodium hydroxide (NaOH), sodium hydrosulfide (NaHS), sodium bicarbonate (NaHCO₃), iodine (I₂), tetrahydrofuran (THF), glacial acetic acid (HAc), chloroform (CHCl₃), ethanol (EtOH), and dimethyl sulfoxide (DMSO), were purchased from Sinopharm Chemical Reagent Co., Ltd. It should be mentioned that tetrahydrofuran (THF) and toluene were respectively dried with metal sodium using benzophenone as the indicator before being used.

3. Synthesis

(*E,E*)-1,5-Di(4-bromophenyl)-1,4-pentadien-3-one (Compound 1). ^[1] 4-Bromobenzaldehyde (75 g, 0.41 mol) and acetone (9.67 g, 0.17 mol), were respectively, added into 270 mL pre-cooled ethanol in cold water. Keeping this temperature, 374 mL 10% NaOH aqueous solution was dropped into the mixture with stirring after the remaining solid dissolved completely. When addition was complete, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The obtained yellow solid by filtration was redispersed in 400 mL dichloromethane under stirring thoroughly. Subsequently, the yellow crystalline solid was collected by filtration and dried to give 45.8 g of compound **1** with the yield of 68.7%. m.p. 216.8~218.3°C; ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, *J* = 15.88 Hz, 2H), 7.55

(AA'BB', $J = 8.16$ Hz, 4H), 7.47 (AA'BB', $J = 8.12$ Hz, 4H), 7.04 (d, $J = 15.88$ Hz, 2H);
 ^{13}C NMR (100 MHz, CDCl_3): δ 186.37, 140.19, 131.74, 130.33, 127.81, 123.89,
122.96; HRMS (EI) calculated for $\text{C}_{17}\text{H}_{12}\text{Br}_2\text{O}$ $[\text{M}]^+$, 391.9234, found 391.9231.

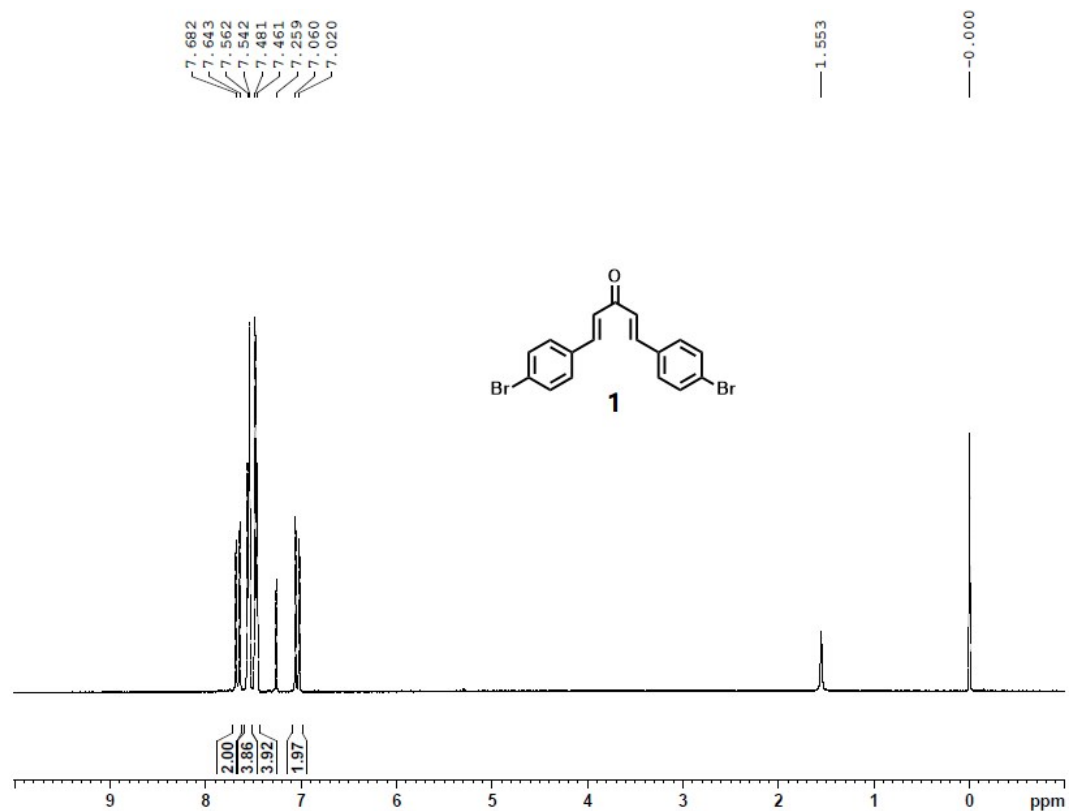


Fig. S1. The ^1H NMR (CDCl_3 , 400 MHz) spectrum of compound **1**.

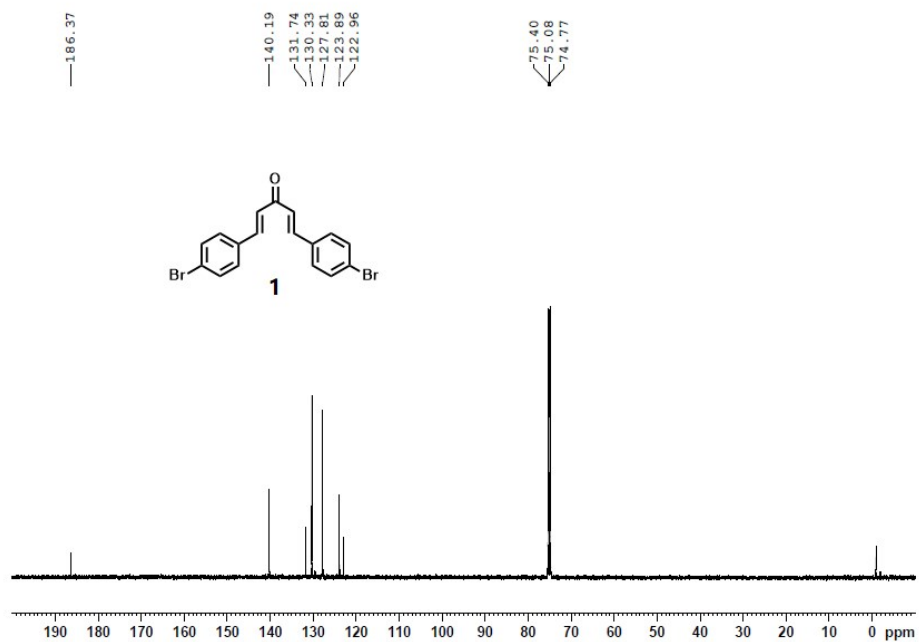


Fig. S2. The ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of compound 1.

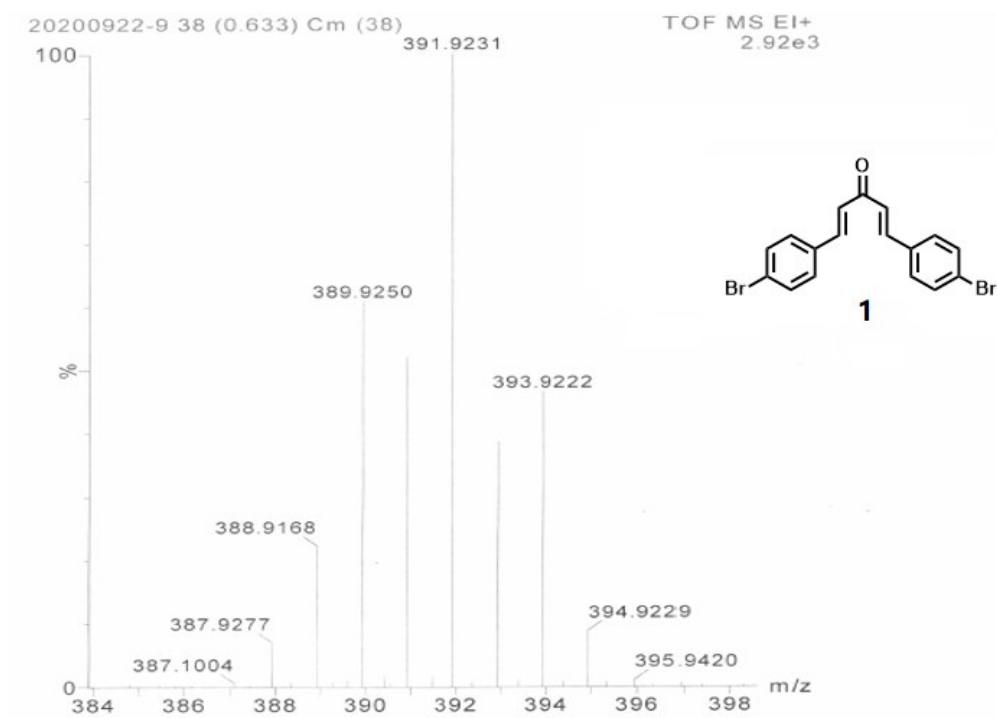


Fig. S3. The HRMS (EI) spectrum of compound 1.

[2,6-Di(4-bromophenyl)-2,3,5,6-tetrahydro-4H-thiopyran-4-one] (Compound 2).

A solution of NaHCO₃ (10.08 g, 0.12 mol) in 40 mL H₂O and a solution of NaHS (36 g, 0.63 mol) in 120 mL H₂O were respectively added into a solution of compound **1** (11.76 g, 0.03 mol) in mixed solvent of 120 mL THF and 60 mL EtOH. The resulting mixture was stirred for 2 hours at room temperature. The reaction mixture was poured into 200 mL water, and the products were extracted with CH₂Cl₂. The combined organic phases were dried over MgSO₄. The solvent was removed in vacuo to afford 14 g crude product as a mixture of *cis*- and *trans*-isomers, a small amount of which was purified by chromatography on silica gel eluted by petroleum/dichloromethane with volume ratio of 1/1 to respectively give the *cis*-isomer (white solid) and *trans*-isomer (white solid) used for structural characterizations, and the remaining part of which was used directly for the next step reaction without further purification. For *cis*-isomer: m.p. 104.2~105.3°C; ¹H NMR (400 MHz, CD₂Cl₂): δ 7.47 (AA'BB', *J* = 8.5 Hz, 4H), 7.24 (AA'BB', *J* = 8.4 Hz, 4H), 4.31 (dd, *J*₁ = 8.4 Hz, *J*₂ = 4.4 Hz, 2H), 3.10 (dd, *J*₁ = 15.2 Hz, *J*₂ = 8.4 Hz, 2H), 2.99 (dd, *J*₁ = 14.8 Hz, *J*₂ = 4.4 Hz); ¹³C NMR (100 MHz, CD₂Cl₂): δ 207.19, 139.56, 131.75, 129.28, 121.45, 48.15, 43.43; HRMS (EI) calculated for C₁₇H₁₄Br₂OS [M]⁺, 425.9112, found 425.9108. For *trans*-isomer: m.p. 158.2~159.9°C; ¹H NMR (400 MHz, CD₂Cl₂): δ 7.47 (AA'BB', *J* = 8.4 Hz, 4H), 7.24 (AA'BB', *J* = 8.4 Hz, 4H), 4.31 (dd, *J*₁ = 12.4 Hz, *J*₂ = 3.2 Hz, 2H), 2.97 (t, *J* = 13.2 Hz, 2H), 2.88 (dd, *J*₁ = 13.2 Hz, *J*₂ = 3.2 Hz); ¹³C NMR (100 MHz, CD₂Cl₂): δ 206.37, 138.61, 132.00, 129.00, 121.85, 47.76; HRMS (EI) calculated for C₁₇H₁₄Br₂OS [M]⁺, 425.9112, found 425.9123.

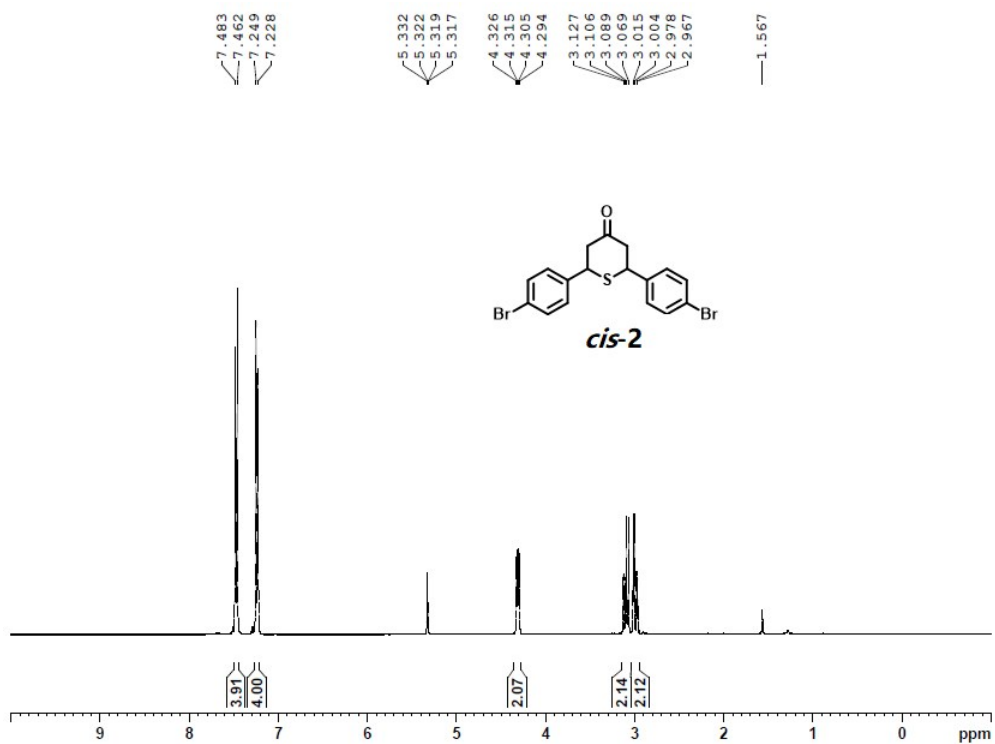


Fig. S4. The ¹H NMR (CDCl₃, 400 MHz) spectrum of compound *cis-2*.

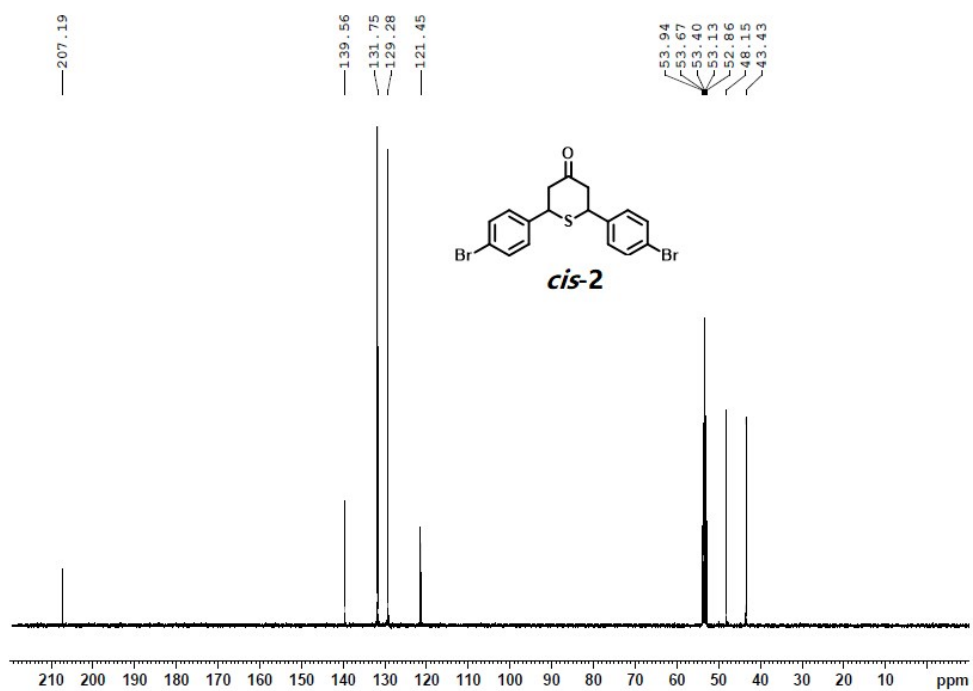


Fig. S5. The ¹³C NMR (CDCl₃, 100 MHz) spectrum of compound *cis-2*.

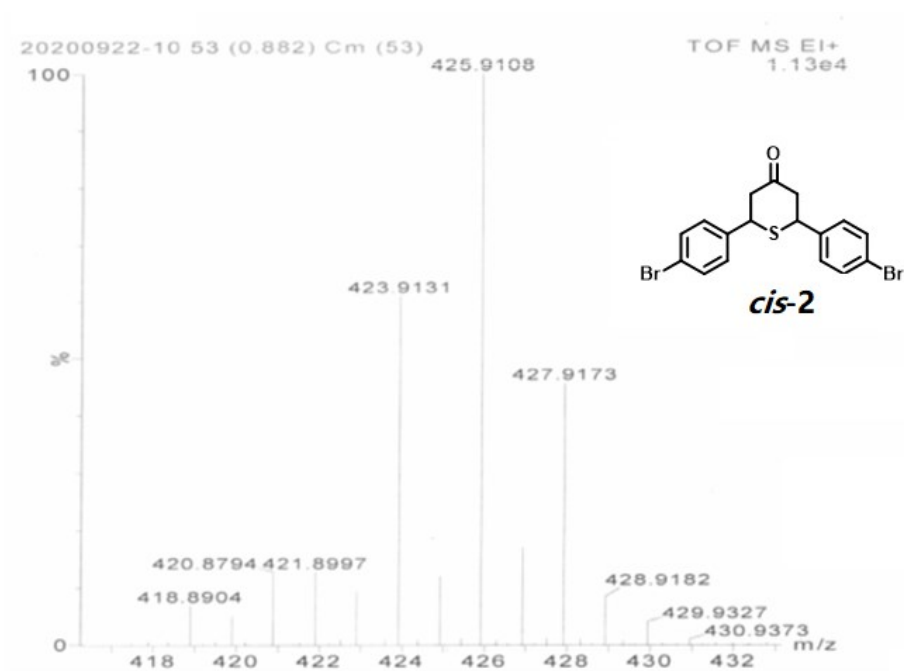


Fig. S6. The HRMS (EI) spectrum of compound *cis-2*.

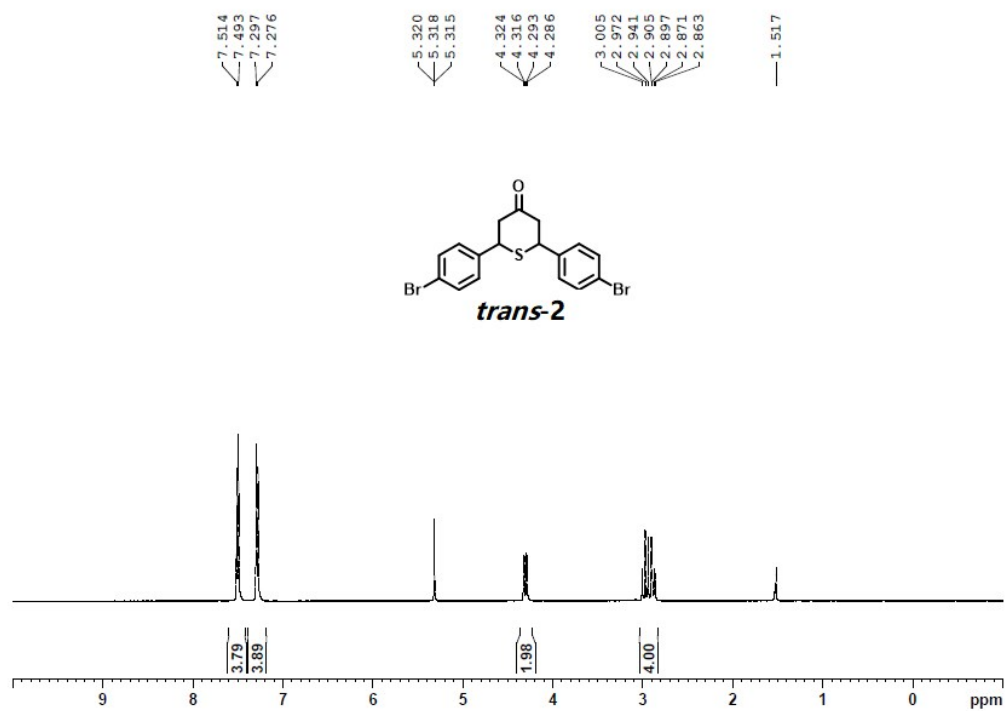


Fig. S7. The ^1H NMR (CDCl_3 , 400 MHz) spectrum of compound *trans-2*.

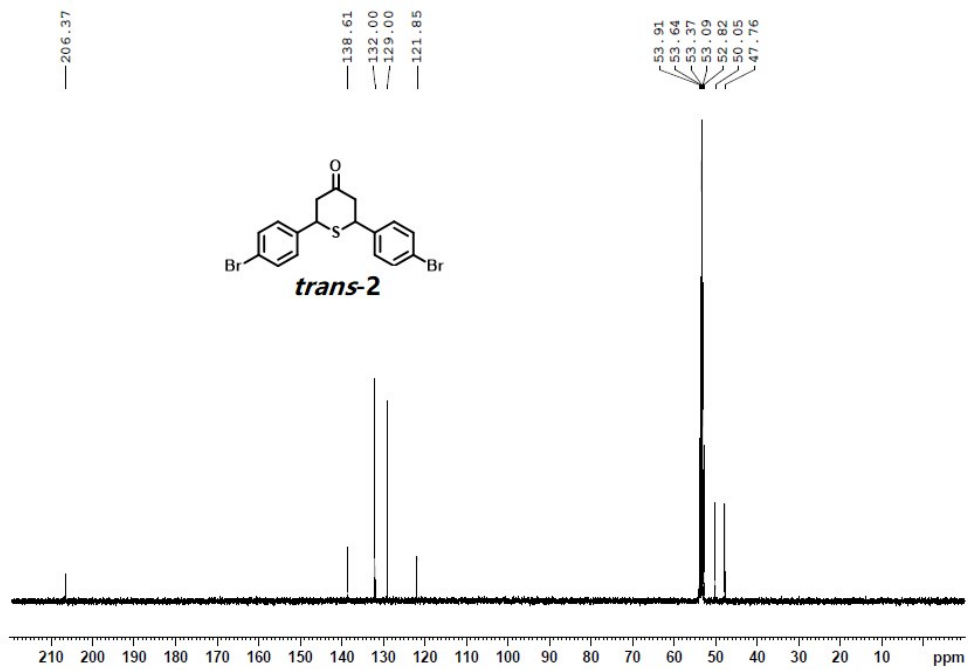


Fig. S8. The ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of compound *trans-2*.

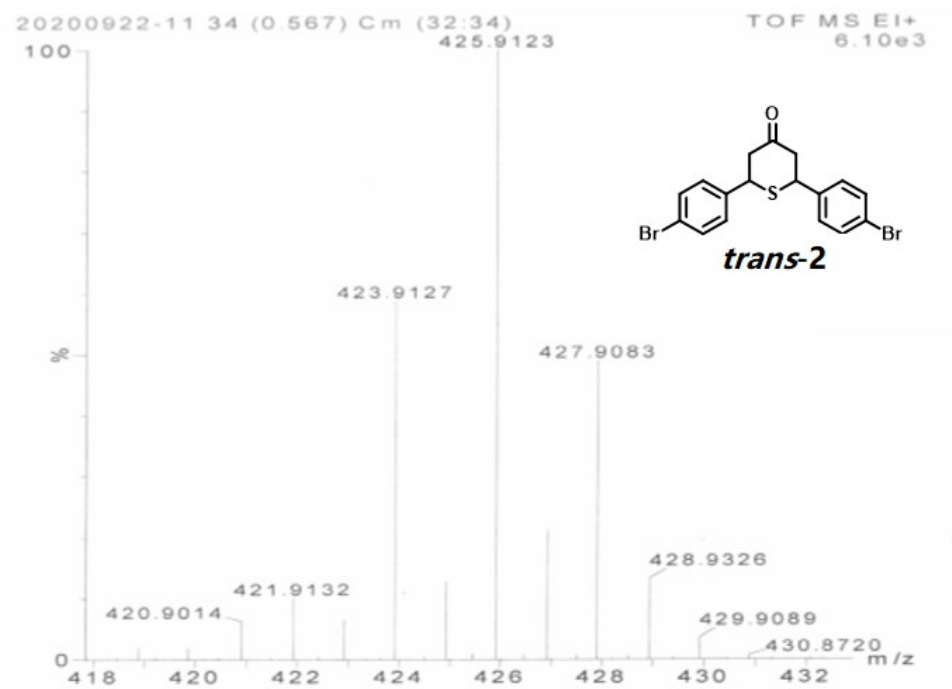


Fig. S9. The HRMS (EI) spectrum of compound *trans-2*.

[1,1-Dioxo-2,6-di(4-bromophenyl)tetrahydro-4H-thiopyran-4-one] (Compound 3). *m*-Chloroperoxybenzoic acid (MCPBA) (20.64 g, 0.12 mol) was added in small portions over 30 min to a solution of compound **2** (as a mixture of isomers) in 80 mL of CH₂Cl₂. After addition was completed, the reaction mixture was stirred 1 hour at room temperature, and then filtrated to remove the excess oxidant. The solid was redissolved in CH₂Cl₂, and washed several times with a dilute aqueous NaOH solution followed by brine. The organic filtrate was dried over MgSO₄ and concentrated, affording 18.5 g mixture of the two isomers of the sulfone as crude product, of which the major part was used directly for the next reaction without further purification, and the other was purified by chromatography on silica gel eluted by petroleum/dichloromethane with volume ratio of 1/2 to respectively give the *cis*-isomer (white solid) and *trans*-isomer (white solid) used for identification and characterization. For *cis*-isomer: m.p. 221.7~224.9°C; ¹H NMR (400 MHz, CDCl₃): δ 7.56 (AA'BB', *J* = 8.4 Hz, 4H), 7.26 (AA'BB', *J* = 8.4 Hz, 4H), 4.45 (dd, *J*₁ = 8.4 Hz, *J*₂ = 5.1 Hz, 2H), 3.48 (dd, *J*₁ = 15.6 Hz, *J*₂ = 8.4 Hz, 2H), 3.36 (dd, *J*₁ = 15.8 Hz, *J*₂ = 5.0 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 202.80, 132.37, 130.97, 128.94, 124.37, 61.01, 44.43; MS (EI) [M-SO₂]⁺ = 392. For *trans*-isomer: m.p. 286.6~288.5°C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (AA'BB', *J* = 8.4 Hz, 4H), 7.31 (AA'BB', *J* = 8.4 Hz, 4H), 4.50 (dd, *J*₁ = 14.0 Hz, *J*₂ = 2.8 Hz, 2H), 3.68 (t, *J* = 14.4 Hz, 2H), 2.96 (dd, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 201.05, 132.37, 131.05, 127.18, 124.55, 64.13, 45.56; MS (EI) [M-SO₂]⁺ = 392.

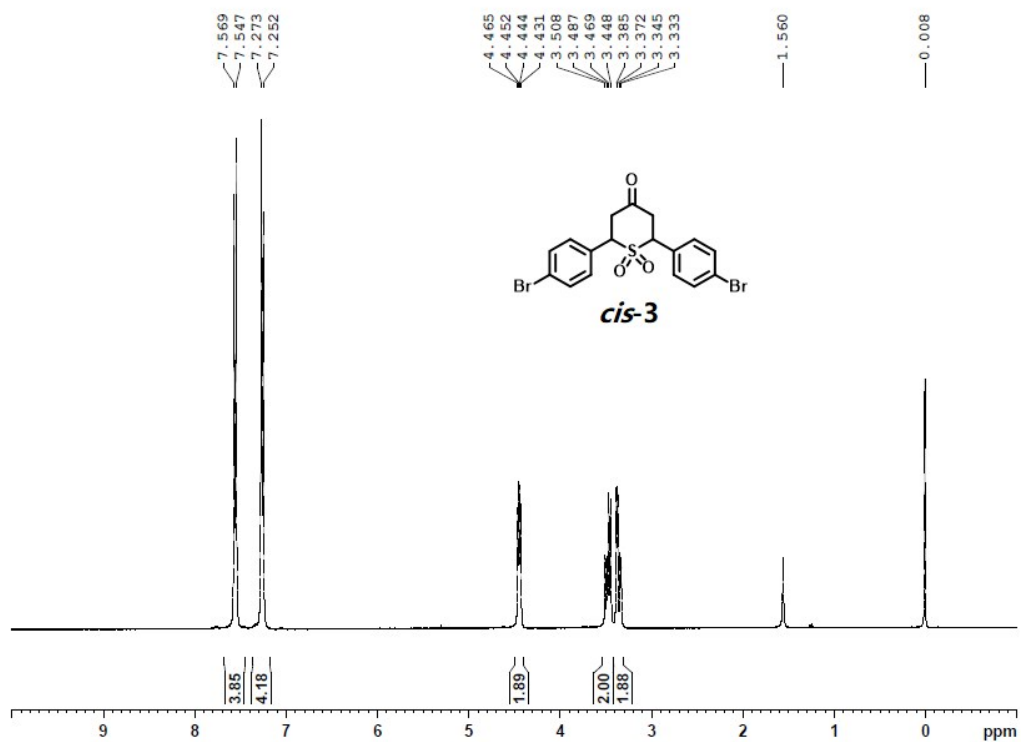


Fig. S10. The ^1H NMR (CDCl_3 , 400 MHz) spectrum of compound *cis-3*.

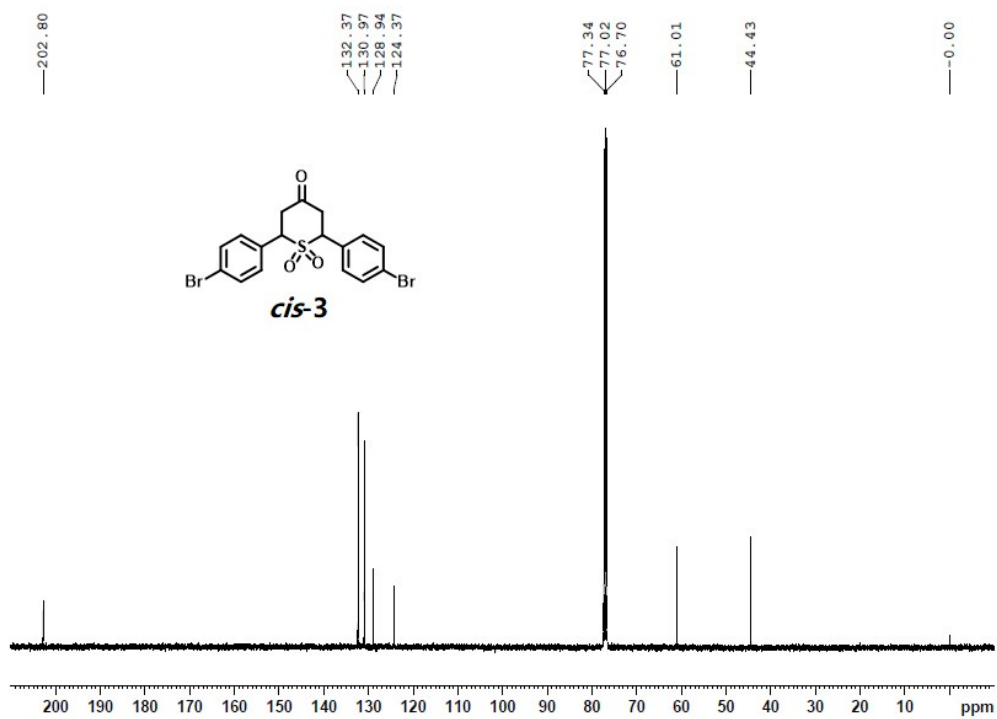


Fig. S11. The ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of compound *cis-3*.

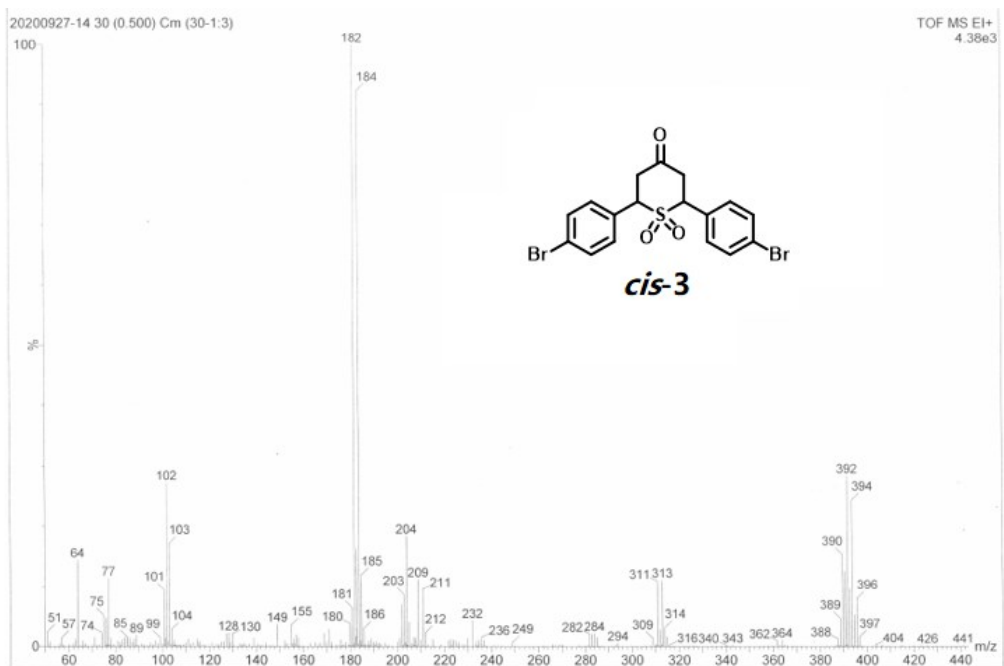


Fig. S12. The MS (EI) spectrum of compound *cis-3*.

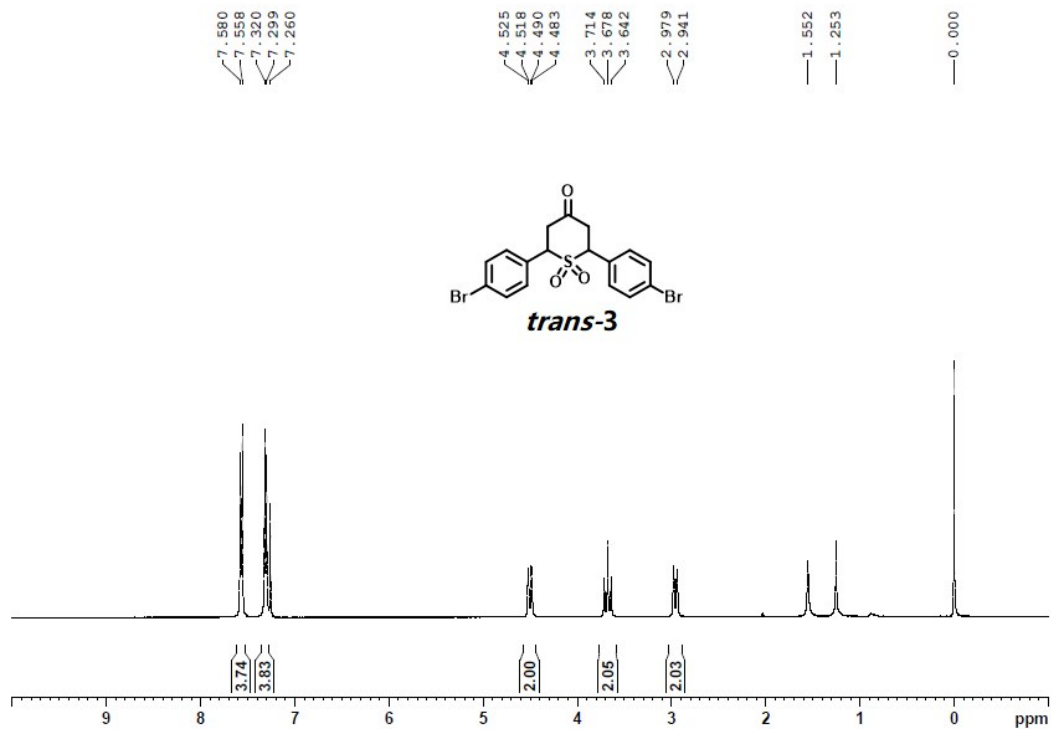


Fig. S13. The ¹H NMR (CDCl₃, 400 MHz) spectrum of compound *trans-3*.

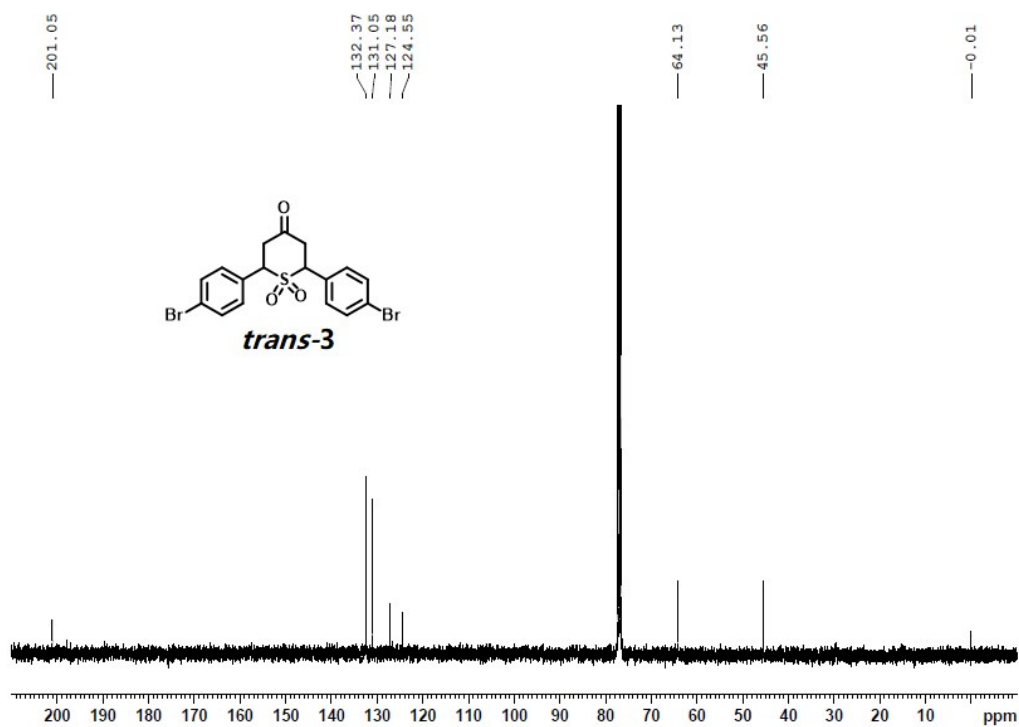


Fig. S14. The ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of compound *trans-3*.

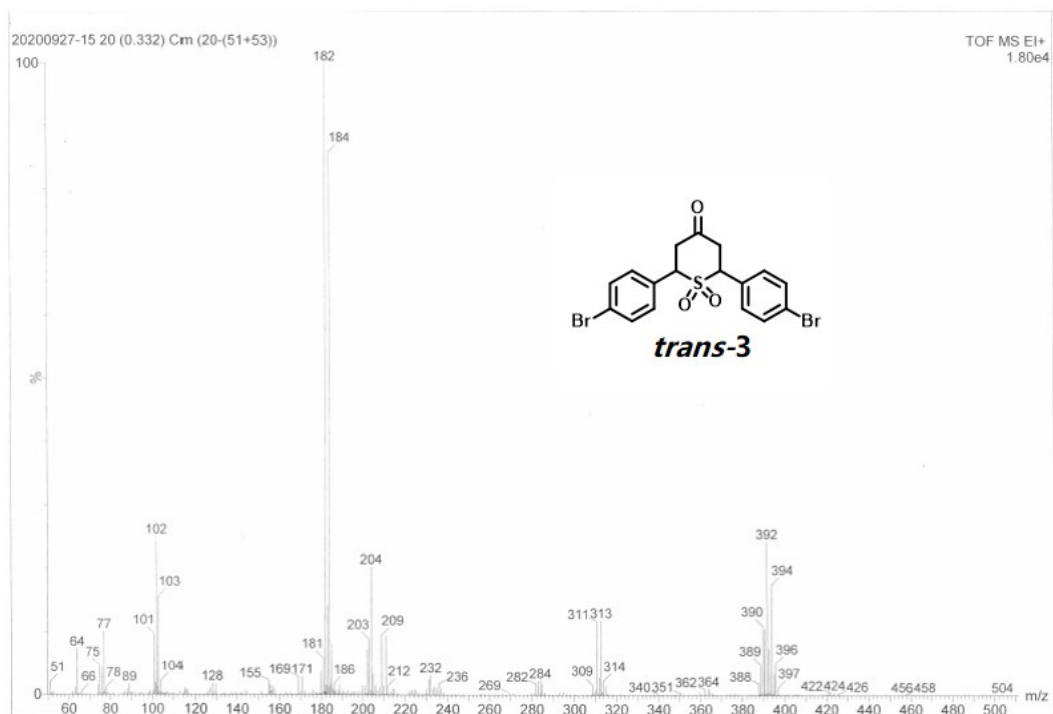


Fig. S15. The MS (EI) spectrum of compound *trans-3*.

1,1-Dioxo-2,6-di(4-bromophenyl)thiopyran-4-one (Compound 4). With magnetic stirring, 8 g of iodine and 1 mL of concentrated H₂SO₄ were respectively added into a solution of compound **3** as a mixture of *cis*- and *trans*-isomers (20 g, 43.7 mmol) in 60 mL of DMSO. The reaction mixture was cooled to room temperature and diluted with 200 ml deionized water after being heated at 100°C for 2 hrs. The product was extracted with CH₂Cl₂, and the combined organic phase was dried over MgSO₄. The residue was purified by column chromatography with a volume ratio of 1:1 of petroleum/CH₂Cl₂ as eluent. The orange-red solid of 18.3 g compound **4** was obtained in 92% yield. m.p. 196.3~196.9°C; ¹HNMR (300 MHz, CDCl₃) δ 7.58–7.78 (m, 8H), 6.68 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 178.86, 152.56, 132.67, 130.31, 127.41, 127.29, 127.11; HRMS (EI) calculated for C₁₇H₁₀Br₂O₃S [M]⁺, 453.8697, found 453.8690.

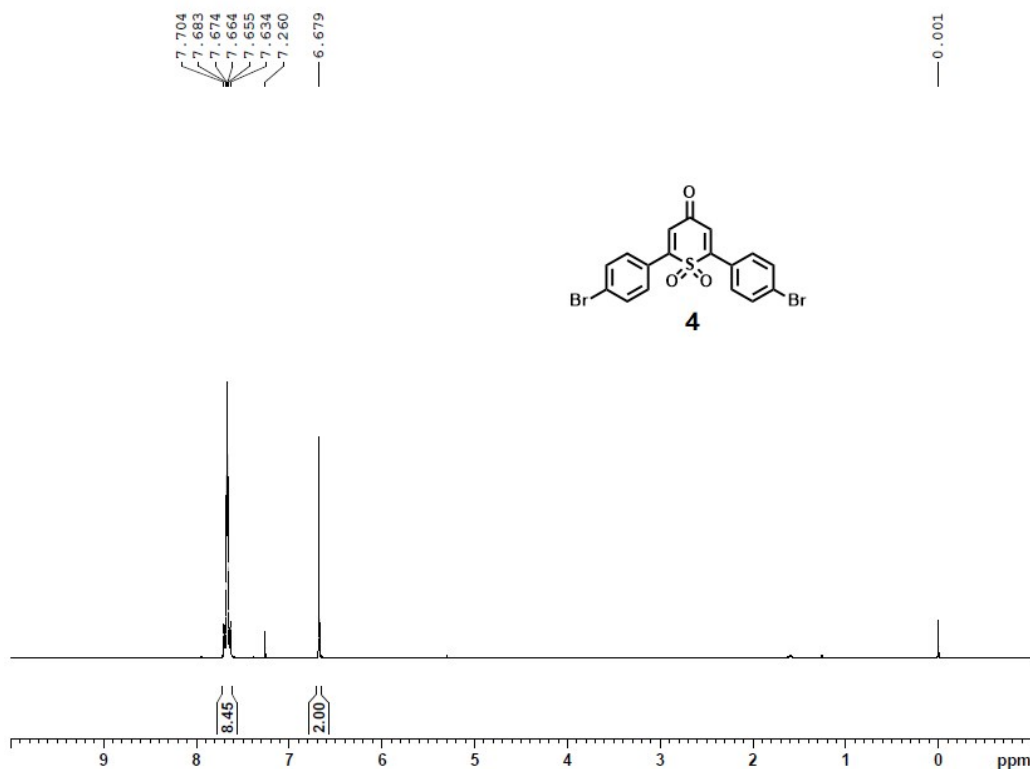


Fig. S16. The ¹H NMR (CDCl₃, 300 MHz) spectrum of compound **4**.

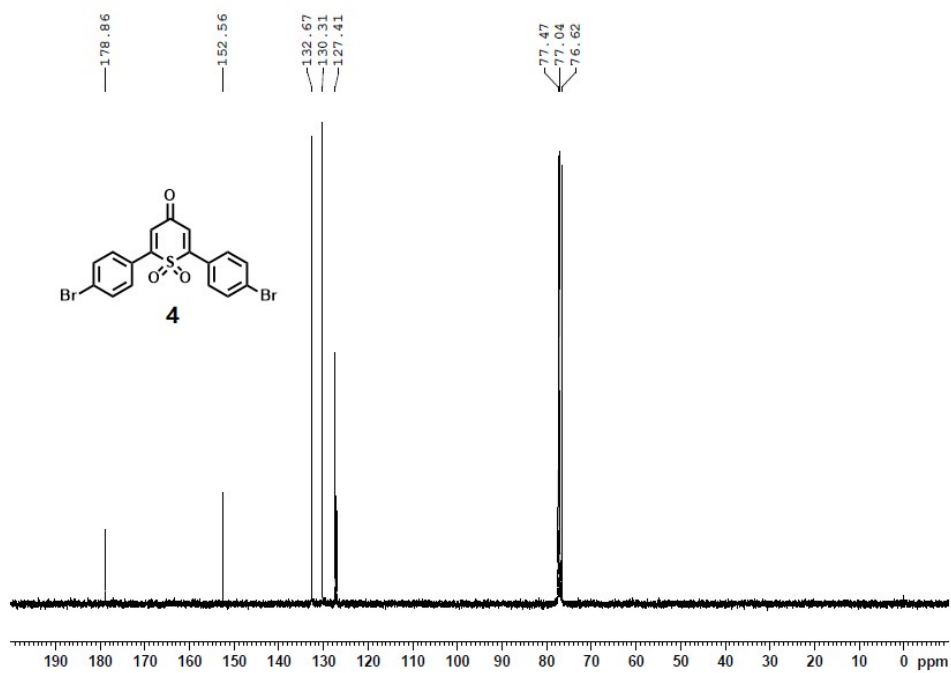


Fig. S17. The ^{13}C NMR (CDCl_3 , 75 MHz) spectrum of compound 4.

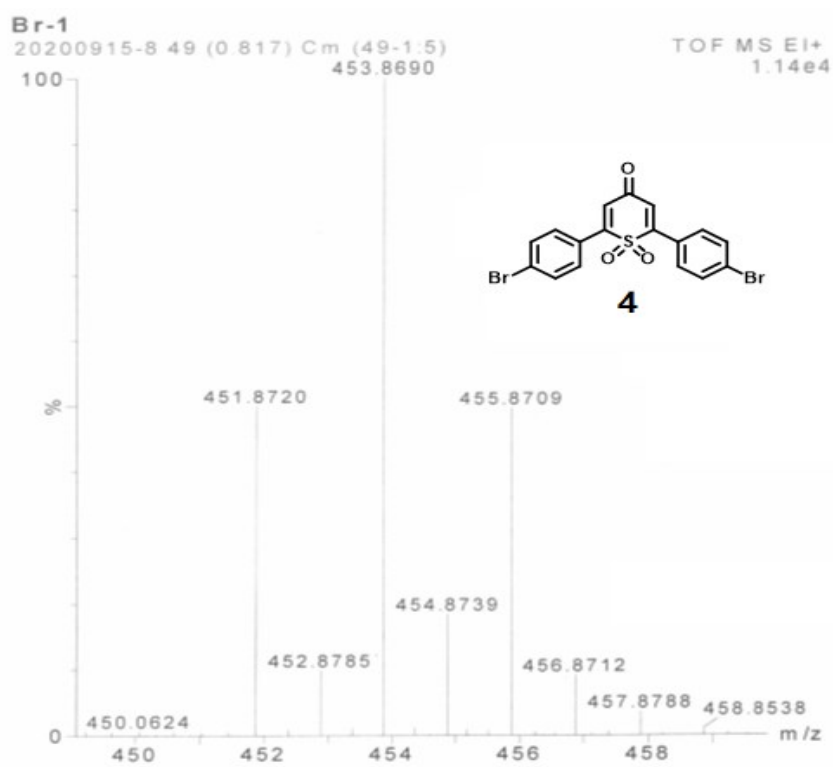


Fig. S18. The HRMS (EI) spectrum of compound 4.

3,3''-Didodecyl-2,2':5',2''-terthiophene (Compound 5). After a 50-mL Schlenk tube charged with Pd(PPh₃)₄ (23.1 mg, 0.02 mmol) was evacuated and backfilled with argon for three times, 2,5-bis(tributylstannyl)thiophene (2.0 mmol), 2-bromo-3-dodecylthiophene (1.66 g, 5.0 mmol) and anhydrous toluene (10 mL) were respectively added under argon. The reaction mixture was stirred at 100 °C for 24 hrs. The resulting brown suspension was cooled to room temperature and filtered. The filtrate was concentrated and the residue was purified by silica gel chromatography with petroleum as eluent to provide the compound **5** (0.75 g, 64%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.18 (d, *J* = 5.20 Hz, 2H), 7.06 (s, 2H), 6.95 (d, *J* = 5.2 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 4H), 1.71–1.60 (m, 4H), 1.43–1.20 (m, 36H), 0.90 (t, *J* = 6.8 Hz, 6H).

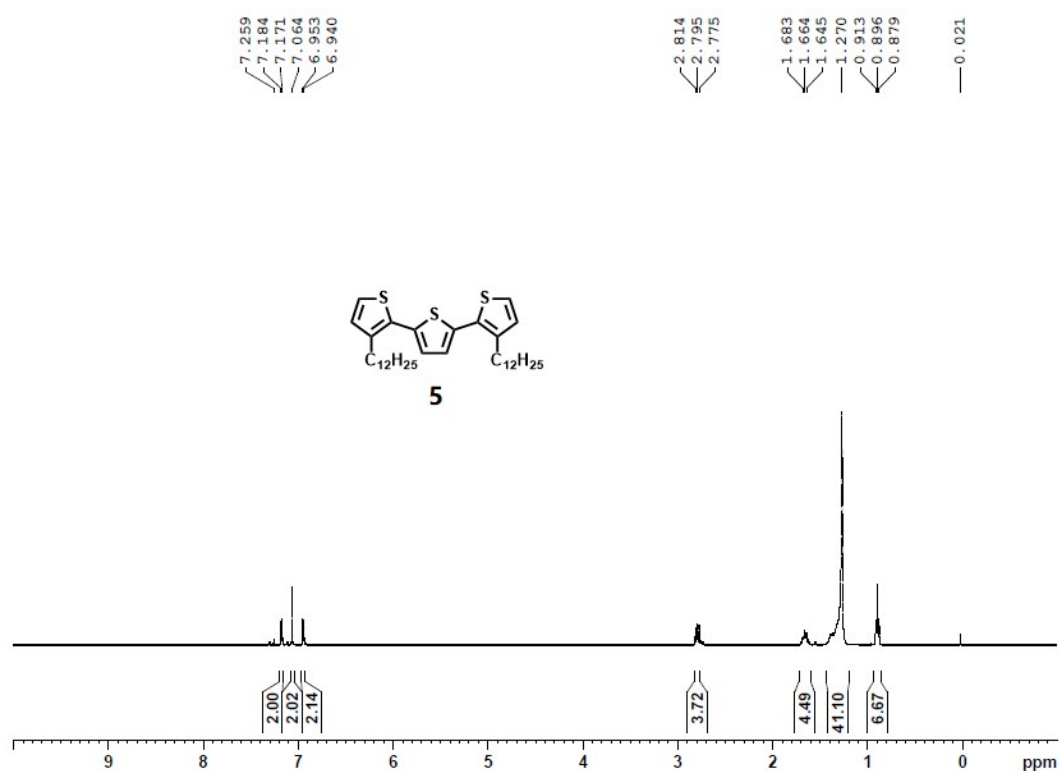


Fig. S19. The ¹H NMR (CDCl₃, 400 MHz) spectrum of compound **5**.

5,5''-Dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene (Compound 6).^[2] Under dark conditions, NBS (0.98 g, 5.48 mmol) was added in portions to a solution of compound **5** (1.60 g, 2.74 mmol) in a mixed solvent of CHCl₃/HAc with volume ratio

of 1/1 and stirred for 12 h at room temperature. After the reaction completion, the reaction mixture was poured into 100 mL of water and extracted several times with chloroform. The combined organic phase was dried over MgSO₄ and concentrated to give the compound **6** (1.98, 98%) as an oil, which was to be used directly in the next reaction without further purification. ¹H NMR (400 MHz, CDCl₃): δ 6.94 (s, 2H), 6.86 (s, 2H), 2.68 (t, *J* = 8.0 Hz, 4H), 1.65–1.50 (m, 4H), 1.38–1.19 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 6H).

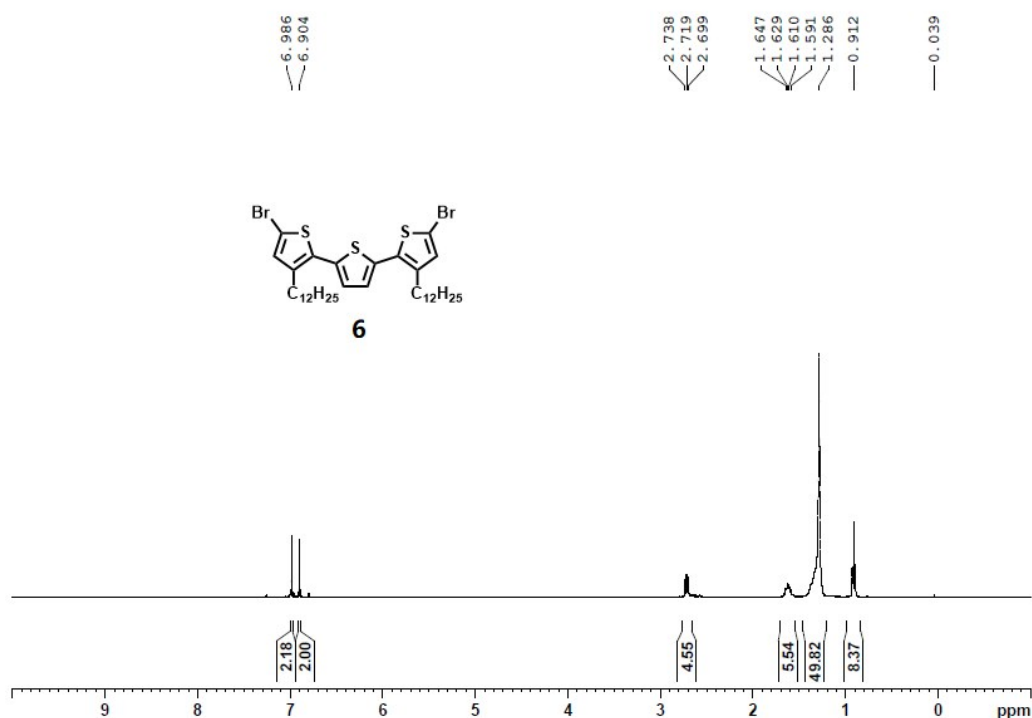


Fig. S20. The ¹H NMR (CDCl₃, 400 MHz) spectrum of compound **6**.

5,5''-Bis(tributylstannyl)-3,3''-didodecyl-2,2':5',2''-terthiophene (Compound 7).^[3] Under N₂ atmosphere, a 2.5 M solution of butyllithium in hexane (2.4 mL, 6.0 mmol) was added dropwise into a solution of compound **6** (1.48 g, 2 mmol) in 60 mL dried THF with vigorous stirring at -78 °C. Maintaining this temperature, a solution of tributylchlorostannane (1.62 mL, 6.0 mmol) in 10 mL dried THF was added after the mixture was continually stirred for 30 min. The resulting mixture was allowed to warm up to room temperature and stirred for 1 hr. Then, the reaction was quenched with an aqueous KF solution and then extracted with AcOEt. The combined organic phase was

dried over MgSO_4 and evaporated under reduced pressure. The crude product of 2.5 g was used for the next reaction without further purification. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.04 (s, 2H), 6.96 (s, 2H), 2.81 (t, $J = 7.6$ Hz, 4H), 1.72–1.65 (m, 4H), 1.48–1.20 (m, 24H), 0.76 (t, $J = 7.6$ Hz, 18H).

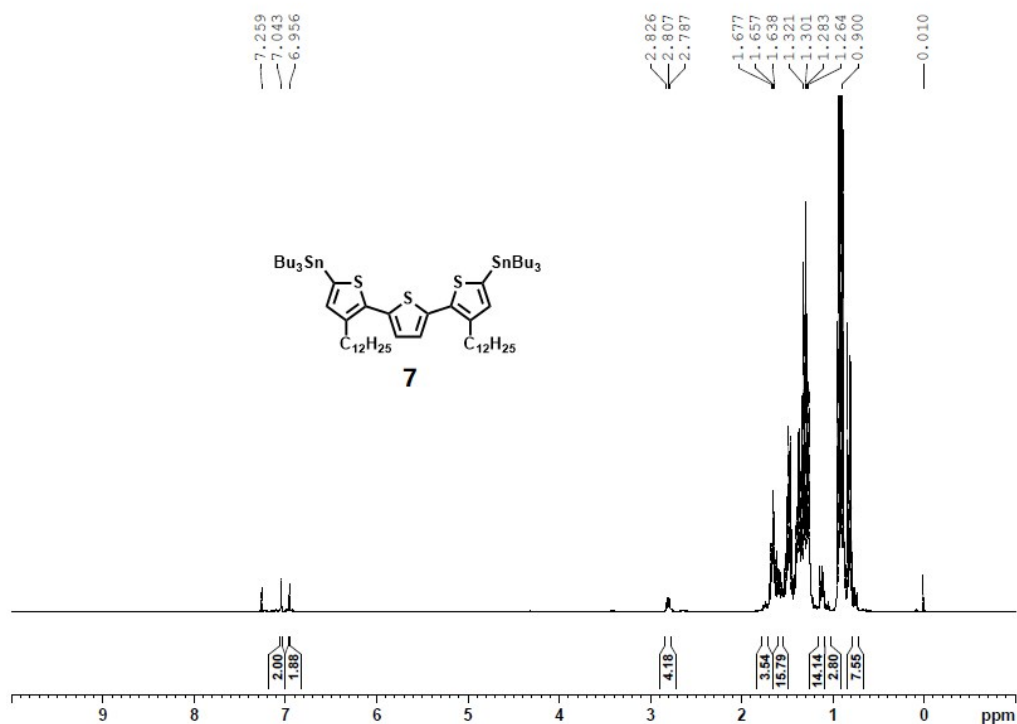


Fig. S21. The $^1\text{H NMR}$ (CDCl_3 , 400 MHz) spectrum of compound 7.

Polymer TPO-TTP12. The polymer TPO-TTP12 was prepared by the Stille reaction. Under argon atmosphere, compound 7 (290.8 mg, 0.25 mmol) and 5 mL of anhydrous toluene were added sequentially to a 25-mL Schlenk bottle, which was pre-charged with compound 4 (113.5 mg, 0.25 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (28.9 mg, 0.025 mmol). The reaction mixtures were heated with stirring at 100°C for 3 days. After cooling to room temperature, the crude polymer was precipitated by decanting the reaction mixture into 100 mL of methanol with stirring for 2 h. The solid was filtered off and washed with methanol, followed by further purification by sequential Soxhlet extraction with methanol, hexanes, and chloroform to remove oligomers and impurities.

Finally, the polymer was re-precipitated once again from chloroform by the addition of excess methanol (80 mL). After dried under vacuum, the polymer of 182.5 mg was obtained as a black-red powder. Mn: 5.17 kg mol⁻¹, PDI: 4.43; ¹H NMR (400 MHz, CD₂Cl₂): δ 7.88 (d, *J* = 7.2 Hz, 4H), 7.74 (d, *J* = 7.2 Hz, 4H), 7.34 (s, 2H), 7.25–6.93 (m, 2H), 6.76 (s, 2H), 2.95–2.56 (m, 4H), 1.80–1.65 (m, 4H), 1.50–0.98 (m, 36H), 0.95–0.65 (m, 6H).

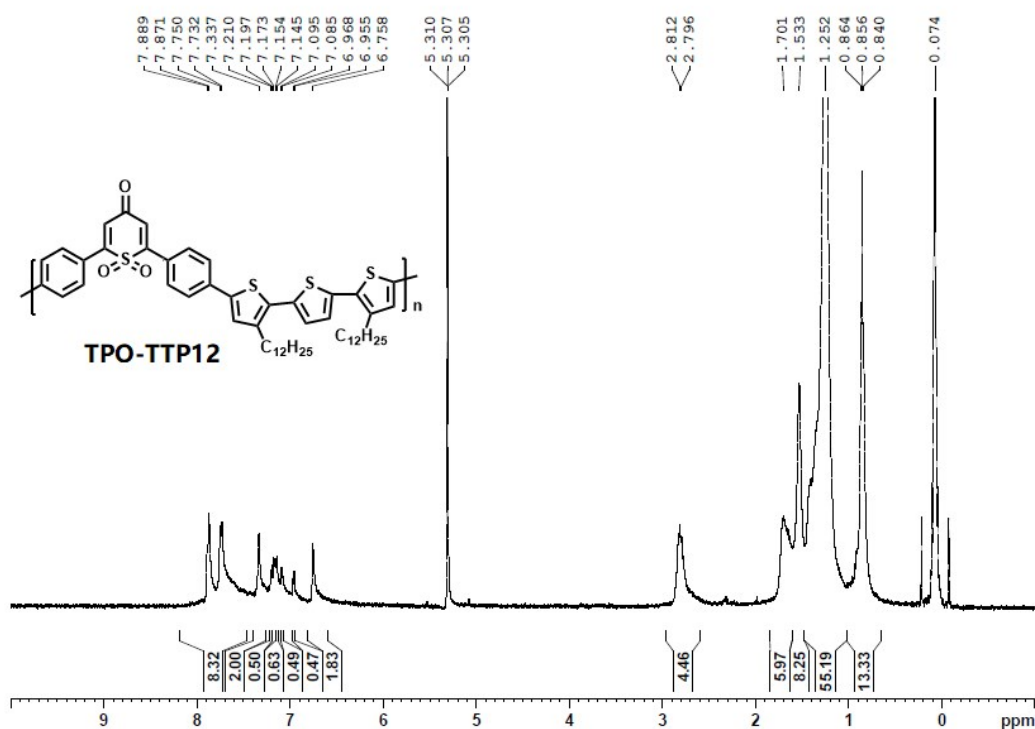


Fig. S22. The ¹H NMR (CD₂Cl₂, 400 MHz) spectrum of polymer **TPO-TTP12**.

4. Preparation of composite films

a. Direct mixing of polymer and single-walled carbon nanotubes (SWCNTs)

A typical procedure for film preparation is shown in the following. First, a suspension of 5 mg SWCNT in 20 mL absolute ethanol was sonicated for 1 h. Keeping it under sonication condition, a solution of a desired amount of polymer in dichloromethane with a concentration of 5 mg mL⁻¹ was added into the aforementioned SWCNT dispersion in one portion, so that the polymer could precipitated rapidly in the

network structure of SWCNTs taking advantage of its extremely low solubility in ethanol. The mixture was continuously sonicated for 3 h to ensure dichloromethane to volatilize completely making use of the heat produced by sonication. The resulting mixture was filtrated by vacuum filtration and washed by ethanol in succession. Finally, a flexible composite film of polymer/SWCNT was obtained after drying at 80 °C under vacuum for 4 h.

b. Simulated *in-situ* compositing of polymer and SWCNTs

The polymer/SWCNT composite film was prepared through a simulated *in-situ* compositing method between polymer and SWCNTs. A typical procedure is shown in the following. Similar to the situation described in the previous section, a suspension of 5 mg SWCNT in 20 mL absolute ethanol was firstly sonicated for 1 h. Keeping it under sonication condition, a solution of a desired amount of polymer in dichloromethane with a concentration of 5 mg/mL was slowly added dropwise into as-prepared SWCNT dispersion in equal portions, making sure that the polymer had enough time to precipitate slowly and then wrap uniformly on the surface of SWCNTs with the assistance of the slow evaporation of dichloromethane and the poor solubility of polymer in the EtOH. After addition was completed, the mixture was stirred in an open system at room temperature for 24 h to ensure dichloromethane to evaporate slowly and thoroughly. Similarly, the resulting mixture was filtrated by vacuum filtration and washed by ethanol. A flexible composite film of polymer/SWCNT was obtained after drying at 80 °C under vacuum for 4 h.

5. TGA curves

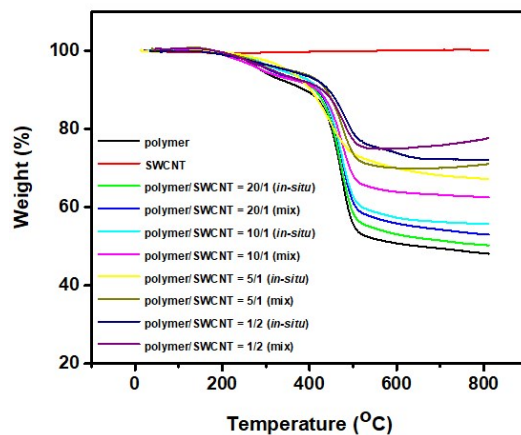


Fig. S23. TGA curves of the pure polymer, pure SWCNTs and several representative composites prepared by two methods.

The TGA analysis in **Fig. S23** suggests that all the samples have high thermal stability below 200 °C. Moreover, the thermal stability for the composites is enhanced with the increase of the content of SWCNTs.

6. The composite films and their flexibility

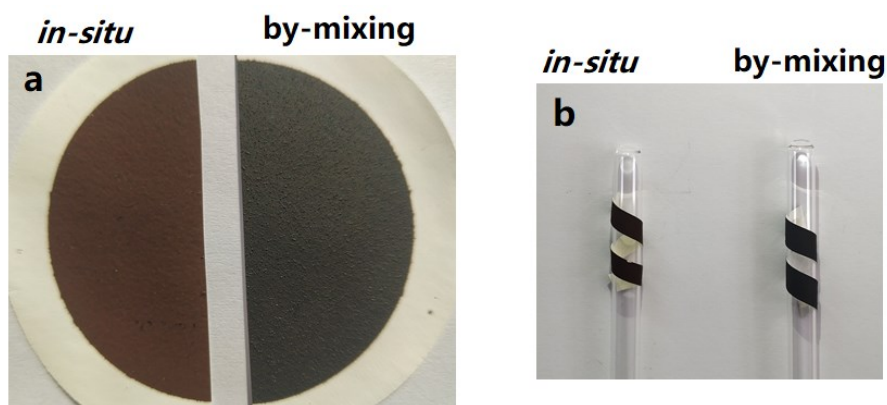
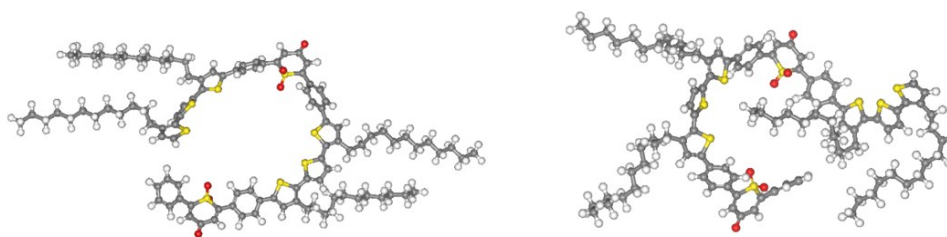
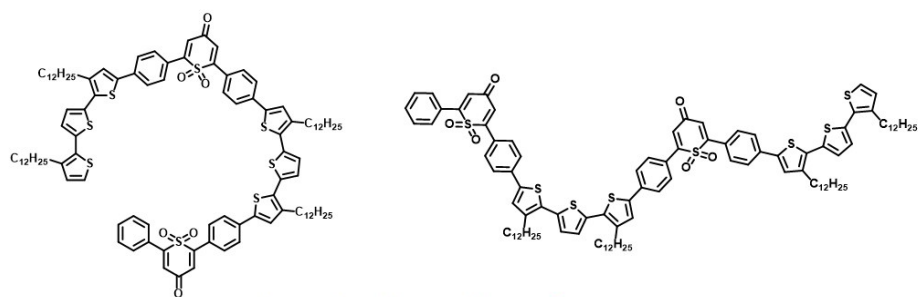


Fig. S24. (a) The photographs of the typical polymer/SWCNT composite films with a mass ratio of 20:1 and (b) displaying their flexibility.

As shown in **Fig. S24**, all the composite films prepared by the two different methods exhibit good flexibility.

7. Theoretical simulation

Theoretical calculations were mainly carried out with the density functional theory (DFT) code DMol³ module [4,5] implemented in the Materials Studio package. Geometry optimizations were performed with the exchange–correlation functional GGA-BLYP [6,7] and the localized double-numerical basis sets with polarization functions (DNP). The frontier molecular energy levels and charge population were then obtained. For ease of analysis, the dimer with two repeated units was chosen as model system.



optimized geometries

the relative energy: **0 kcal mol⁻¹**

17.36 kcal mol⁻¹

Fig. S25. Two main conformations and optimized geometries of dimer with two repeated units and their relative total energies calculated at the GGA/BLYP level.

8. TEM image of SWCNTs

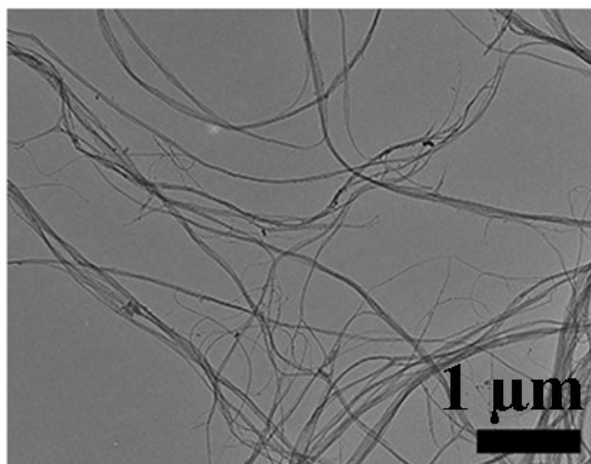


Fig. S26. The TEM image of SWCNTs.

9 Elemental mapping distributions

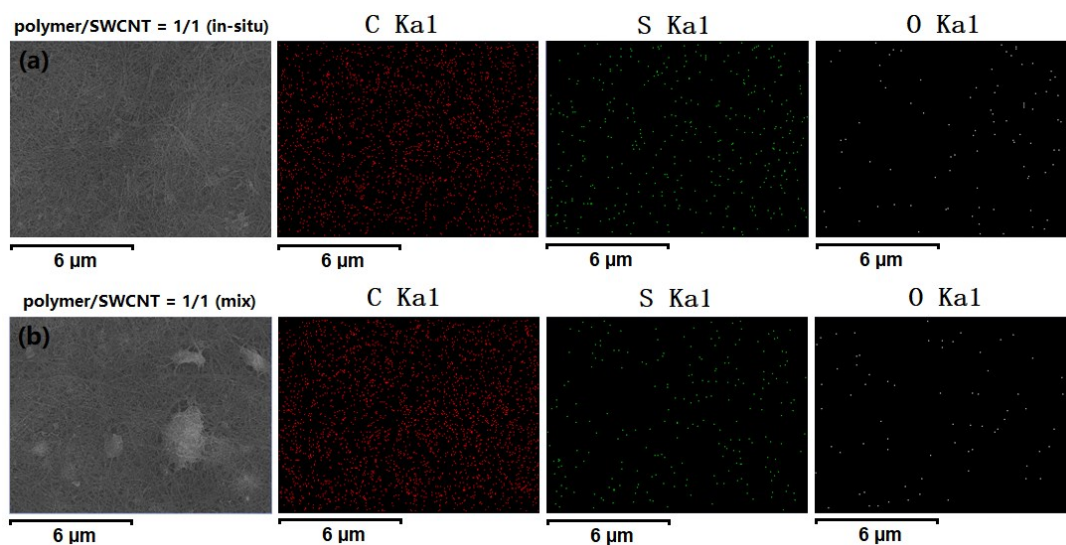


Fig. S27. Elemental mapping distributions of carbon C, sulfur S, and oxygen O obtained by EDS area scan for the polymer/SWCNT composite with a mass ratio of 1:1.

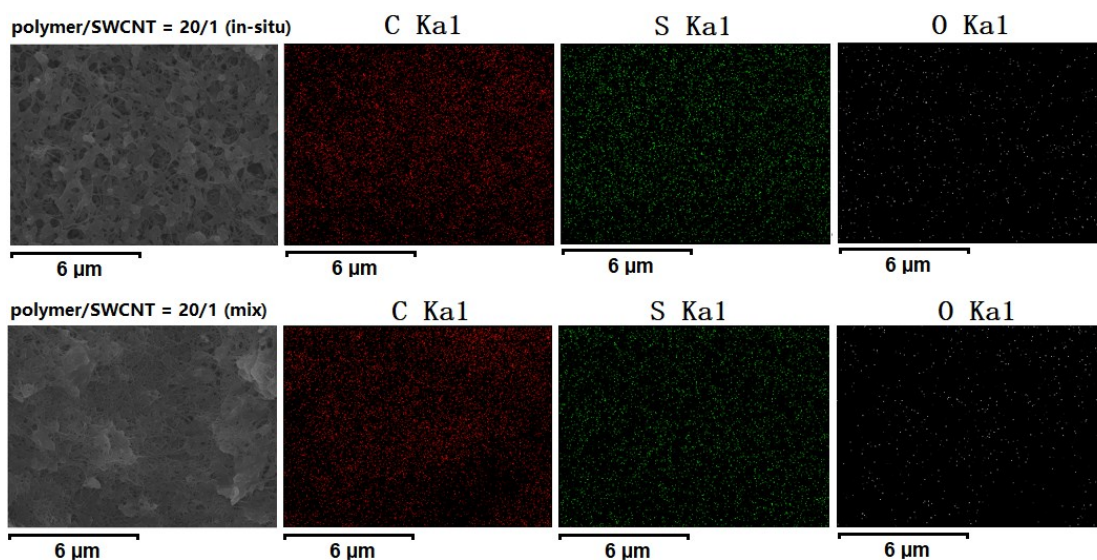


Fig. S28. Elemental mapping distributions of carbon C, sulfur S, and oxygen O obtained by EDS area scan for the polymer/SWCNT composite with a mass ratio of 20:1.

10 XPS spectra

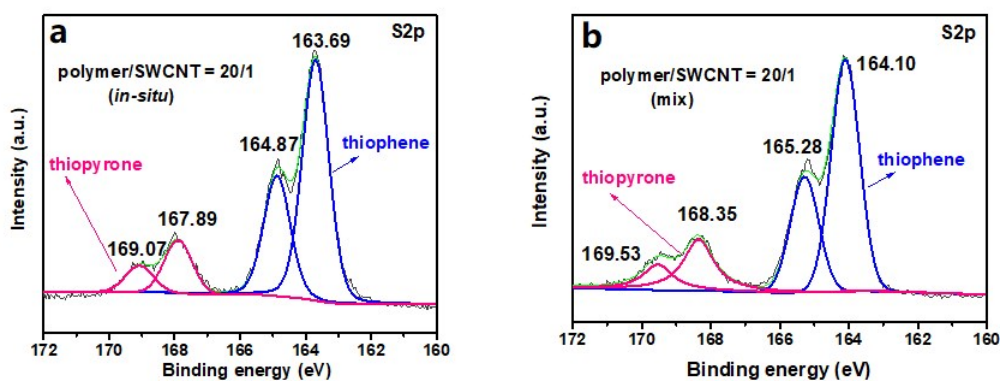


Fig. S29. XPS deconvolution spectra of S2p for (a) the in-situ and (b) the by-mixing prepared composite films with polymer/SWCNT mass ratio of 20/1.

11. References

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