

Significantly Enhanced Thermoelectric Performance of Solution-processable Organic Polymer and Carbon Nanotubes Composite via Molecular Packing Engineering

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Abstract:

Combining solution-processable organic polymers and carbon nanotubes (CNT) with excellent electric conductivity has been demonstrated to be an effective strategy to elevate the thermoelectric performance. Nevertheless, the seriously inadequate attentions in constructing superior polymers and ambiguous correlation between polymeric architectures and thermoelectric properties of polymer/CNT composites largely impede the further improvement of thermoelectric parameters. Herein, three one-step synthetic organic polymers named BTC8, BTSC8 and BTSC12 are constructed with the same main building units but different alkyl side chains and molecular rigidity/planarity to reveal the significative structure-property relationship. The condensed alkyl chains and simultaneously enhanced rigidity/planarity could reduce electron reorganization energy, facilitate molecular packing effectively and thus provide excellent charge transport channel in BTSC8/SWCNT based blend films, affording a superior power factor of $241.4 \mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ with satisfactory air stability comparing to those of 188.8 and $159.7 \mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ for BTSC12 and BTC8 based blend films, respectively. Our work demonstrated conjugated polymers/CNT based thermoelectric performance could be dramatically increased by balancing the trade-off between Seebeck coefficient and electric conductivity via molecule packing engineering such as improving molecular rigidity/planarity, reducing reorganization energy and strengthening molecular packing.

Keywords: *Thermoelectric performance, Organic polymer, Molecular packing engineering, Carbon nanotubes, Structure-property relationship.*

Introduction

Organic thermoelectric materials with abundant merits of solution processing^{1, 2}, lightweight³, intrinsic flexibility,^{4, 5} low cost,⁶ and environmental friendliness^{4, 6, 7} have been acknowledged as one of the most attractive candidates for thermoelectric generators to alleviate the excessive energy demand by directly converting waste heat into electricity.^{1-4, 6, 8-10} The energy conversion efficiency as the foremost parameter of organic thermoelectric materials is commonly evaluated by using power factor (PF) instead of the dimensionless figure of merit (ZT) involved with thermal conductivity, considering the extremely low thermal conductivity of organic polymers ($0.1\text{--}0.8\text{ W m}^{-1}\text{ K}^{-1}$)^{11, 12} and invariable temperature difference between the cold and hot sides in many scenarios for thermoelectric generators.¹³ To improve the thermoelectric properties largely, the Seebeck coefficient (S) and electrical conductivity (σ) of thermoelectric materials are preferably promoted simultaneously based on the defined power factor by $PF=S^2\sigma$.¹⁴ Unfortunately, the greatly increasement in Seebeck coefficient is generally accompanied by a serious decrease in conductivity, due to their reverse correlation with the carrier concentration and intrinsically low charge carrier concentration for most conjugated polymers.^{15, 16} Subsequently, how to balance and even break through the trade-off between S and σ to some extent will be a challenging and meaningful problem.

Considerable efforts on molecular structure designing have been devoted to address the conflict between S and σ , significantly promoting the conversion efficiency and enriching the diversity of organic thermoelectric materials.¹¹ The molecular optimizing strategies predominantly focus on introducing preferable constructing

blocks and linkage units,^{17, 18} heteroatom substitution (such as N, Se, Te),¹⁹⁻²¹ functionalization on polymer skeletons²², regulating the length/types and position of alkyl side chains²³⁻²⁵, as well as extending conjugate length of molecular skeletons^{26, 27} etc. The ultimate understanding of these effectual strategies to improve thermoelectric performance should be considered from the following perspectives. Firstly, at the level of single molecular structure, these strategies can increase the molecular planarity and rigidity through powerful intramolecular conformation locking,^{28, 29} regulating steric hindrance and releasing torsional tension.²⁸ Furthermore, the alternant donor-acceptor (D-A) features could be precisely controlled owing to the abundant variety and arrangement of D and A units along with multiple chemical modification sites, accelerating the intramolecular/intermolecular charge transfer.³⁰ For the other thing, the intermolecular π - π stacking and aggregation behaviors can be optimized, attributing to the intensified intermolecular non-covalent bond interactions and the advancement in single molecular structure including improved planarity/rigidity and D-A feature.^{17, 18} All above these together will result in a fundamentally optimal morphology in favor of charge transfer and transport, which can increase the carrier mobility to elevate σ and balance carrier concentration to maximize the PF with the most suitable S and σ . However, due to the inherent nature of most organic polymers with extremely low carrier concentration, the satisfactory PF with hundreds of values can be obtained via profound chemical doping in overcautious atmosphere,^{8, 31} otherwise only a few tens $\mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ of PF is afforded.¹⁸ Subsequently, extensive dopants will disturb the ordered polymer packing/aggregation behaviors, bringing a possible decrease in effective

carrier mass and mobility.^{3, 18, 22, 26, 31} Even worse, the inevitably added complexity to the device postprocessing and sacrificial device stability along with chemical doping will hinder the practical application of organic thermoelectric materials in future.^{8, 32}

The composite of organic polymers with highly conductive material could effectively decouple S from σ induced by an energy filtering effect through the formed heterointerfaces.^{13, 33-35} The carbon nanotubes (CNTs), especially SCNT¹³, with unique structures and excellent electrical properties have been one of the most frequently-used and appropriate thermoelectric materials to composite with conjugated polymer, which boosts the fast upgrade of thermoelectric conversion efficiency.^{36, 37} In addition, the superiority of solution-processable for organic polymers can well maintained because the powerful intermolecular interaction between polymers and high-surface CNTs.³⁷⁻³⁹ Given such an effective strategy and the significant role of polymer structure innovation in increasing thermoelectric parameters, it is interesting to see that the related researches mainly concentrate on some traditional polymers such as PEDOT, P3HT, PPy and PANI,^{34, 35, 37, 40, 41} but only several cases developed organic materials with novel structures.⁴²⁻⁴⁴ Despite some progress, this structure-property relationship remains ambiguous so far, disturbing the further improvement of thermoelectric properties for organic polymers/CNT based materials.^{34, 42, 43, 45, 46} If more high-efficiency polymers are developed and the relationship between polymer structure and thermoelectric performance based on polymer/CNT is elucidated, it is beyond doubt that the thermoelectric performance would be further promoted.

Herein, three organic polymers poly4-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-

5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (**BTC8**), poly4-(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-5,6-bis(octyloxy)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**BTSC8**) and poly4-(5-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)thiophen-2-yl)-5,6-bis(dodecyloxy)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**BTSC12**) are constructed with the same conjugate units including an electron-deficient benzo-2,1,3-thiadiazole (BT) with two alkoxy chains and an electron-rich 3,4-(ethylenedioxy) thiophene (EDOT) but only inserting a thiophene unit as interlinkage between donor and acceptor units of BTSC8 and BTSC12 to release the torsional tension and extend conjugate extent. The only structural difference of BTSC8 compared to BTSC12 is that the alkyl chains on benzothiadiazole are shortened to C8 from C12. The inserted thiophenes and condensed alkyl chains endows BTSC8 with improved molecular rigidity/planarity/crystallinity, low electron reorganization energy and enhanced intermolecular interaction, leading to more ordered molecular packing and superior phase separation between SCNT and polymers in BTSC8-CNT based blend films. The excellent film morphology provides excellent charge transport channel, leading to a high electric conductivity of $> 2400 \text{ S/cm}$ with a decent Seebeck coefficient of $31.6 \text{ } \mu\text{V/K}$, compared to that of a σ of 1480 S/cm with an S of $36.8 \text{ } \mu\text{V/K}$ for BTSC12-CNT based films and a σ of 1178 S/cm with an S of 35.7 for BTC8-CNT based films, respectively. The ultrahigh σ is primarily due to optimized CNT percolation network, while polymer crystallinity enhances interfacial charge transfer. Therefore, a significantly elevated PF of $241.4 \text{ } \mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ for BTSC8-CNT based films is achieved, comparing to those of 188.8 and $159.7 \text{ } \mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ for BTSC12-CNT

and BTC8-CNT based films, respectively. It is worth noting that the highest PF for BTSC8-CNT films should ascribe to the soaring electric conductivity due to optimized CNT dispersion and strengthened polymer-CNT interfacial coupling, as well as the moderate S by suppressed carrier overshooting,^{14, 47} induced by the structure-controlled molecule packing. Furthermore, over 92% of initial efficiency can be kept for all three polymers based composite films after more than 30 days of exposure in mild environment, presenting outstanding air stability for thermoelectric materials with such structure. Our work has demonstrated polymers/CNT films based thermoelectric performance could be improved dramatically by enhancing molecular packing through constructing three novelly easy-synthesized D-A conjugated polymers and revealed the key crucial role of regulating molecular structure such as releasing torsional tension, improving molecular rigidity/planarity, increasing crystallinity in optimizing the morphology of polymers/CNT films.

Results and Discussions

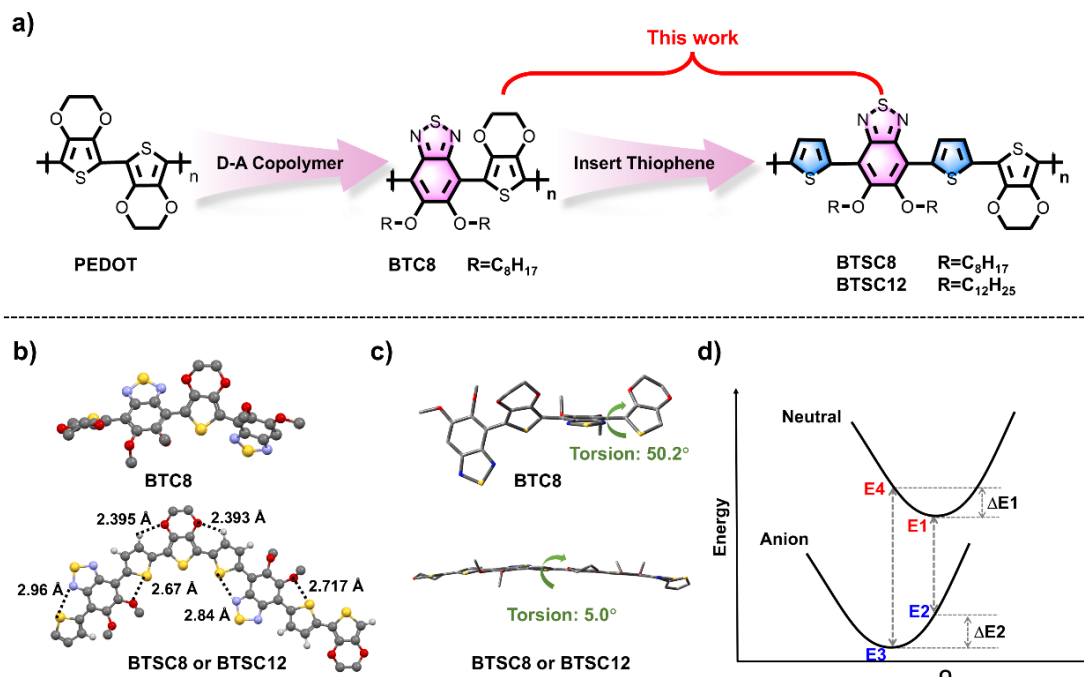


Figure 1. **a)** Molecular structures of PEDOT and BT-series molecules (BTC8, BTSC8 and BTSC12). **b)** The optimized molecular geometries in top view and **c)** side view of BTC8, BTSC8 and BTSC12 by Density Functional Theory (DFT) in vacuum within the Gaussian 16 software **d)** The reorganization energy (λ) calculation diagram, $\lambda = [E2 - E3] + [E4 - E1]$. E1 and E3 represent the single point energy of the neutral molecule at the ground state and anion via optimization of the anion, respectively. E2 is the single point energy of anion after simple optimization of the neutral molecule. E4 is the energy of the neutral molecule via the optimized geometry of the anion. The electron reorganization energy of BTSC8/BTSC12 and BTC8 are 187 meV and 282 meV, respectively.

PEDOT constructed with only electron-donor 3,4-(ethylenedioxy) (EDOT) has displayed remarkable thermoelectric properties, but its inevitable drawbacks such as insolubility, complex post-processing, potentially inferior electrical property than D-A copolymers are receiving increasing attentions.⁴⁸ To fully take advantages of PEDOT on remarkable thermoelectric property but avoiding its inferior aspects mentioned above, 3,4-(ethylenedioxy) (EDOT) and another electron-deficient benzo-2,1,3-thiadiazole (BT)^{49, 50} with largely potential quinoid characteristics⁵¹ are selected as the

building blocks to construct BTC8 (**Figure 1a**). Note that a couple of alkoxy chains on BT unit is to ensure its solution in many organic solvents and afford the conformational locking effect by oxygen-sulfur interactions.⁵² The apparent donor-acceptor feature is displayed by comparing the electron distribution in HOMO and LUMO showed in **Figure S1** and **S2**. Unfortunately, as showed in **Figure 1b** and **1c**, a large torsion angle over 50° calculated by Density Functional Theory (DFT) is presented for BTC8 skeleton due to the overly compact building blocks with ignoring the oxygen-sulfur interactions. Therefore, an additional thiophene unit as a linkage is embedded between BT and EDOT to constructed BTSC8 and BTSC12 (**Figure 1a**). The only difference for BTSC8 and BTSC12 is the alkyl chain length (C8 and C12 for BTSC8 and BTSC12, respectively), aiming to figure out the influence of crystallinity and molecular packing behavior on thermoelectric performance by tuning alkyl chain length. Predictably, the whole molecular skeleton is almost on a plane with a sharply reduced torsion angle of 5° for BTSC8 and BTSC12, attributed to the multiple non-covalent interactions and the release of tension by inserting a thiophene unit (**Figure 1b and 1c**). The increased planarity also is favorable to the extended conjugate length, which can be verified by the narrower bandgap calculated from the energy levels of HOMO and LUMO for BTSC8 and BTSC12 (1.96 and 2.95eV for BTSC8/ BTSC12 and BTC8, respectively, which are displayed in **Figure S1** and **S2**). The narrowed bandgap obtained from energy level for BTSC8 and BTSC12 is consisted with the experimental optical band gap that would be discussed below. Furthermore, the electron reorganization energy of BTSC8 and BTSC12 is also decreased to 187 meV from 282 meV of BTC8 (**Figure 1d**),

indicating BTSC8 and BTSC12 have the superior molecule rigidity and potentially preferable charge transport properties.⁵³⁻⁵⁵ It is worthy to note that the improved rigidity/planarity, extended effective conjugate extent, condensed alkyl chains and low reorganization energy support the more ordered and tightened molecular packing and thus provide excellent charge transport channel in **BTSC8**/SWCNT based blend films, which would be demonstrate in below discussion. In addition, all three polymers are synthesized with only one-step Stille coupling reaction (**Scheme S1-S3**) and exhibit a good thermal stability with a decomposition temperature over 300 °C, measured by the TGA (thermal gravimetric analysis) (**Figure S3**). The number-average molecular weights of BTC8, BTSC8 and BTSC12 were 51.0, 15.5 and 7.7 KDa with a polydispersity (PDI) index of 1.41, 1.18 and 1.42 (**Figure S11-S13**), respectively.

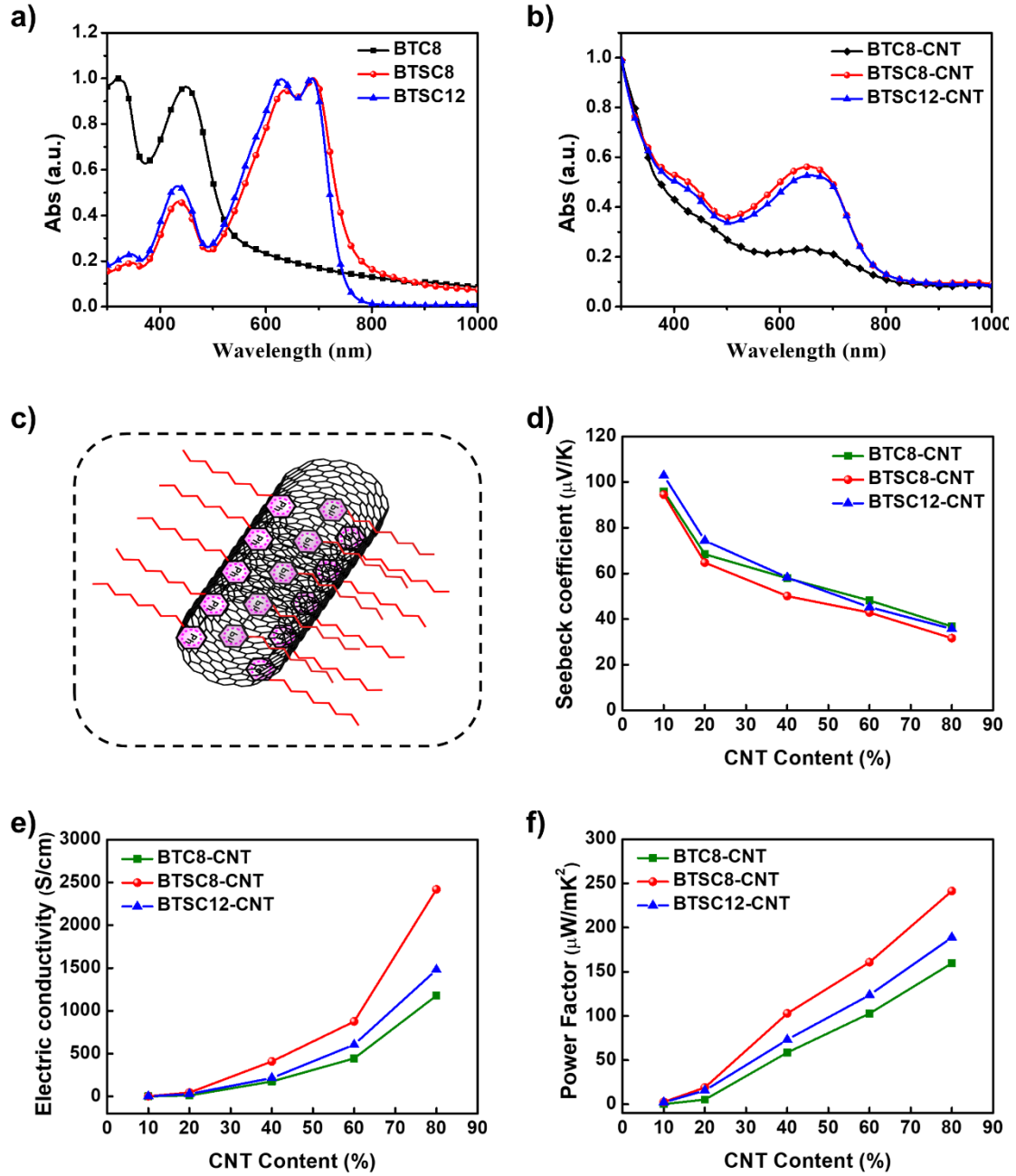


Figure 2. a) Normalized absorption spectra of BTC8, BTSC8 and BTSC12 films. b) Normalized absorption spectra of BTC8-CNT, BTSC8-CNT and BTSC12-CNT films. c) The diagram of the interaction between polymers and SCNT. d) The Seebeck coefficient of BTC8-CNT, BTSC8-CNT and BTSC12-CNT along with the incremental CNT content. e) The electric conductivity of BTC8-CNT, BTSC8-CNT and BTSC12-CNT along with the incremental CNT content. f) The power factor of BTC8-CNT, BTSC8-CNT and BTSC12-CNT along with the incremental CNT content.

To elucidate the influence of different structural polymers on polymers/CNT based thermoelectric performance, the UV-vis absorption spectra of composited BTC8-CNT,

BTSC8-CNT and BTSC12-CNT films and corresponding pure polymer films were measured and compared with each other. As shown in **Figure 2a** and **Table S1**, the two main absorption peaks named λ_{P1} and λ_{P2} of BTSC8 films located at 635 and 690 nm, respectively, showing the largely redshift than that of BTC8 (320nm for λ_{P1} and 449nm for λ_{P2}) and slightly redshift than BTSC12 (630nm for λ_{P1} and 687nm for λ_{P2}). Meanwhile, the optical bandgap (E_g^{onset}) of BTSC8 is also located at the lowest energy of 1.64 eV (2.34 and 1.65 eV for BTC8 and BTSC12 solid films, respectively), which is consisted with the bandgaps from energy level differences discussed above. Comparing to the absorption in solution (**Figure S4** and **Table S1**), BTSC8 and BTSC12 films respectively have the best and middle performance on peaks redshift instead of the only blueshift for BTC8 films. These absorption differences confirmed that BTSC8 possessed the most effective conjugate extent and strongest molecular interactions produced by the improved planarity and shortened alkyl chain.^{56, 57} As shown in **Figure 2b**, the noticeable changes in absorption peak shapes and locations took place, suggesting that all three polymers had strong interaction with CNT, mainly caused by π - π packing. Given the intense π - π stacking between CNT and conjugate skeletons of polymers, the alkyl chains on polymers would expose outside, just like multiple flexible chains being embedded on the CNT (**Figure 2c**), ensuring the favorable solubility of polymers-CNT composites.⁵⁸ Therefore, three composites all behaved satisfyingly solution-processable feature (**Figure S5**), which is conducive to the film preparation for thermoelectric performance test. To better understand the interaction between BT-series polymers and CNT, the Raman test has also been

conducted to further reveal the interfacial interactions between the BT-series polymers and CNTs. The most concerned G^+ is related to sp^2 carbon-atom vibration, which can indicate doping levels of CNT in composites by comparing its variation. As shown in **Figure S6**, BTSC8-CNT film presents an impressive blue shift of 3.3 cm^{-1} in the G^+ band, being larger than those of 1.4 and 2.1 cm^{-1} for BTC8-CNT and BTSC12-CNT composite films respectively. The larger G^+ band variation of BTSC8-CNT film suggested the more effective of p-doping, thereby contributing to the electrical conductivity enhancements, which should attribute to the improved interface interactions induced by the enhanced intermolecular packing between BTSC8 and CNT. Furthermore, the more obvious G^+ band peak broadening of BTSC8-CNT than BTC8-CNT and BTSC12-CNT also demonstrated the more intensive interactions between the polymers and nanotubes.^[42]

Table 1. Summary of thermoelectric parameters for optimized films.

Films	S ($\mu\text{V/K}$)	σ (S/cm)	PF ($\mu\text{W/m}^{-1}\text{K}^{-2}$) ^[a]
BTC8-CNT	36.8 (36.5 ± 0.86)	1177.7 (1160.5 ± 50.31)	159.7 (154.4 ± 6.58)
BTSC8-CNT	31.6 (31.7 ± 0.40)	2419.2 (2370.9 ± 40.02)	241.4 (237.4 ± 3.88)
BTSC12-CNT	35.7 (35.4 ± 0.44)	1480.2 (1465.9 ± 25.44)	188.8 (183.7 ± 3.36)

[a] $PF=S^2\sigma$

To further evaluate the influence of planarity/rigidity and alkyl chain length on thermoelectric performance, the measurements of Seebeck coefficient, electrical conductivity and corresponding power factor for BTC8, BTSC8 and BTSC12 based SCNT composites with different CNT content were conducted immediately. The detailed preparation procedures of devices and test condition were described in

supporting information. As shown in **Figure 2d** and **2e**, the Seebeck coefficient goes down gradually and electrical conductivity goes up steadily along with the increasing CNT content, due to the intrinsically higher S and σ for BT- series polymers and CNT respectively. Interestingly, the power factor of three polymers based composite films also improved following the growing CNT content (**Figure 2f**), benefiting from the soaring electrical conductivity despite slowly decreasing Seebeck coefficient. Considering the fine solution-processable advantage with the polymer-CNT system, the maximum CNT content was controlled at 80 wt-%. Consequently, the highest PF s of 159.7, 188.8 and 241.4 $\mu\text{W}/\text{m}^1\text{K}^{-2}$ with 1177.7, 2419.2 and 1480.2 S/cm of σ and 36.8, 31.6 and 35.7 $\mu\text{V}/\text{K}$ of S for BTC8-CNT, BTSC8-CNT and BTSC12-CNT films were afforded, respectively. The detailed thermoelectric data was summarized in **Table 1** and **Table S2-S3**. Please note the excited PF for BTSC8-CNT is better than that of traditional polymer P3HT based CNT composites^{37, 59} and comparable to that of most classical PEDOT based CNT composites^{35, 36}, which attributed to the excellent electrical conductivity and simultaneously decent Seebeck coefficient, illustrating that the more balanced trade-off between the two parameters was well achieved. This should be explained through the preferable charge transport channel originates from more optimized CNT dispersion and strengthened polymer-CNT interfacial coupling (**Figure 2b, 2c**), while the moderate S is maintained by suppressed carrier overshooting, which might originate from the suitable morphology in corresponding solid states. Furthermore, considering the similar structures, BTSC8 neat films should have a same-level low thermal conductivity around 0.3 $\text{W m}^{-1} \text{K}^{-1}$ to that of undoped organic

materials. Due to the difficulty in testing the thermal conductivity of organic films, especially in the in-plane direction, the reported values are usually the thermal conductivity in the out-of-plane direction (κ_z). Here, the κ_z was speculated to be 0.4~0.6 for $\text{W m}^{-1} \text{K}^{-1}$ BTSC8-CNT composite films based on the reported data.³⁶

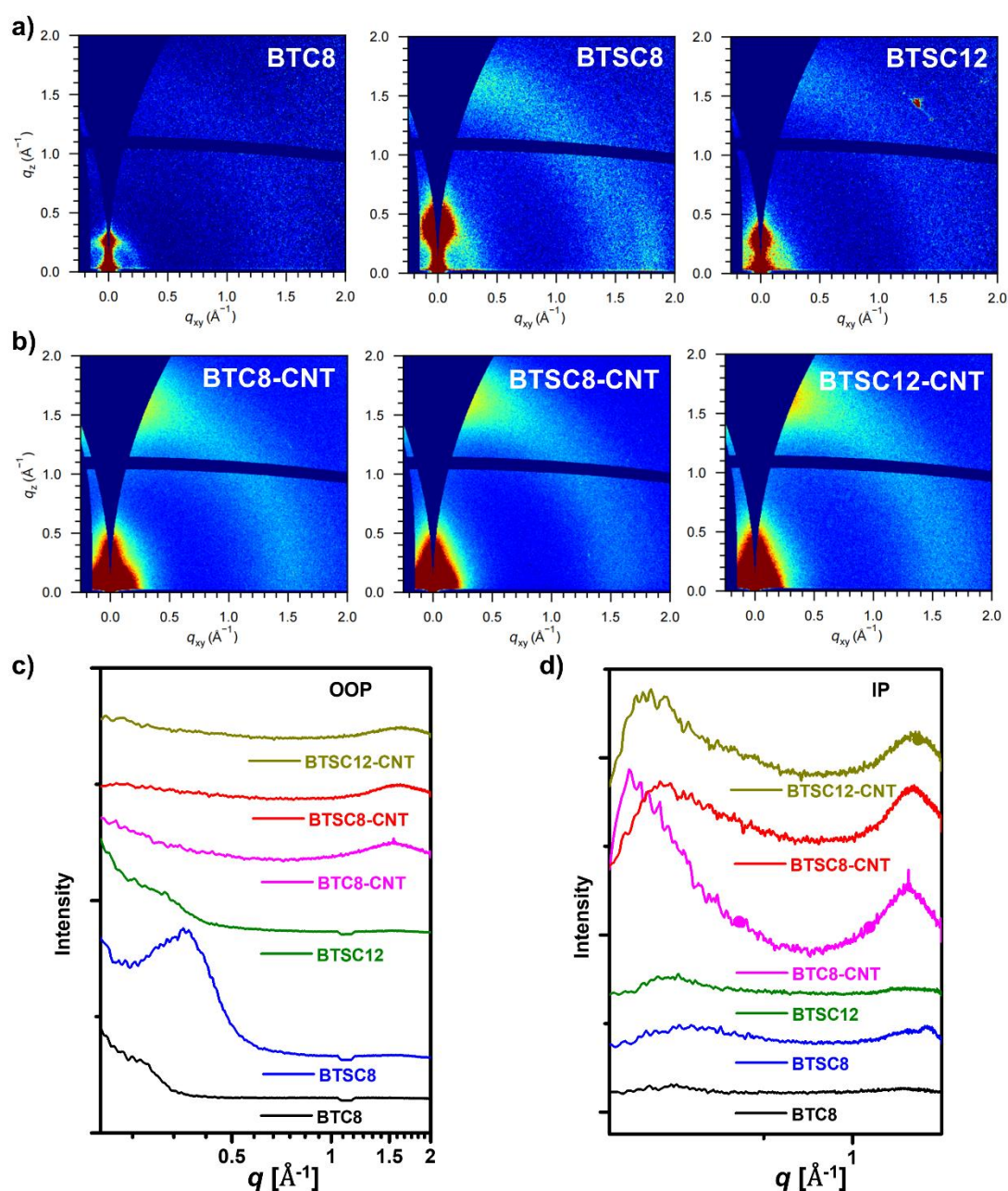


Figure 3. a) 2D GIWAXS patterns of BTSC8, BTSC8 and BTSC12 based films and b) BTSC8-CNT, BTSC8-CNT and BTSC12-CNT based composite films. c) The

corresponding 1D line-cuts in OOP direction and **d)** in IP direction from the corresponding 2D GIWAXS patterns.

As we have discussed above, the remarkable difference of film morphology would be achieved among three BT- series polymers as well as their mixed films, which is deduced from the largely different thermoelectric parameters and molecular structure. Grazing incident wide-angle X-ray scattering (GIWAXS) measurements were thereby conducted to uncover the molecular orientations and packing behaviors.⁶⁰⁻⁶³ As illustrated in **Figure 3a**, **Table S4** and **S5**, BTSC8 neat film displayed an obviously edge-on packing orientation suggested by the strong (010) diffraction peak at $1.70 \text{ \AA}^{-1}$ with a π - π packing distance of $3.69 \text{ \AA}$ in in-plane (IP) direction and a (100) diffraction peak at $0.34 \text{ \AA}^{-1}$ with a packing distance of $18.56 \text{ \AA}$ in out-of-plane (OOP) direction. Although the (010) diffraction peak at $1.59 \text{ \AA}^{-1}$ with a π - π packing distance of $3.95 \text{ \AA}$ in IP direction and the (100) diffraction peak at $0.23 \text{ \AA}^{-1}$ with a packing distance of $27.17 \text{ \AA}$ in OOP direction were relatively weaker than those in BTSC8 neat film, the edge-on packing orientation also was achieved in BTSC12 neat films. In theory, the improved alkyl chain length can lead to greater steric hindrance, thereby interfering with intermolecular π - π stacking and making the packing distance increase. Meanwhile, there is no diffraction peak detected in BTC8 neat films due to the extremely weak molecular packing caused by the overlarge torsion angle. Note the stronger diffraction peaks and smaller intermolecular packing distance manifested the significantly strengthened and more ordered and close intermolecular stacking in BTSC8 neat film, which should be kept in its corresponding blended films and made a profoundly positive difference on thermoelectric performance. Therefore, the enhanced

intermolecular packing including the emergence of molecular packing orientation and the reduction of molecular packing distance was achieved by BTSC8, which originated from the strengthened planarity and reduced steric hindrance caused by introducing thiophene and shortening alkyl chain respectively. As displayed in 2D GIWAXS images of the three blend films and their corresponding 1D curves (**Figure 3a**, **Table S4** and **S5**), all peaks of three blended films based BTC8-CNT, BTSC8-CNT and BTSC12-CNT located at $0.15\text{--}0.26\text{ \AA}^{-1}$ and $1.55\text{--}1.62\text{ \AA}^{-1}$ for (100) and (010) diffraction signals respectively, showing that the molecular structure variation made no difference on the molecular packing orientation in composite films between polymers and CNT. This same packing orientation should attribute to the powerful interaction between CNT and all three conjugated polymers through π - π stacking, which was illustrated in **Figure 2c**. But the overall smallest intermolecular packing distance and largest crystal coherence length (CCL) (**Table S4** and **S5**) were observed in BTSC8-CNT based blended film, illustrating that the enhanced crystallinity and intermolecular packing of BTSC8 based neat films caused by the improved molecular planarity/rigidity and condensed alkyl chain, were well maintained in BTSC8-CNT based blend films. Furthermore, although the lower M_w of BTSC₁₂ ($M_n = 7.7\text{ kDa}$) may limit long-range order, the local packing at interfaces is still promoted, as evidenced by reduced π - π distance ($3.87\text{ \AA}$ vs. $3.95\text{ \AA}$ in BTSC12-CNT and BTSC12 films respectively in the IP direction, **Table S4**). These results are consistent with film XRD showed in **Figure S7**, which verified the superiority of BTSC8 based neat and blend films morphology.

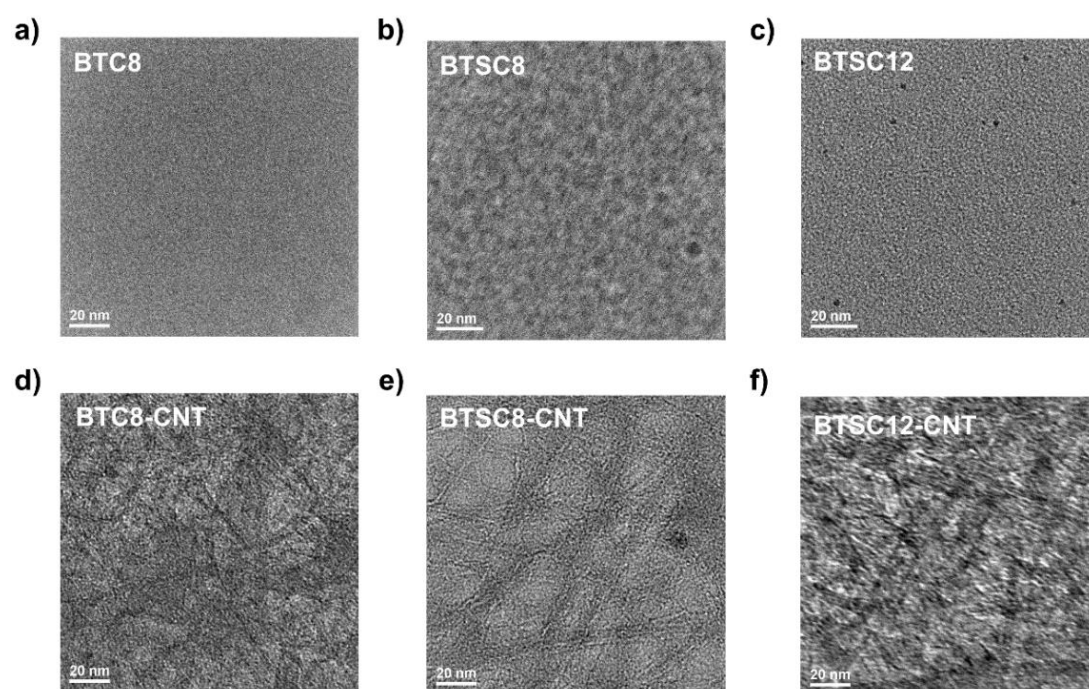


Figure 4. TEM images of **a)** BTC8; **b)** BTSC8; **c)** BTSC12; **d)** BTC8-CNT; **e)** BTSC8-CNT; and **f)** BTSC12-CNT.

Furthermore, transmission electron microscopy (TEM) measurements of three neat polymer films and three blended films were carried out to investigate the molecular aggregation behaviors. As shown in **Figure 4a-4c**, the more prominent aggregation behaviors were gained in BTSC8 neat film compared to that of BTSC12, which should be caused by the condensed alkyl chains on benzothiadiazole and enhanced intermolecular π - π stacking. Expectedly, BTC8 based neat films acquired the most inferior aggregation behaviors indicated by the most unsatisfactory crystallinity among the three BT- series polymers, resulting from the unnecessary torsion angle on the molecular structure level. With respect to the blended films, the most ordered and efficiently unbundling phenomenon of carbon nanotubes was achieved in BTSC8-CNT based blend films (**Figure 4d-4f**), demonstrating the enhanced interactions between polymers and polymers to facilitate phase separation, as well as polymers and CNT to

unbundle CNT happened simultaneously. The better phase separation of BTSC8 based blend films could be demonstrated by the EDS mapping images of sulfur element presented in **Figure S8**, proving the tightest packing of BTSC8 again. From a deeper perspective, the molecular orientation behaviors in polymer/CNT composite films should be created through forming interlocking network architectures of CNT based on the above experimental GIWAXS and TEM analysis, because the profound π - π stacking exists among CNT by P orbital fully overlapping. Then, the organic polymers would play a crucial role in connecting these relatively dispersed CNT, thus affording more effective charge transport channels through polymers and charge transfer at polymer/CNT interfaces, which is favorable to the increased electric conductivity. In other words, the ultrahigh σ is primarily due to optimized CNT percolation network (**Figure 4d-4f**), while polymer crystallinity enhances interfacial charge transfer. Furthermore, abundant alkyl chains on polymers are attached to CNT by aromatic skeleton's π - π stacking could ensure the solution-processable advantage of polymer/CNT composites by unbounding the easily excessively aggregated CNT^{38, 39} and regulating the aggregation behavior of the polymer/CNT systems. More importantly, the resulting heterojunction interfaces (**Figure 4d-4f**) between CNT and organic polymers could suppress carrier overshooting to potentially prevent Seebeck coefficient from declining sharply or even elevate the Seebeck coefficient despite the raised electric conductivity. Consequently, the trade-off between Seebeck coefficient and electric conductivity of polymer/CNT could be well balanced to improved thermoelectric properties dramatically by enhancing molecular packing, tuning

molecular crystallinity and adjusting phase separation behavior through constructing or modifying efficiently conjugated polymers.

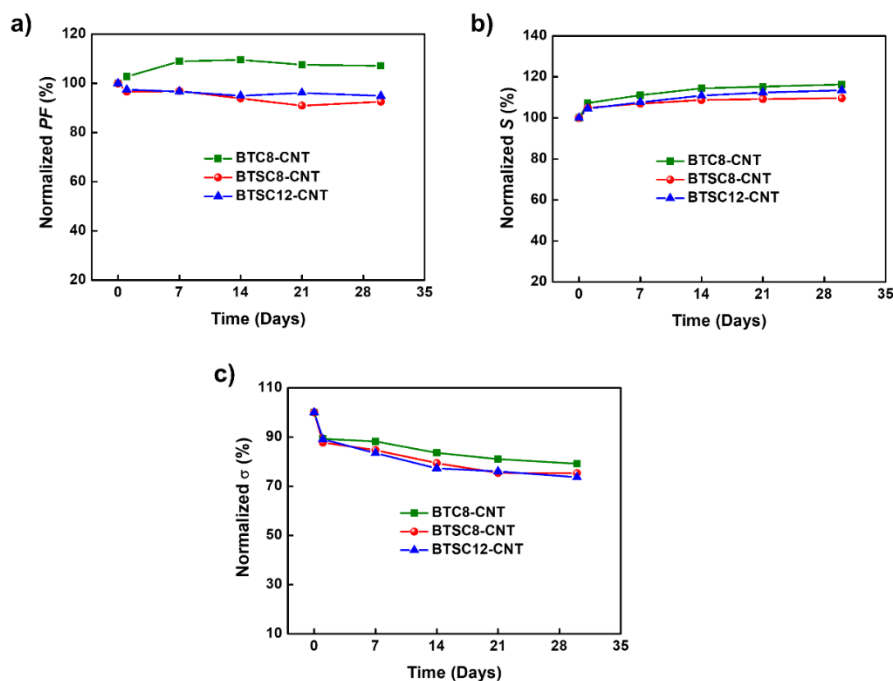


Figure 5. The thermoelectric parameters variation versus the operating time in mild air condition at room temperature. The variations of **a)** normalized PF , **b)** normalized Seebeck coefficient and, **c)** normalized Electric conductivity along with time.

In view of the great significance of stability in practical application, the thermoelectric parameters based on BT- series blend films were tested. As shown in **Figure 5a** and **Table S6**, the PF s of the BTCS8-CNT and BTCS12-CNT based thermoelectric films could maintain 93% and 95% respectively compared to their initial PF s after 30 days of exposure in mild air condition. Interestingly, the PF of the BTC8-CNT based film presented a slightly increasement than the initial PF . The remarkable air stability greatly surpassed the most studied PEDOT/CNT based thermoelectric films,³⁶ making it to be one of the potential materials in future application. This should seemingly attribute to the growing Seebeck coefficient and slightly reduced electric

conductivity in **Figure 5b** and **5c**. The slight PF rise in BTC8-CNT may stem from oxidative doping under air exposure, which moderately optimizes carrier concentration. This warrants further study but does not compromise overall stability. Furthermore, we also performed the FI-IR of three composites before and after exposing in air for ~3 months. As illustrated in **Figure S9**, there is no shift for these characteristic peaks of three composites after a long time of exposure in air, although the infrared peaks are very weak due to a very low polymer content. These provide powerful evidence for the excellent stability of BT-series-CNT composites. Actually, such fantastic stability of BT-series based CNT composites should come from the stable morphological features due to the enhanced intermolecular interactions between polymers and CNT without complex post-processing and deeply doping.

Conclusion

To conclude, a sequence of BT-series organic conjugated polymer (BTC8, BTSC8 and BTSC12) with the identical constructing units but different planarity/rigidity and alkyl chains have been built through only one-step synthesis to disclose the underlying relationship between polymer structures and thermoelectric properties. After a comprehensive investigation, BTSC8 among BT-series polymers exhibits the lower electron reorganization energy and enhanced intermolecular packing due to the released tension, more extended conjugate extent and condensed alkyl chain, which are conducive to preferable charge transport and favorable phase separation in its corresponding composited films. The ordered and strengthened π - π stacking was also

achieved between polymers and carbon nanotubes in BTSC8-CNT based blend films, not only increasing conductivity through optimized CNT dispersion and strengthened polymer-CNT interfacial coupling, but also maintaining the moderate S by suppressed carrier overshooting. Finally, a superior power factor of $241.4 \mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ with a high electric conductivity of $> 2400 \text{ S/cm}$ and a decent Seebeck coefficient of $31.6 \mu\text{V/K}$ was achieved for BTSC8-CNT based films compared to those of 188.8 and $159.7 \mu\text{W}\cdot\text{m}^{-1}\text{K}^{-2}$ for BTSC12 and BTC8 respectively. The ultrahigh σ is primarily due to optimized CNT percolation network, while polymer crystallinity enhances interfacial charge transfer. Moreover, these BT-series molecules based composite films possess excellent air stability, making them to be potentially applied material in future. In consequence, our work has not only offered a series of novelly organic polymers as high-efficiency and stabilized thermoelectric materials through only one-step synthesis, but also revealed the structure-property relationship to help boost the thermoelectric performance through molecular packing optimizing.

Author contributions

The synthetic works were carried out by H.C., and three polymers were characterized by H.C.. H.C., S. L. and J. G. carried out most of the device fabrication and measurements. Y. L. and B. H. provided assistances in device characterization and instrument usage. Y. Z., Y. Z. and X. C. performed the morphology characterization and analyzed the data. G.L. carried out the theoretical computation of three acceptors and helped to revise the manuscript. C. H. supervised and directed this project; C. H. and H. C. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Conflict of interest

The authors declare no conflict of interest.

Data availability

Data available in article supplementary information.

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