

Recent progress in design of conductive polymers to improve the thermoelectric performance

Zhen Xu (徐真), Hui Li (李慧), and Lidong Chen(陈立东)

Citation: Chin. Phys. B, 2022, 31 (**2**): 028203. DOI: 10.1088/1674-1056/ac22a4、
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Substrate tuned reconstructed polymerization of naphthalocyanine on Ag(110)

Qi Zheng(郑琦), Li Huang(黄立), Deliang Bao(包德亮), Rongting Wu(武荣庭), Yan Li(李彦), Xiao Lin(林晓), Shixuan Du(杜世萱), and Hong-Jun Gao(高鸿钧)

Chin. Phys. B, 2022, 31 (**1**): 018202. DOI: 10.1088/1674-1056/ac3500

Polymer/silica hybrid waveguide Y-branch power splitter with loss compensation based on $NaYF_4$: Er^{3+}, Yb^{3+} nanocrystals

Yue-Wu Fu(符越吾), Tong-He Sun(孙潼鹤), Mei-Ling Zhang(张美玲), Xu-Cheng Zhang(张绪成), Fei Wang(王菲), Da-Ming Zhang(张大明)

Chin. Phys. B, 2019, 28 (**10**): 104206. DOI: 10.1088/1674-1056/ab3f24

Polymer waveguide thermo-optical switch with loss compensation based on $NaYF_4$: 18% Yb^{3+}, 2% Er^{3+} nanocrystals

Gui-Chao Xing(邢桂超), Mei-Ling Zhang(张美玲), Tong-He Sun(孙潼鹤), Yue-Wu Fu(符越吾), Ya-Li Huang(黄雅莉), Jian Shao(邵健), Jing-Rong Liu(刘静蓉), Fei Wang(王菲), Da-Ming Zhang(张大明)

Chin. Phys. B, 2018, 27 (**11**): 114218. DOI: 10.1088/1674-1056/27/11/114218

Optical nonlinearities of tetracarbonyl-chromium triphenyl phosphine complex

M D Zidan, A W Allaf, A Allahham, A AL-Zier

Chin. Phys. B, 2017, 26 (**4**): 044205. DOI: 10.1088/1674-1056/26/4/044205

TOPICAL REVIEW — Organic and hybrid thermoelectrics

Recent progress in design of conductive polymers to improve the thermoelectric performance

Zhen Xu (徐真)[1,2], Hui Li (李慧)[1,2,†], and Lidong Chen(陈立东)[1,2,]

[1] *State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai* 200050, *China*

[2] *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing* 100049, *China*

(Received 30 July 2021; revised manuscript received 26 August 2021; accepted manuscript online 1 September 2021)

Organic semiconductors, especially polymer semiconductors, have attracted extensive attention as organic thermoelectric materials due to their capabilities for flexibility, low-cost fabrication, solution processability and low thermal conductivity. However, it is challenging to obtain high-performance organic thermoelectric materials because of the low intrinsic carrier concentration of organic semiconductors. The main method to control the carrier concentration of polymers is the chemical doping process by charge transfer between polymer and dopant. Therefore, the deep understanding of doping mechanisms from the point view of chemical structure has been highly desired to overcome the bottlenecks in polymeric thermoelectrics. In this contribution, we will briefly review the recently emerging progress for discovering the structure–property relationship of organic thermoelectric materials with high performance. Highlights include some achievements about doping strategies to effectively modulate the carrier concentration, the design rules of building blocks and side chains to enhance charge transport and improve the doping efficiency. Finally, we will give our viewpoints on the challenges and opportunities in the field of polymer thermoelectric materials.

Keywords: conductive polymer, organic thermoelectric material, chemical doping, side chain engineering

PACS: 82.35.−x, 36.20.−r, 42.70.Jk, 64.70.km **DOI:** 10.1088/1674-1056/ac22a4

1. Introduction

Thermoelectric (TE) material can realize the direct conversion of a temperature difference into an electric voltage by using the migration of carriers inside the materials.[1] Because of the advantages of simple device structure, controllable size, no pollution to the environment, the thermoelectric energy conversion technologies have attracted extensive attention from both the academic community and the industry in recent years.[2] Compared with traditional inorganic TE materials, organic TE materials, especially conjugated polymer semiconductors, have the merits of solution processibility, mechanical flexibility, low-cost fabrication. They are of great expectation to be widely used in the field of wearable electronic devices for power supply.[3]

The thermoelectric performance of a given material can be evaluated by the dimensionless thermoelectric merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the temperature. For polymer semiconductors, due to their low thermal conductivity (< 0.5 W·m^{-1}·K^{-1}), the power factor, $PF (PF = S^2\sigma)$, is often used to compare their thermoelectric properties instead. The intrinsically low carrier concentration of organic semiconductors and the complex charge transport model, compared with traditional inorganic semiconductors, lead to a low electrical conductivity and thus a low power factor. Moreover, the S and σ are oppositely dependent on the carrier concentration and often show unfavorable opposing trends, therefore, the optimization of the power factor is not straightforward and great attention should be paid to the synergistic control of carrier concentration and carrier mobility by chemical doping associated with the design of molecular structures.

In this review, we summarize the latest research progress on organic polymer thermoelectric materials from the view of chemical doping methods and materials design rules. Firstly, we discuss some efficient doping strategies for significantly improving the thermoelectric performance. And then, structure design of polymer backbone and polymer side chains will be described. Finally, we give our viewpoints on the challenges and opportunities in this emerging field.

2. Molecular doping of polymer semiconductors

2.1. Understanding about doping mechanism

Chemical doping has been a key method to adjust the carrier concentration of polymer semiconductors based on redox reactions. In a p-type doping process, a dopant with a deep-lying lowest unoccupied molecular orbital (LUMO) level can extract an electron from the polymer with a high-lying highest occupied molecular orbital (HOMO) level. Similarly, in a

†Corresponding author. E-mail: lihui889@mail.sic.ac.cn

© 2022 Chinese Physical Society and IOP Publishing Ltd

n-type doping process, a dopant with a shallow HOMO level can donate an electron to the polymer with a low-lying LUMO level (Fig. 1). Great efforts have been made to optimize the doping methods. Shirakawa *et al.* exposed polyacetylene to iodine vapor to achieve the doping of polyacetylene and the electrical conductivity of the doped film reached up to 10 S·cm^{-1}.[4] The small size of iodine molecule has strong volatility and high reactivity, leading to an obvious performance degradation in ambient, which is not suitable for accurate control of carriers concentration and commercial application. Nowadays, the widely used dopants consist of Lewis-acid dopants,[5–8] Brønsted-acid dopants,[9,10] organic conjugated small molecule,[11–13] etc. Nevertheless, deep understating about doping mechanism is urgently desired. We will discuss the recent progress about small conjugated molecules as dopants below.

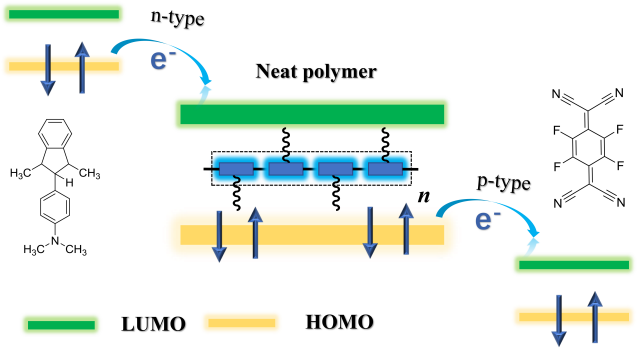


Fig. 1. Charge transfer process for n-type and p-type doping process.

2.1.1. Degree of charge transfer

The ideal molecular doping process is to form an ion pair within the matrix and then all carriers along polymer chains are mobile and contribute to the electrical conductivity. However, numerous experiments have shown that complete integer charge transfer (ICT) is difficult to occur during the doping process. On the contrary, charge transfer complexes (CTC) will simultaneously appear and the uncompleted electron transfer results in a decrease of the amount of carriers per dopant. Therefore, the existence of CTC, which is ubiquitous in conjugated molecular dopant and oligomer,[14–17] has become a main drawback to improving the doping efficiency.

The formation of CTC state is related to the stability of charge transfer state. Many works have proved that the ICT state is kinetically occurred in the process of molecular doping while CTC is a more thermodynamically favored state. Watts *et al.* systematically studied the conversion process from ICT to CTC in the P3HT/F4TCNQ system over time (Fig. 2).[18] Through a combination of infrared and photoelectron spectroscopies, the conversion of ICT state to the CTC state was monitored over time accompanied by a significant conductivity decline.

To improve the doping efficiency, it is necessary to suppress the formation of CTC. Stanfield *et al.* have found that polymers with high crystallinity could restrain the formation of CTC, but that fractional charge transfer would still occur to some extent even in the doped crystalline film by vapor deposition of dopant.[19] It also has been proved that thermal annealing could effectively convert CTC to ICT. It is known that the formation of CTC requires π-stacking of the dopant and polymer, which is kinetically difficult to achieve in highly crystalline regions. This makes sense that the design of conductive polymers should pursue crystalline ICT states for charge transport and let possible CTC states stay in amorphous regions to avoid the deleterious effect on the charge transport.

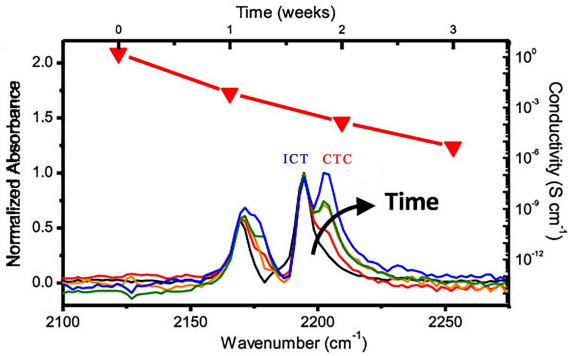


Fig. 2. The Fourier infrared spectrum and conductivity changes of ICT transition to CTC over time.[18]

2.1.2. Double doping of conjugated polymers

Conventional wisdom posits that each dopant produces only one carrier. However, due to the existence of incomplete charge transfer, the doping efficiency is usually below 10%.[9] Therefore, large amounts of dopants are needed to pursuing a high doping efficiency and excess dopants act as impurities impeding the charge transport. Surprisingly, Kiefer *et al.* has shown that small conjugated p-dopants, such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ), can truly accept two electrons per dopant (Fig. 3) from conjugated polymers with a low ionization potential.[13] The characteristic peaks of F4TCNQ dianions were detected in the doped films, confirming the occurrence of the double doping process. This means that the doping efficiency can even reach up to 200%. Therefore, this "double doping" can effectively improve the electrical conductivity of the polymer up to 100 S·cm^{-1}. This work demonstrates that, to achieve double doping, the ionization energy (IE^0) of the polymer should be lower than both the electron affinity (EA^0) of the neutral dopant and the electron affinity (EA) of its anion. That suggests that the low ionization energy of the polymer is the key factor for high doping efficiency and all-donor backbone with polar oligoethylene glycol side chains would be a good design strategy for achieving double doping and high electrical conductivity.

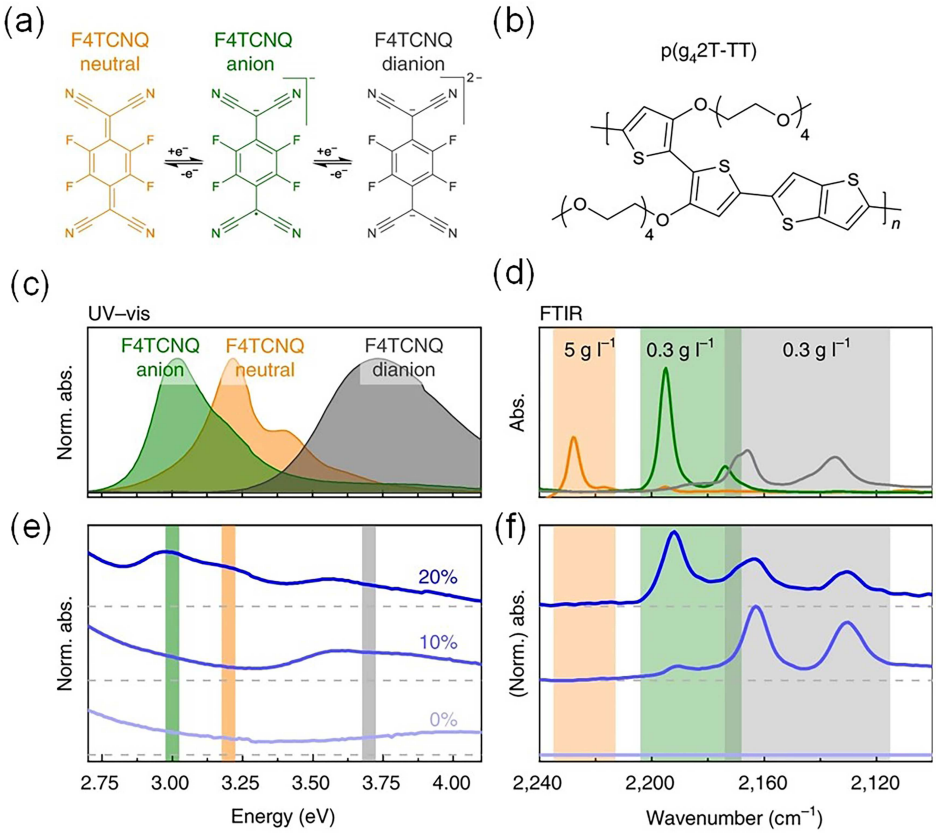


Fig. 3. Chemical structures of (a) F4TCNQ, $Li^{+}F4TCNQ^{\bullet-}$ $2Li^{+}F4TCNQ^{2-}$ and (b) p($g_4$2T-TT). UV-vis absorption spectra (c) and FTIR absorption (d) of the cyano stretch vibrations of neutral F4TCNQ, $Li^{+}F4TCNQ^{\bullet-}$ and $2Li^{+}F4TCNQ^{2-}$. UV-vis absorption spectra (e) and FTIR absorption (f) of the cyano stretch vibrations of undoped p($g_4$2T-TT) films and films doped with 10 and 20 mol% F4TCNQ.[13]

2.2. Generals of doping strategies for high thermoelectric performance

Electrochemical doping was employed to dope polymer semiconductors in an early stage. Electrochemical doping often involves heavy doping of polymer materials accompanying with electrochemically polymerization, such as the preparation of PEDOT:PSS.[20] The polymers obtained by this method usually show high electrical conductivity. Nevertheless, the polymers cannot be dissolved in common solvents, resulting in difficulty to control the film microstructure. In contrast, the chemical doping method shows a wider range of applications in electronic devices. Traditional chemical doping methods include dipping doping,[21,22] single-solution blending[23–25] and sequential doping.[26–29] The development of the doping method aims to reduce the interruption from dopants on the packing of polymer chains. For example, for sequential doping, the pure polymer is deposited first and then the molecular dopant is deposited on the polymer film so that the morphology of the polymer is largely preserved. Recently, a hybrid doping method (Fig. 4) was proposed by Kim's group, in which the solution blending and the sequential doping method were combined together.[30] They proved that the crystalline region and amorphous region of P3HT and PIDF-BT films could be fully doped, and the conductivity could be increased to 81.5 S·cm^{-1} and 639.1 S·cm^{-1}, respectively, which is 2–3 times higher than that of the sequential doping method.

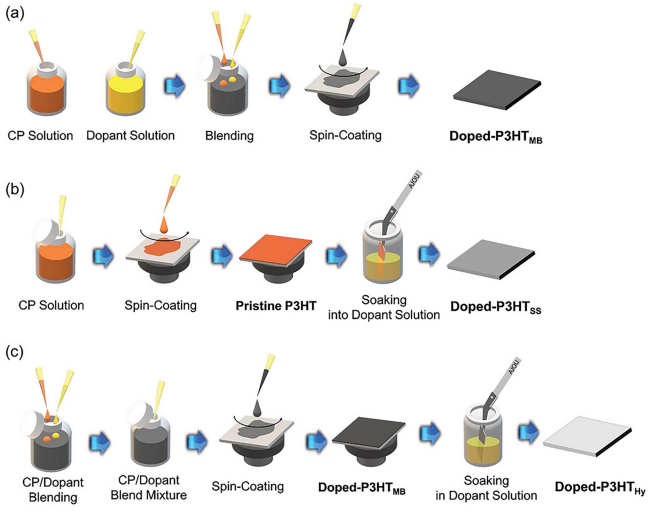


Fig. 4. Schematic diagram for (a) mixture blending, (b) sequential soaking, and (c) hybrid doping processes of the pristine and doped-P3HT.[30]

Traditional chemical doping is the charge transfer between the polymer semiconductor and the dopant to generate polarons on the polymer backbone. When the polarons or charge complexes can be successfully dissociated into free carriers, the doping efficiency can be greatly increased. Anion-exchange doping, different from chemical doping, was proposed by Yamashita *et al*. In their work, negative F4TCNQ

ions produced by chemical doping could be exchanged by ionic liquid (Fig. 5), which results in high doping efficiency as almost one charge per monomer unit.[31] The driving force of spontaneous anion exchange progress is mainly derived from the entropy increase effect of the mixed system. The doped film was immersed in an ionic liquid (such as EMIM-TFSI) with high swelling characteristics to complete the ion–anion exchange process. By changing the anions and cations of ionic liquids, they found that an ionic liquid composed of small cations and large anions would achieve the high doping concentration and anion exchange efficiency.[31]

Murrey *et al.* found that ion exchange is beneficial for polymers with high ionization energy to achieve high doping efficiency.[32] For a polymer, PDPP-2T, with a high ionization energy, the anion exchange of $FeCl_3$-doped film with TFSI spontaneously occurs and the doping level can be increased by approximately $> 10\%$ after anion exchange. Much research is needed to address the effect of anion exchange on polaron delocalization, the polymer film morphology, and the stability of the doped film in the presence of external ions. Furthermore, the high Seebeck coefficient possibly attributed to the ionic Seebeck coefficient after ion exchange should be carefully taken into consideration.

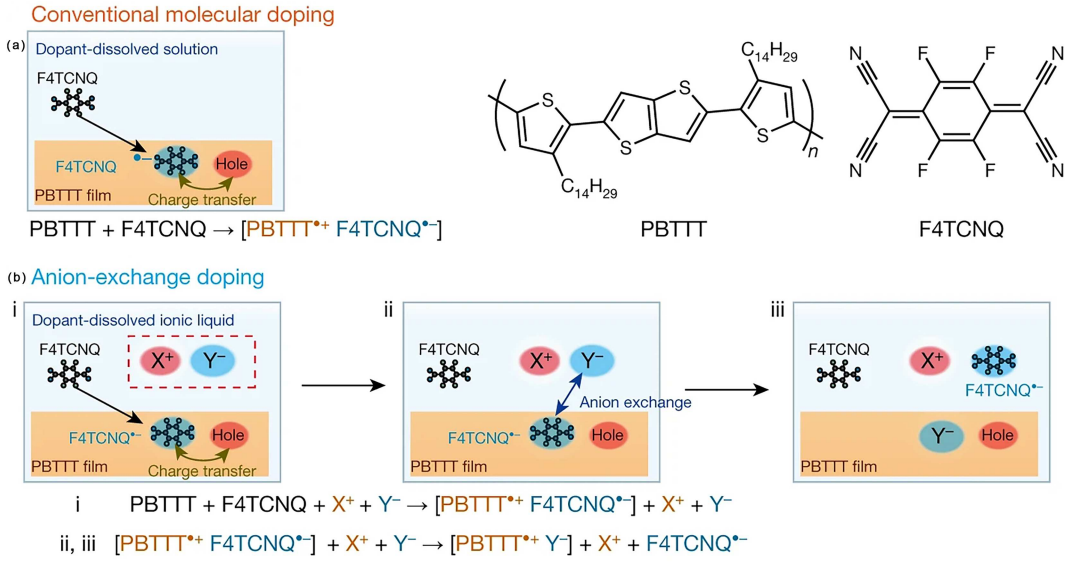


Fig. 5. Anion-exchange doping process. (a) Conventional molecular doping and (b) anion-exchange doping. The inset at the top right shows the chemical structures of PBTTT and F4TCNQ.[31]

3. Optimization of polymer chemical structure

3.1. Design and optimization of polymer backbone

The polymers should have suitable HOMO/LUMO energy levels to achieve charge transfer in the process of molecular doping.[33] The modulation of backbone has been demonstrated to be an effective approach to adjust the energy level in organic thin film transistors and solar cells.[34–36] Therefore, the design of the polymer backbone is important to regulate the molecular orbital energy level and band gap to achieve effective molecular doping (Fig. 6). The representative TE polymers are donor–donor polymers with low ionization energy, such as PEDOT, P3HT or PBTTT (Table 1). Recently, Gregory *et al.* synthesized three analogues of poly (3-alkylthiophene) by substituting S atom with Se and Te in the thiophene cores.[37] It is found that the polymer with Te atom was the easiest one to be doped compared with other two polymers. The electrical conductivity increases as they change the heteroatom from S to Se and to Te, while the thermopower follows the opposite trend. Finally, an optimized thermoelectric performance with a power factor of 13 $\mu W \cdot m^{-1} \cdot K^{-2}$ was obtained for the Te-substituted polymer. Scholes *et al.* achieved the control of polymer energy levels by statistically replace some of the 3-hexylthiophene units with 3-heptylselenophene units along the main chain of P3HT.[38] Although the increase of 3-heptylselenophene content decreases the band gap of the polymer, the change of conductivity is not monotonic with fractional selenophene composition. They further proved that the crystallinity of the doped state is the dominant factor that influences the properties of the highly doped semiconducting polymer films.

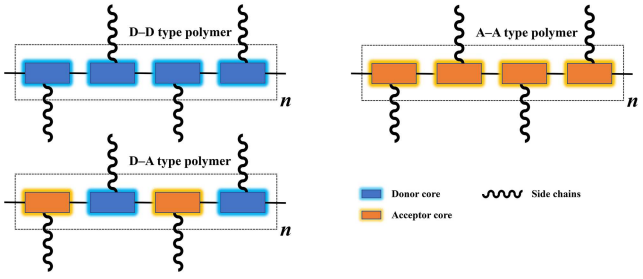


Fig. 6. Structures of D-D type polymer, A-A type polymer, and D-A type polymer.

Table 1. The electrical conductivity, Seebeck coefficient and power factor of representative p-type thermoelectric materials recently reported.

Polymer/dopant	$\sigma_{\text{at max PF}}$ (S·cm^{-1}))	$S_{\text{at max PF}}$ (μV·K^{-1})	PF_{max} (μW·m^{-1}·K^{-2})	Doping method	Ref.
PEDOT:PSS	265	400	23.5	Electrochemical de-doping	[39]
PEDOT:PSS	2170	39.2	334	Treated with H_2SO_4/NaOH	[40]
PBTTT/F4TCNQ	670	42	120	Vapor doping-annealed/OTS treated	[41]
P3HT/TFSI	50	N/A	26	Soaking	[42]
P3HT/$FeCl_3$	45	122	56	Sequential-drop-cast	[43]
PDPP3T/$FeCl_3$	86	226	276	Sequential-drop-cast	[43]
P3RSe/$FeCl_3$	52	89	13	Soaking	[37]
PDPPSe-12/$FeCl_3$	997	70	300	Soaking	[44]
PCQ/Gav	N/A	600	10	Solution blending	[45]
pBBTa26-2T/F4TCNQ	43.1	N/A	11.8	Soaking	[46]
PPy/Nap	78.27	5.23	0.21	Solution blending	[47]
pBBT-2T-TT/ $FeCl_3$	287	65.4	65.2	Sequential solution	[48]
PCDTFBT/F4TCNQ	8.73	946	31.5	Solution blending	[49]
PCDTPT/F4TCNQ	5.13	878	21.8	Solution blending	[49]
PDPP(6-DO)$_2$TT/CN6-CP	70	N/A	N/A	Solution blending	[33]
p($g_4$2T-T)/ F4TCNQ	100	N/A	N/A	Solution blending	[50]
PCPDTSBT/B(C_6H_5)$_3$	7.47	426.75	7.73	Solution blending	[51]
PDPP-$g_3$2T$_{0.3}$/ $FeCl_3$	360	56	110	Soaking	[52]

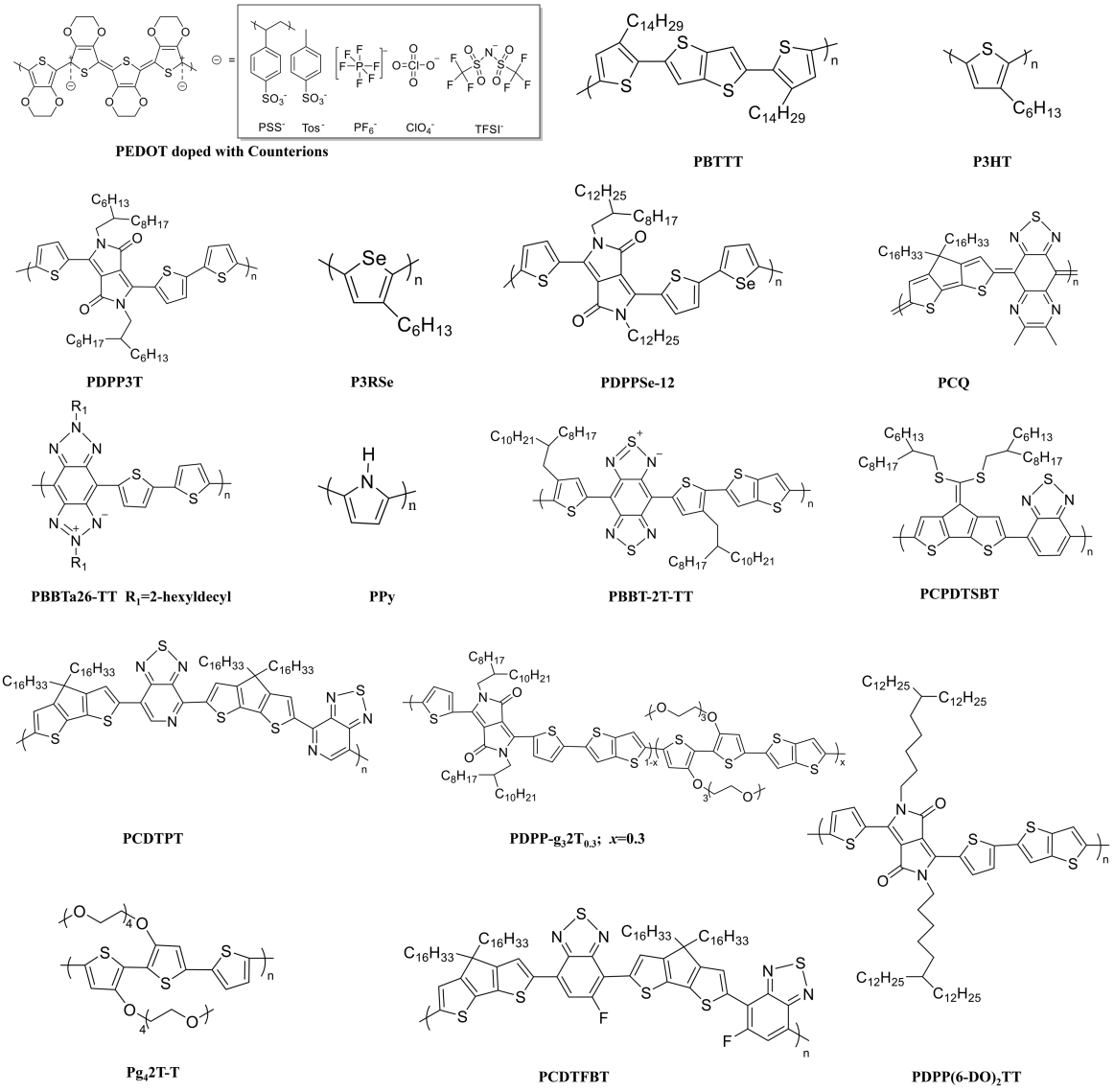


Fig. 7. Chemical structures of p-type thermoelectric polymers mentioned in Table 1.

The polymer crystallinity plays a key role in film mobility. The proper choice of building block for polymer backbone would allow strong interchain interaction providing smooth charge transport paths. Compared to all-donor conjugated polymers, alternative donor–acceptor (D-A) polymers have been used as thermoelectric materials due to their high intrinsic carrier mobility. So far, few D-A polymers have shown promising TE performance.[53] Most D-A polymers are difficult to be doped because of their low-lying HOMO level mismatched with common dopants.[54] Therefore, improving the doping efficiency of the D-A polymer is challenging and meaningful for high thermoelectric properties. The doping efficiency of the D-A polymers can be improved by introducing strong donor units. By copolymerizing two different donors with a typical electron acceptor unit, diketopyrrolopyrrole (DPP), Zhong *et al.* synthesized two D-A polymers.[55] By adjusting the the initial carbazole (CZ) donor unit to regulate the electron donating ability, the polymer with strong donor cores, dithieno[3,2-b:2′,3′-d] pyrrole (DTP), was easier to be doped. The power factor of PDTP-DPP can be enhanced up to 85.5 $\mu W \cdot m^{-1} \cdot K^{-2}$ through the synergistic effect of thermal activation and thermal induced dedoping.

Li *et al.* synthesized a polymer P(BDTTT-DPP) with two-dimensional structure by introducing a highly two-dimensional electron donor unit, BDTTT, into the main chain of the polymer.[56] Compared with its analogue with one-dimensional conjugated backbone, P(BDTTT-DPP) shows a higher doping efficiency and its power factor is 26 times higher than that of its analogue doped with $FeCl_3$. The morphology analysis further indicates that P(BDTTT-DPP) maintains short π–π stacking (010) distance after the doping process and the longer lamellar stacking distance allows $FeCl_3$ dopant staying between the side chains, resulting in favorable crystallinity and carrier transport.

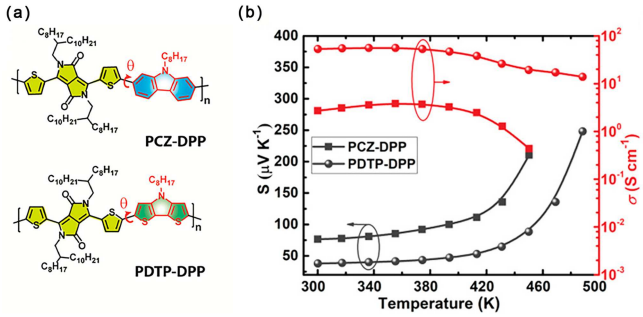


Fig. 8. (a) Molecular structures of studied polymers PCZ-DPP and PDTP-DPP. (b) The temperature-dependence of σ curves of the samples doped with 0.025 mol/L $FeCl_3$ at 10 min.[55]

Many works have demonstrated that the mobility of doped films decreases with the addition of dopants due to the disruption of the nanostructure at high dopant concentration, which limits the improvement of conductivity and thus power factor. Li *et al.* proposed that the random copolymerization of functional building blocks is a simple but effective strategy to synergistically improve the doping efficiency and mobility.[52] They polymerized the D-A type and all-donor type building blocks with glycol side chains to obtain a series of new random copolymers (Fig. 9). Strong D-A interchain interactions maintain a high degree of crystallinity for efficient charge transport while electron-rich units contribute to the increased doping level. In addition, these polymers show higher Seebeck coefficients than that of all-donor polymers because of the alternative monomer sequence providing more energetic disorder and tuning the shape of density of states (DOS).[57] As a result, high PF over 110 $\mu W \cdot K^{-2} \cdot m^{-1}$ is obtained for PDPP-$g_3$2$T_{0.3}$ copolymers.

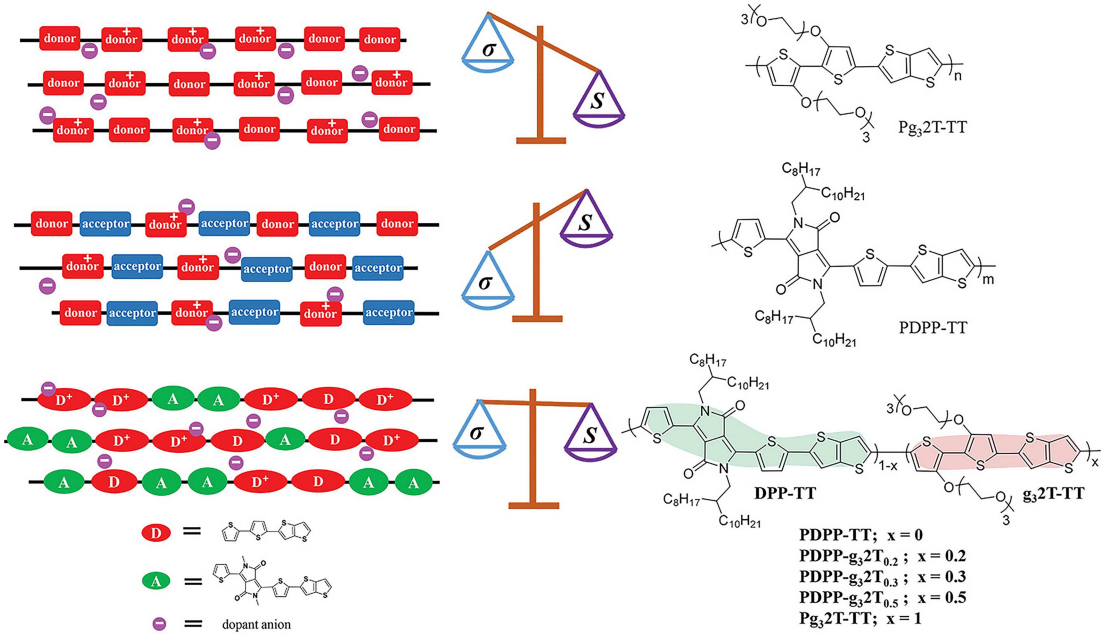


Fig. 9. Schematic diagram of different types of polymer doping. Random copolymer structure and thermoelectric lifting mechanism.[52]

Table 2. The electrical conductivity, Seebeck coefficient and power factor of some representative n-type thermoelectric materials recently reported.

Polymer/dopant	$\sigma_{\text{at max PF}}$ (S·cm^{-1})	$S_{\text{at max PF}}$ (μV·K^{-1})	$PF_{\max}$ (μW·m^{-1}·K^{-2})	Doping method	Ref.
P(NDI2OD-T2)/N-DPBI	2×10^{-3}	3074 ± 77	1.84 ± 0.13	Solution blending	[60]
PNDIClTVT/NDI-TBAF	0.20	1854	67	Solution blending	[61]
ClBDPPV/N-DMBI	4	-206	17	Solution blending	[62]
FBDPPV/N-DMBI	14	141	28	Solution blending	[62]
LPPV/N-DMBI	1.1	−133	1.96	Solution blending	[59]
P(PzDPP-CT2)/N-DMBI	32.1	/	/	Solution blending	[63]
TBDOPV-T/N-DMBI-H	62	−130	106	Solution blending	[64]
FBDPPV/(RuCp*mes)$_2$	0.86	−113	1.1	Solution blending	[65]
FBDPPV/(N-DMBI)$_2$	8	−93	7	Solution blending	[65]
UFBDPPV/N-DMBI-H	16.0 ± 2.1	−94 ± 3.5	11.6 ± 0.3	Solution blending	[66]
PBN-19/TDAE	7.8	178.8	24.8	Sequential vapor	[67]
PCNI-BTI/N-DMBI-H	14.5	−83	10	Sequential solution	[68]
PDTzTI/TDAE	4.6	−128	7.6	Sequential vapor	[69]
pNB-TzDP/*N*-DMBI	11.6	−214	53.4	Solution blending	[70]
PNDI2C8TEG-2Tz	1.5	−346	18	Solution blending	[71]

The design rules of backbone for high mobility and doping efficiency are also suitable for n-type TE polymers (Table 2). Reducing the LUMO level of n-type polymer is a key point for high doping level and film stability. Han *et al.* reported high electron conductivity of 38.3 S·cm^{-1} and 16.1 S·cm^{-1} by coupling difluoro and dichloro-substituted BDOPV with dichlorodithienylethene, respectively. Chlorinated polymer doped by N-DMBI shows excellent air stability due to its high crystallinity and ordered molecular packing.[58] Yang *et al.* gave an example that the introduction of carbon–carbon double bonds and strong electron-withdrawing carbonyl groups into polymer backbone (Fig. 10) leads to a n-type polymer with torsion-free backbone and deep LUMO levels.[59] The new polymer showed a high electrical conductivity up to 1.1 S·cm^{-1} and power factor up to 1.96 μW·m^{-1}·K^{-2} with excellent air stability.

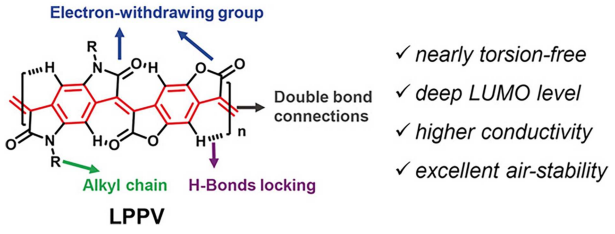


Fig. 10. The design rules and chemical structure of rigid coplanar LPPV.[59]

3.2. Advances of polymer side chain optimization

The modification of side chains is an important design consideration in addition to the polymer backbone. The function of side chains includes controlling energy level, adjusting dielectric constant, and ensuring compatibility with dopants, which goes beyond its common ability to increase polymer solubility. Many studies have shown that the structures of polymer side chain have a great impact on the crystallization behavior, morphology and electronic properties of polymers.[11,50,72] Thus, the modification of polymer side chains has become promising strategy to optimize the TE performance. Next, we will introduce some representative achievements in side chain design of conductive polymers.

Oligo ethylene glycol side chains have been demonstrated to improve the polymer doping efficiency as well as film processability. Kroon *et al.* synthesized a polymer, p(g$_4$2T-T) (Fig. 12), with oligo ethylene glycol side chains attached on the thiophene units.[50] It was verified that the dopant F4TCNQ prefers to interact with the polar side chain, greatly improving the doping efficiency and gaining a high conductivity of about 100 S·cm^{-1}.

Compared with traditional alkyl side chains, polar side chains can significantly reduce the aggregation of dopant molecules, which contributes to the homogenous distribution of dopant molecules in the matrix. By introducing polar side chains, the doping efficiency and thermal stability can be enhanced in n-type TE materials. Liu *et al.* synthesized polymer semiconductors with polar side chain substituted D-A structure (Fig. 13) and obtained the highest conductivity up to 0.17 S·cm^{-1} doped with n-DMBI.[73] In addition, they further proved that the existence of amphipathic side chain, containing an alkyl chain segment as a spacer between the polymer backbone and an ethylene glycol type chain segment, can reduce Coulombic interaction and contribute to a higher Seebeck coefficient for a given electrical conductivity. As a result, an optimized power factor of 18 μW·m^{-1}·K^{-2} was achieved in the doped n-type polymer film.[71]

Li *et al.* synthesized a series of polythiophene polymers (Fig. 14) by inserting sulfur atoms between the main chain conjugated unit and the alkyl side chain.[74,75] The results showed that the sulfur in the side chain acted as the binding sites for the dopants so that the addition of dopant will negligibly affect the packing of polymers and induce strong interchain interactions, resulting in smooth charge transport channels along π–π stacking direction. Moreover, the alkylthio-substituted polymers have high thermal stability and environmental stability after doping.

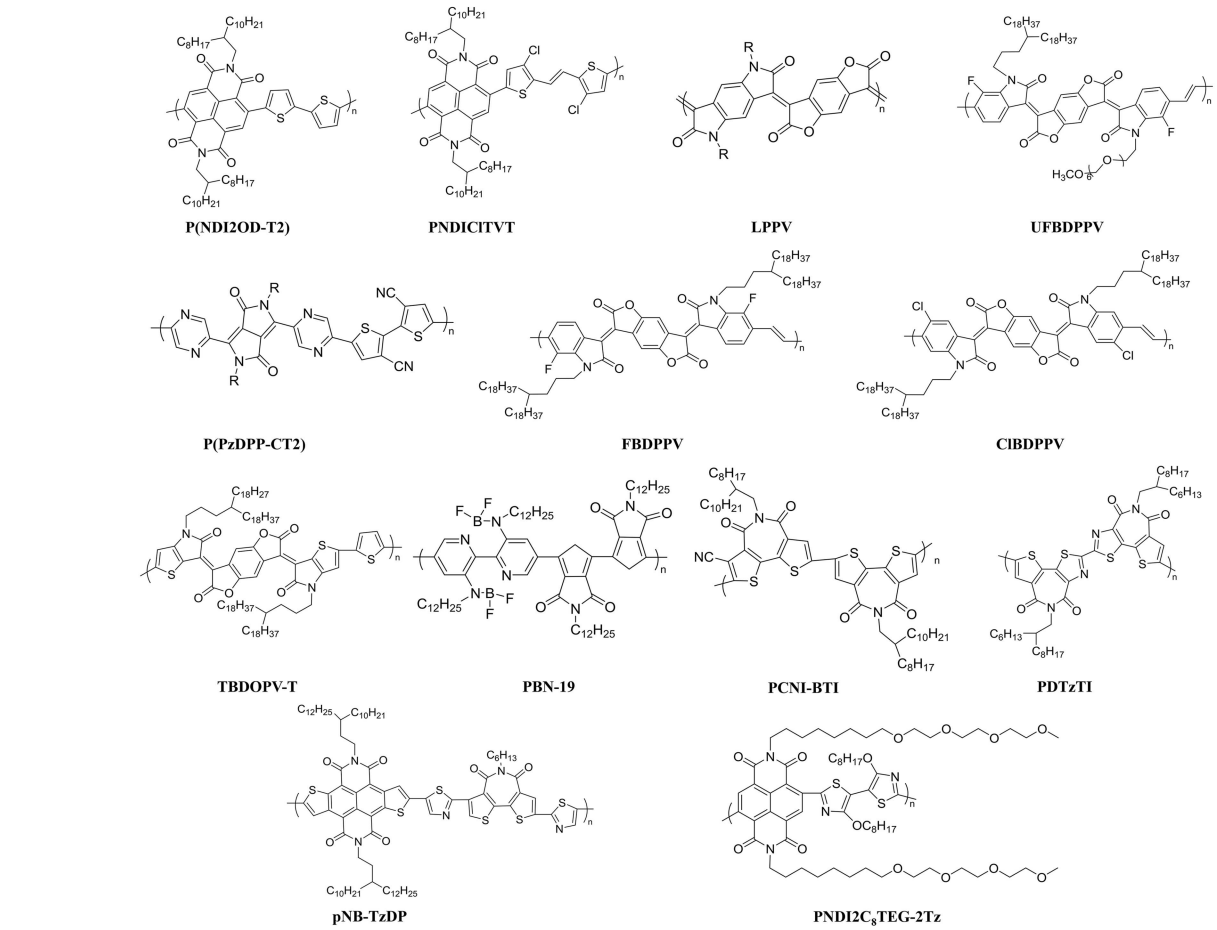


Fig. 11. Chemical structures of n-type thermoelectric polymers mentioned in Table 2.

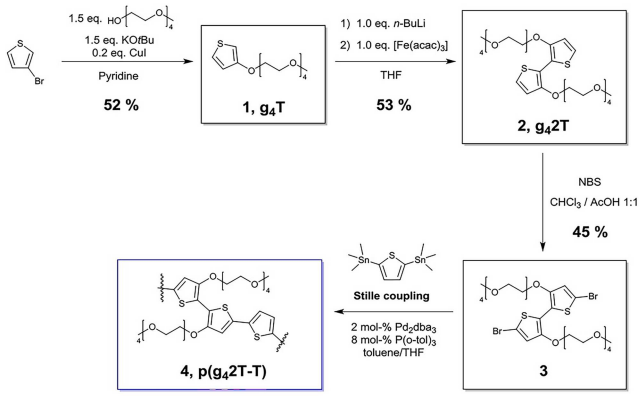


Fig. 12. Synthesis scheme of p(g42T-T) and its chemical structure.[50]

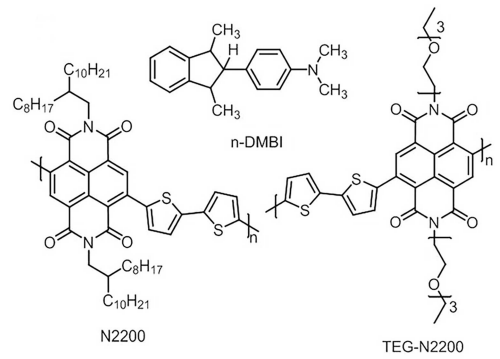


Fig. 13. The chemical structures of N2200, n-DMBI, and TEG-N2200.[73]

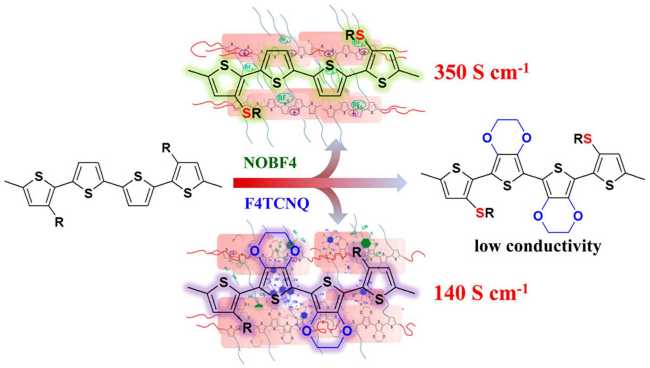


Fig. 14. Chemical structure, conductivity after doping of PTQ12, PTQS12 and PDTDE12.[75]

The conductivity of the doped polymer can be greatly affected by the length of the alkyl side chain. Liang *et al.* synthesized fluorene benzothiazole conjugated polymers with different lengths of alkyl side chains.[72] Although three polymers show similar optical, thermal and mechanical properties, the length of the alkyl chain has an obviously effect on the morphology of the conjugated polymers. The polymer with short alkyl chain shows a higher conductivity than that of the polymers with long alkyl chain while the Seebeck coefficient is negligibly influenced by the alkyl chain length. In addition, the isomerization of the side chain

also has a great influence on the crystallinity of the polymer. The existence of side chain branching site reduces the stacking of the main chains and improve the doping efficiency ascribed to the steric hindrance effect. Yoon *et al.* synthesized four indigo polymers with different types of alkyl chains (Fig. 15).[76] They found that charge carrier mobilities and diffusion efficiencies of the molecular dopant

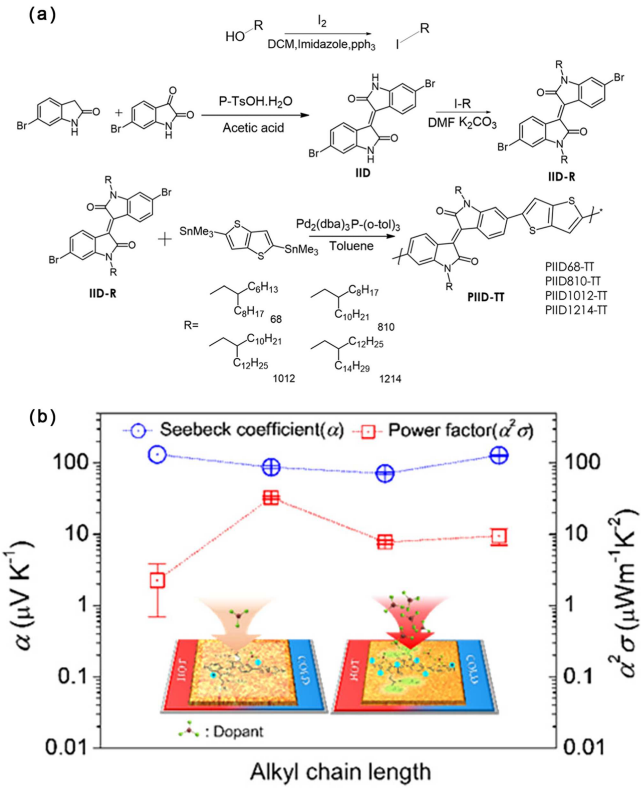


Fig. 15. Chemical structures and synthesis routes of PIID-TT derivatives with different side chains (a) and the TE properties of polymers with different alkyl length (b).[76]

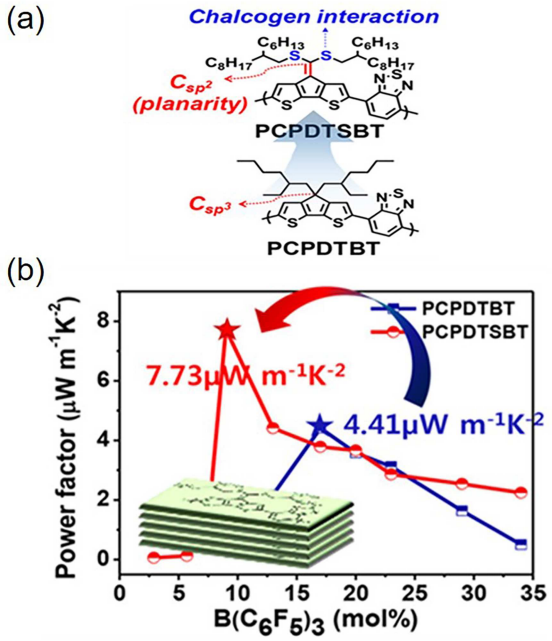


Fig. 16. Chemical structures and power factor of PCPDTSBT and PCPDTBT.[51]

are dependent on the size of the alkyl chains. That means amorphous polymers with bulkier alkyl chains show efficient dopant diffusion although their carrier mobility is relatively lower than that of crystalline polymers. The trade-off relationship between mobility and dopant diffusion by side-chain modification gave an optimized power factor up to 37.8 $\mu W \cdot m^{-1} \cdot K^{-2}$.

Lee *et al.* proved that the introduction of sp^2-hybridized olefinic bis(alkylsulfanyl)methylene side-chains with the extended chain planarity has a great contribution to the strong interchain packing and film mobility.[51] Compared to PCPDTBT with normal ethylhexyl substituents, the sp^2-hybridized olefinic substituted PCPDTSBT, doped with Lewis acid $B(C_6F_5)_3$, shows a higher electrical conductivity of 7.47 $S \cdot cm^{-1}$ and thus an enhanced power factor of 7.73 $\mu W \cdot m^{-1} \cdot K^{-2}$ (Fig. 16).

4. Conclusions and perspectives

Compared with inorganic semiconductors, there is still a long way for thermoelectric polymers to approach commercial applications. Although the *ZT* value has been improved up to 0.2 profited from materials design and film processing, the conductive polymers with high TE performance are still rare. Polymer design strategies based on in-depth understanding of the structure-property relationship are urgently required. Especially, two crucial factors, carrier concentration and carrier mobility, are strongly related to the modulation of carrier transport property. The carrier concentration is generally adjusted by chemical doping which can cut both ways. The increased carrier concentration is usually accompanied by the addition of a large amount of dopants with part of them acting as impurities to damage the charge transport. Therefore, high doping efficiency with much low dopant concentration is of great importance to break the balance between carrier concentration and mobility. To realize this, more attention should be paid to the development of new dopants as well as the rational design of polymer structure to obtain good miscibility and overcome Coulomb binding energy between dopant anion and holes along the polymer backbone.

Molecular doping mechanism is still inadequately understood. It is well known that the charge transfer process plays a key role in the doping efficiency. However, how the charge transfer complexes overcome Coulomb binding energy, then convert into free carrier and finally contribute to conductivity is still a controversial issue. In particular, a myriad of transport models can be used for doped polymers. It is still challenging to propose a general description for transport in lightly doped film or heavily doped film. The lack of deep understanding how charges move through polymers has been one of bottlenecks for designing high-performance TE materials.

The optimization of Seebeck coefficient during the improvement of electrical conductivity is largely unexplored. Since Seebeck coefficient and electrical conductivity are inversely correlated, the decoupling of these two parameters is tough but of vital importance for developing thermoelectric materials with high power factors. The modulation of density-of-states has been demonstrated to obtain high Seebeck coefficients. However, this method is just realized in two polymer blends. A simple and universal system with comprehensively physical explanation is lacking so far.

Besides the alternative D-A polymers, emerging block copolymers, random copolymers, and so on, can be new design strategies to control the morphology and electronic property of conductive polymers. All these progresses in material design combined with processing strategies and nonconventional module architectures open opportunity to realize practical application of polymer-based thermoelectric materials and devices. It is a promising direction for future research to realize large-area and printed polymer TE films applied in flexible power generators, thermal management devices, and multi-parameter sensors.

Acknowledgements

Project supported by the National Natural Science Foundation of China (Grant No. 21905294) and the Shanghai Sailing Program.

References

[1] Heremans J P, Jovovic V, Toberer E S, Saramat A, Kurosaki K, Charoenphakdee A, Yamanaka S and Snyder G J 2008 *Science* **321** 554
[2] Harman T C, Taylor P J, Walsh M P and Laforge B E 2002 *Science* **297** 2229
[3] Ding T, Chan K H, Zhou Y, Wang X Q, Cheng Y, Li T and Ho G W 2020 *Nat. Commun.* **11** 6006
[4] Shirakawa H, Louis E J, MacDiarmid A G, Chiang C K and Heeger A J 1977 *J. Chem. Soc., Chem. Commun.* **16** 578
[5] Li H, Shi W, Song J, Jang H J, Dailey J, Yu J and Katz H E 2018 *Chem. Rev.* **119** 3
[6] Huang W, Besar K, Lecover R, Rule A M, Breysse P N and Katz H E 2012 *J. Am. Chem. Soc.* **134** 14650
[7] Kang Y H, Ko S J, Lee M H, Lee Y K and Song Y C 2020 *Nano Energy* **82** 105681
[8] Yamamoto, Jun, Furukawa and Yukio 2015 *J. Phys. Chem. B* **119** 4788
[9] Lüssem B, Keum C M, Kasemann D, Naab B, Bao Z and Leo K 2016 *Chem. Rev.* **116** 13714
[10] Kim G H, Shao L, Zhang K and Pipe K P 2013 *Nat. Mater.* **12** 719
[11] Gao, Weiying, Kahn and Antoine 2001 *Appl. Phys. Lett.* **79** 4040
[12] Kulkarni C, van Son M H C, Di Nuzzo D, Meskers S C J, Palmans A R A and Meijer E W 2019 *Chem. Mater.* **31** 6633
[13] Kiefer D, Kroon R, Hofmann A I, Sun H, Liu X, Giovannitti A, Stegerer D, Cano A, Hynynen J, Yu L, Zhang Y, Nai D, Harrelson T F, Sommer M, Moulé A J, Kemerink M, Marder S R, McCulloch I, Fahlman M, Fabiano S and Müller C 2019 *Nat. Mater.* **18** 149
[14] Aziz E F, Vollmer A, Eisebitt S, Eberhardt W and Koch N 2010 *Adv. Mater.* **19** 3257
[15] Méndez H, Heimel G, Opitz A, Sauer K, Barkowski P, Oehzelt M, Soeda J, Okamoto T, Takeya J, Arlin J B, Balandier J Y, Geerts Y, Koch N and Salzmann I 2013 *Angew. Chem. Int. Ed.* **52** 7751
[16] Pahner P, Kleemann H, Burtone L, Tietze M L, Fischer J, Leo K and Lussem B 2013 *Phys. Rev. B* **88** 195205
[17] Salzmann I, Heimel G, Duhm S, Oehzelt M, Pingel P, George B M, Schnegg A, Lips K, Blum R P, Vollmer A and Koch N 2012 *Phys. Rev. Lett.* **108** 035502
[18] Watts K E, Neelamraju B, Ratcliff E L and Pemberton J E 2019 *Chem. Mater.* **31** 6986
[19] Stanfield D A, Wu Y, Tolbert S H and Schwartz B J 2021 *Chem. Mater.* **33** 2343
[20] Robert B, Felipe F G J, Kosala W, Eleni P, Daniela G, Xianjie L, Roudabeh V, Zozoulenko I V and Xavier C 2018 *J. Mater. Chem. A* **6** 21304
[21] Endrdi B, Mellar J, Gingl Z, Visy C and Janaky C 2014 *Rsc Advances* **4** 55328
[22] Wu L, Li H, Chai H, Xu Q, Chen Y and Chen L 2021 *ACS Applied Electronic Materials* **3** 1252
[23] Zheng W, Min Y, M Acd Iarmid A G, Angelopoulos M, Liao Y H and Epstein A J 1997 *Synthetic Metals* **84** 109
[24] Duong D T, Wang C, Antono E, Toney M F and Salleo A 2013 *Organic Electronics* **14** 1330
[25] Tolbert, Sarah H, Scholes, Tyler D, Hao, Schwartz, Benjamin J, Yee, Patrick Y and Lindemuth 2015 *J. Phys. Chem. Lett.* **6** 4786
[26] Zhang G Y, Huber R C, Ferreira A S, Boyd S D, Luscombe C K, Tolbert S H and Schwartz B J 2014 *J. Phys. Chem. C* **118** 18424
[27] van Franeker J J, Kouijzer S, Lou X, Turbiez M, Wienk M M and Janssen R A J 2015 *Adv. Energy Mater.* **5** 1500464
[28] Ferreira A S, Aguirre J C, Subramaniyan S, Jenekhe S A, Tolbert S H and Schwartz B J 2016 *J. Phys. Chem. C* **120** 22115
[29] Fontana M T, Stanfield D A, Scholes D T, Winchell K J and Schwartz B J 2019 *J. Phys. Chem. C* **123** 22711
[30] Yoon S E, Kang Y, Jeon G G, Jeon D, Lee S Y, Ko S J, Kim T, Seo H, Kim B G and Kim J H 2020 *Adv. Funct. Mater.* **30** 2004598
[31] Yamashita Y, Tsurumi J, Ohno M, Fujimoto R, Kumagai S, Kurosawa T, Okamoto T, Takeya J and Watanabe S 2019 *Nature* **572** 634
[32] Murrey T L, Riley M A, Gonel G, Antonio D D, Filardi L, Shevchenko N, Mascal M and Moulé A J 2021 *J. Phys. Chem. Lett.* **12** 1284
[33] Karpov Y, Erdmann T, Raguzin I, Al-Hussein M, Binner M, Lappan U, Stamm M, Gerasimov K L, Beryozkina T, Bakulev V, Anokhin D V, Ivanov D A, Günther F, Gemming S, Seifert G, Voit B, Di Pietro R and Kiriy A 2016 *Adv. Mater.* **28** 6003
[34] Li G, Zhu R and Yang Y 2012 *Nat. Photon.* **6** 153
[35] Kim A, Lee J H, Kim H J, Choi S, Kim Y U, Park C G, Jeong C H, Cho M J and Choi D H 2018 *Synthetic Metals* **236** 36
[36] Heeney M, Zhang W, Crouch D J, Chabinyc M L, Gordeyev S, Hamilton R, Higgins S J, McCulloch I, Skabara P J, Sparrowe D and Tierney S 2007 *Chemical Communications* **2007** 5061
[37] Gregory S A, Menon A K, Ye S, Seferos D S, Reynolds J R and Yee S K 2018 *Adv. Energy Mater.* **8** 1802419
[38] Scholes D T, Yee P Y, Mckeown G R, Li S, Kang H, Lindemuth J R, Xia X, King S C, Seferos D S and Tolbert S H 2018 *Chem. Mater.* **31** 73
[39] Bubnova O, Berggren M and Crispin X 2012 *J. Am. Chem. Soc.* **134** 16456
[40] Fan Z, Li P, Du D and Ouyang J 2017 *Adv. Energy Mater.* **7** 1602116
[41] Patel S N, Glaudell A M, Peterson K A, Thomas E M and Chabinyc M L 2017 *Science Advances* **3** 1700434
[42] Zhang Q, Sun Y M, Xu W and Zhu D B 2012 *Energy & Environmental Science* **5** 9639
[43] Jung I H, Hong C T, Lee U H, Kang Y H, Jang K S and Cho S Y 2017 *Scientific Reports* **7** 44704
[44] Ding J, Liu Z, Zhao W, Jin W, Xiang L, Wang Z, Zeng Y, Zou Y, Zhang F and Yi Y 2019 *Angewandte Chemie* **131** 19170
[45] Joo Y, Huang L, Eedugurala N, London A E, Kumar A, Wong B M, Boudouris B W and Azoulay J D 2018 *Macromolecules* **51** 3886
[46] Dexter Tam T L, Ng C K, Lim S L, Yildirim E, Ko J, Leong W L, Yang S W and Xu J 2019 *Chem. Mater.* **31** 8543
[47] Park J, Lee Y, Kim M, Kim Y, Tripathi A, Kwon Y W, Kwak J and Woo H Y 2020 *ACS Appl. Mater. Interfaces* **12** 1110
[48] Tam T L D, Wu G, Chien S W, Lim S F V, Yang S W and Xu J 2020 *ACS Materials Letters* **2** 147
[49] Suh E H, Jeong Y J, Oh J G, Lee K, Jung J, Kang Y S and Jang J 2019 *Nano Energy* **58** 585
[50] Kroon R, Kiefer D, Stegerer D, Yu L, Sommer M and Müller C 2017 *Adv. Mater.* **29** 1700930

[51] Lee J, Kim J, Nguyen T L, Kim M, Park J, Lee Y, Hwang S, Kwon Y W, Kwak J and Woo H Y 2018 *Macromolecules* **51** 3360

[52] Li H, Song J, Xiao J, Wu L, Katz H E and Chen L 2020 *Adv. Funct. Mater.* **30** 2004378

[53] Goel M, Heinrich C D, Krauss G and Thelakkat M 2019 *Macromolecular Rapid Communications* **40** 1800915

[54] Karpov Y, Erdmann T, Stamm M, Lappan U, Guskova O, Malanin M, Raguzin I, Beryozkina T, Bakulev V and Günther F 2017 *Macromolecules* **50** 914

[55] Zhong F, Yin X, Chen Z, Gao C and Wang L 2020 *ACS Appl. Mater. Interfaces* **12** 26276

[56] Li B, Li X, Yang F, Chen Y, Mao X, Wan S, Xin H, Yan S, Wang M, Gao C and Wang L 2021 *ACS Appl. Energy Mater.* **4** 4662

[57] Zuo G, Liu X, Fahlman M and Kemerink M 2018 *Adv. Funct. Mater.* **28** 1703280

[58] Han J, Fan H, Zhang Q, Hu Q, Russell T P and Katz H E 2021 *Adv. Funct. Mater.* **31** 2005901

[59] Lu Y, Yu Z D, Zhang R Z, Yao Z F, You H Y, Jiang L, Un H I, Dong B W, Xiong M, Wang J Y and Pei J 2019 *Angew. Chem. Int. Ed.* **58** 11390

[60] Kluge R M, Saxena N, Chen W, Körstgens V, Schwartzkopf M, Zhong Q, Roth S V and Müller-Buschbaum P 2020 *Adv. Funct. Mater.* **30** 2003092

[61] Han J, Ganley C, Hu Q, Zhao X, Clancy P, Russell T P and Katz H E 2021 *Adv. Funct. Mater.* **31** 2010567

[62] Shi K, Zhang F, Di C A, Yan T W, Zou Y, Zhou X, Zhu D, Wang J Y and Pei J 2015 *J. Am. Chem. Soc.* **137** 6979

[63] Xiong M, Yan X Y, Li J T, Zhang S, Cao Z Q, Prine N, Lu Y, Wang J Y, Gu X D and Lei T 2021 *Angewandte Chemie* **133** 8270

[64] Lu Y, Yu Z D, Un H I, Yao Z F, You H Y, Jin W, Li L, Wang Z Y, Dong B W, Barlow S, Longhi E, Di C a, Zhu D, Wang J Y, Silva C, Marder S R and Pei J 2021 *Adv. Mater.* **33** 2005946

[65] Un H I, Gregory S A, Mohapatra S K, Xiong M, Longhi E, Lu Y, Rigin S, Jhulki S, Yang C Y, Timofeeva T V, Wang J Y, Yee S K, Barlow S, Marder S R and Pei J 2019 *Adv. Energy Mater.* **9** 1900817

[66] Lu Y, Yu Z D, Liu Y, Ding Y F, Yang C Y, Yao Z F, Wang Z Y, You H Y, Cheng X F, Tang B, Wang J Y and Pei J 2020 *J. Am. Chem. Soc.* **142** 15340

[67] Dong C, Deng S, Meng B, Liu J and Wang L 2021 *Angew. Chem. Int. Ed.* **60** 16184

[68] Feng K, Guo H, Wang J, Shi Y, Wu Z, Su M, Zhang X, Son J H, Woo H Y and Guo X 2021 *J. Am. Chem. Soc.* **143** 1539

[69] Liu J, Shi Y, Dong J, Nugraha M I, Qiu X, Su M, Chiechi R C, Baran D, Portale G, Guo X and Koster L J A 2019 *ACS Energy Letters* **4** 1556

[70] Wang Y and Takimiya K 2020 *Adv. Mater.* **32** 2002060

[71] Liu J, Ye G, Potgieser H G O, Koopmans M, Sami S, Nugraha M I, Villalva D R, Sun H, Dong J, Yang X, Qiu X, Yao C, Portale G, Fabiano S, Anthopoulos T D, Baran D, Havenith R W A, Chiechi R C and Koster L J A 2021 *Adv. Mater.* **33** 2006694

[72] Liang A, Zhou X, Zhou W, Wan T, Wang L, Pan C and Wang L 2017 *Macromolecular Rapid Communications* **38** 1600817

[73] Liu J, Qiu L, Alessandri R, Qiu X, Portale G, Dong J, Talsma W, Ye G, Sengrian A A, Souza P C T, Loi M A, Chiechi R C, Marrink S J, Hummelen J C and Koster L J A 2018 *Adv. Mater.* **30** 1704630

[74] Li H, Decoster M E, Ming C, Wang M and Katz H E 2019 *Macromolecules* **52** 9804

[75] Li H, Decoster M E, Ireland R M, Song J, Hopkins P E and Katz H E 2017 *J. Am. Chem. Soc.* **139** 11149

[76] Yoon S E, Shin S J, Lee S Y, Jeon G G, Kang H, Seo H, Zheng J and Kim J H 2020 *ACS Applied Polymer Materials* **2** 2729