RESEARCH HIGHLIGHTS

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To enhance the performance of n-type organic thermoelectric materials

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Organic thermoelectric (OTE) materials that can convert waste heat to electricity have aroused interests due to their unique advantages over traditional inorganic TE materials, such as light weight, mechanical flexibility, low thermal conductivity, and solution processability[1–4]. In general, TE devices require both p-type and n-type semiconductors. The p-type polymers have been extensively studied, showing rapid advances, but there are few efficient n-type TE polymers[5, 6]. Therefore, the development of high-performance n-doped conjugated polymers is demanded.

The TE performance is evaluated by the figure of merit, $ZT = S^2\sigma T/\kappa$, where S, σ, T, and κ are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. As the κ values of polymers are much lower than that of inorganic materials, the TE performance of polymers can also be determined by the power factor (PF = $S^2\sigma$)[7]. Thus, enhancing σ and S is the key to improve TE performance. The inferior performance for n-type OTE materials is mainly due to their low σ, so we focus on the σ issue in this article. To enhance the conductivity, some strategies can be applied, which will be discussed as follows.

Lowering LUMO energy level is an effective approach to improve n-doping[8–10]. Introducing strong electron-withdrawing groups or atoms to the backbone can lower the LUMO level[11–13]. The D–A copolymer P(NDI2OD-T2) has deep-lying LUMO level (–3.80 eV). When doped with *n*-DMBI, a conductivity of ~10^{-3} S/cm was achieved[7]. To further down-shift LUMO level, Facchetti *et al.* designed polymer P(NDI2OD-Tz2) (Fig. 1)[14]. By introducing bithiazole unit, the polymer possesses a more planar backbone than N2200, resulting in a close π–π stacking. The electron-deficient nature of bithiazole enhances electron affinity of the polymer, yielding an enhanced σ of 0.1 S/cm and a reasonable PF of 1.5 μW/(m·K^2) (Table 1). To reduce steric hindrance of NDI, thiophene-fused NDI derivative, naphtho[2,3-b:6,7-b']dithiophenediimide (NDTI), was developed by Takimiya *et al.* Then they developed a polymer PNDTI-BBT-DP with strong electron affinity. It has a low LUMO level (~ –4.4 eV), which is sufficiently low for being doped by *n*-DMBI. The doped film offered a σ of 5.0 S/cm and a PF of 14 μW/(m·K^2)[15]. Recently, Wang *et al.* reported PNB-TzDP that offered an excellent σ of 11.6 S/cm and a PF of 53.4 μW/(m·K^2)[16]. Another strong electron-accepting unit BDOPV was developed by Pei *et al.*, and the derivative polymers have low LUMO levels and have been investigated in various devices[17]. Among them, FBDPPV delivered a high σ of 14 S/cm and a PF of 28 μW/(m·K^2). Subsequently, a σ over 90 S/cm was obtained from TBDPPV polymer doped with *n*-DMBI[18, 19]. Guo *et al.* synthesized thiazolothienyl imide dimer (DTzTI) unit by replacing thiophene with thiazole to further push down LUMO level. PDTzTI was studied in OTFT[20, 21]. When doped with TDAE, a σ of 4.6 S/cm and a PF of 7.6 μW/(m·K^2) were obtained[22]. PCNI-BTI was developed, offering a σ of 23.3 S/cm and a PF of 10 μW/(m·K^2)[23]. B←N coordination bonds show electron-withdrawing properties, gifting polymers with low LUMO levels[24]. Liu *et al.* reported a polymer PBN-19 with BNBP unit. After n-doping, PBN-19 exhibited a σ of 7.8 S/cm and a PF of 24.8 μW/(m·K^2)[25].

Introducing polar triethylene glycol (TEG) side chains into polymers can improve the miscibility between dopant and polymer. Liu *et al.* found that the σ and PF of TEG-N2200 can be increased by a factor of 200 after replacing alkyl side chains of N2200 with TEG side chains[26]. It delivered a σ of 0.17 S/cm and a PF of 0.4 μW/(m·K^2) (Table 1) after being doped with *n*-DMBI. They also designed polymer PNDI2TEG-2Tz by replacing thiophene with thiazole unit, and the doped material showed a higher σ of 1.8 S/cm and a higher PF of 4.5 μW/(m·K^2) as compared with N2200[27]. Similar methods were also used by other groups[28].

In short, we discussed the strategies of lowering LUMO energy level and incorporating polar side chains for making high-performance n-type OTE materials. More efforts should be focused on molecular engineering.

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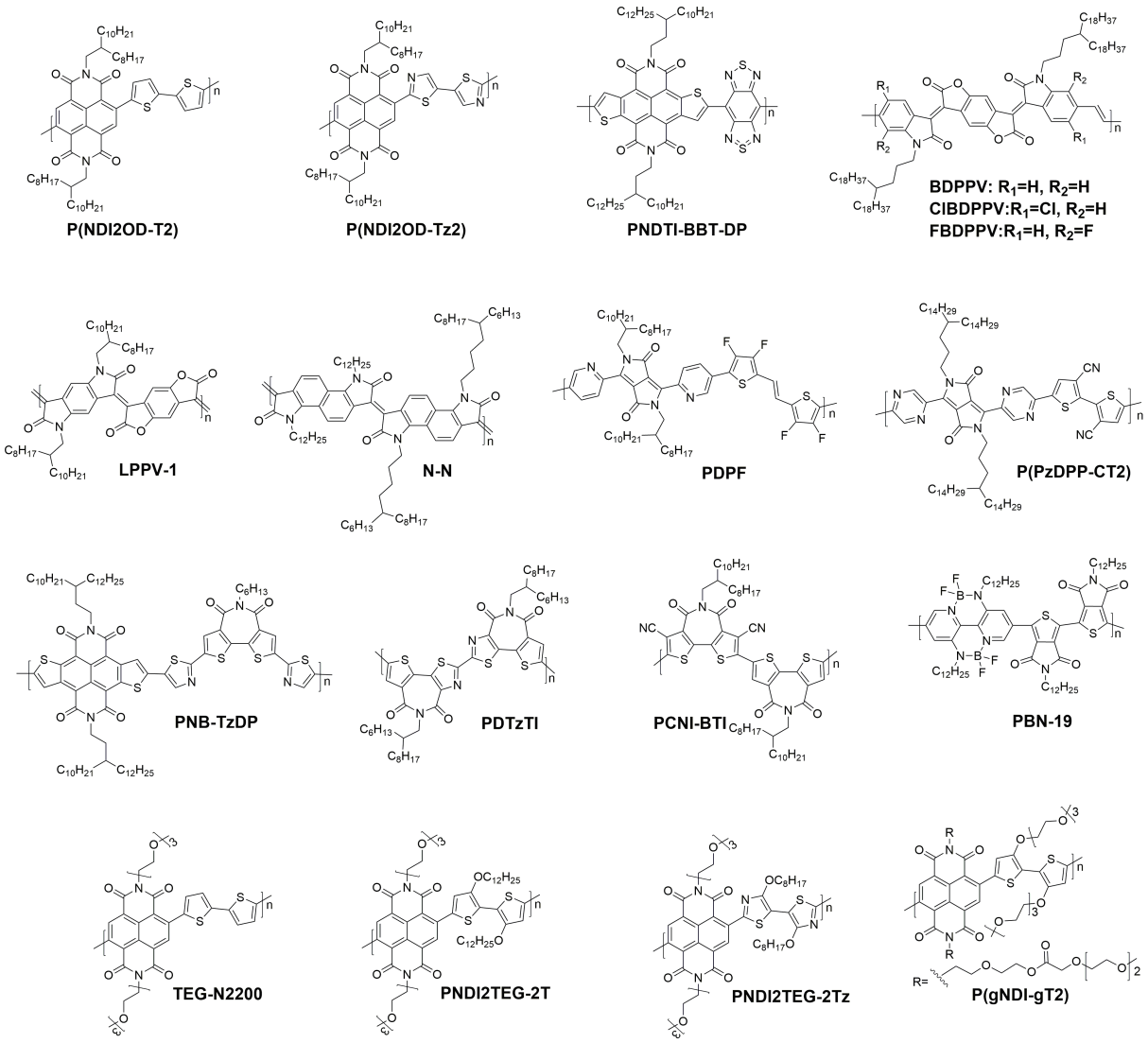

Fig. 1. The chemical structures of representative n-type OTE materials.

Table 1. Performance data for n-type OTE materials.

Polymer	σ (S/cm)	S (μV/K)	PF (μW/(m·K^2))	Ref.
P(NDI2OD-T2)	0.003	–	0.012	[7]
P(NDI2OD-Tz2)	0.1	−447 ± 15	1.5	[14]
PNDTI-BBT-DP	5	−169	14.2	[15]
FBDPPV	14	−141	28	[17]
LPPV-1	1.1	−170	1.96	[8]
N-N	0.65	–	3.2	[9]
PDPF	1.30	−235	4.65	[10]
P(PzDPP-CT2)	8.4	–	57.3	[19]
PNB-TzDP	11.6	–	53.4	[16]
PDTzTI	4.6	−129	7.6	[22]
PCNI-BTI	23.3	−83.3	10.0	[23]
PBN-19	7.8	−178.8	24.8	[25]
TEG-N2200	0.17	–	0.40	[26]
PNDI2TEG-2Tz	0.18	−159 ± 158	4.6 ± 0.2	[27]
P(gNDI-gT2)	0.3	−93	0.4	[28]

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