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Full paper

Side-chain effects on N-type organic thermoelectrics: A case study of fullerene derivatives

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ABSTRACT

In this contribution, the two key parameters, the polarity and side chain length have been changed to study their effects on n-type organic thermoelectrics of a series of fullerene derivatives. Fullerene derivatives bearing either an alkyl side chain or ethylene glycol (EG) side chains of different lengths are used as the host molecules for molecular doping. It is found that the polar EG side chains can enable better miscibility with the polar dopant than the alkyl side chain, which leads to more than 5-fold enhancement of doping efficiency. Beyond the doping efficiency, another crucial parameter of molecular doping, the molecular order, is readily acquired by simultaneous control of the polarity and the length of the side chain. A polar side chain with an appropriate chain length can contribute to increasing Seebeck coefficients of doped fullerene derivatives more effectively than an alkyl side chain, likely due to the resultant good miscibility and high molecular order. As a result, an optimized power factor of $23.1 \mu\text{W m}^{-1} \text{K}^{-2}$ is achieved in the fullerene derivative with a tetraethylene glycol side chain. This represents one of the best n-type organic thermoelectrics. Additionally, EG side chains can improve the air stability of n-doped fullerene derivatives films as compared to an alkyl side chain. Our work sheds light on the design of side-chains in efficient n-type small molecules thermoelectric materials and contributes to the understanding of their thermoelectric properties.

1. Introduction

Molecular doping of organic semiconductors (OSCs) plays a key role in advancing the performance of organic electronic devices by filling traps in organic field-effect transistors, extracting and injecting charge carriers in organic/hybrid solar cells and organic light-emitting diodes, tuning the polarity (p-type legs or n-type legs) in organic thermoelectrics [1–7]. For organic thermoelectrics, the carrier density of OSCs is usually modulated by doping to optimize the figure of merit value $ZT = \sigma S^2 T / \kappa$, where σ , S , κ , and T are the electrical conductivity, the Seebeck coefficient, the thermal conductivity and the absolute temperature, respectively [8–10]. The simplicity of molecular doping by low-temperature solution co-deposition from a host/dopant mixture is one of its intrinsic advantages over other doping strategies, such as electrochemical doping [11,12]. However, the incorporation of dopant molecules can disrupt the packing of the host material or induce orbital hybridization between host and dopant molecules, which brings

additional structural/energetic disorder [13]. Consequently, efficient molecular doping is desirable for generating sufficient carrier density with limited loading of dopant molecules. Both efficient p- and n-doping of OSCs are required for the practical thermoelectric application. P-doping of OSCs has already been well studied and sufficiently high doping efficiency can be achieved [14–17]. However, most of the n-type OSCs, possess high-lying lowest unoccupied molecular orbital (LUMO) levels ($\geq -4.0 \text{ eV}$), which causes a narrow window for optional stable n-type dopants and typically low doping efficiency [18]. Additionally, the two key parameters, S and σ , show opposite trends when modulating the carrier density to optimize the power factor (σS^2). One effective way to increase σ without sacrificing S is to increase the intrinsic mobility by enhancing the molecular order [19]. However, maintaining the molecular order upon molecular doping is a challenge given the large size of organic dopants and the low efficiency of n-doping.

Currently, the best organic n-type thermoelectric performance, with

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a power factor of $453 \mu\text{W m}^{-1} \text{K}^{-2}$, was achieved with electrochemically prepared poly(nickel 1,1,2,2-ethenetetrathiolate) [20]. However, this method is complex and not amenable to solution-processing. The pioneering work of utilizing solution-processed n-type conjugated polymers for thermoelectrics was conducted by Chabinyk and co-workers [18]. An optimized conductivity of $\sim 10^{-3} \text{ S/cm}$ with a power factor of $\sim 0.1 \mu\text{W m}^{-1} \text{K}^{-2}$ was achieved based on molecularly doped poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)–2,6-diyl]-*alt*-5,5'-(2,2'-bithiophene)}(P(NDI2OD-T2)). The researchers attribute the low electrical conductivity to the limited solubility of organic dopants in the host matrix and a doping efficiency of only $\sim 1\%$. Shin et al. incorporated 'kinked' monomers to a naphthalene-based copolymer to improve the host/dopant miscibility and achieved a conductivity of $\sim 10^{-3} \text{ S/cm}$ [21]. Perry et al. reported a nonplanar naphthalene-based copolymer with an optimized conductivity of 0.45 S/cm after a sequential doping [22]. Pei and coworkers demonstrated that rational modification of the n-type polymer backbone can simultaneously increase the charge mobility and the doping level, leading to a high conductivity of 14 S/cm [23]. Wang et al. reported a conductivity of 2.4 S/cm and a power factor of $0.43 \mu\text{W m}^{-1} \text{K}^{-2}$ by n-doping polybenzimidazobenzophenanthroline (BBL) [24]. Huang et al. recently investigated the effects of the conjugated backbone of organic small molecules on the n-type thermoelectric behavior and achieved an optimized conductivity of 3.1 S/cm and a power factor of $105 \mu\text{W m}^{-1} \text{K}^{-2}$ [25]. Most of those works focus on the influences of the structure of the backbone on the n-type thermoelectric properties while neglecting the effects of side chains. Therefore, the study of the role of side chains in n-doping can provide a complementary design towards efficient n-type organic thermoelectric materials.

So far, alkyl side chains are most widely used in organic semiconductors and have proven successful in organic electronic devices [26–29]. Alkyl side chains are, therefore, an obvious choice for designing solution-processable organic thermoelectric materials [18,30]. Recently, we reported a novel type of fulleropyrrolidine with a triethylene glycol side chain (PTEG-1), which has a high dielectric constant and can passivate the interfacial trap states as the electron transport layer in perovskite solar cells [31–34]. Moreover, this polar side chain increases the polarity of the fullerene derivative, resulting in good miscibility in the host/dopant blend and leading to high n-doping efficiency of 18% [35,36]. The same concept of using polar side chains has been found to apply to both molecular p- and n-doping of conjugated polymers [17,21,37]. However, a comprehensive study of the influence of the type and length of side chains in n-type organic thermoelectric materials is lacking.

In this contribution, the two key parameters of the side chain, i.e. the polarity and the length, are changed to investigate their effects on the n-type organic thermoelectric behavior. A series of fullerene derivatives with an *n*-dodecyl side chain (PPA) or oligoethylene glycol (EG) side chains of different lengths (PDEG-1, PTEG-1, PTEG-1 and PPEG-1) are used as the host molecules, and (4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)phenyl)dimethylamine (n-DMBI) is used as the dopant. Their chemical structures are displayed in Scheme 1 arranged with coordinates of the polarity and the chain length. The previously reported PTEG-1-based system, with the same-length side chain but different polarity as PPA, is used for a comparison [35]. We will explore in detail the effects of side chains on molecular packing in the undoped/doped states, on the n-doping process and on the thermoelectric transport properties in the following sections. By using the polar side chains, the miscibility in the host/dopant system is greatly improved, which causes less phase aggregation and increases the doping efficiency by more than a factor of five. Additionally, the molecular order can also be improved by simultaneous control of the polarity and the length of side chains. The enhanced doping efficiency and molecular order lead to a simultaneous increase in conductivity and Seebeck coefficient. Finally, an optimized power factor of $23.1 \mu\text{W m}^{-1} \text{K}^{-2}$ is achieved by the side chain engineering. Additionally, we show that EG side chains can

Scheme 1. The chemical structures of the fullerene derivatives with varying polarity and length of side chain and n-DMBI dopant.

improve the air stability of n-doped fullerene derivatives films as compared to an alkyl side chain. It is anticipated that our work will offer insights into the role that side chains play in n-type organic small molecules thermoelectrics.

2. Experimental details

2.1. Materials

PPEG-1 was synthesized in our lab as described in the [Supporting information](#). The synthetic routines of PPA, PDEG-1, and PTEG-1 are reported somewhere else [38]. n-DMBI was purchased from Sigma Aldrich.

2.2. Device fabrication

The borosilicate glass substrates were sequentially washed using detergent, acetone, and isopropanol. Then, the substrates were dried using a nitrogen gun and treated by UV-ozone for 20 min. The doped fullerene derivative films were prepared by spin-coating their solution (5 mg/ml in chloroform) mixed with different amounts of dopant in a glovebox with a nitrogen atmosphere. For the electrical conductivity measurements, parallel line-shape Au electrodes with a width (w) of 13 mm and a channel length (L) of $100\text{--}300 \mu\text{m}$ were deposited as the top contact. Voltage-sourced two-point conductivity measurements were conducted in a probe station in an N_2 glovebox and variable temperature conductivity was measured under vacuum in a cryogenic probe station. The electrical conductivity (σ) was calculated according to the following formula: $\sigma = (J/V) \times L/(w \times d)$. The Seebeck coefficient was measured using a home-built setup reported previously [35], and a continuously changing temperature gradient was imposed across the devices to measure the thermal voltage at varying temperatures.

2.3. Characterization of thin films

The thicknesses of all films were measured by ellipsometry. AFM topographical images were recorded in tapping mode using a Bruker MultiMode 8 microscope with TESP probes. GIWAXS measurements were performed at the Dutch-Belgian beamline (DUBBLE) BM26B at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. An X-ray beam with an energy of 12 keV was used (flat field, solid angle, and polarization). The beam center was estimated using the known position of the diffracted rings from standard silver behenate and Al_2O_3 powders. The scattering vector q was defined with respect to the center of the incident beam and had a magnitude of $q = (4\pi/\lambda)\sin(\theta)$, where 2θ is the scattering angle, and λ is the wavelength of the X-ray beam. Herein, we opted to present the wedge-shaped corrected images, where q_{xy} and q_z are the in-plane and near out-of-plane scattering vectors, respectively. The scattering vectors are defined as follows: $q_x = (2\pi/\lambda)$

$(\cos(2\theta_f)\cos(\alpha_f)-\cos(\alpha_i))$, $q_y = (2\pi/\lambda) (\sin(2\theta_f)\cos(\alpha_f))$, $q_z = (2\pi/\lambda) (\sin(\alpha_f) + \sin(\alpha_i))$, $q_{xy}^2 = q_x^2 + q_y^2$, where α_f is the exit angle in the vertical direction, and $2\theta_f$ is the in-plane scattering angle, in agreement with standard GIWAXS notation. An incident angle of $\alpha_i = 0.14^\circ$ was used for all samples. The TEM samples were prepared on glass substrates coated with water-soluble PEDOT: PSS, then the thin films were lift-off by dipping into the water and scalvaged on copper mesh. HR-TEM was performed on a Tecnai T20 electron microscope (FEI) operating at 200 keV. Images were recorded under low-dose conditions using a slow-scan CCD camera.

3. Results and discussion

First, we assess the influence of the side chains on the amount of disorder in films consisting of the fullerene derivatives under study. To do so, we perform space-charge-limited current (SCLC) measurements at different temperatures. The current-voltage characteristics of pristine PPA, PDEG-1, PTEG-1, and PPEG-1 based devices are displayed in Fig. S1 (symbols). In the case of a Poole-Frenkel type mobility, the SCLC is given by [39,40]:

$$J_{SCL} = \frac{9}{8} \epsilon_0 \epsilon_r \mu_0(T) \exp\left(0.89 \sqrt{\frac{V_{in}}{L}}\right) \frac{V_{in}^2}{L^3} \quad (1)$$

where J_{SCL} is the SCLC current, $\mu_0(T)$ is the zero-field mobility as a function of temperature, V_{in} is the internal voltage, and L is the thickness of the active layer. By fitting Eq. (1) (solid lines) to the data, $\mu_0(T)$ is derived as shown in Fig. 1. The classic Arrhenius equation can describe $\mu_0(T)$; the activation energies (E_μ) are determined to be 0.38, 0.46, 0.32 and 0.34 eV for PPA, PDEG-1, PTEG-1 and PPEG-1 films, respectively. The zero-field mobilities μ_0 at the room temperature are also extracted to be 5×10^{-4} , 6×10^{-3} , 3.0×10^{-4} and 3.7×10^{-4} $\text{cm}^2\text{Vs}^{-1}$ for PPA, PDEG-1, PTEG-1 and PPEG-1, respectively. The fullerene derivatives with different side chains show very similar carrier mobilities, except for PDEG-1, which shows the highest mobility, probably due to the short side chain.

Tailoring the side chains of the fullerene derivatives may influence the molecular packing, which translates to energetic disorder. The activation energy (E_μ) can be used to estimate the width (σ_d) of the Gaussian density of states ($E_\mu = (\sigma_d^2/(kT))$) [41]. We find σ_d to be 91 ± 1 , 100 ± 1.5 , 85 ± 1 and 86 ± 1 meV for PPA, PDEG-1, PTEG-1 and PPEG-1 thin films, respectively. Previously, Torabi et al. found $\sigma_d = 75$ meV for PTEG-1 [34]. PDEG-1 exhibits the highest disorder parameters, probably because it has the shortest side chain, while PTEG-1, PTEG-1 and PPEG-1 show a reduced energetic disorder as compared to PPA.

Fig. 1. Zero-field mobility of charge carriers versus temperature for PPA, PDEG-1, PTEG-1 and PPEG-1 (symbols) and corresponding Arrhenius fit (lines) yield activation energies (E_μ) of 380 meV, 460 meV, 320 meV and 340 meV, respectively.

The effects of the type and length of the side chains on the structural order of the fullerene derivatives were assessed by grazing incidence wide-angle X-ray scattering (GIWAXS). GIWAXS measurements were carried out on both pristine and doped thin films for the whole family of fullerene derivatives under study. All pristine samples show a crystalline structure with the 001 planes preferentially oriented parallel to the substrate (see Fig. 2a-d). The samples all exhibit similar crystallinity. However, the order of the crystallinity is PTEG-1 > PPEG-1 > PPA > PDEG-1 if we compare the intensity of the 001 peak and the number of observed high-order reflections. The 001 peaks for the fullerene derivatives are 2.7, 3.0, 2.8 and 2.6 nm^{-1} for PPA, PDEG-1, PTEG-1 and PPEG-1, respectively. Using Bragg's law, these values give the following spacing for the 001 plane: 2.3, 2.1, 2.2 and 2.4 nm for PPA, PDEG-1, PTEG-1 and PPEG-1, respectively. Previously, we found 001 spacing of 2.2 nm for PTEG-1 [35]. The crystal sizes in the direction perpendicular to the substrate, estimated from the width of the 001 reflections, are approximately 13, 17, 12 and 10 nm for PPA, PDEG-1, PTEG-1 and PPEG-1 pristine thin films, respectively. The vertical intensity cuts along the q_z direction for the pristine thin films are reported in Fig. S2. It was previously shown that doping of these fullerene derivatives can have an impact on the crystallinity of the film [35]. GIWAXS images have thus been acquired for the doped thin films (see Fig. S2). No significant influence of the n-DMBI dopant agent on the crystalline structure was observed for PPA and PDEG-1 samples. Previously, we observed that the crystalline structure was slightly improved upon doping of PTEG-1, although its side chain is of the same length as that of PPA [35]. Molecular doping seems to have a relatively large impact on the structure of the fullerene derivatives with longer side chains, namely, PTEG-1 and PPEG-1. For these latter samples, a negative impact of the doping on the crystalline structure was observed, especially for PPEG-1.

The microstructures of the different fullerene derivatives can be visualized by high resolution (HR) transmission electron microscopy (TEM). In the HR-TEM images (Fig. 2e, Fig. 2f and Fig. S3) of the doped fullerene derivatives with the polar side chains, we can clearly observe superlattice nanostructures formed by the in-plane packing of fullerene cages highlighted by the black dashed circles. In contrast, the ordered domains are not seen in the doped fullerene derivative with alkyl side chains (PPA, Fig. 2e). Additionally, the length of the polar side chain appears to also influence the formation of those ordered nanostructures as the doped PTEG-1 shows the most superlattice domains (Fig. 2f and Fig. S3). These results further confirm the significance of the type and the length of side chains in the n-type doping of OSCs.

Fig. 3a-c show the electrical conductivities, Seebeck coefficient and power factors of the fullerene derivatives as a function of the doping concentration, respectively. By modulating the dopant concentration from 5% to 40 mol%, the conductivity σ of the doped PPA with the alkyl side chain increased from 1.83×10^{-5} to 0.10 S/cm. At a conductivity of 0.069 S/cm, the doped PPA film gave a Seebeck coefficient S of $-193 \mu\text{V/K}$, resulting in an optimized power factor $S^2\sigma$ of $0.385 \mu\text{W K}^{-2} \text{m}^{-1}$. This is comparable to those of the doped n-type conjugated polymers [18,24]. By contrast, doped PTEG-1, with the same chain length but different polarity, shows an optimized electrical conductivity of 2.05 S/cm and power factor $16.7 \mu\text{W K}^{-2} \text{m}^{-1}$ [35]. By changing the side-chain length, PDEG-1, PTEG-1 and PPEG-1 films exhibited a conductivity σ of 1.49, 2.27 and 1.38 S/cm at doping concentrations of 40%, 30% and 30%, respectively. The electrical conductivity achieved in the 30%-doped PTEG-1 film is the highest value reported thus far for solution-processed fullerene derivatives. Importantly, the most conducting PTEG-1 film exhibits a relatively large Seebeck coefficient S of $-319 \mu\text{V/K}$, which is much larger than that of recently reported n-doped BBL films at a similar conductivity σ level ($S \sim -60 \mu\text{V/K}$) [24]. Fullerene derivatives with too long oligoethylene glycol side chains and fullerene derivatives at excessive dopant loadings do not present suitable thermoelectric parameters, which can be explained by the dilution of conjugated moieties negatively impacting charge transport. The

Fig. 2. GIWAXS patterns for the pristine PPA (a), PDEG-1 (b), PTeEG-1 (c) and PPEG-1 (d) thin films with an incidence angle of $\alpha_i = 0.14^\circ$, and the HR-TEM images of the doped PPA (e) and PTeEG-1 (f) films.

power factor $S^2\sigma$ for doped PDEG-1, PTEG-1, PTeEG-1 and PPEG-1 films was optimized, via doping engineering, yielding maximum values of 9.18, 16.7 [35], 23.1 and $9.76 \mu\text{W K}^{-2} \text{m}^{-1}$, respectively. Table 1 summarizes the thermoelectric properties of previously reported solution-processed n-type organic materials together with the results of this work. Given the extremely low thermal conductivity κ ($0.03\text{--}0.06 \text{ W K}^{-1} \text{m}^{-1}$) of pristine fullerene derivative films and the weak carrier density dependence of thermal conductivity at moderate doping [8,42], molecularly doped fullerene derivative films with high power factor hold promise for efficient n-type organic thermoelectrics. We also studied the effects of side chains on the air stability of doped fullerene derivatives. Fig. 3d displays the decay of electrical conductivity of films of doped fullerene derivatives after air exposure. The EG side chain greatly improves the air stability of the doped fullerene derivatives as compared to an alkyl side chain, and the longer EG side chains provide better air stability. Our results indicate that both the polarity and the length of the side chains have a strong influence on the thermoelectric properties.

The surface morphologies of PPA, PDEG-1, PTeEG-1 and PPEG-1 films before and after doping were characterized by atomic force microscopy (AFM) (Fig. S4 and Fig. S5). Pristine PPA showed a very smooth surface morphology, while many surface features were visible in PDEG-1, PTeEG-1 and PPEG-1 films. Spheroid domains were clearly observed in PDEG-1 films, and fibrous structures were observed in PTeEG-1 and PPEG-1 films. Upon n-DMBI doping (30%), most features still remained in those films in addition to large aggregates that appeared in the doped films. These aggregates are considered to originate from the limited solubility of polar dopants or doping products in the host matrix [18,43]. As observed, PPA with an apolar alkyl side chain exhibits the strongest aggregation among the four fullerene derivatives, due to the low polarity of its side chains.

It is of significance to know the doping efficiency of the doped film, which has been rarely reported in previous works on n-type doping of organic materials. Recently, we have reported a general relationship

between the carrier density and activation energy of electrical conductivity (E_A) at a given disorder parameter for disordered OSCs [35]. The activation energies are obtained from the temperature dependence of the electrical conductivity (see Fig. 4a). The carrier density- E_A plots at different disorder parameters are given in Fig. S6. Accordingly, the doping efficiencies of differently doped fullerene derivatives were estimated as displayed in Fig. 4b. The doped PPA film exhibits a peak doping efficiency of only 3.7% at a doping concentration of 30%, which is consistent with the previously reported results for doped OSC with alkyl side chains [18]. The doped fullerene derivatives with polar side chains show strongly increased doping efficiencies, with the highest value of 27% achieved for the doped PTeEG-1, which is comparable to those of p-type doped organic films [44]. Fig. S7 displays the conductive AFM (c-AFM) images of doped PPA and PTeEG-1 films. Via c-AFM, the effective doping sites could be easily visualized as white regions in both images. The doped PTeEG-1 film shows a background current of 1.0 nA, 10 times that of the doped PPA film, indicating a higher electrical conductivity. Clearly, in both films, the aggregates are not conductive, indicating that they are composed of dopant or insulating doping products. This finding validates the previously proposed phase-separation mechanism responsible for the deteriorating electrical conductivity [18,35].

The molecular doping of OSCs is understood as a two-step process: i) ionization of the dopant with donation of an electron to the host for n-doping, and ii) dissociation of these charged pairs, effectively generating a free charge carrier [45]. For the first step, the host/dopant miscibility plays a key role as the two types of molecules must be spatially close to each other for charge transfer. In Fig. 4c (the left panel), we use a cartoon to analyze the spatial distribution of neutral dopants in different fullerene derivative matrixes. For the fullerene derivative with an alkyl side chain (PPA), which differs greatly in polarity from the polar n-DMBI dopant, it is unlikely that the dopant molecules mainly reside in the plane of the alkyl side chain in crystalline regions. Therefore, the dopants may disrupt the π - π^* stacking of

Fig. 3. The electrical conductivity (a), Seebeck coefficient (b), power factor (c) and the decay of electrical conductivity after air exposure (d) for doped PPA, PDEG-1, PTEG-1 (from Ref. [35]), PTeEG-1 and PPEG-1 films at different doping concentrations.

Table 1
Thermoelectric properties of solution-processed n-type organic semiconductors.

Material	Conductivity [S/cm]	Seebeck coefficient [$\mu\text{V K}^{-1}$]	Power factor [$\mu\text{W m}^{-1} \text{K}^{-2}$]	Refs.
PPA	10.1	– 193	0.38	this work
PDEG-1	106	– 294	9.18	this work
PTEG-1	2.05	– 284	16.7	[35]
PTeEG-1	227	– 319	23.1	this work
PPEG-1	138	– 266	9.76	this work
TEG-N2200	0.17	– 153	0.4	[37]
N2200	8×10^{-3}	– 850	0.6	[18]
BBL	1.2	– 60	0.43	[24]
p(gNDI-gT2)	0.3	– 93	0.4	[21]
FBDDPV	14	– 140	28	[23]
PNDTI-BBT-DP	5	– 169	14	[30]
P(BTP-DPP)	0.45	–	–	[22]
A-DCV-DPPTT	3.1	– 568	105	[25]

fullerene cages or aggregate with themselves as observed in AFM images, causing the low doping efficiency and additional molecular disorder in PPA. In contrast, the polar oligoethylene glycol side chain phase can accommodate most of the dopant molecules in the crystalline regions without sacrificing π - π^* stacking order [35]. This explains the enhanced doping efficiency in the doped fullerene derivatives with the polar side chains. As the polar side chain becomes too long, the dopant molecules are supposed to be embedded in the polar side chains as well.

However, the crystalline structure may become too fragile to survive from the disruption of dopants as evidenced by GIWAXs data. Eventually, the dopants mainly reside in regions with large disorder. In case of poly(3-hexylthiophene), there are several recent works that claim that the doping is less efficient if the dopant is localized in disordered regions rather than in crystalline regions [46,47]. We think that this mechanism might also hold for doped PPEG-1 with a long polar side chain. Another reason for the enhanced doping efficiency with the polar side chain may be related to the second step. As shown in Fig. 4c (the right part), as the ionized dopant molecules are charged, they should prefer the polarizable environment of the oligoethylene glycol ether phase. The main barrier for creating a free charge carrier is the Coulomb force from the positive charge n-DMBI⁺. The polar oligoethylene side chains possess permanent dipoles [48], and those dipoles can potentially screen up the electrostatic field of n-DMBI⁺. Thereby, the ionized n-DMBI⁺ is stabilized by such a polarizable environment, which lets free charge carriers more easily be created. A more detailed study of the effects of such a polar environment on the second step of doping is on the way, but beyond the scope of this work.

Fig. 5a displays the experimental S - σ relationship in differently doped PPA, PDEG-1, PTEG-1 [35], PTeEG-1 and PPEG-1 films. As the five fullerene derivatives showed similar intrinsic charge mobilities extracted from the SCLC measurement, the electrical conductivity can be considered as being representative of the carrier density for the doped fullerene derivatives, which is consistent with the estimation of the charge densities in Fig. 4b. In principle, it is expected that a high (absolute) Seebeck coefficient S is found for the doped fullerene

Fig. 4. The activation energy values (a) and estimated doping efficiencies (b) as a function of doping concentration in doped PPA, PDEG-1, PTEEG-1 and PPEG-1 films, and (c) the proposed cartoon model for clarifying how the polarity and the length of side chain impact the n-doping process. This scheme is not intended to show a full mechanism including all the chemical species that form as a result of the doping process.

derivatives with low electrical conductivity σ . However, we observed the opposite trend: the doped fullerene derivatives with a polar side chain show higher electrical conductivity and (absolute) Seebeck coefficient than the doped and less polar PPA. Recently, an empirical relation of $S \sim \sigma^{-1/4}$ was observed in many doped conjugated polymers, which is considered as an indicative of the high molecular order in the doped state [24,49]. We found that only the doped PTEEG-1 film followed this empirical relation, as shown in Fig. 5a (the red dashed line).

In disordered systems with mostly localized charge carriers, the Seebeck coefficient largely depends on the details of the mechanism by which they move [50]. Generally, the Seebeck coefficient is determined by the difference between the Fermi level (E_F) and the transport energy level (E^*) as described [51]:

$$S = \frac{1}{q} \frac{E_F - E^*}{T} \quad (2)$$

Therefore, the characteristic Seebeck energy ($E_S = E_F - E^*$) can be derived from the Seebeck coefficient according to the following equation [50,52]:

$$E_S = |S| \cdot T \cdot q \quad (3)$$

Fig. 5b displays plots of E_S versus E_A in differently doped PPA, PDEG-1, PTEEG-1 and PPEG-1 thin films, together with those from our previously reported PTEG-1 system [35]. PTEEG-1 and PTEG-1 show the best agreements between the characteristic Seebeck energy E_S and activation energy E_A , followed by PPEG-1, PDEG-1 and PPA, respectively. The good agreement between E_S and E_A in PTEG-1 and PTEEG-1 has also been observed in doped evaporated C₆₀, which has high molecular order [52]. The large discrepancy between E_A and E_S observed in doped PPA and PDEG-1 may be caused by the relatively high

Fig. 5. (a) the S versus σ relationship in differently doped PPA, PDEG-1, PTEG-1, PTeEG-1, and PPEG-1 (the red dash line represents a fit to the empirical $S \propto \sigma^{-1/4}$ for doped PTeEG-1 film); (b) their corresponding plots of E_s versus E_a (the arrows represent the direction of increasing doping concentration, *Ref.35); and (c) the analysis of variable temperature conductivities with the approach developed by Zabrodskii and Zinoveva ($W(T) = d \ln \sigma(T) / d \ln T$).

molecular disorder, which is evidenced by the SCLC measurement, GIWAXS data and the HR-TEM images.

The electrical conductivity through hopping in disordered materials is temperature dependent: $\sigma = \sigma_0 \exp(-(T_0/T)^d)$, where T_0 and d are the characteristic temperature and a hopping exponent related to different charge transport behaviors [53,54]. $d = 0.25$ and $d = 1$ represent the Mott variable range hopping (VRH) and nearest-neighbor hopping (NNH), respectively. The hopping exponent d is calculated using the approach developed by Zabrodskii and Zinoveva as shown in Fig. 5d [54]. By changing the polarity and chain length, values of $d = 0.36$, 0.67, 1.1 and 0.48 are obtained in doped PPA, PDEG-1, PTEG-1 and PPEG-1, respectively. This suggests that the transport in PTeEG-1, in particular, is of the NNH type whereas the transport in PPA is much closer to VRH. This is also reflected in the Seebeck coefficients: due to the limited number of neighbors a carrier can hop to in the NNH-regime, the transport energy will be higher than in the case of VRH, resulting in a larger absolute Seebeck coefficient in NNH. Interestingly, the trend of the d value going from PPA to PPEG-1 correlates well with that of the S - σ relationship: the d value approaching 1 gives an upper right shift of the S - σ plot. The increase in d value indicates an improved molecular order, which is consistent with the SCLC measurement, GIWAXS data, and HR-TEM images. These results further indicate that the unusual trend of S - σ relationship observed in this study is mainly caused by the molecular order, which can be improved by simultaneous control of the polarity and side chain length.

4. Conclusions

In summary, we systematically investigated the impact of the polarity and the length of side chain on n-type thermoelectrics in a series of fullerene derivatives. The miscibility and thus doping efficiency in host/dopant system can be improved by using polar EG side chain rather than an alkyl side chain. Beyond the doping efficiency, another key parameter, the molecular order, is readily tuned by simultaneously controlling the polarity and the length of side chains. A polar side chain

of the appropriate length is beneficial for a high molecular order, which leads to both increases in Seebeck coefficient and electrical conductivity. By optimizing the two key parameters of the side chain, a conductivity of 2.3 S/cm and a power factor of $23 \mu\text{W K}^{-2} \text{ m}^{-1}$ are achieved in the doped PTeEG-1 film. Additionally, polar EG side chains can significantly improve the air stability of n-doped fullerene derivatives as compared to an alkyl side chain. This represents one of the best results for solution-processed n-type organic thermoelectrics. We believe that the effectiveness of the side-chain engineering can be potentially transferred to other organic thermoelectrics. Moreover, due to the versatility of n-doped fullerene derivatives, our work may spur broad interests in the community of organic electronics, such as organic field-effect transistors, organic light-emitting diodes, organic/hybrid solar cells and organic biosensors.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nanoen.2018.07.056](https://doi.org/10.1016/j.nanoen.2018.07.056).

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