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A review of carrier thermoelectric-transport theory in

organic semiconductors

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Abstract:

Carrier thermoelectric-transport theory recently is of growing interest and numerous thermoelectric-transport models have been proposed in organic semiconductors, due to the most pressing current issues from energy and environment. The purpose of this review is to provide a theoretical description of the thermoelectric Seebeck effect in organic semiconductors. Special attention is devoted to the carrier concentration, temperature, polaron effect, and dipole effect dependence of Seebeck effect and its relationship to hopping transport theory. Furthermore, various theoretical methods are used to discuss the carrier thermoelectric transport. Finally, an outlook of remaining challenges for future theoretical research is provided.

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1. Introduction

With the development of human and the society's progressing, the questions from energy and environment have become some of the most pressing current issues. Thermoelectric technology offers a promising conception to convert heat from the sun and to recover waste heat from industrial sectors and automobile exhausts [1-6]. For this favorable technology, the most intrinsic parameter is the Seebeck effect which plays an indispensable role in converting temperature differences directly into electrical voltages [7-9]. Although the thermoelectric Seebeck effect was firstly discovered by Thomas Johann Seebeck in 1821 [10], the basic principle for harvesting electricity from a temperature gradient was utilized and developed as the contemporary technology in inorganic semiconductors until the late 1950's [11, 12]. Other contributions to the field were from Jean Charles Peltier in 1834 (Peltier effect) [13], and Lord Kelvin in 1854 (Thomson effect) [14]. Experimentally, the thermoelectric Seebeck effect, generally evaluated by Seebeck coefficient (also referred to as thermopower), can be obtained via $S=\Delta V/\Delta T$ [15-17]. A Seebeck voltage (ΔV) can be measured between two ends of the sample along with the corresponding temperature difference (ΔT) after the establishment of a thermal gradient over the sample, as illustrated in Figure 1. The Seebeck coefficient, which is determined by the sign and concentration of the dominant charge carrier, can provide direct insights in the energetics of dominant charge transport processes and determine the average transport energy of carriers [18-20].



Figure 1. A typical set-up for measuring Seebeck coefficient. Carrier is impelled to move from hot side to cold side by the temperature difference.

For a long time, the mobility, which provides a quantitative estimate for the performance of organic semiconductor, is widely regarded as the most important parameter of the charge transport in organic semiconductors. However, with the decrease of the device size accompanying the channel length, the contact effect in the interface plays an important role in the charge transport characteristics [21]. Since the Seebeck voltage does not depend on the interfacial contact [22], hence the Seebeck effect would be a novel way to uncover the intrinsic charge carrier transport. In the past decade, the carrier thermoelectric transport has been received much attention in organic semiconductors. Figure 2 shows the Thomson Reuters Web of Science publication report for the topic "organic thermoelectric Seebeck effect" for the last 16 years. Research interest in organic thermoelectric Seebeck effect has been growing remarkably over the last 5 years.



Figure 2. Thomson Reuters Web of Science publication report for the topic "organic thermoelectric Seebeck effect" from 2000 to 2015.

Organic semiconductors are mainly based on earth-abundant elements, that is, C, H, and O. Although compared with inorganic thermoelectric materials, the organic semiconductors still exhibit a lower ZT (approximately 0.5) so far [23-25], there are several more advantages in organic semiconductors instead of inorganic materials [26-29], for example, the non scarcity of raw materials, the non toxicity, and the large area applications, etc. Due to these excellent properties, along with their specific charge thermoelectric transport properties, organic semiconductors are of growing interest in some cases unique for various applications, particularly for thermoelectric

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devices, where demands on the higher thermoelectric effect and relatively low thermal conductivity [30, 31]. In organic systems, conducting polymer, such as polyacetylene, was first developed to act as the thermoelectric technology in the late 1980s [32, 33]. Thereafter, researchers devoted a lot of enthusiasm to the experimental works in the organic thermoelectric technology [34-41]. While the thermoelectric-transport theory in organic semiconductors lags far behind the experimental investigation. The earliest theory of thermoelectric-transport was usually based on the Boltzmann theory in organic crystal semiconductors proposed by L. Friedman [42]. However, the more difficult problem within the band approximation from Boltzmann theory was a proper treatment of the scattering, although Friedman followed the previous in assuming the existence of a constant relaxation time τ . Otherwise, it was likely that, under some circumstances, the relaxation time assumption may be entirely unjustified, and that, due to the narrow bandwidths, the scattering may not be amenable to a standard, one-phonon deformation potential treatment [42]. Therefore, as Friedman felt, the simulation results from the present Boltzmann theory was only a semi-quantitatively correct result. Then, *ab initio* techniques (first-principles calculations) combining with Boltzmann theory have also been applied to simulate the thermoelectric effect [43-46]. Although the thermoelectric transport theory took a big step forward in terms of Boltzmann theory combining the first-principles theory, it has an ineluctable shortcoming that it cannot go beyond the crystal systems and hence fails to the disordered organic semiconductors. To achieve a general thermoelectric-transport theory of the disordered systems, in the last few years, hopping transport theory and Monte Carlo simulation were widely employed to describe the thermoelectric Seebeck effect of disordered organic semiconductors [47-51]. Based on these theoretical models, several new physical phenomena of thermoelectric Seebeck effect, such as unusual thermoelectric behavior, temperature-independence, and dipole effect, etc., have been interpreted or predicted. There is no doubt that theoretical model of carrier thermoelectric transport is essential in order to better develop design strategies and predict characteristics.

There have been some good reviews published recently with emphasis on

theoretical description of thermoelectric technology in organic semiconductors [45, 52,53], however, the current reviews inclined to the scope of organic crystal materials, as well as the thermoelectric figure of merit. The review underlining the thermoelectric-transport theory of the disordered organic semiconductors is still scarce. In this review, we mainly focus on the thermoelectric Seebeck effect in organic semiconductors, including not only the crystal but also disordered organic semiconductors. In Section 2, theory basic of thermoelectric transport, included hopping transport, Boltzmann transport equation and general expression of Seebeck effect, is discussed. Theoretical study of Seebeck effect including unified theoretical model, carrier concentration dependence of Seebeck effect, polaron effect and dipole effect, are discussed in Section 3. In Section 4-7, percolation theory of Seebeck effect, hybrid model of Seebeck effect, Monte Carlo simulation and first-principles theory then are summarized. Finally, a future outlook of this field is briefly discussed in Section 8.

2. Theory basic of thermoelectric transport

2.1 Hopping transport

Organic semiconductors generally can be sorted as crystalline or amorphous materials, depending on the degree of their crystallinity (static disorder) [54-56]. All organic semiconductors are generally characterized by weak van der Waals bonding, which gives them weak intermolecular interactions. This weak coupling of molecules leads to weak interaction energy to give narrow electronic bandwidths. Otherwise, the statistical variation of width in the energy level distribution of the molecules will overcome the already narrow electronic bands to create Anderson charge localization. For the crystalline organic semiconductors, the localization of charge carriers is mainly induced by intermolecular thermal fluctuations (dynamic disorder), where the size of the localized wave function is expected to be on the order of the molecular spacing and transport in this weakly localized carrier regime is classified as "intermediate hopping transport regime" [57-60]. For disordered organic semiconductors, because a large concentration of crystal imperfections (e.g.,

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impurities, grain boundaries, dangling bonds) breaks the periodicity of a crystal, the localization of charge carriers is attributed to spatial and energetic disorder due to weak intermolecular interactions [61-63]. Although the variety of such materials is very rich [64-65], due to the presence of disorder the basic charge transport mechanism in organic semiconductors is common: incoherent tunneling (hopping) of carriers between localized states [66-68]. The probability of hopping between two states of spatial separation R and energy separation W is generally given by Millar-Abrahams (M-A) transition rate (detailed description for M-A transition rate will be discussed in Section 3). For the localized states with their energies and positions, the distribution of the site energies and positions is called density of states (DOS), distribution of states or energy spectrum. Gaussian DOS (G-DOS) or exponential DOS are the general two forms of distribution in organic semiconductors [59, 69, 70]. So far, most of the researches for the charge carrier transport are based on the assumption of M-A jump rate and a DOS distribution in organic semiconductors [71-73].

2.2 Boltzmann transport equation

As mentioned above, the earliest theory of thermoelectric effect in organic semiconductors is based on Boltzmann transport proposed by Friedman [42]. Friedman's transport approach simulating thermopower used the existence of a constant relaxation for an anisotropic energy band. At the same time, it was assumed that, in the general case of applied dc electric and magnetic fields and a nonvanishing temperature gradient, the steady-state Boltzmann equation reads as

$$\frac{f_k - f_k^{(B)}}{\tau} = -v_k \cdot grad_k f_k + \frac{e}{h} \left(F + \frac{[v_k \times \mathbf{H}]}{c} \right) \cdot grad_r f_k, \tag{1}$$

where $f_k^{(B)}$ is the Boltzmann distribution function, *F* and *H* are the external electric and magnetic fields, $v_k = \hbar^{-1} grad_k E_k$ is the velocity of an electron in Bloch relaxation time. Taking the applied electric field and thermal gradient along the *i*th crystallographic direction, Eq. (1) may be readily solved for f_k . From this, one gets the standard expressions for the electronic and thermal currents, given, respectively, by

$$j_{i} = \left(\frac{eF_{i}}{k_{B}T} + \frac{\partial}{\partial x_{i}}lnA\right)K_{1}^{i} + \frac{e}{k_{B}T}\left(\frac{\partial}{\partial x_{i}}lnT\right)K_{2}^{i},$$
(2)

and

$$w_{i} = -\left(\frac{eF_{i}}{k_{B}T} + \frac{\partial}{\partial x_{i}}lnA\right)K_{2}^{i} - \frac{1}{k_{B}T}\left(\frac{\partial}{\partial x_{i}}lnT\right)K_{3}^{i},$$
(3)

here, A is the normalization constant for the Boltzmann distribution function, and

$$K_{s}^{i} = \frac{2}{(2\pi)^{2}} \int d^{3}k \tau(v_{k})_{i}^{2} E_{k}^{s-1} f_{k}^{(B)}, \qquad (4)$$

which is the standard transport integrals for a non-degenerate carrier distribution. In the above integrals, E_k , is understood to mean the carrier kinetic energy, and is therefore measured from the relevant band minimum (or downward from the band maximum, in the case of hole conduction).

To obtain the absolute thermoelectric power, one solves Eq. (2) under the constraint that $j_i = 0$, giving

$$S^{i} \equiv \left(\frac{F_{i}}{\frac{\partial T}{\partial x_{i}}}\right)_{j_{i}=0} = -\frac{1}{eT} \frac{K_{2}^{i}}{K_{1}^{i}} - \frac{k_{B}T}{e} \frac{\partial lnA}{\partial T},$$
(5)

where it be recalled that e is positive (i.e., the charges on the electron is -e). Taking $A = \exp(E_f/k_BT)$, where E_f is the Fermi level. Finally, the thermopower equation becomes

$$S^{i} = -\frac{1}{(eT)} \left(\frac{K_{2}^{i}}{K_{1}^{i}} - E_{f} \right).$$
(6)

As Friedman pointed out [42] that the main purpose by using Boltzmann theory aimed to calculate the order of magnitude thermoelectric power of a large class of organic semiconductors which crystallize in the base-centered monoclinic structure.

2.3 General expression of Seebeck effect

Since the organic semiconductors consist of the amorphous and crystal structure, the theoretical model of the carrier thermoelectric-transport should be more general, as well as the mobility. The present expression of Seebeck effect derived was inspired by the work of Cutler and Mott [74]. The basis expression was in terms of the conductivity, σ . Based on the definition of Cutler and Mott, for a hopping system in a disordered lattice at zero and finite temperature, σ was expressed as,

$$\sigma = -\int \sigma(E) \frac{\partial f}{\partial E} dE, \qquad (7)$$

Otherwise, one can start out by writing the conductivity as integral over the single states neglecting electron correlation effects [75]

$$\sigma = e \int g(E)\mu(E)f(E)[1 - f(E)]dE, \qquad (8)$$

then, the energy dependence of the conductivity is written as

$$\sigma(E) = eg(E)\mu(E)f(E)[1 - f(E)]dE, \qquad (9)$$

here g(E) is the density of states, $\mu(E)$ is the mobility and f(E) is the Fermi distribution function. The thermopower *S* is related to the Peltier coefficient \prod as [76, 77]

$$S = \frac{\Pi}{T}.$$
 (10)

The Peltier coefficient is the energy carried by the electrons per unit charge. The energy carried is measured relative to the Fermi energy E_f . Each electron contributes to \prod in proportion to its relative contribution to the total conduction. The weighting factor for electrons in the interval dE at energy E is thus $\sigma(E)dE/\sigma$, where $\sigma(E)$ is the energy dependence of conductivity as Eq. (9). One can obtain therefore the general expression of Seebeck effect as [76]

$$S = -\frac{k_B}{e} \int \left(\frac{E - E_f}{k_B T}\right) \frac{\sigma(E)}{\sigma} dE, \qquad (11)$$

To distinguish crystalline inorganic solids, the general Seebeck coefficient also can be defined the shape of transport energy with the mean energy of conducting charge carriers as [77]

$$S = -\frac{1}{eT}(E_{trans} - E_f), \qquad (12)$$

where E_f is the Fermi energy, the transport energy E_{trans} is defined as the averaged energy weighted by the conductivity distribution

$$E_{trans} = \int \frac{E\sigma(E)}{\sigma} dE, \qquad (13)$$

The general expression of Seebeck coefficient was applied early in doped organic semiconductors by Roland Schmechel in 2003 [77]. In Schmechel's literature, a detailed approach to the complex hopping transport in doped organic semiconductors

(p-doped zinc-phthalocyanine) was presented and used to describe experimental data from Maennig et al. [78], on the effect of doping on conductivity, mobility and thermopower.

3. Theoretical study of Seebeck effect

3.1 Unified theoretical model

It is well known that, differing from nearly perfect crystals where the electronic states are delocalized, in organic semiconductors charge carriers are usually localized over spatially and energetically distributed transport sites [79,80]. It is widely accepted that the transport mechanism is hopping of charge carriers from one localized state to another within a lattice of molecular sites [59,62]. Pioneering hopping transport model in disordered systems was the Gaussian disorder model (GDM) carried out by Bässler [81]. The disorder models are conventionally based on a Miller-Abrahams jump rate. Since the energy of the localized states is randomly distributed, the density of states (DOS) can be described by a Gaussian function as

$$g(\varepsilon) = \frac{N_t}{\sqrt{2\pi}\Delta_0} \exp(-\frac{\varepsilon^2}{2\Delta_0^2}),$$
(14)

where N_t is the concentration of randomly distributed localized states (also called localization sites) where charge carries can transport by hopping, ε is the normalized energy and $\Delta_0 = \Delta/k_BT$ indicates the energy scale of the density of states (DOS) which also implies the degree of energetic disordered, k_B is the Boltzmann constant.

Based on the generalized Einstein relation [77], the energy-dependent carrier mobility is written as follows

$$\mu(E) = \eta \frac{eR(E)^2 v_{esc}(E)}{k_B T \left[1 + exp\left(\frac{E_f - E}{k_B T}\right) \right]},\tag{15}$$

where η is a dimensionless fit parameter, R(E) is the average hopping range of the carriers at the energy E, $v_{esc}(E)$ is the total escape rate at the energy E, E_f is the Fermi energy.

Monroe had reported that the carrier transport includes two thermalization mechanisms: (a) hopping directly to deeper states; (b) thermal excitation to shallower

states (transport states), transport, and subsequent retrapping at deeper states [82]. Therefore, the escape rate for carriers will cover these two transport processes, i.e., the carrier transition rate from a site with energy *E* to another site with a different energy is given by the sum of average downward and upward hopping rates [47]. Based on Ambegaokar et al. [83], the intrinsic transition rate for a carrier hopping from an initial site *i* to an empty site *j* is expressed by $\gamma_{ij}=\gamma(R_{ij}, E_i-E_j)$. The average transition rate from site *i* to site *j* is then

$$v_{ij} = \langle n_i(1-n_j) \gamma_{ij} \rangle,$$
 (16)

where n_i and n_j are the occupation numbers, respectively. The energy dependence of γ_{ij} is then a good approximation to write as

$$\gamma_{ij} = \begin{cases} \gamma_0 \exp\left(-2\alpha R_{ij} - \frac{E_j - E_i}{k_B T}\right), & \text{for } E_j > E_i \\ \gamma_0 \exp\left(-2\alpha R_{ij}\right). & \text{for } E_j < E_i \end{cases}$$
(17)

with γ_0 is the constant which depends on the electron-phonon coupling strength, α is the inverse localized length, R_{ij} is the hopping distance, E_i and E_j are the energies at sites *i* and *j*, respectively, and k_B is the Boltzmann constant. Therefore, based on the energy dependence of γ_{ij} , the total escape rate as Miller-Abrahams jump rate is expressed as [84,85]

$$\nu_{esc} = \nu_0 \exp(-r_{ij}) = \nu_0 \begin{cases} \exp\left(-2\alpha R_{ij} - \frac{E_j - E_i}{k_B T}\right), & E_j - E_i > 0\\ \exp(-2\alpha R_{ij}). & E_j - E_i < 0 \end{cases}$$
(18)

where v_0 is the attempt-to-jump frequency. The hopping range with normalized energy ($\varepsilon = E/k_BT$) can therefore be rewritten as

$$R = \begin{cases} 2\alpha R_{ij} + \varepsilon_j - \varepsilon_i, & \varepsilon_j - \varepsilon_i > 0\\ 2\alpha R_{ij}, & \varepsilon_j - \varepsilon_i < 0 \end{cases}$$
(19)

The average hopping range of the carriers at energy E is given by [86]

$$R(E) = \left[\frac{4\pi}{3B_c} \int_{-\infty}^{E} g(E)(1 - f(E)) dE\right]^{-\frac{1}{3}}.$$
 (20)

here, the numerical value of parameter B_c is determined to be 2.8 or 2.7 in terms of percolation criteria [59,87], $f(E) = 1/(1 + ex p(E - E_f(x)))$ is the Fermi-Dirac distribution, 1 - f(E) is the probability that the final site is empty.

Substituting Eqs. (19) and (20) into Eq. (15), the energy-dependent carrier 10/56

mobility is calculated as

$$\mu(E)) = \frac{\eta e \nu_0}{k_B T} [1 - f(E)] R(E)^2 \exp(-r_{ij}).$$
(21)

According to a Kubo-Greenwood type calculation of conductivity, the total conductivity can be written as

$$\sigma = \int \sigma(E)dE = \int_{-\infty}^{0} eg(E)\mu(E)f(E)dE.$$
 (22)

Then, the energy-dependent conductivity can be calculated as

$$\sigma(E) = eg(E)\mu(E)f(E)dE.$$
(23)

Finally, by substituting Eq. (21)-(23) into Eq. (11), the Seebeck coefficient can be expressed as [88]

$$\begin{cases} S = \frac{1}{eT} \frac{\int_{0}^{\varphi_{S}} \int_{-\infty}^{0} (E - E_{f}) g(E) A(x) B(E) dE d\varphi(x)}{\int_{-\infty}^{0} g(E) A(x) B(E) dE} \\ A(x) = f(E)^{2} exp(E - E_{f}) \\ B(E) = R(E)^{2} exp(-r_{ij}) \end{cases}$$
(24)

3.2 Carrier concentration dependence of Seebeck effect

In general, the carrier concentration in organic semiconductors is written as

$$n = \int_{-\infty}^{\infty} g(E) f(E, E_f) dE.$$
⁽²⁵⁾

In an organic thin-film transistor (OTFT), carriers are always accumulated in the semiconductor-insulator interface under the effect of gate voltage and decrease with a distance x (see in Fig. 3(a)). The gate-induced potential $\varphi(x)$ shifts the difference between the transport band edge and the Fermi level. Therefore, the quasi-Fermi level $E_f(x)$ is

$$E_f(x) = E_{f0} + q\varphi(x). \tag{26}$$



Figure 3. (a) Geometric definition and channel configuration of Organic layer, and (b) schematic of carrier transport in variable-range hopping theory. The difference between the conduction band edge and Fermi level may be shifted by applied potential φ .

Then, the carrier concentration in a transistor can be written as

$$n = \int_{-\infty}^{\infty} \frac{\frac{N_t}{\sqrt{2\pi\Delta_0}} \exp\left(-\frac{\varepsilon^2}{2\Delta_0^2}\right)}{1 + \exp\left(\varepsilon - \varepsilon_{f_0} - \frac{e\varphi(x)}{k_BT}\right)} d\varepsilon.$$
(27)

The variation of $\varphi(x)$ with respect to the distance x is determined by the Poisson equation as [89]

$$F(x)^{2} = \frac{2e}{\varepsilon_{s}}n = \frac{2e}{\varepsilon_{s}}\left[\int_{0}^{\varphi(x)}\int_{-\infty}^{\infty}\frac{g(\varepsilon)}{1 + \exp\left(\varepsilon - \varepsilon_{f_{0}} - \frac{e\varphi(x)}{k_{B}T}\right)}d\varepsilon d\varphi(x)\right], \quad (28)$$

where ε_s is the dielectric constant and F(x) is the electric field perpendicular to the interface. At the interface, the electric field F(0) can be expressed through Gauss law as

$$\varepsilon_{s}F(0) = C_{i}(V_{g} - V_{fb} - \varphi_{s}) = \sqrt{2e\varepsilon_{s}\int_{0}^{\varphi_{s}}\int_{-\infty}^{\infty}\frac{g(\varepsilon)}{1 + exp\left(\varepsilon - \varepsilon_{f0} - \frac{e\varphi(x)}{k_{B}T}\right)}d\varepsilon d\varphi(x), (29)$$

where V_g is the gate voltage, V_{fb} is the flat-band voltage, C_i is the insulator capacitance per unit area, φ_s is the potential at the semiconductor-insulator interface.

Figure 4 shows the carrier concentration dependence of the Seebeck coefficient comparing the theoretical result calculated by the theoretical model above with the experimental data for PEDOT:Tos [90], and for a high-quality rubrene single crystal [91], respectively. To convert oxidation level to carrier density for PEDOT:Tos, one

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can use the same approach with the literature [47], and the carrier density here is calculated by using Eq. (25). The fitting parameters are similar to the Ref., such as the total DOS $N_t=1\times10^{21}$ cm⁻³[47] and $N_t=1.4\times10^{21}$ cm⁻³[91].



Figure 4. Comparison between calculated [88] and experimental values of the Seebeck coefficient for PEDOT:Tos and Rubrene, respectively. The input parameters for PEDOT:Tos are: $N_t=1\times10^{21}$ cm⁻³, $\alpha^{-1}=1$ nm, $C_t=1.5\times10^{-4}$ F/m², $\Delta_0/k_BT=2$, $E_{f0}=-0.65$ eV, $\varepsilon_s=3$, P=0 D, $V_g-V_{fb}=5$ V, and T=300 K. The input parameters for Rubrene in inset are: $N_t=1.4\times10^{21}$ cm⁻³, $C_t=3\times10^{-5}$ F/m², $\Delta_0/k_BT=1.3$, $E_{f0}=-0.52$ eV, and T=294 K, the other parameters are the same as those of PEDOT:Tos.

In OTFTs, the carrier concentrations are connected with the gate-voltage by using Eqs. (27)-(29). Lu et al. also discussed the gate-voltage dependence of the Seebeck coefficient for the OTFTs [92], as shown in Fig. 5. In Fig. 5, the Seebeck coefficient depends strongly on the gate-voltage at different polaron activation energy (the polaron effect will be discussed in Section 3.4). The strong gate-voltage dependence is attributed to the change of carrier concentration in deep or shallow energy states. In general, the deeper energy states will be occupied gradually with the increase of gate voltage (the larger gate voltage corresponding to a high density) and the quasi-Fermi level will move close or above the conduction band, hence a growing number of charge carriers are firstly trapped in the deeper energy states. As the carriers are 13/56

trapped in the deeper energy states, the movement of carriers to the shallower energy states would be difficult, which could result in the decrease of the carrier concentration in shallower energy states. Since the Seebeck coefficient is actually proportional to the flow of entropy transported by an electrical current, the decrease of carrier concentration in shallower energy states results in the decrease of the flow of entropy transported. As a result, the Seebeck coefficient decreases with the increasing gate-voltage.



Figure 5. Gate voltage dependence of Seebeck coefficient at different polaron activation energy [92]. The input parameters are: $N_t=1\times10^{20}$ cm⁻³, $\alpha^{-1}=0.1$ nm, $C_t=1\times10^{-4}$ F/m², $\Delta_0=3$ k_BT , $\varepsilon_s=3$, $\varepsilon_{f0}=-20$ k_BT and T=300 K.

3.3 Effect of temperature on Seebeck effect

As described above, the Seebeck effect is attributed to the gradient of temperature in the device, the effect of temperature on the Seebeck coefficient (*S*) is greatly important. Kim et al. [47] discussed the relation of *S* vs *T* in organic semiconductors by examining fits which exhibits that for different organic materials the Seebeck effect demonstrates the different temperature dependence, as shown in Fig. 6. Kim et al. showed that, for Naphthalenetetracarboxylic dianhydride (NTCDA) [93], *S* shows an activated (~1/*T*) temperature dependence. For polyacetylene [94], the result

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shows that *S* increases with T and that the increase is approximately linear (similar to the predicted temperature dependence of VRH for an exponential DOS [95]). Finally, for a pentacene FET [96], the results show S(T) predicted by their model that the available *S* vs *T* data are somewhat noisy, which do appear to follow the predicted trend. As a result, one can conclude from the results of Kim et al. that the temperature dependence is various for different energetic disorder in organic semiconductors.



Figure 6. Fits of the model to further experimental data, demonstrating how d|S|/dT changes as α increases from an activated ($|S| \sim 1/T$) regime in NTCDA to an intermediate ($|S| \sim \text{const.}$) regime in pentacene to a VRH ($|S| \sim T$) regime in polyacetylene.

Differing from the results of Kim et al., Henning Sirringhaus et al. [97] have reported that the Seebeck coefficient displays the temperature-independent property for the organic semiconductors with the disorder-free (IDTBT) (as shown in Fig. 7), as well as the results from Batlog et al. for single crystals (pentacene and rubrene) [91]. In Fig. 7, the Seebeck coefficient shows the variable decreased trend with temperature for PBTTT, that is, at low temperature the carrier density dependence is stronger than that at higher temperature. As mentioned in Ref. [97], the energetic disorder in IDTBT is significantly lower than that in PBTTT. Therefore, the temperature-independent feature of Seebeck coefficient could be induced by the 15/56

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smaller energetic disorder.



Figure 7. Temperature dependence of Seebeck coefficient for PBTTT and IDTBT. Symbols and solid lines are experimental [97] and simulated [98] results used percolation theory in Section 4, respectively.

To better understand the temperature-independent feature of Seebeck coefficient, Lu et al. discussed the effect of energetic disorder and temperature on the Seebeck coefficient, as shown in Fig (8) and (9). Figure 8(a) shows the energetic disorder dependence of Seebeck coefficient at 200 K and 300 K based on the following percolation theory (the detailed theoretical theory described in Section 4 [98]). The Seebeck coefficient shows a strong energetic disorder dependence. This dependence under the larger energetic disorder will enhance with decreasing the temperature. For the smaller energetic disorder, such as $\Delta/k_BT < 1$, this dependence is similar for different temperatures. Temperature dependence of Seebeck coefficient for different energetic disorders is plotted in Fig. 8(b). The observed results clearly show that the temperature dependence enhances with increasing energetic disorder.

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Figure 8. (a) Energetic disorder dependence of Seebeck coefficient at 200 K and 300 K, and (b) temperature dependence of Seebeck coefficient for different energetic disorder [98].

Generally, carriers in deep states will move by thermal excitation to shallower states, while carriers in shallow states will move by hopping to other shallow states. If the carrier is initially generated randomly within the DOS, it tends to relax towards tail states, the typical rate at which carriers hop away from a state is much smaller for deeper initial energy. Otherwise, the Seebeck coefficient is dominated by the entropy of mixing associated with adding a carrier into the density of states, which is determined by the density of thermally accessible transport states [96, 99, 100]. Therefore, for the smaller energetic disorder, the density of thermally accessible transport states will remarkably decrease. As a result, the Seebeck coefficient shows the temperature-independent. Fig. 9 clearly shows the contribution to Seebeck 17/56

coefficient of carriers above Fermi level (shallow state) and below Fermi level (deeper state), respectively. Here $S_{(E < E_f)}$ and $S_{(E > E_f)}$ denote the contributions of carriers below or above the Fermi level, respectively. The overall Seebeck coefficient is calculated as $S = S_{(E > E_f)} - S_{(E < E_f)}$. One can see that the Seebeck coefficient from the contribution of carriers below Fermi level reduces remarkably with the decrease of the energetic disorder. Thus the Seebeck coefficient is attributed to the carriers in shallow states by hopping to other shallow states and will imply the temperature-independent for the smaller energetic disorder.



Figure 9. Contribution to overall Seebeck coefficient of carriers below $S_{(E < E_f)}$ or above $S_{(E > E_f)}$ Fermi level as a function of carrier density at $\Delta/k_BT=3.5$ (a) and energetic disorder (b) [98]. The input parameters are $N_t=5\times10^{20}$ cm³, $\alpha^{-1}=0.15$ nm, T=300 K.

Otherwise, the effect of temperature on Seebeck effect induced by energetic disorder is consistent with the various temperature-dependent in Kim et al. [47]. In Kim et al., being different from polyactylene [94] which has a lager energetic disorder and showing an increasing trend with temperature, pentacene is the crystal organic with smaller energetic disordered [96] and thus shows almost temperature-independence.

3.4 Polaron effect

About 20 years ago, Bässler et al. suggested that the effective zero-field activation energy of the charge transport in a system can be approximated by a sum of superimposed disorder and polaron contribution [101]. Shortly afterward, by using Monte Carlo simulations in a disordered organic solid, Parris et al. based on the Marcus rate model demonstrated that polaronic carriers with moderate polaron binding energy are consistent with experimental observations [102]. Subsequently, Arkhipov et al. formulated an analytic model of low-temperature energy relaxation of polarons, and proved that the energy relaxation of polarons is much slower than that of charge carriers in a similar disordered system [103]. The polaron effect can obviously affect the charge transport properties. So far, numerous studies have shown that hopping transport of charge carriers in disordered organic materials can, in principle, be controlled by both energy disorder and polaron effects [58, 79, 86, 104].

Generally speaking, a polaron is a quasi-particle composed of the charge and its surrounding polarization cloud. After the formation of the polaron in disordered system, the strong charge-phonon coupling could lead to carrier self-trapping and carry an adjacent molecule along the associated molecular deformation. This strong charge-phonon coupling weakens the energy of the charge to create a bigger barrier for charge removal. Polaron formation in organic materials is usually treated according to small-polaron model suggested by T. Holstein [105] and L. Friedman [106], and further developed for nonadiabatic polaron transfer between sites with different energies by D. Emin [107]. At high enough temperatures, the small polaron

model gives a jump rate equivalent to a Marcus expression. The jump rate of Marcus expression is given by the following [108, 109]

$$v = \frac{|J_{ij}|^2}{\hbar k_B T} \sqrt{\frac{\pi}{E_a}} exp\left(-\frac{(E_j - E_i + E_a)^2}{4E_a k_B T}\right),$$
(30)

where \hbar is the Planck constant divided by 2π , $J_{ij} \propto \exp(-2\alpha R_{ij})$ is the transfer integral, i.e., the wave function overlap between sites *i* and *j*, E_a is the polaron activation energy. Based on the hopping range derived from Miller-Abrahams jump rate in Eq. (17), the hopping range derived from Marcus jump rate with normalized energy ($\varepsilon = E/k_BT$) can be represented as

$$R = 4\alpha R_{ij} + \frac{\left(\varepsilon_j - \varepsilon_i + \varepsilon_a\right)^2}{4\varepsilon_a},$$
(31)

Then, the average hopping range R can be obtained following the approach used in Ref. [110] by solving the following equation

$$\frac{\pi}{2B_{c}\alpha^{3}}\int_{0}^{R/2}r^{2}dr\int_{\varepsilon_{i}-\varepsilon_{a}-\sqrt{4\varepsilon_{a}(R-2r)}}^{\varepsilon_{i}-\varepsilon_{a}+\sqrt{4\varepsilon_{a}(R-2r)}}g(\varepsilon)(1-f(\varepsilon))d\varepsilon = 1.$$
(32)

Here, parameter $B_c=2.8$ or 2.7 is determined according to percolation criteria [59,87].

Replacing Eq. (20) by Eq. (32) to calculate the average hopping range R, the corresponding polaron effect dependence of Seebeck effect can be obtained.

A polaron effect dependence of Seebeck coefficient at different carrier density has been shown in Fig. 10 [92], at which the carrier density is calculated by Eq. (25). The simulated Seebeck coefficient displays completely different dependence of polaron. For example, for E_a <0.01 eV, S decreases with the increase of polaron activation energy (E_a), while for E_a >0.01 eV, is remarkably dependent on the polaron effect. The different influence of polaron effect on Seebeck coefficient can be attributed to different polaronic contribution to the carrier transport.



Figure 10. Polaron activation energy dependence of Seebeck coefficient at different carrier density. The input parameters are $N_t=1\times10^{20}$ cm⁻³, $\alpha^{-1}=0.1$ nm, $C_t=1\times10^{-4}$ F/m², $\Delta_0=3 k_BT$, $\varepsilon_s=3$, $\varepsilon_{f0}=-20 k_BT$ and T=300 K.

As is well known that the effect of polaron effect on mobility is comparable to energetic disorder effect [79,86], for the Seebeck coefficient, the similar results are also obtained. Fig. 11 shows energetic disorder dependence of the Seebeck coefficient for different polaron activation energy. In Fig. 11, the Seebeck coefficient increases with energetic disorder, which is consistent with Kim et al.'s result under the assumption of negligible polaron effects [47]. However, please note that, the Seebeck coefficient remarkably exhibits the different dependence on energetic disorder for the variable polaron activation energy. To explicitly understand the effect from polaron effects and energetic disorder, the Seebeck coefficient for different E_a/Δ ratios was calculated, as shown in Fig. 12. In Fig. 12, the Seebeck coefficient reduces with the increase of E_a/Δ ratios, i.e., with increasing the relative strength of the polaron effects. Otherwise, the reduced trend under $E_a/\Delta > 1$ is obviously larger than that for $E_a/\Delta < 1$. The results suggest that the effect of the polaron effect on Seebeck coefficient may be comparable to energetic disorder.



Figure 11. Energetic disorder dependence of Seebeck coefficient at different polaron activation energy. The input parameters are $N_t=1\times10^{20}$ cm⁻³, $n/N_t=0.001$, $V_g-V_{fb}=1.78$ V, $\alpha^{-1}=0.1$ nm, $C_t=1\times10^{-4}$ F/m², $\Delta_0=3$ k_BT , $\varepsilon_s=3$, $\varepsilon_{f0}=-20$ k_BT and T=300 K.



Figure 12. Seebeck coefficient as a function of E_a/Δ ratios. The blue dash line is a guide to the eye.

3.5 Dipole effect

To discuss the effect of dipole on the Seebeck effect, we now propose a theoretical model based on the OTFTs. In physics, an electric dipole refers to a separation of electric charge. The electric dipole moment is a measure of the $\frac{22}{56}$

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separation of positive and negative electrical charges in a system of electric charges. A surface dipole is a neutral charge with an electric dipole moment per unit area directed perpendicular to the surface. OTFTs usually operate in accumulation mode. Because the charge carrier transport is typically confined to the first few monolayers of the organic semiconductors adjacent to the gate dielectric, the transistor performance is greatly influenced by the interface [110,111]. Fig. 13(a) shows the device structure of the OTFT, at which the dipole layer lies in the interface between the insulating layer and organic semiconductor. The dipole is randomly distributed in the dipole layer, which would change the energy distribution of nearby hopping sites because of the Coulomb interactions between the charge in the localized states and electric dipole within the dipole layer.



Figure 13. (a) The device structure of OTFT with the dipole layer, and (b) schematic diagrams of variable-range hopping theory with a simple Gaussian DOS (G-DOS) or a deviated DOS (D-DOS) induced by dipole, respectively. SAMs: a self-assembled monolayers.

Richards et al. [112] and Diechmann et al. [113] have reported that surface dipole effect could induce a deviation in the DOS distribution and broaden the tail states of the DOS in organic semiconductors. Fig. 13(b) displays the schematic diagrams of variable-range hopping theory for the cases of a simple Gaussian DOS and a deviated DOS induced by surface dipole effect. Generally, a dipole moment P for a charge pair

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is $\vec{P} = E\vec{L}$, where the vector \vec{L} points from the negative charge to the positive charge. As a given dipole moment change the energy distribution of the system, the probability density w(r) is determined by the Poisson distribution as [66]

$$w(r) = 4\pi r^2 N_t exp\left(-\frac{4}{3}\pi r^3 N_t\right),$$
(33)

where r is the distance between the carrier and center of a dipole. By taking into account the electrostatic interaction energy E_{cc} between a charge e in the semiconducting layer and a specific dipole moment in the gate dielectric, one can express the potential energy of this interaction as [113]

$$E_{cc} = \frac{e\mathbf{p}\cdot\mathbf{r}}{4\pi\varepsilon_s r^3} = \frac{ep_0 cos\theta}{4\pi\varepsilon_s r^3},\tag{34}$$

where **p** is an effective dipole strength calculated from the dipole moment p_0 of the monomer groups of the dielectric, and the dielectric constants of the semiconductor ε_s , and θ is the angle between the dipole moment and the vector **r**. Because the dipole orientation is random, the total energy of the interaction between the charge and total dipole moment of the interface is calculated as

$$E_{c} = \int_{-\pi/2}^{\pi/2} \int_{0}^{\pi/2} E_{cc} d\theta d\varphi.$$
 (35)

For a localized state, the total energy *E* of the hopping site can be obtained as $E = E_c + E_0$, where E_0 is the intrinsic disorder energy. Finally, the deviated DOS with the dipole effect can be rewritten as [115]

$$g_{d}(E) = 2\pi N_{t} \left(\frac{eP}{8\pi\varepsilon_{s}}\right)^{\frac{3}{2}} \int_{-\infty}^{0} exp\left(-\frac{4\pi N_{t}}{3} \left(-\frac{eP}{8\pi\varepsilon_{s}E_{c}}\right)^{\frac{3}{2}}\right) (-E_{c})^{-\frac{5}{2}} g(E-E_{c}) dE_{c}.$$
 (36)

Replacing the Gaussian DOS in Eq. (14) by using deviated DOS, the dipole effect dependence of Seebcek coefficient can be calculated.

Figure 14 shows the gate-voltage dependence of the Seebeck coefficient at different dipole moments. The simulated results show that the Seebeck coefficient depends strongly on the gate-voltage under the surface dipole effect. More remarkably, the dependence of the Seebeck coefficient on the gate-voltage will enhance when the dipole moment increases. The characteristics of Seebeck coefficient on one hand derived from the increasing carrier concentration in the systems. On the other hand,

with increasing the dipole effect, the DOS can be broadened, as well as the increase of disorder [115]. The broadened DOS and increased disorder can shift the Fermi level upward [116], which will decrease the occupied probability of charge carriers in shallow energy states. According to the results from Germs et al. [48], within the variable-range hopping (VRH) transport, the Seebeck coefficient is proportional to the Fermi level (E_f), such as $S \propto \frac{E_t - E_f}{qT}$ (here E_t is the transport energy). Otherwise, although the carrier concentration increases with the increase of gate voltage, the increasing carriers will prior to be trapped by deep energy states when Fermi level shift upward. Therefore the increasing carriers don't contribute to the flow of entropy transported by an electrical current. Consequently, the gate-voltage dependence of the Seebeck coefficient becomes much more intense when the dipole moment is increased.



Figure 14. Gate-voltage dependence of the Seebeck coefficient for different dipole moments. The input parameters are: $N_t=1\times10^{20}$ cm⁻³, $\alpha^{-1}=0.5$ nm, $C_i=1\times10^{-4}$ F/m², $\Delta_0/k_BT=4$, $E_{f0}=-0.65$ eV, $\varepsilon_s=3$, and T=300 K.

Figure 15 shows the dependence of the Seebeck coefficient on the dipole moment

for different energetic disorders. The results in Fig. 15 demonstrate that the Seebeck coefficient varies non-monotonically as the dipole moment is increased. For example, as P < 5 D, the Seebeck coefficient decreases with the increase of the dipole moment, while increases for P > 5 D. As mentioned above, the dipole moment can broaden DOS and increase the disorder, which results in an increasingly large number of shallow sites into deep states and accordingly decrease the mobility. Therefore the Seebeck coefficient decreases remarkably with the increase of the dipole moment in the lower dipole moment. When the dipole moment is larger, such as P > 5 D, the strength of Coulomb interaction between carrier and dipole will increase and hence promote the carrier transport. As a result, the Seebeck coefficient will increase with the increase of the dipole moment, as the surface dipole effect is larger, which is consistent with the results reported at which increasing the strength of the Coulomb interaction can increase the Seebeck coefficient [117].



Figure 15. Seebeck coefficient as a function of dipole moment for different energetic disorder.

4. Percolation theory of Seebeck effect

So far, the percolation theory is considered as the best way known to analytically

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describe charge hopping transport characteristics in disordered systems. The percolation problem for a charge transport properties in a disordered semiconductor has been argued early by Ziman and a number of workers [118-120], at which the charge transport should be proportional to the percolation probability P(p). A brief definition is that a first approximation to the conductivity as [121]

$$\sigma(\mathbf{E}) = \sigma_0 P(p(E)), \tag{37}$$

where P(p), the percolation probability, is the fraction of the volume allowed but not isolated, i.e., lying in infinitely extended channels; and σ_0 has a value characteristic of large allowed regions of the material. P(p) is known to vanish for p less than a critical value B_c , falls sharply to zero as $p \rightarrow B_c$. To simplify the percolation question, two kinds of standpoints for the critical value B_c have been confirmed. One is $B_c = 1$ from Arkhipov et al. [122] and Li et al. [110] for the Gaussian DOS, another is $B_c = 2.8$ from B. N. Limketkai et al. for the exponential DOS [123] or $B_c = 2.7$ from Rubel et al. for the Gaussian DOS [124]. Although the unified agreement is not achieved among researchers, the percolation theory in hopping system was widely developed to describe the charge transport characteristics.

In general, the charge transport happens to be in a four-dimensional (4D) hopping space, including three spatial coordinates and one energy coordinate, where the probability of carrier hopping between localized states depend on the spatial and energy coordinates. Therefore the percolation approach addressing the charge transport would be more complicated, if one considers not only spatial positions of sites but also their energies and the occupation of sites. In Eq. (36), to calculate the electrical conductivity $\sigma(E)$, the key is to find the percolation path in a hopping system. Thus, a random-resistor network connecting each molecular site under a percolation model is often used. Figure 16 shows the schematic diagram of the charge transport in a hopping system and the corresponding percolation current through the polymer matrix for carrier to travel through.



Figure 16. (a) Schematic diagram of carrier transport in hopping space with the density of states, and (b) the corresponding percolation current in disordered organic semiconductor.

Based on the following general definition through Kelvin-Onsager relation to the Peltier coefficient Π , a percolation theory to calculate Seebeck coefficient S in hopping transport is expressed as in Eq. (10). Π is generally identified with the average site energy on percolation cluster and can be written as

$$\Pi = \int E_i P(E_i) dE_i, \tag{38}$$

where $P(E_i)$ is the probability that a site of energy E_i is on the current-carrying percolation cluster and was further given by

$$P(E_i) = \frac{g(E_i)P_1(Z_m|E_i)}{\int_{-E_m}^{E_m} g(E_i)P_1(Z_m|E_i)dE_i},$$
(39)

where $g(E_i)$ is the density of states per unit volume, E_m is the maximum site energy, and $P_1(Z_m|E_i)$ is the probability that the second smallest resistance emanating from a site with energy E_i is not larger than the maximum resistance on the percolation cluster, Z_m . The expression of the probability $P_1(Z_m|E_i)$ is written as

$$P_1(Z_m|E_i) = 1 - exp[-P(Z_m|E_i)][1 + P(Z_m|E_i)],$$
(40)

where $P(Z_m|E_i)$ is the bonds density, which means the average number of resistance of Z_m or less connected to a site energy E_i . To calculate the Peltier coefficient (or Seebeck coefficient), an expression for $P(Z_m|E_i)$ is essential.

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According to the percolation theory, the disordered organic semiconductor is viewed as a random-resistor network (see in Fig. 16(b)). To determine the total conductivity in disordered system, the first step is to take a reference conductance H and remove all conductive pathways between sites *i* and *j* with $H_{ij} < H$. The conductance between sites *i* and *j* is given by $H_{ij} \propto exp(-S_{ij})$ with [87]

$$S_{ij} = 2\alpha R_{ij} + \frac{|E_i - E_f| + |E_j - E_f| + |E_i - E_j|}{2k_B T}.$$
(41)

The density of bonds $P(Z_m|E_i)$ then can be written as

$$P(Z_m|E_i) = \int 4\pi R_{ij}^2 g(E_i) g(E_j) dR_{ij} dE_i dE_j \theta(S_c - S_{ij}).$$
(42)

If the density of participating sites is P_s , the critical parameter S_c is found by solving equation

$$P(Z_m|E_i) = B_c P_s = B_c \int g(E) dE\theta \left(S_c k_B T - \left| E - E_f \right| \right).$$
(43)

Based on the numerical studies for a three-dimensional amorphous system, the formation of an infinite cluster corresponds to $B_c = 2.7$ [123,125].

By connecting Eqs. (41-43), the bond density can be formulated as

$$P(Z_m|E_i) = \frac{4\pi}{3(2\alpha)^3} \times \begin{cases} \int_{\epsilon_f}^{\epsilon_i} (S_c - \epsilon_j + \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_i}^{S_c + \epsilon_f} (S_c - \epsilon_j + \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_i - S_c}^{\epsilon_f} (S_c - \epsilon_i + \epsilon_j)^3 g(\epsilon_j) d\epsilon_j, \ \epsilon_i > \epsilon_f \\ \int_{\epsilon_i}^{\epsilon_f} (S_c + \epsilon_i - \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_f - S_c}^{\epsilon_i} (S_c + \epsilon_i - \epsilon_f)^3 g(\epsilon_j) d\epsilon_j + \int_{\epsilon_f}^{\epsilon_i + S_c} (S_c - \epsilon_j + \epsilon_i)^3 g(\epsilon_j) d\epsilon_j, \ \epsilon_i < \epsilon_f \end{cases}$$
(44)

here ϵ is the normalized energy as $\epsilon = \frac{E}{k_B T}$. This expression has been split into two regimes of $\epsilon_i > \epsilon_f$ and $\epsilon_i < \epsilon_f$, which are corresponding to the contributions of ϵ_i above or below Fermi level to $P(Z_m | E_i)$ and therefore Seebeck coefficient *S*, respectively. Above Fermi level, carriers in shallow states will move by hopping to other shallow states. While below Fermi level, carriers in deep states will move by thermal excitation to shallower states.

By substituting Eqs. (38-40), and (44) into Eq. (10), one can obtain the final result of Seebeck coefficient.

The validity of the proposed percolation model in Seebeck effect has been demonstrated by fitting the experimental results. Figure 17 shows the calculated Seebeck coefficient as a function of carrier density based on the percolation theory,

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comparing the simulation results with the experimental data measured by using FET from three kinds of conjugated polymers, i.e., IDTBT, PBTTT and PSeDPPBT [97]. The proposed model can reasonably reproduce the experimental data under the whole range of carrier density for different conjugated polymers. Otherwise, except for the carrier concentration dependence of Seebeck coefficient, the presented percolation theory also can well explain the temperature-independence of Seebeck effect, as discussed above in Section 3.3. In a word, the temperature-independence of Seebeck effect is induced by the smaller energetic disorder.



Figure 17. Carrier density dependence of Seebeck coefficient for different materials at room temperature. Symbols and solid lines are experimental and simulated results, respectively.

5. Hybrid model of Seebeck effect

As mentioned in Section 3.2, the usual behavior for the Seebeck coefficient is to decrease with increasing charge carrier density [90, 97]. However, Germs et al. measured the Seebeck coefficient of pentacene in a TFT [48], and observed that at room temperature the increase of charge density indeed results in the expected decrease of S, while when decreasing the temperature to below room temperature, an increase of S with increasing charge carrier density at T=250 K and even more pronounced at T=200 K, as shown in Fig. 18.



Figure 18. Measurements (symbols) and calculations (lines) of the Seebeck coefficient vs gate bias in a pentacene thin film transistor. The gate bias V_g is corrected for the threshold voltage V_{th} of the TFT.

Such an unusual thermoelectric behavior cannot be explained using VRH or ME alone, as both predict a strictly monotonously decreasing density dependence. To explain this unusual thermoelectric behavior, Germs et al. developed a simplified hybrid model that incorporates both variable range hopping (VRH) and the mobility edge (ME) transport [48]. In general, charge transport in organic semiconductors is often described within the framework of strong localization as developed by Anderson and Mott [126,127]. This transport mechanism is then described in terms of ME (or multiple trapping and release) model or by the VRH model. The ME model implies bandlike conduction, the later does not. For the bandlike transport within the ME model, where the current is carried by charges that are thermally excited over the mobility edge at energy E_c as illustrated in Fig. 19(a). Fig. 19(b) shows the schemetic diagram of VRH model.



Figure 19. The density of states used in (a) the ME model, (b) the VRH model, and (c) the hybrid model, including the relevant energy levels. The gray area below E_C represents the density of occupied localized states.

The corresponding schematic diagram of the hybrid model is shown in Fig. 19(c). It accounts for the contributions to the charge and energy transport by two processes that are treated as independent: VRH-type processes that occur within an exponential tail of localized states and transport by charges that are thermally excited to bandlike states above a mobility edge. Then, the Seebeck coefficient of the hybrid model is calculated as the conductivity-weighted average of the two contributing transport channels:

$$S = \frac{S_{ME}\sigma_{ME} + S_{VRH}\sigma_{VRH}}{\sigma_{ME} + \sigma_{VRH}},$$
(45)

where S_{ME} and σ_{ME} is the Seebeck coefficient and conductivity in the ME part, and S_{VRH} and σ_{VRH} is the Seebeck coefficient and conductivity in the VRH part, respectively.

Then, the general expression of Seebeck effect in Eq. (11) reduces

$$S_{ME} = \frac{(E_c - E_f)}{eT} + A, \tag{46}$$

with

$$A = \frac{\int_0^\infty \frac{\varepsilon}{eT} \sigma(\varepsilon) d\varepsilon}{\int_0^\infty \sigma(\varepsilon) d\varepsilon},\tag{47}$$

where $\varepsilon = E - E_C$.

In Eq. (46), the second term on the right-hand side accounts for excitations beyond the band edge and is typically 1%–20% of S_{ME} . Similarly, within the VRH

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model, where the transport is assumed to be dominated by a characteristic hop from the equilibrium energy to a relatively narrow transport energy $E^*[128]$ as illustrated in Fig. 19(b), Eq. (11) becomes $S_{VRH} = \frac{(E^* - E_f)}{eT}.$ (48)

The conductivity in ME part is calculated as

$$\sigma_{ME} = e n_{free} \mu_{free}(T), \tag{49}$$

with a power law dependence on temperature, $\mu_{free}(T) = \mu_0 T^{-m}$.

The VRH part is described by the Mott-Martens model that assumes transport to be dominated by hops form the Fermi level to the transport level E^* . The conductivity in VRH part is subsequently calculated by optimizing a Miller-Abrahams-type expression as

$$\sigma_{VRH} = \sigma_0 \exp[-2\alpha R^* - (E^* - E_f)/(k_B T)],$$
 (50)

where the position of this level and the typical hopping distance R^* are connected via a percolation argument,

$$B_c = \frac{4}{3}\pi R^{*3} \int_{E_f}^{E^*} G(E) dE, \qquad (51)$$

With $B_c=2.8$ the critical number of bonds. G(E) represents the density of states (DOS), which here is simplified to a single exponential trap tail below the mobility edge and a constant density of extended states above E_C ,

$$G(E) = \begin{cases} \frac{n_{trap}}{k_B T_0} exp\left(-\frac{E}{k_B T_0}\right) & for \ E < E_C, \\ \frac{n_0}{k_B T_0} & for \ E \ge E_C, \end{cases} (E_C = 0), \tag{52}$$

where n_0 is divided by $k_B T_0$ for dimensional reasons. The number of charge carriers above E_C , n_{free} , follows from the Fermi-Dirac distribution.

Figure 20 shows the measured and calculated Seebeck coefficients at T=200 K. One can see that at 200 K the heat transported at the mobility edge (E_C-E_f) and the heat transported at the transport level (E^*-E_f) both decrease with increasing charge carrier density, accounting for the downward trends in S_{ME} and S_{VRH} . Consequently, the weight-averaged Seebeck coefficient S_{hyb} shifts from the S_{VRH} curve at small gate bias up towards S_{ME} for large gate bias. The relatively large value of S_{ME} at lower temperatures follows from Eq. (46) and the temperature independence of E_c .



Figure 20. (a) Measured (symbols) and calculated (lines) Seebeck coefficients at T=200 K. S_{hyb} is the conductivity-weighted average of S_{VRH} and S_{ME} .

6. Monte Carlo simulation

So far we discussed the analytical model of thermoelectric Seebeck effect. However, in spite of exhibiting the large number of advantages as compared with numeric model, such as more context and physical property, these current analytical models have an inevitable shortcoming due to the use of plenty of free parameters during the simulation and calculation. In order to eliminate these hindrances, a universal method is based on the Monte Carlo (MC) simulation in describing the hopping transport for insuring the validity and accuracy of thermoelectric Seebeck coefficient.

The kinetic Monte Carlo simulation generally includes six steps as follows [49].

(i) Initializing site energies E_i . The random energy E_i at site *i* derives from Gaussian or exponential DOS.

(ii) Initial placement of charges. The Fermi-Dirac occupation probabilities will be used in randomly placing $N_{charges}$ charges.

(iii) Choosing hopping events. If neglecting the polaron effect, the hopping rates v_{ij} from site i to site j are based on the Miller- Abrahams transition rate in Eq. (18). The corresponding setting is: a) hopping rates equals to 0 to prevent hopping into

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already occupied sites; b) introducing a cut-off distance and set $v_{ij}=0$ for the jumps longer than this distance.

Otherwise, renormalizing the hopping rates Γ_{ij} as $p_{ij} = \frac{\Gamma_{ij}}{\sum_{i'j'} \Gamma_{i'j'}}$. The sum of rates only include jumps from the occupied to unoccupied, i.e., $\Gamma_{ij}=0$ for occupied site j or unoccupied site i. For every pair ij, an index k (i.e., $ij \rightarrow k$, and $p_{ij} = p_k$), where $k \in \{1, ..., k_{max}\}$, with k_{max} being the total number of all possible hopping events. Then a partial sum S_k is defined for every index k,

$$S_k = \sum_{k'=1}^k p_{k'}.$$
 (53)

Apparently, for every k the length of the interval $[S_{k-1}, S_k]$ is equal to the probability p_k for the kth jump, and the total length of all intervals is equal to 1, i.e., $S_{kmax} = 1$. Then drawing a random real number r from the interval [0, 1] and finding the index k such that $S_{k-1} \ll r \ll S_k$, which gives us the hopping event that will occur. Having chosen the hopping event and moving a charge between the corresponding sites i and j.

(iv) Calculating the waiting time. After determining every hopping event, one adds to the total simulation time t and the waiting time τ that has passed until the event took place. This time is obtained by drawing a random number from the exponential waiting time distribution $P(\tau) = v_i \exp(-v_i \tau)$ with $v_i = \sum_j v_{ij}$ being the total hopping rate of hopping from site *i*. It is therefore given by

$$\tau = -\frac{1}{v_i} \ln(x),\tag{54}$$

where a random number x is drawn from the interval [0, 1].

(v) Calculating the current density. Every time that a predefined number of jumps has occurred, the current density J(t) can be expressed as

$$J(t) = \frac{e(N^{+} - N^{-})}{tN_{y}N_{z}a^{2}},$$
(55)

where N^+ and N^- are the total number of jumps along and against the electric field for a cross section slice in the *yz* plane.

(vi) Calculating the Seebeck coefficient. The Seebeck coefficient is given by the expression

$$S(T) = \frac{E_f - E_{trans}}{|e|T},\tag{56}$$

where the transport energy is defined as the averaged energy weighted by the conductivity distribution

$$E_{trans} = \frac{\int E\sigma(E,T) \left(-\frac{\partial f_{FD}}{\partial E}\right) dE}{\sigma(T)},$$
(57)

with $\sigma(T) = \int dE \sigma(T, E) \left(-\frac{\partial f_{FD}}{\partial E}\right)$.

Although the kinetic Monte Carlo technique provides a direct modeling of the hopping transport in organic semiconductors and therefore it gives the most accurate description of the electronic conductivity, its disadvantage is that it demands extensive computational resources, which makes it difficult to use this technique to analyze and fit experimental data. A comparison between the analytical model and MC simulation for Seebeck coefficient has been shown in Fig. 21 [49]. It is seen in Fig. 21 that they exhibit a qualitative agreement for all values of the parameter α . For large α in Fig. 21(a), S_{sa} and S_{MC} show not only qualitative, but even a relatively good quantitative agreement in the energy interval E<0 (corresponding to the relative corresponding to the relative concentrations) the difference between S_{sa} and S_{MC} increases. As the parameter α decreases, the functional dependencies S_{sa} and S_{MC} remain very close to each other, but S_{sa} gets shifted with respect to S_{MC} (Fig. 21(b)).



Figure 21. The Monte Carlo and semianalytical calculations of the Seebeck coefficient for different values of the localization length (a) $\alpha = a$, (b) $\alpha = 0.2 a$. E_f is in units of Δ . $\Delta = 4 k_B T$, and T = 300 K. Here and hereafter (unless stated otherwise) $\frac{36}{56}$

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the numerical Monte Carlo calculation are performed on the lattice $50 \times 50 \times 50$ with a lattice constant *a*=1 nm and the results are averaged over 16 different samples.

For the sake of comparison between neglecting and including polaron transport, N. Tessler et al. have reported that both Miller-Abrahams hopping and Marcus theory charge transfer were used in the MC simulation [51]. In the MC simulation from N. Tessler, a three-dimensional cubic lattice, where periodic boundary conditions were defined, firstly was implemented. For the three-dimensional lattice, each site representing a localized carrier wave function, was then assigned an energy drawn randomly from the system density of states (DOS) with a Gaussian function. The hopping event time and destination was determined by drawing a random dwell time as in Eq. (54).

Otherwise, Tessler et al. also induced the spatial correlations (correlated GDM) and off-diagonal disorder (off diagonal GDM) to expand the physical picture. Spatial correlations were introduced following Ref. [129], where initially all sites were assigned energy values U_i drawn randomly from the DOS function and subsequently were replaced by the spatially averaged energy values calculated as

$$E_i = N^{1/2} \sum_j M(r_{ij}) U_j,$$
(58)

where

$$M_{(r_{ij})} = \begin{cases} 1 & r_{ij} \le K \\ 0 & r_{ij} > K \end{cases},$$
(59)

In Eqs. (58) and (59), N is the normalization factor set to yield the desired DOS standard deviation, and K is the cutoff radius determining the number of sites over which averaging is performed.

Figure 22 shows a comparison of the Seebeck coefficient between measured and calculated results. The various lines correspond to the different models used. These are the GDM (diamonds), the correlated GDM (circles), the off-diagonal disorder GDM (squares), and the GDM under the premise of polaron transport (triangles). The functional form of the Seebeck coefficient is similar for all of the physical scenarios tested and cannot be used to experimentally differentiate between them.



Figure 22. Seebeck coefficient values obtained from MC simulation (a) as a function of temperature with carier density $n=10^{17}$ cm⁻³, and (b) as a function of the carrier density at temperature T = 300 K.

Figure 23 shows the Seebeck coefficient and transport energy dependence on the disorder parameter δ under the premise of the different model variants for a range of parameter values. The data were obtained from simulations run at T = 300 K and carrier density of n= 10¹⁷ cm⁻³. In Fig. 23, the lowering of the transport level and decrease of the Seebeck coefficient due to the incorporation of spatial correlations within the system energetic landscape can be seen to be augmented as δ increases. The predominant effect seems to follow the actual incorporation of correlations (K=1), while a further increase of the spatial correlation parameter leads to a somewhat weaker effect.



Figure 23. (a), (c), (e) Seebeck coefficient and (b), (d), (f) transport energy as a function of δ for different physical scenarios. (a), (b) Correlated GDM, (c), (d) off-diagonal GDM, and (e), (f) the GDM implemented under the premise of polaron transport. All corresponding model parameter values are presented in subfigure legends.

7. First-principles theory

A first-principles (*ab initio*) theory would be deemed to the best type of theory for hopping charge transport in organic semiconductors, since it starts from the particular

chemical and geometrical structure of the system, and it starts directly at the level of established science and does not make assumptions such as empirical model and fitting parameters. In the recent years, the first-principles approach has been developed to address the charge transport. However, as S. D. Baranovskii remarked that the current state of theoretical research on charge transport in disordered organic semiconductors is yet far behind this desired level [59]. The inapplicability of first-principles theory in the disordered organic semiconductors derives from the disordered structure and transport sites of localized distribution over spatially and energetically. The first-principles theory for investigating the Seebeck effect indeed is more suitable to the systems with the crystal structure.

So far, a few researches on charge transport properties based on the first-principle theory are hardly beyond the scope of crystalline. Otherwise, the direct calculation of Seebeck effect is hardly realistic. The current method generally combines the first-principles calculations with the transport theory. For example, Gao et al. have investigated theoretically the thermopower of low-band-gap crystalline polymers, including the crystalline solids β -Zn₄Sb₃ and AuIn₂ and these polymers, based on muffin-tin orbital and full-potential linearized augmented-plane-wave (FLAPW) electronic structure code [43]. In essence, Gao et al.'s method for the calculation of transport properties of a crystalline solid is firstly based on the semiclassical Boltzmann theory, following as

$$\sigma_0(T) = \frac{e^2}{3} \int dE \tau(E, T) N(E) v^2(E) \left(-\frac{\partial f(E)}{\partial E} \right), \tag{60}$$

where *e*, τ , *f*, and *v* represent the charge of the electron, electronic relaxation time, Fermi distribution function, and Fermi velocity, respectively. If one assumes the relaxation time for the electron scattering processes is a constant, i.e., $\tau(E,T)$ =Const., which has been shown to yield reasonably good results in several materials, then the temperature dependence of $\sigma_0(T)$ can be calculated in terms of the constant relaxation time τ ,

$$\frac{\sigma_0(T)}{\tau} = \frac{e^2}{3} \int dE N(E) v^2(E) \left(-\frac{\partial f(E)}{\partial E}\right),\tag{61}$$

Then, the Seebeck coefficient is calculated from the ratio of the zeroth and first

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moments of the electrical conductivity with respect to energy,

$$S(T) = \frac{1}{eT} \frac{I^1}{I^0},$$
(62)

where

$$I^{x}(T) = \int dE\tau(E,T)N(E)v^{2}(E)(E-E_{f})^{x}\left(-\frac{\partial f(E)}{\partial E}\right).$$
 (63)

A product of the density of states N(E) and arbitrary quantity g which has energy and k-vector dependence as in the expressions (60) and (63) can be obtained by integration on the constant energy surface S in k space. The electronic band structure can be calculated by using the WIEN97 and WIEN2K FLAPW [130] or the pseudopotential plane-wave code in Vienna ab initio simulation package (VASP) [131].

Figure 24 shows the Seebeck coefficients calculated as a function of pressure at 300 K. The theoretical trend in the variation of the Seebeck coefficient with pressure is in qualitative agreement with experiment. Otherwise, the magnitude of the calculated Seebeck coefficient within the spin-orbit (SO) approximation is evidently in better agreement with experiment.



Figure 24. Calculated Seebeck coefficient (*S*) as a function of pressure for $AuIn_2$ with and without spin-orbit interactions.

Figure 25(a) and (b) shows the calculated energy band structure of the polythiophene polymer. For this calculation, the internal structural parameters of the

polymer are fully optimized and the electronic band structure is obtained from pseudopotential plane-wave calculations employing an ultrasoft Vanderbilt pseudopotential and a generalized gradient scheme. The calculated results show that polythiophene has a very simple band structure and is a semiconductor with a band gap of 0.9 eV. The neutral polythiophene is an electrical insulator. Otherwise, the inspection of the band structure shows that except very close to the zone center, where the density of states is high, the band dispersions are considerable. The special band structure thus leads to the very low Seebeck coefficient ($\sim 20 \mu$ V/K), as shown in Fig. 25.



Figure 25. Calculated energy band structure (a), (b), and Seebeck coefficient (*S*) (c), (d), for polythiophene (left) and polyaminosquarine (right), respectively. Isolated planar polymer chains were used for this calculation.

As well as the calculated method from Gao et al., Shuai et al. also combined the first-principles band structure calculations coupled with the Boltzmann transport theory to study the thermoelectric in pentacene and rubrene crystals [44]. In the constant relaxation time and rigid band approximations, the electronic contribution to the Seebeck coefficient is obtained, as shown in Fig. 26. The calculated results also 42/56



exhibited the similar trend compared with the experimental Seebeck coefficient.

Figure 26. The Seebeck coefficient calculated as a function of carrier concentration (a) for pentacene and rubrene at room temperature and compared to the field-effect transistor measurements. The calculated Seebeck data have been averaged over three crystal directions (b) for rubrene at temperatures in the range between 200 and 300 K.

Otherwise, Shuai et al. also applied a combined computational scheme to predict the thermoelectric properties of organic semiconductors, taking *a*-from phthalocyanine crystals H2Pc, CuPc, NiPc, and TiOPc [46]. Their computational approach combined first-principles band structure calculations, Boltzmann transport theory, deformation potential theory. In the work, the first-principles calculations of the Seebeck effect is performed in VASP. Figure 27 shows the structures of *a*-from phthalocyanine crystals.



Figure 27. Structures of *a*-from (a) H2Pc, (b) CuPc, (c) NiPc, and (d) TiOPc crystals.

After finishing the band structure calculations, the Boltzmann transport theory was applied to calculated properties related to the charge carrier transport, as in Eqs. (60) and (61).

Differing from Gao et al's and their previous works, in the work the relaxation time $\tau(i, k)$ isn't assumed to be a constant, which can be evaluated by the deformation potential theory for treating the electron-phonon scattering. According to the literatures [46, 132], the acoustic phonon scattering in both pristine and doped system was modeled by the deformation potential theory with the scattering matrix element for electrons from the **k** state to the **k**' state taking the form as

$$|M(\mathbf{k}, \mathbf{k}')|^2 = \frac{E_1^2}{c_{ii}} k_B T,$$
(64)

where E_1 is the deformation potential constant that represents the energy band shift caused by the crystal lattice deformation, and C_{ii} is the elastic constant in the direction of propagation of the lattice wave. The relaxation time then can be expressed by the scattering probability

$$\frac{1}{\tau(i,k)} = \sum_{k' \in BZ} \left\{ \frac{2\pi}{\hbar} |M(\boldsymbol{k}, \boldsymbol{k}')|^2 \delta[\varepsilon(i,k) - \varepsilon(i,k')] (1 - \cos\theta) \right\}, \quad (65)$$

where $\delta[\varepsilon(i,k) - \varepsilon(i,k')]$ is the Dirac delta function and θ is the angle between k and k'. In Bardeen and Shockley's treatment, it is assumed that scattering is isotropic and the matrix element of interactions $M(\mathbf{k}, \mathbf{k}')$ is independent of \mathbf{k} and \mathbf{k}' .

The calculated band structures and the density of states (DOS) of H2Pc, CuPc, NiPc, and TiOPc are displayed in Fig. 28. The band gaps of H2Pc, CuPc, NiPc, and TiOPc are calculated to be 1.179, 1.253, 1.337, and 0.912 eV, respectively. A localized state is observed in the band gap of CuPc. It is noted that to calculate the electrical transport properties, the authors ignored the trap state. Otherwise, the authors also noted that the underestimation of band gaps from the DFT calculations have little influence on the charge carrier transport, since the transport properties is determined by the bandwidth. The calculated Seebeck coefficient S is shown in Fig. 29. The calculated Seebeck coefficient displays different properties, such as, positive S for holes and negative S for electrons. The Seebeck coefficient is isotropic at first glance, and it decreases rapidly as the charge carrier concentration increases.



Figure 28. Band structures and DOS for (a) H2Pc, (b) CuPc, (c) NiPc, and (d) TiOPc. Band energies are shifted so that Fermi levels are at the zero point. The reciprocal coordinates of high-symmetry points are $\Gamma = (0, 0, 0)$, Y = (0.5, 0, 0), K = (0.5, 0, 0.5), B = (0, 0.5, 0), Z = (0, 0, 0.5), A = (0.5, 0.5, 0), and D = (0.5, 0.5, 0.5). The highest valence bands and lowest conduction bands, including all of the sub-bands arising from inequivalent molecules in the unit cell, are highlighted in red.



Figure 29. The Seebeck coefficient as a function of the logarithm of the carrier concentration. The solid lines represent holes, and the dashed lines represent electrons.

In case of electrons, the absolute value of the Seebeck and the concentration is used.

More recently, utilizing the similar method as mentioned above, Shuai et al. have investigated the thermoelectric properties of a novel class of excellent hole transport organic materials, 2,7-dialkyl[1]benzothieno[3,2-b]benzothiophene derivatives (Cn-BTBTs). The first-principles calculations show that BTBTs exhibit high mobility and large Seebeck coefficients (0.3 mV/K) [133]. The structure of C8-BTBT, band structures and DOS of C8-BTBT and calculated Seebeck coefficient are shown in Fig. 30. Based on the predicted excellent performance, the authors suggested that if controlled doping is achieved without significantly decrease of the charge transport properties of the materials, BTBTs will become ideal candidates for thermoelectric applications.



Figure 30. (a) Lamella-like alternating structure of C8-BTBT in the *ac* plane. (b) Herringbone arrangement of C8-BTBT in the *ab* plane; the red dashed lines represent the crystal lattices. (c) Calculated band structures and DOS of C8-BTBT. (d) Seebeck coefficient (S), along the a-direction (blue lines) and the b-direction (red lines) for C8-BTBT as a function of carrier concentration at 298 K.

Otherwise, Shuai et al. also have identified a close-to-unity charge transfer from PEDOT to the dopant, and found that the ionized impurity scattering dominates over the acoustic phonon scattering in the doped PEDOT [132]. The authors revealed that the lightly doped PEDOT would exhibit thermoelectric properties superior to the heavily doped one, and the thermoelectric transport is highly anisotropic in ordered crystals.

8. Conclusions and outlook

In this work, we have reviewed the origin and development of organic thermoelectric Seebeck effect under the scope of thermoelectric applications. It looks that the theoretical progress of organic thermoelectric Seebeck effect lags far behind the experimental investigation in the last 30 years, but has been changed remarkably until the recent five years. From the enormous number of contributions, we have tried to describe several of the effect on thermoelectric Seebeck and the theories or approaches abundant in the literature concerned with carrier thermoelectric transport characteristics in organic semiconductors. Some possible merit and demerit for the current theoretical methods have also been discussed. Otherwise, to advance the thermoelectric effect in organic semiconductors, the theoretical model and predict is essential and promising for fundamental understanding of organic thermoelectric Seebeck effect and can provide the motivation for enlarging the thermoelectric application in organic semiconductors.

Acknowledgement

This work was supported in part by the Opening Project of Key Laboratory of Microelectronic Devices & Integrated Technology, Institute of MicroElectronics Chinese Academy of Sciences, by the Beijing Training Project For The Leading Talents in S&T under Grant Z151100000315008, by the National Natural Science Foundation of China (Nos. 61574166 and 61306117), by the National 973 Program

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under Grant 2013CB933504, Grant 2011CB808404 and Grant 2013CB933504, by the Strategic Priority Research Program of the Chinese Academy of Sciences, Grant No. XDB12030400, by the CAEP Microsystem and THz Science and Technology Foundation under the Grant No. CAEPMT201504.

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