

# Thermally assisted charge transfer and charge separation in organic donor-acceptor solar cells

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## ABSTRACT

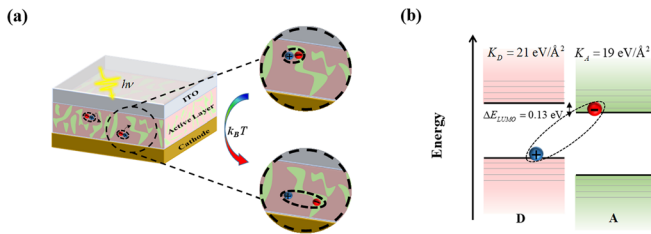
We propose a mechanism based on thermally assisted charge transfer (CT) to study the thermal effect on the formation of CT states and subsequent charge separation in an organic donor-acceptor solar cell. We reveal that the difference between phonons in the donor and acceptor caused by elastic energy acts as a thermally assisted driving force for charge transfer. It is found that the system exhibits a quite different CT process in the high and low temperature regions. Remarkably, combined with the entropy driving mechanics, the thermally assisted CT yields charge separation probability as high as 70% at room temperature. Our model and results provide a microscopic quantum understanding of the relevant recent experiments and open up a route to realize high-efficiency organic solar cells by effectively taking advantage of the thermal effect.

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In recent years, thanks to the rapid development of material synthesis technology and the optimized design of the device, the power conversion efficiencies (PCEs) of organic solar cells (OSCs) have reached 18%.<sup>1,2</sup> To enhance the dissociation rate of excitons, blends of electron-donor (D) and electron-acceptor (A) materials, known as bulk heterojunctions (BHJs), have become the mainstream in the design of OSC devices.<sup>3</sup> In a BHJ, exciton (tightly bound electron-hole pair) can be generated in the donor or acceptor materials after photon absorption due to Coulomb interaction together with electron-phonon (*e-ph*) coupling. An exciton migrates or transports to the donor/acceptor (D/A) interface where it dissociates into a bound charge transfer (CT) state with full or partial electron transferring to the other molecule, as depicted schematically in Fig. 1(a). Finally, the free carriers are extracted at electrodes to yield a current.

It is known that the thermal effect plays an important role in the photovoltaic processes.<sup>4–6</sup> There is no doubt that thermal effects accompany the entire process of exciton migration, charge transfer, and CT state dissociation. Mikhnenko *et al.* and Lin *et al.* studied experimentally the temperature-dependence of exciton diffusion.<sup>7,8</sup> In our recent work, the thermal effect on exciton movement within donor (or acceptor) polymers was studied theoretically.<sup>9</sup> It is found that an inhomogeneous temperature field is one possible mechanism for an exciton to move toward the interface to form the CT state. Traditionally, as CT states are precursors of free carriers in an organic solar cell based on the BHJ,<sup>10,11</sup> the thermal effect on the processes of

charge transfer and separation has received more attention recently.<sup>12,13</sup> The temperature dependence of photoluminescence (PL) quenching has indicated that the PL quenching related to charge transfer becomes less efficient at low temperature.<sup>14</sup> In 2019, Liu *et al.* measured the charge transfer rate as a function of temperature for two non-fullerene-based BHJs, in which they adopted 4,4,10,10-tetrakis(4-hexylphenyl)-5,11-(2-ethylhexyloxy)-4,10-dihydro-dithienyl[1,2-b:4,5b'] benzodi-thiophene-2,8-diyl]bis(2-(3-oxo-2,3-dihydroinden-1-ylidene)-malononitrile (BT-IC) and 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d':2',3'-d']-s-indaceno[1,2-b:5,6-b']dithiophene (IT-IC) as acceptors, respectively, and poly[(2,2'-bithiophene-4,4'-didodecyl)-*alt*-2,2'-bithiophene] (PBDBT) as the donor. They found that both systems show two distinct regimes with a critical temperature  $T_X \approx 150$  K. At  $T > T_X$ , the charge transfer rate increases rapidly with temperature, which is characteristic of thermally activated behavior for charge transfer. At  $T < T_X$ , the charge transfer rate is relatively temperature-independent due to the dominance of tunneling in the charge transfer process.<sup>15</sup> In the same year, researchers have considered an open quantum system approach to model the complex-solvent interaction theoretically, and they have stressed that the electron transfer rates are the highest at room temperature.<sup>16</sup> Moreover, it was observed that the dissociation of a CT state is also a temperature-dependent process.<sup>17,18</sup> Gao *et al.* investigated the effect of temperature on charge generation by examining the open-circuit voltage ( $V_{OC}$ ) in a wide temperature range and observed a



**FIG. 1.** Schematic diagram of thermally assisted charge transfer in a BHJ. (a) Photon absorption in the donor or acceptor materials generates an exciton. Then, it migrates or transports to a donor/acceptor interface where the exciton dissociates into the CT state, corresponding to full or partial electron transfer from an electron donor to an acceptor. With increasing temperature, the thermal potential across the donor/acceptor interface drives a further separation of the electron and hole. (b) Energy level diagram of the donor (D) and acceptor (A) molecules with band offset  $\Delta E_{LUMO} = 0.13$  eV.

decrease in  $V_{OC}$  at low temperatures, which was attributed to reduced charge generation.<sup>19</sup> The pump-push photocurrent (PPP) spectroscopy kinetics at different temperatures for the PffBT4T-2OD:EH-IDTBR device showed that at lower temperatures, fewer CT states can overcome the electrostatic barrier and directly dissociate into free carriers.<sup>20</sup> Theoretically, for the thermal effect on the CT state dissociation, it was also studied by considering energetic disorder<sup>21</sup> and entropy driving mechanisms.<sup>22–24</sup> These recent studies show that the thermal effect could potentially provide valuable information to improve the OSC efficiency. However, the thermal effect on the processes of charge transfer and separation is still elusive in theory and the underlying physical mechanisms of these interesting experimental phenomena need to be clarified.

In this Letter, we report our theoretical study about the thermal effect on the process of charge transfer in the framework of the tight-binding model. Combined with the entropy driving mechanism, the dependence of the probability of charge separation on temperature is obtained. The influence of the factor, elastic energy of the materials, on the thermally assisted charge transfer is discussed.

Type-II organic photovoltaics (OPVs) are composed of two coupled molecules, i.e., the electron donor and acceptor, each of which is described by a one-dimensional polymer chain. The Hamiltonian of the system can be written as

$$H = H_D + H_A + H_{\perp}. \quad (1)$$

The term  $H_j$  ( $j = D$  or  $A$ ) denotes the Hamiltonian of an isolated donor (D) or acceptor (A). Through secondary quantization in the tight-binding approach, we obtain

$$\begin{aligned} H_j = & \sum_{n,s} \Delta_j C_{j,n,s}^{\dagger} C_{j,n,s} + \sum_{n,s} \beta_j u_{j,n}(T) C_{j,n,s}^{\dagger} C_{j,n,s} \\ & - \sum_{n,s} \{ t_{j,n,n+1} - \tau_{j,n,n+1} [u_{j,n}(T) + u_{j,n+1}(T)] \} \\ & \times (C_{j,n+1,s}^{\dagger} C_{j,n,s} + C_{j,n,s}^{\dagger} C_{j,n+1,s}) \\ & + \sum_n \frac{1}{2} K_j [(u_{j,n+1} + u_{j,n+1}(T)) - (u_{j,n} + u_{j,n}(T))]^2 \\ & + \sum_n U_j \left( C_{j,n,\uparrow}^{\dagger} C_{j,n,\uparrow} - \frac{1}{2} \right) \left( C_{j,n,\downarrow}^{\dagger} C_{j,n,\downarrow} - \frac{1}{2} \right), \end{aligned} \quad (2)$$

where  $C_{j,n,s}^{\dagger}$  ( $C_{j,n,s}$ ) denotes the creation (annihilation) operator of an electron at site  $n$  of the  $j$ th chain with spin  $s$ . The first term in Eq. (2) is the on-site energy of the  $j$ th chain with  $\Delta_j$ . The second term describes the thermal correction of the on-site energy, which has usually been neglected in some previous investigations.<sup>25,26</sup> The third term refers to  $\pi$ -electron transfer between the nearest-neighbor sites along the chain. The transfer integral  $t_{j,n,n+1}$  between sites  $n$  and  $n+1$  is written as  $t_{j,n,n+1} = t_j^0 - \alpha_j(u_{j,n+1} - u_{j,n}) - (-1)^n t_j'$ , with  $t_j^0$  being the transfer integral in a uniformly arranged lattice,  $\alpha_j$  being the  $e$ - $ph$  coupling constant,  $t_j'$  being the symmetry-breaking term,<sup>27</sup> and  $u_{j,n}$  being the lattice displacement. We write separately the thermal correction term  $\tau_{j,n,n+1}$ , where  $u_{j,n}(T)$  stands for thermal fluctuation (or thermal phonon) of the lattice displacement. The fourth term describes the lattice elastic energy, where  $K_j$  is the lattice elastic constant. The thermal correction on the elastic energy is also included in this term. The Hubbard electron-electron interaction is included in Eq. (2) as the last term.

The inter-chain coupling between the donor and acceptor is written as

$$H_{\perp} = - \sum_{n,s} t_{\perp} (C_{A,n,s}^{\dagger} C_{D,n,s} + C_{D,n,s}^{\dagger} C_{A,n,s}), \quad (3)$$

where  $t_{\perp}$  is the inter-chain transfer integral.

The  $\mu$ -th electronic state  $\psi_{\mu} = \sum_{j,n,s} Z_{\mu,j,n,s} |j, n, s\rangle$  with energy  $\varepsilon_{\mu}$  is obtained by solving the equation

$$\begin{aligned} \beta_j u_{j,n}(T) Z_{\mu,j,n,s} - [t_{j,n,n-1} - \tau_{j,n,n-1}(u_{j,n-1}(T) + u_{j,n}(T))] Z_{\mu,j,n-1,s} \\ - [t_{j,n,n+1} - \tau_{j,n,n+1}(u_{j,n}(T) + u_{j,n+1}(T))] Z_{\mu,j,n+1,s} \\ + U_j \left( \rho_{j,n,-s} - \frac{1}{2} \right) Z_{\mu,j,n,s} - t_{\perp} Z_{\mu,j',n,s} = \varepsilon_{\mu} Z_{\mu,j,n,s}, \end{aligned} \quad (4)$$

where the charge density matrix is defined as  $\rho_{j,n,s} = \sum_{\mu} Z_{\mu,j,n,s}^* f_{\mu,s} Z_{\mu,j,n,s}$ , with  $f_{\mu,s}$  being the Fermi-Dirac distribution for the  $\mu$ -th energy level.

We assume that the thermal fluctuation remains time independent, and the displacement  $\{u_n\}$  is determined by the following equation:

$$\begin{aligned} u_{j,n+1} - u_{j,n} = & \frac{2\alpha_j}{(N_j - 1)K_j} \sum_{n,\mu,s} Z_{\mu,j,n,s} f_{\mu,s} Z_{\mu,j,n+1,s} \\ & - \frac{2\alpha_j}{K_j} \sum_{\mu,s} Z_{\mu,j,n,s} f_{\mu,s} Z_{\mu,j,n+1,s}. \end{aligned} \quad (5)$$

Equations (4) and (5) are solved by the self-consistent iterative calculation from which the lattice displacement and the electronic states at a given thermal field are obtained.

We suppose that the thermal fluctuation of the lattice displacement is random and obeys Boltzmann statistics,  $u_{j,n}(T) = (k_B T / K_j)^{1/2} R_n$ , where  $\{R_n\}$  is a set of random numbers with square-distribution in the range of  $[-1, 1]$ . Without loss of generality, we choose each conjugated polymer chain with 100 sites. The following parameters are adopted:  $t_j^0 = 2.5$  eV,  $t_j' = 0.05$  eV,  $U_j = 1.0$  eV,  $\beta_j = 10$  eV/Å, and  $\tau_{j,n,n+1} = \alpha_j = 4.1$  eV/Å referring to *cis*-polyacetylene.<sup>28,29</sup> The results are averaged for 200 samples to reduce the statistical errors.

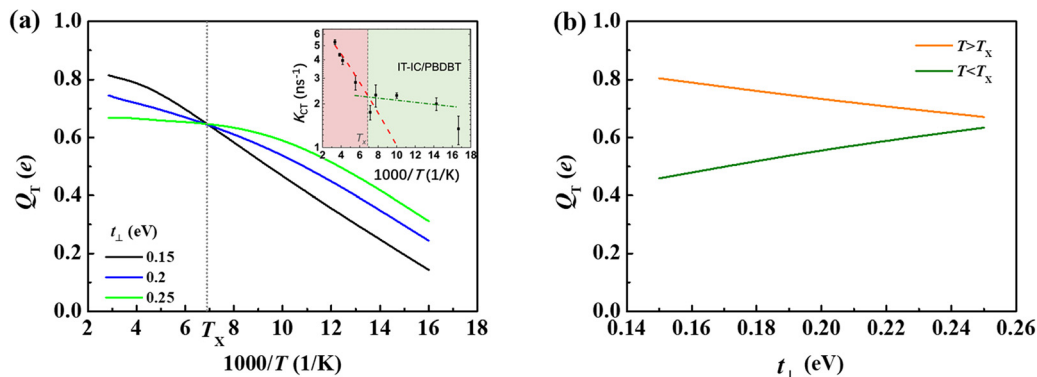
As is known, the electron and hole are bounded by the Coulomb interaction in an inorganic semiconductor. In contrast, in an organic

semiconductor, the electron and hole interact not only by the Coulomb interaction but also by the  $e$ - $ph$  interaction. Actually, in an organic semiconductor, the strong  $e$ - $ph$  interaction can bound the electron and hole pair in an exciton or a charge transfer state, which is spatially localized. In this case, the thermal phonon, or lattice thermal fluctuation, will play an important role in the confinement or dissociation of an exciton in OSCs. Moreover, since the OSCs usually are made up of light atoms, the thermal fluctuation can be much more significant than that in an inorganic one. In particular, in a BHJ, the different thermal phonon modes in the donor and acceptor will produce a thermal potential around the interface, which can act as a potential source to cause dissociations of either the electron-hole pair or CT state.

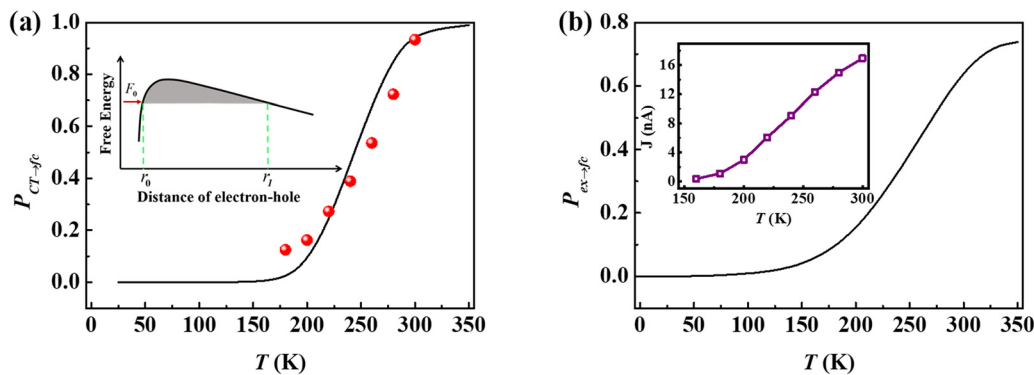
A CT state is the precursor of free carriers at the D/A interface. Hence, its formation rate essentially influences the photovoltaic performance of a BHJ solar cell device. We first investigate the thermal effect on the formation of a CT state. In our model framework, we choose a donor molecule with  $K_D = 21 \text{ eV}/\text{\AA}^2$  and an acceptor molecule with  $K_A = 19 \text{ eV}/\text{\AA}^2$ . Setting the on-site energy difference between the donor and acceptor as  $\Delta_j = 0.3 \text{ eV}$ , we can obtain the band offset or energy difference between the lowest unoccupied molecular orbitals (LUMO),  $\Delta E_{LUMO} = 0.13 \text{ eV}$ , as depicted schematically in Fig. 1(b). Usually, in a system with small  $\Delta E_{LUMO}$ , photon absorption in either the donor or acceptor material can generate a hybrid local exciton-charge transfer state,<sup>30,31</sup> as shown in Fig. 1(b). To quantify the forming ratio of CT states, we define the quantity of transferred charge from the donor to acceptor as  $Q_T = e \sum_{n,s} (\rho_{A,n,s} - 1)$ , where  $e$  is the unit charge. The dependence of the transferred charge on temperature in different coupling systems is presented in Fig. 2(a), where the inset shows experimental data of charge transfer rates vs temperature for IT-IC/PBDBT from Ref. 15. It is found that the transferred charge increases with temperature, indicating that the thermal effect is beneficial for the formation of the CT state. We note that, due to the different elastic constants  $K_D$  and  $K_A$ , even though there is a uniform temperature distribution, the thermal phonons are different in the donor than that in the acceptor. The difference in phonon modes will induce a thermally assisted driving force for the charge transfer at the interface. Therefore, as the temperature increases, the charge transfer

is favorable, which shows a process of thermally assisted charge transfer and is qualitatively consistent with the experimental results.<sup>15</sup> The experimental measurement also accessed that charge transfer is dominant by electron tunneling in the low temperature region but is characteristic of thermally activated behavior in the high temperature region, as shown in the inset of Fig. 2(a). Here, it is interesting to note that the thermal assistance is related to the inter-chain coupling and there also exists a critical temperature  $T_X \simeq 150 \text{ K}$ . We present the dependences of the transferred charge on the inter-chain coupling in different temperature regions, as shown in Fig. 2(b). Contrast to the increasing transferred charge with the inter-chain coupling in the low temperature region, the transferred charge decreases with the inter-chain coupling in the high temperature region. The two distinct features show that the thermal effect and the inter-molecule coupling effect coexist and are competitive in the process of charge transfer. In the case of  $T < T_X$ , i.e., the driving force provided by the thermal effect is not very large, and charge transfer is dominated by intermolecular tunneling due to a strong inter-chain coupling. While in the case of  $T > T_X$ , the transferred charge decreases rapidly with inter-chain coupling due to strong energy level mixing, but the charge transfer quantity is still a lot, which shows a process of thermally assisted charge transfer. This conclusion is consistent with the experimental measurements, that is, the charge transfer is dominated by tunneling at low temperature while by thermal assistance at high temperature.<sup>15</sup> Recently, OPV systems can achieve efficient charge separation with a negligible band offset.<sup>32</sup> The thermal driving force may be one of the reasons for efficient charge separation in the system with a negligible band offset.

When a CT state forms in the BHJ, it will further dissociate into a free electron or hole (negative or positive polaron in organic materials) to functionalize the OPV. The charge transfer quantity calculated above also reflects the probability  $P_{ex \rightarrow CT}(T)$  that an exciton is converted to a CT state or an electron-hole pair. Furthermore, we suppose the probability that a CT state is converted to free charges to be  $P_{CT \rightarrow fc}(T)$ , then the total probability that a photoexcited exciton is converted to free electron and hole is  $P_{ex \rightarrow fc} = P_{ex \rightarrow CT}(T) \cdot P_{CT \rightarrow fc}(T)$ . We employ the entropy driving mechanism to calculate  $P_{CT \rightarrow fc}(T)$ . The free energy of an electron-hole pair with separation  $r$  is given by  $F(r, T) = \frac{e^2}{4\pi\epsilon_0\epsilon_r r} - TS$ .  $\epsilon_0(\epsilon_r)$  is the vacuum



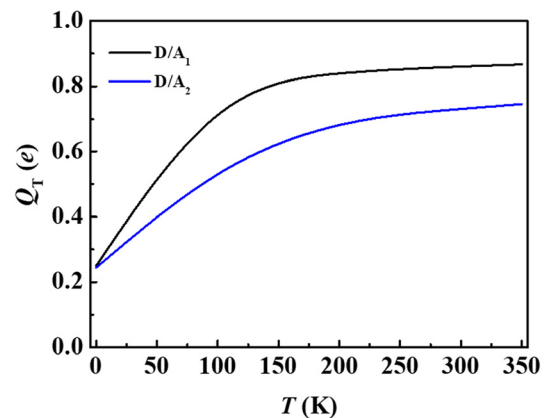
**FIG. 2.** Thermal effect on the process of charge transfer. (a) Dependence of the charge transfer on temperature in a polymer heterojunction with  $t_{\perp} = 0.15 \text{ eV}$  (black),  $t_{\perp} = 0.2 \text{ eV}$  (blue), and  $t_{\perp} = 0.25 \text{ eV}$  (green), respectively. The inset shows the experimental data of charge transfer rates vs temperature for IT-IC/PBDBT.<sup>15</sup> Reproduced with permission from Liu *et al.*, Phys. Rev. Appl. **11**, 024060 (2019). Copyright 2019 American Physical Society. (b) Dependence of the charge transfer on the inter-chain coupling in the cases of  $T < T_X$  (olive line) and  $T > T_X$  (orange line).



**FIG. 3.** Thermal effect on the process of charge separation. (a) Dependence of  $P_{CT \rightarrow fc}$  on temperature. The red balls represent experimental data.<sup>18</sup> The inset shows the free energy barrier required for the electron tunneling to escape from the bound state. (b) Dependence of  $P_{ex \rightarrow fc}$  on temperature. The inset is the experimental measurement of photocurrent at different temperatures.<sup>18</sup> Reproduced with permission from Zhang *et al.*, J. Mater. Chem. A **5**, 11949 (2017). Copyright 2017 Royal Society of Chemistry.

(effective) dielectric constant and the entropy  $S \approx k_B \ln(2\pi r^2/a_0^2)$  is given by counting the possible microscopic configuration of the electron-hole pair setting an immobile hole.  $a_0 = 1$  nm is the lattice constant. Then, the probability  $P_{CT \rightarrow fc}(T)$  is simply given by the WKB approximation  $P_{CT \rightarrow fc}(T) = \exp\left[-\frac{2}{\hbar} \left| \int_{r_0}^{r_1} \sqrt{2m(F_0 - F(r, T))} dr \right| \right]$ , where  $F_0$  is the energy of an electron confined at the interface. In our study, delocalization effects can take place due to the existence of the thermal effect. The initial distance  $r_0$  between the electron and hole is set to 6.5 nm according to a Coulomb capture radius of about 6–8 nm<sup>23</sup> and  $r_1$  is the distance where the CT state dissociation occurs. We present a schematic diagram of the free energy barrier required for the electron tunneling to escape from the bound state in the inset of Fig. 3(a). The dependence of  $P_{CT \rightarrow fc}$  on temperature is obtained as shown in Fig. 3(a). The result indicates that a drastic increase with temperature is the probability that an electron-hole pair is converted to free charges in the high temperature region, whereas the probability is almost zero in the low temperature region. For a given initial distance  $r_0$ , the free energy barrier required for the electron tunneling becomes significantly wide as the temperature decreases, making it so easy for electrons to tunnel in the high temperature region and almost impossible to tunnel in the low temperature region. Therefore, the thermal effect can assist CT state separation by reducing the energy barrier. We compare the result with the experimental data measured by the temperature-dependent PPP response from 160 K to 300 K as shown by the red balls in Fig. 3(a), and the theoretical result is in good agreement with the experimental measurement.<sup>18</sup> The dependence of  $P_{ex \rightarrow fc}(T)$  on temperature is shown in Fig. 3(b). The result shows that it is hard for an exciton to dissociate into the free electron and hole in the low temperature region, and the probability  $P_{ex \rightarrow fc}(T)$  increases rapidly with increasing temperature in the high temperature region. At room temperature, the probability of charge generation can reach about 70%. The yield of free carriers directly affects the photocurrent. The inset of Fig. 3(b) shows the experimental measurement of photocurrent at different temperatures.<sup>18</sup> Recently, the non-fullerene solar cell based on the PM6: Y6 bulk heterojunction shows high photocurrent down to  $\sim 100$  K despite the small driving force.<sup>33</sup> Our theoretical results confirm the experimental conclusions that the process of free carrier generation is a process of temperature activation<sup>17,18,34,35</sup> and provide a possible explanation for the charge generation in non-fullerene systems.<sup>33</sup>

It should be stressed that the thermal effect in an organic BHJ system is more important. Due to the different bond structures, the reorganization energy of the donor is different from that of the acceptor, which is reflected by the elastic energy in the present model. From the Boltzmann statistics,  $\langle \frac{1}{2} K_j u_{j,n}^2(T) \rangle = \frac{1}{2} k_B T$ , we obtain that the lattice fluctuation  $u_{j,n}(T)$  is related to the elastic constant  $K_j$  or the phonons of the donor (acceptor). As a result, charge transfer at the D/A interface is strongly influenced by thermal phonons. Due to the different elastic constants, the thermal effect in the donor will be different from that in the acceptor even when the temperature distribution is the uniform. Based on this, we study the thermal effect on charge transfer in the BHJ systems with different elastic constant ratios ( $D/A_1$  with  $K_D/K_{A1} = 21/17$  and  $D/A_2$  with  $K_D/K_{A2} = 21/19$ ). We set the same initial LUMO band offset of 0.13 eV as in the previous case. Figure 4 shows the dependence of charge transfer on temperature. It is found that the charge transfer is more pronounced in the system with  $K_D/K_{A1} = 21/17$  than that with  $K_D/K_{A2} = 21/19$ . Notice that even though the temperature distribution is uniform, there exists a thermal driving force in a BHJ structure. As analyzed above, the thermal driving force results from the different thermal phonons in the donor and



**FIG. 4.** Dependence of transferred charges on temperature in the  $D/A_1$  system with  $K_D/K_{A1} = 21/17$  (black line) and the  $D/A_2$  system with  $K_D/K_{A2} = 21/19$  (blue line).



acceptor. We analyze that the acceptor molecule with  $K_A = 17 \text{ eV}/\text{\AA}^2$  responds to the thermal effect more sensitively than the acceptor molecule with  $K_A = 19 \text{ eV}/\text{\AA}^2$ , which further causes a larger thermally assisted driving force for charge transfer in D/A<sub>1</sub> than in D/A<sub>2</sub>. We conclude that, for type-II OPVs, the larger the ratio of  $K_D/K_A$ , the better the charge transfer, which is attributed to the thermal effect on charge transfer in a BHJ. In an isolated organic material, we have suggested that a non-uniform temperature distribution can drive and even dissociate an exciton.<sup>9</sup> Here, we demonstrate that, in a BHJ, even a uniform temperature distribution can drive a CT state formation and dissociation. As most of the OPVs host BHJ structures, the present investigation reveals an additional tunneling for CT state dissociation.

The photovoltaic processes in OSCs are sensitive to the thermal effect. In this Letter, we propose a thermally assisted dissociation mechanism in a BHJ structure. Interestingly, unlike usual temperature gradient-induced thermal dissociation, we demonstrate that the formation and dissociation of a CT state can be driven thermally even under a uniform temperature distribution. At the interface, the band offset, inter-molecule coupling, and the thermal driving are all important factors for the charge transfer and separation. Our calculation reveals that, in the low temperature region, the inter-molecule coupling facilitates the charge transfer, but it does not in the high temperature region. Combined with the entropy driving mechanism, the thermally assisted charge separation probability can reach 70% at room temperature. In addition, a large difference in the elastic energy between the donor and acceptor induces a large thermal driving force, which causes a pronounced charge transfer. Our results provide a route to improve the efficiency of organic solar cells.

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## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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