Seebeck Effects in N-Type and P-Type Polymers Driven Simultaneously by Surface Polarization and Entropy Differences Based on Conductor/Polymer/Conductor Thin-Film Devices

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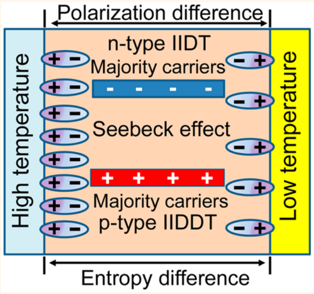

ABSTRACT This paper reports Seebeck effects driven by both surface polarization difference and entropy difference by using photoinduced intramolecular charge-transfer states in n-type and p-type conjugated polymers, namely IIDT and IIDDT, respectively, based on vertical conductor/polymer/conductor thin-film devices. We obtain large Seebeck coefficients of −898 μV/K from n-type IIDT and 1300 μV/K from p-type IIDDT when the charge-transfer states are generated by a white light illumination of 100 mW/cm^2, compared with the values of 380 and 470 μV/K in dark condition, respectively. Simultaneously, the electrical conductivities are increased from almost insulating state in dark condition to conducting state under photoexcitation in both n-type IIDT and p-type IIDDT based devices. The large Seebeck effects can be attributed to the following two mechanisms. First, the intramolecular charge-transfer states exhibit strong electron–phonon coupling, which leads to a polarization difference between high and low temperature surfaces. This polarization difference essentially forms a temperature-dependent electric field, functioning as a new driving force additional to entropy difference, to drive the energetic carriers for the development of Seebeck effects under a temperature difference. Second, the intramolecular charge-transfer states generate negative or positive majority carriers (electrons or holes) in the n-type IIDT or p-type IIDDT, ready to be driven between high and low temperature surfaces for developing Seebeck effects. On the basis of coexisted polarization difference and entropy difference, the intramolecular charge-transfer states can largely enhance the Seebeck effects in both n-type IIDT and p-type IIDDT devices. Furthermore, we find that changing electrical conductivity can switch the Seebeck effects between polarization and entropy regimes when the charge-transfer states are generated upon applying photoexcitation. Therefore, using intramolecular charge-transfer states presents an approach to develop thermoelectric effects in organic materials-based vertical conductor/polymer/conductor thin-film devices.

KEYWORDS: Seebeck effects · charge-transfer states · surface polarization · entropy difference · n-type organic polymer · p-type organic polymer

When a temperature difference (ΔT) is applied across a medium, an electrical voltage (ΔV) can be generated between the high and low-temperature surfaces, leading to Seebeck effects. The Seebeck coefficient (S) can be calculated by using the applied temperature difference and the obtained electrical potential difference (ΔV):$S = (\Delta V/\Delta T)$. Primarily, the Seebeck effects originate from the diffusion of energetic carriers driven by the entropy difference between high and low temperature surfaces.[1−3] Specifically, high/low temperature surface can exhibit higher/lower density of energetic carriers through thermal activation, generating an entropy difference in carrier concentration across a medium. This entropy difference has been functioning as the basic driving force to diffuse the energetic carriers from high to low temperature surface for developing Seebeck effects. However, the entropy difference can often cause an inverse relationship between the Seebeck coefficient and electrical conductivity in the thermoelectric developments. Here, we explore an additional driving force

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by using temperature-dependent surface polarization to drive energetic carriers to enhance the Seebeck effects in n-type IIDT and p-type IIDDT materials based on intramolecular charge-transfer states in the vertical conductor/polymer/conductor thin-film devices. The intramolecular charge-transfer states can provide two important properties for enhancing Seebeck effects: (i) generating energetic carriers through photoexcitation, and (ii) increasing temperature-dependent surface polarization through electron–phonon coupling in conductor/polymer/conductor devices. On one hand, the energetic carriers are ready to contribute to the carrier concentration difference (ΔN) between high and low temperature surfaces, facilitating the entropy difference for developing Seebeck effects. On the other hand, the electron–phonon coupling can establish a temperature-dependent polarization on polymer surfaces, leading to a temperature-dependent electric field, functioning as an additional driving force, to drive the energetic carriers between high and low temperature surfaces for developing Seebeck effects. Essentially, the Seebeck effects are driven by coexisted polarization and entropy differences between high and low-temperature surfaces. In particular, the coexisted polarization and entropy differences provide a new method to enhance Seebeck effects in conductor/polymer/conductor devices.

RESULTS AND DISCUSSION

Figure 1a,b shows the Seebeck coefficients generated from the vertical ITO/polymer/Au thin-film devices at various temperatures based on two polymers, namely IIDT and IIDDT. The early studies have shown that the IIDT and IIDDT can function as n-type and p-type materials.[4] Here, we can see that in dark condition both n-type IIDT and p-type IIDDT devices exhibit the positive Seebeck coefficients with the values of exceeding 380 and 470 μV/K at 80 °C. However, under photoexcitation n-type IIDT device changes the Seebeck coefficient from positive to negative value. The negative Seebeck coefficient reaches -898 μV/K at the photoexcitation intensity of 100 mW/cm^2. In contrast, the p-type IIDDT device only shows a positive Seebeck coefficient under photoexcitation. The positive Seebeck coefficient approaches 1300 μV/K at the photoexcitation intensity of 100 mW/cm^2. In general, the vertical conductor/polymer/conductor thin-film devices can exhibit both polarization difference and entropy difference between high and low-temperature surfaces.[5] Specifically, the polarization difference between high and low-temperature surfaces is essentially developed by the electron–phonon coupling on polymer surfaces. The electron–phonon coupling comes from the interactions between electrical polarizations and thermal vibrations, which can be widely observed through temperature-dependent dielectric constants in organic materials.[6–10] Considering that organic materials can have certain electron-donating properties, we can suggest that the polymer surfaces become positively polarized in the conductor/polymer/conductor devices. In this situation, the high and low-temperature surfaces correspond to stronger and weaker polarizations due to electron–phonon coupling. As a consequence, a temperature-dependent potential difference across polymer film can be established with the direction pointing from high-temperature surface to low-temperature surface, as schematically shown in Figure 1c. In addition, the different electron donating properties between the conductor and polymer

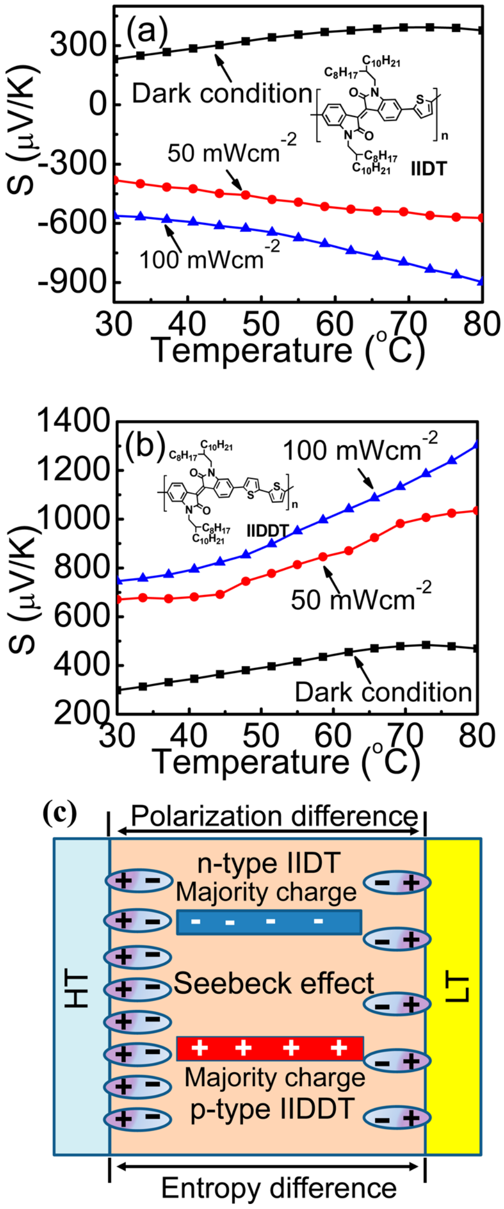

Figure 1. Seebeck effects in n-type and p-type thin-film devices. (a) An n-type ITO/IIDT/Au device; (b) p-type ITO/IIDDT/Au device; (c) schematic diagram to show Seebeck effects driven by polarization and entropy differences under temperature difference in the vertical thin-film conductor/polymer/conductor devices. HT, high temperature surface; LT, low temperature surface.

phases can shift the electron clouds at the conductor/polymer interface, leading to interfacial dipoles. Because the electron clouds can be thermally mediated, the interfacial dipoles can become temperature-dependent. As a consequence, the interfacial dipoles can contribute to the temperature-dependent polarization difference between high and low-temperature surfaces. Nevertheless, the temperature-dependent potential difference established by surface polarization difference provides a new driving force, additional to entropy difference, to drive the energetic carriers between high and low-temperature surfaces for enhancing Seebeck effects in conductor/polymer/conductor devices. Specifically, the temperature-dependent potential difference can drift the energetic electrons from low to high-temperature surface but the energetic holes from high to low-temperature surface, leading to a positive Seebeck effect in both n-type IIDT and p-type IIDDT devices. In contrast, the entropy difference between the high and low-temperature surfaces always generates negative and positive Seebeck effects in n-type and p-type materials. Essentially, the observed Seebeck effects are driven by both polarization difference and entropy difference in conductor/polymer/conductor devices under a temperature difference, leading to polarization and entropy regimes to develop Seebeck effects, as shown in eq 1.

$$S = S_{\mathrm{Drift}} + S_{\mathrm{Diffusion}} \tag{1}$$

where S_{Drift} and $S_{\mathrm{Diffusion}}$ are Seebeck coefficients generated by the drift driven by surface polarization difference and the diffusion driven by entropy difference, respectively.

On the one hand, in the n-type IIDT device, the surface-polarization difference and entropy difference drive Seebeck effects with opposite directions. Specifically, the polarization difference leads to a positive Seebeck effect, while the entropy difference generates a negative Seebeck effect. The overall Seebeck coefficient is then determined by the combination of polarization-driven and entropy-driven Seebeck effects. Here, we observe positive and negative Seebeck effects (380 and -898 μV/K at 80 °C) in dark and photoexcitation conditions, respectively, in the n-type IIDT device. This result can experimentally indicate that increasing electrical conductivity can change the Seebeck coefficient from positive value to a negative value in the n-type device. In particular, this experimental observation suggests that increasing the electrical conductivity changes the Seebeck effects from polarization-dominated regime to entropy dominated regime when the majority carriers are electrons. On the other hand, in the p-type IIDDT device, the polarization difference and entropy difference both drive the Seebeck effects in the same direction when the majority carriers are holes, leading to a large positive Seebeck coefficient. In this situation, increasing the electrical conductivity can further increase the positive Seebeck coefficient in the p-type device. Nevertheless, we can experimentally see that low and high electrical conductivities correspond to polarization-dominated and entropy-dominated regimes, respectively, in the development of Seebeck effects. Increasing electrical conductivity can switch the Seebeck effects between polarization and entropy regimes in n-type IIDT and p-type IIDDT devices. On the basis of these experimental results, we can propose the following arguments. The energetic carriers can decrease the polarization difference effect between high and low-temperature surfaces through Coulomb screening effects at high conductivities in the conductor/polymer/conductor devices. However, we should note that the energetic carriers are normally generated by thermal activation to establish entropy difference. Here, photoexcitation can generate a large number of energetic carriers through intramolecular charge-transfer states, ready for thermal activation to contribute to entropy difference. In this situation, increasing electrical conductivity can facilitate the entropy difference toward the development of Seebeck effects at high conductivities. Clearly, increasing electrical conductivity can switch the Seebeck effects from polarization regime to entropy regime in the conductor/polymer/conductor devices.

We should note that photoexcitation can generate both Seebeck voltage and photovoltage in the vertical conductor/polymer/conductor thin-film devices. In our measurements we have removed the photovoltage in the determination of Seebeck voltage by separating these two effects.[11] Here, we can compare the total voltage measured with a forward temperature difference (3 °C) and the total voltage measured with negligible temperature difference (<0.1 °C) in the ITO/polymers/Au device under photoexcitation. The difference between these two measurements can determine the Seebeck effect under photoexcitation in the ITO/polymers/Au device under a temperature difference (Figure 2). For the p-type IIDDT based device, the total voltage measured with a forward temperature difference exhibits larger values than the photovoltaic voltage measured with a negligible temperature difference at different temperatures under photoexcitation. Therefore, in this situation, the Seebeck voltages and photovoltaic voltages have the same direction. On the contrary, the total voltage measured with a forward temperature difference from the n-type IIDT based device is lower than the photovoltaic voltage measured with a negligible temperature difference under photoexcitation. In this situation, the Seebeck voltages and photovoltaic voltages have the opposite direction. Clearly, the difference of the total electrical voltage between the forward and the negligible temperature difference in both IIDT and IIDDT confirms that our data processing (see Methods section) of subtracting the

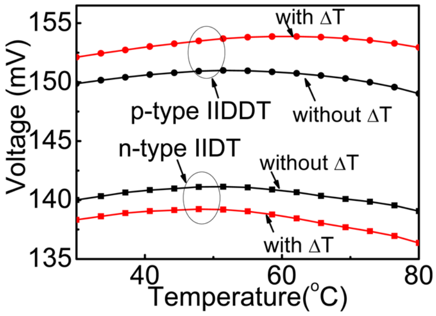

Figure 2. Total voltages measured under forward temperature difference (around 3 °C) as compared with negligible temperature difference at different temperatures under photoexcitation for ITO/n-type IIDT/Au and ITO/p-type IIDDT/Au devices.

photovoltage from the total electrical voltage can indeed be used to determine the Seebeck voltage in the vertical conductor/polymers/conductor thin-film devices under photoexcitation.

Now we discuss the electron–phonon coupling associated with the charge-transfer states based on photoluminescence (PL) studies at different temperatures. Figure 3 shows the PL spectra measured at different temperatures for the IIDT and IIDDT films. It is well-known that the electron–phonon coupling strength could be determined by the Huang–Rhys parameter, S, which is defined by[12,13]

$$S = \frac{k(\Delta Q)^2}{2\hbar\omega_p} \tag{2}$$

where k is the elastic constant, ΔQ is the change of the configuration coordinate from ground states to excited states and ω_p is the angular frequency of the phonon mode of energy E_p. According to eq 2, a larger change (ΔQ) in the configuration coordinate corresponds to stronger electron–phonon coupling in excited states. We can see in Figure 3 that the IIDT and IIDDT films show a main peak around 750 nm with a shoulder peak around 820 nm. On the basis of photophysics in organic semiconductors, the 750 and 820 nm peaks can be assigned to the nominal 0–0 and 0–1 vibrational transitions.[14,15] It is clear that increasing temperature causes an increase in the 0–0/0–1 intensity ratio. The early studies have shown that such temperature-dependent PL characteristics can be attributed to the weakly coupled H aggregates in the IIDT and IIDDT.[14,15] Specifically, the increase in the 0–0/0–1 peak intensity ratio implies that increasing temperature leads to large disorders in polymer chain configuration through thermal vibrations. Consequently, increasing the disorders in polymer chain configuration can enhance the electron–phonon coupling, as shown by the temperature dependence of 0–0/0–1 intensity ratio in eq 2.[16−19] The electron-coupling can generate a polarization difference between high and low-temperature surfaces through charge-transfer states, functioning as an additional driving force for developing Seebeck effects in the IIDT and IIDDT devices.

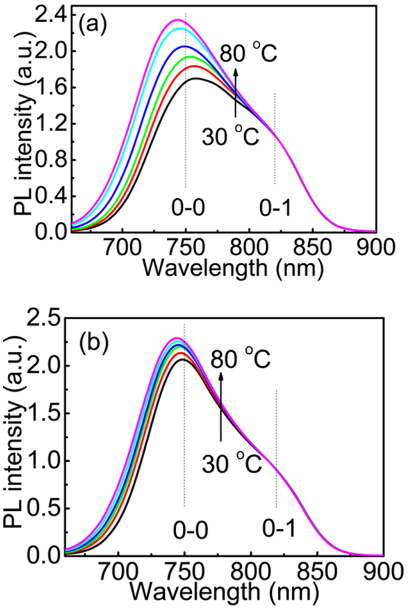

Figure 3. PL spectra at different temperatures for n-type IIDT and p-type IIDDT devices based on ITO/polymer/Au architecture. (a) An n-type IIDT device; (b) p-type IIDDT device. The PL spectra show that increasing temperature causes an increase on the 0–0/0–1 ratio for both n-type IIDT and p-type IIDDT.

Now we confirm the temperature-dependent surface polarization by using temperature-dependent capacitance measurements in the IIDT and IIDDT devices. The device capacitance can essentially reflect the surface polarization on the IIDT and IIDDT films when the thin-film devices are measured in capacitance mode. Figure 4a,b shows the capacitance–voltage (C–V) characteristics for ITO/IIDT/Au and ITO/IIDDT/Au devices at different temperatures under photoexcitation. We can see that the device capacitance at zero bias increases with increasing temperature for both IIDT and IIDDT. Here, the observed temperature dependence of device capacitance characteristics provides an experimental evidence that the surface polarization is temperature dependent in the IIDT and IIDDT devices. It is known that the electrical conductivities can be largely increased under photoexcitation.[20,21] Figure 5 shows the current–voltage (I–V) characteristics for both IIDT and IIDDT devices in dark and photoexcitation conditions. We can see that the photoexcitation can lead to a significant increase in the electrical current as compared with dark condition. Here we use the Cheung's equation[22] to determine the electrical conductivities in the IIDT and IIDDT devices. The Cheung's equation is given by

$$\frac{dV}{d\ln(I)} = n_1\frac{kT}{q} + IR_s \tag{3}$$

where V is the voltage, I is the current, n_1 is the ideality factor, k is the Boltzmann constant, q is the electronic

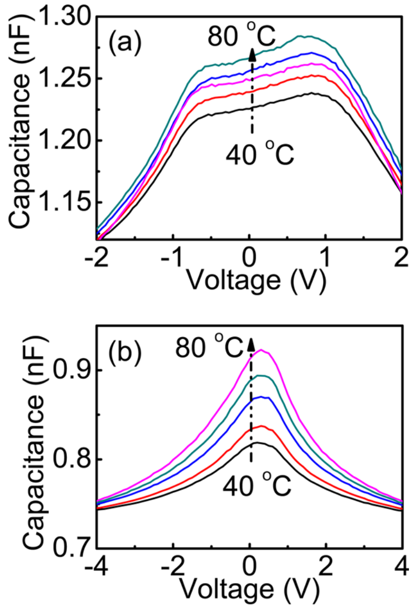

Figure 4. Capacitance−voltage (*C*−*V*) characteristics at different temperatures under photoexcitation. (a) ITO/n-type IIDT/Au device.; (b) ITO/p-type IIDDT/Au device.

charge, and R_s is the series resistances of these devices. On the basis of the *I*−*V* characteristics in Figure 5, the slope of d*V*/d ln*I*−*I* plot can be determined to be 4.0 × 10^{-5} and 4.3 × 10^{-5} Ω for IIDT and IIDDT in photoexcitation condition, respectively. By using the series resistances, the electrical conductivities can be calculated to be 7.5 × 10^{-8} and 6.9 × 10^{-8} S/m for the IIDT and IIDDT under photoexcitation condition, respectively. Clearly, applying photoexcitation can largely increase the electrical conductivities in both n-type IIDDT and p-type IIDDT devices. Simultaneously, we can see that increasing electrical conductivities leads to an enhancement on the Seebeck coefficient in both n-type IIDT and p-type IIDDT devices.

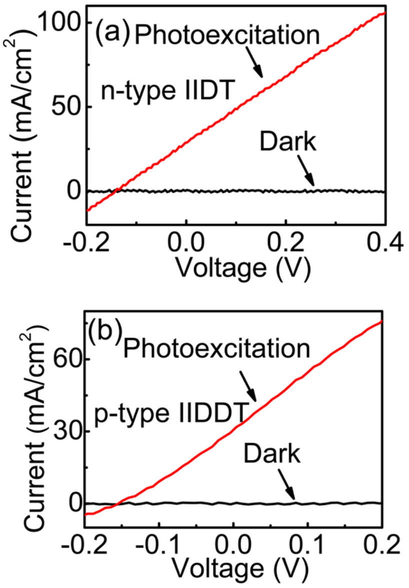

Figure 5. Current−voltage (*I*−*V*) characteristics at dark and photoexcitation conditions. (a) ITO/n-type IIDT/Au device; (b) ITO/p-type IIDDT/Au device.

CONCLUSION

In summary, we explored Seebeck effects by using intramolecular charge-transfer states in n-type IIDT and p-type IIDDT devices based on vertical architecture of conductor/polymer/conductor design. We found that the vertical conductor/polymer/conductor thin-film devices provide a new driving force, namely temperature-dependent surface-polarization difference, additional to entropy difference, to drive the energetic carriers between high and low-temperature surfaces. This leads to coexisted polarization and entropy regimes for developing Seebeck effects. The Seebeck coefficient is essentially determined by the combination of two Seebeck effects driven by polarization and entropy differences. In n-type device, the polarization and entropy difference drive the energetic electrons with opposite directions from low to high-temperature surface and from high to low-temperature surface, respectively. In p-type device, the polarization and entropy differences drive the energetic holes with the same direction from high to low-temperature surface. Here, the intramolecular charge-transfer states can generate two critical contributions to enhance Seebeck effects: (i) increasing surface polarization difference between the high and low-temperature surfaces through electron−phonon coupling and (ii) generating energetic carriers contributing to entropy difference. By using charge-transfer states, we observed large positive and negative Seebeck coefficients of 1036 and −898 μV/K from the p-type IIDDT and n-type IIDT devices under photoexcitation. Furthermore, we found that changing electrical conductivity can switch the Seebeck effects between polarization and entropy regimes. Therefore, using intramolecular charge-transfer states provides promising possibilities to develop thermoelectric effects tunable between polarization and entropy regimes in n-type and p-type materials based on vertical conductor/polymer/conductor thin-film devices.

METHODS

The intramolecular charge-transfer polymers, IIDT and IIDDT, were synthesized by using previously reported procedures.[4] The vertical thin-film devices were fabricated with a sandwiched architecture of ITO/polymer/Au. The polymer films were spin-cast with the thickness of about 300 nm on previously cleaned ITO substrates. The spin-cast polymer films were thermally annealed at 120 °C for 10 min. The top Au conducting layers were deposited with a thickness of 60 nm on the polymer films in the vacuum of 2 × 10^{-6} Torr. The K-type thermocouple wires were connected to the ITO and Au layers to measure the surface temperatures. The heating was applied to the ITO surface in the ITO/polymer/Au devices by using electrically controllable hot plate. At the same time the top Au layer was cooled with an aluminum heat sink to generate a controllable temperature difference for developing Seebeck effects. A white light from Thermal Oriel 96000 300-W solar simulator was used to generate charge-transfer states in the n-type IIDT and p-type IIDDT devices. The voltage and temperature data were collected by a Labview acquisition system. The Seebeck coefficients are calculated by $S = (\Delta V/\Delta T)$. The accuracies for ΔV and ΔT were within about 10 μV and 0.1 K, respectively. It should be noted that the photoexcitation leads to both photovoltage and Seebeck voltage when photoexcitation and temperature differences are simultaneously applied. However, the photovoltage was removed in our Seebeck measurements by using the following precedures. First, the total electrical voltage containing the Seebeck and photovoltaic components was measured under a temperature difference of around 3 °C at different temperatures from 40 to 80 °C under constant photoexcitation intensity, denoted as the $V_{\rm all}$. Second, the photovoltage ($V_{\rm ph}$) was recorded immediately with a zero temperature difference ($\Delta T < 0.1$ °C) at different temperatures when the same photoexcitation was applied. Third, the Seebeck voltage ($V_{\rm TE}$) was calculated by subtracting the photovoltage from the total electrical voltage, $V_{\rm TE} = V_{\rm all} - V_{\rm ph}$. The capacitance measurements were performed by using an Agilent E4980A LCR meter with a 50 mV AC bias to explore surface polarizations at different temperatures. The current−voltage ($I-V$) measurements were measured to characterize the electrical conductivities in the n-type IIDT and p-type IIDDT thin-film devices by using Keithley 2400 electrometer.

Conflict of Interest: The authors declare no competing financial interest.

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