P-Type Chemical Doping-Induced
High Bipolar Electrical Conductivities
in a Thermoelectric Donor–Acceptor
Copolymer

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Typically, conducting polymers transfer either electrons or holes. It is rare to see high bipolar (p- and n-type) electrical conductivities within a single bulk doped organic polymer without the assistant of gate voltage. Herein, we report that FeCl3-doped solution-processable D–A copolymer poly (2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)diketopyrrolo[3,4-c]pyrrole-1,4-dione-alt-thieno[3,2-b]thiophen) (DPPTTT) could exhibit a high p-type electrical conductivity of 130.6 S/cm and a good n-type electrical conductivity of 14.2 S/cm by engineering the doping level. Both p- and n-type electrical conductivities were superior to most solution-processable D–A copolymers, including monopolar polymers. The high electrical conductivity resulted in high thermoelectric performance of DPPTTT in both p- and n-type, leading to a high current density of 3 A/cm² for a fully organic planar p–n junction created with only one material. Structural and spectroscopic tests were performed to provide a fundamental understanding of the polarity-switch mechanism. Our results open up an opportunity of making p- and n-type modules with a single conducting polymer for modern organic electronics in the future and might arouse research interest in exploring novel conducting polymers to enrich the knowledge of charge transport in organic materials.

Keywords: polarity switching, donor–acceptor copolymer, thermoelectric, organic diode, p-type doping

Introduction

Conducting polymers have the potential advantages of low manufacturing cost by using traditional printing techniques to produce electronic modules at a large scale,1 which makes them very attractive for innovative electronic applications, especially for flexible electronic devices.2 Remarkable progress has been achieved in developing functional conducting polymers in many fields such as organic thermoelectrics,1,2,4 organic solar cells,1 organic field-effect transistors (FETs),5 organic light-emitting diodes,6 and so on, since the conducting
polymer was first discovered by Heeger et al. in 1977. However, the transport of holes and electrons in conducting polymers is still far from being well understood and controlled.

Making p- and n-type modules with a single conducting polymer is still very challenging for organic materials; though, it can be easily realized for inorganics such as doping silicon with phosphorus and boron to make n- and p-type semiconductors, respectively. For modern organic electronics, p- and n-type materials are equally important and desired. Making p- and n-type modules with a single conducting polymer would simplify the fabrication processes of organic devices with high scalability and low cost using traditional printing techniques to pattern a single conducting polymer with p- and n-type dopants. Besides, it may improve the performance of organic devices. For example, Roncali suggested that single-material solar cells would be the next frontier for organic photovoltaics since they would have a longer lifetime due to the strong stabilization of the morphology of the interface. Toffanin and co-workers reported that single-layer light-emitting transistors might ensure good charge transport together with an efficient light-emission in the solid-state. Wang et al. reported that a novel organic Schottky barrier diode created in a single planar polymer film exhibited a remarkable current density of 30 A/cm² that is 2–3 orders in a higher magnitude and superior to that of previously reported organic materials. This is because it excluded interfaces that generally existed between p- and n-type modules, resulting in smooth current flow and subsequent improvement in the performance of the devices. These promising results of single-material devices light the enthusiasm in making p- and n-type modules with a single conducting polymer.

However, not many conducting polymers can transport both holes and electrons. In general, the carrier polarity of a conducting polymer strongly depends on its molecular structure. Once a conducting polymer is synthesized, it may prefer to transport either electrons or holes. Most conducting polymers exhibit a unipolar transport property and can transport only holes or electrons. In contrast, ambipolar conducting polymers that exhibit both positive and negative Seebeck coefficients have been reported in limited cases. Especially, it is very challenging to achieve conducting polymers with high bipolar electrical conductivities (possessing high electrical conductivity for both p- and n-type).

Currently, a popular strategy employed to make ambipolar conducting polymer is to co-polymerize electron-rich groups (donors, D) and electron-deficient groups (acceptors, A). However, only a small portion of the D–A copolymers exhibit appreciable bipolar transport properties. Although D–A copolymers have been reported to have very high mobilities of over 20 cm²/(V·s) recently, the electrical conductivity for the D–A copolymers are often in the range of 10⁻²–10⁻³ S/cm. These ambipolar conducting polymers with low electrical conductivities are mainly used in organic FETs or organic solar cells. Moreover, most of these ambipolar conducting polymers exhibit bipolar electrical conductivities in FET devices, which require the assistance of a gate voltage. Very rare examples were reported to have bipolar electrical conductivities for bulk-doped conducting polymers without the assistant of the gate voltage.

To the best of our knowledge, bipolar electrical conductivities (both p- and n-type) of over 10⁻² S/cm have never been reported for D–A copolymers to date. Here, we report that a solution-processable D–A copolymer, poly(2,5-bis(2-octyldodecyl)-3,6-di(thiophen-2-yl)diketopyrrolo[3,4-c]pyrrole-1,4-dione-alt-thieno[3,2-b]thiophen) (DPPTTT; Figure 1), could achieve high bipolar electrical conductivities after being doped with FeCl₃ (DPPTTTFeCl₃). This fabricated copolymer exhibited the highest p-type electrical conductivity of 130.6 S/cm and a high n-type electrical conductivity of 14.2 S/cm, superior to most solution-processable D–A copolymers (Supporting Information Tables S1 and S2). Its high electrical conductivity led to the establishment of a high

Figure 1 | (a) Molecular structure of the polymers, DPPTTT and P3HT, and commercially available dopants. (b) Electrical conductivities of DPPTTT after being p-type doped by six commercially available dopants at MDR = 1.
p-type thermoelectric power factor of 23.4 µW/(mK²) and a high n-type thermoelectric power factor of 0.66 µW/(mK²), which are the highest attainable for p- and n-type solution-processable ambipolar D–A copolymers, respectively. The conversion mechanism was addressed after relevant structural and spectroscopic tests. A p–n junction was created in a planar thin film, exhibiting a high rectification ratio of 2 × 10² at ±5 V for fully printed organic diodes, which further demonstrated the conversion of the p-type D–A copolymer to n-type. The rectification performance met the requirement for high-frequency radio-frequency identification (R-ID) tags. These results might uncover an opportunity for developing new organic electronic devices with single organic materials.

**Experimental Section**

**Materials**

DPPTTTT (Mw = 22.47 kDa) was purchased from Derthon Optoelectronic Materials Science Technology Co. Ltd. (Shenzhen, China). Poly(3-hexylthiophene) (P3HT) (Mw = 85,000 kDa) was purchased from 1-material (Dorval, Quebec, Canada). Ferric chloride was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). Nitromethane was purchased from Aladdin Chemical Reagent Factory (Tianjin, China). Iron sulfate hydrate and iron nitrate nonahydrate were purchased from Damao Chemical Reagent Factory (Tianjin, China). Ferric chloride was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). All chemicals were used as received. Hexacyanotrimethylene-cyclopropane (CN6-CP) was synthesized in our lab, as described previously.

**Film preparation**

The polymers and dopants solutions were prepared in advance by dissolving them in O-dichlorobenzene and nitromethane. Then mixed solutions were obtained at different weight ratios by adding the dopants solutions to the polymers. After each mixture was vigorously stirred for ~15 min, it was dropped onto a glass substrate and dried at room temperature. All the experiments were performed in a glove box. The detailed film preparation process has been described in the Supporting Information.

**P–N junction preparation**

The DPPTTT O-dichlorobenzene solution with 21 wt % FeCl₃ was dropped onto half of the copolymer-dopant glass substrate. After drying at room temperature, the DPPTTT O-dichlorobenzene solution with 84 wt % FeCl₃ was dropped onto the rest half of the glass substrate. The p–n junction was tested after both sides of the films were dry.

**Computational methods**

Ionization potential (IP) and electron affinity (EA) potentials were used to evaluate the ambient stability and the charge injection properties of the DPPTTT and P3HT polymers, respectively. The adiabatic IP and EA (AIP, AEA) were calculated according to the following formulas:

\[
\text{AIP} = E^+ (G^+ ) - E^0 (G^0 )
\]

\[
\text{AEA} = E^0 (G^0 ) - E^- (G^-)
\]

where \(G^0\), \(G^+\), and \(G^-\) represent the geometric configurations of optimized cationic, anionic, and neutral states, respectively. \(E^+\), \(E^-\), and \(E^0\) are the energy of cationic, anionic, and neutral states, respectively. The calculation was implemented in the Gaussian 09 Program Package. All of the optimized and the frequency analysis of cationic, anionic, and neutral states were obtained using functional theory methods of B3LYP with a 6-31G(d) basis set. By taking the calculation efficiency and cost into account, only the DPPTTT monomer and P3HT polymers were calculated. Also, the long alkyl side chains of P3HT and DPPTTT were replaced with methyl groups, which would reduce the calculation cost in the determination of the electronic structure of the polymer without significantly decreasing the calculation accuracy.

**Results and Discussion**

The molecular structures of DPPTTT, P3HT, and the p-type dopants: F4TCNQ, PTS-Fe, CN6-CP are shown in Figure 1a. A solution-processable method was used to prepare the DPPTTT and P3HT films on glass substrates, as shown in Supporting Information Figure S1. Six commercially available p-type dopants were studied at the same molar doping ratio (MDR = 1, repeat units: dopant ratio of 1:1). Pristine DPPTTT is almost an insulator with a significant decrease in the electrical conductivity after being doped with the six p-type dopants, with their electrical conductivities arranged in the following order: 

\[
\sigma_{\text{FeCl}_3} > \sigma_{\text{CN6-CP}} > \sigma_{\text{PTS-Fe}} > \sigma_{\text{CNQ}} > \sigma_{\text{F4TCNQ}} > \sigma_{\text{SO_4}}
\]

(Figure 1b). The trend is mainly related to the doping ability of the p-type dopants relative to their molecular orbital occupancy. For example, CN6-CP had the lowest unoccupied molecular orbital (LUMO) of ~5.87 eV than F4T CNQ (LUMO = ~5.24 eV), leading to a higher electrical conductivity of DPPTTT-CN6-CP than that of DPPTTT-F4TCNQ. DPPTTT-FeCl₃ showed the highest p-type electrical conductivity among the six p-type dopants.
which might be due to the small size and high EA of FeCl₃, as reported in the previous literature. Electromagnetic and Seebeck coefficient of DPPTTT doped with FeCl₃ at different concentrations were measured at room temperature, as shown in Figure 2. The electrical conductivity of DPPTTTFeCl₃ increased with a rise in FeCl₃ concentration until it reached a maximum of 130.6 S/cm at the FeCl₃ concentration of 21 wt %. Then the electrical conductivity decreases while further increasing the concentration of FeCl₃. Scanning electron microscopy (SEM) was performed to understand the electrical conductivity dropping from the FeCl₃ concentration of 21 wt %. Figures 2d–2f show SEM images of pristine DPPTTT, DPPTTTFeCl₃ − 21 wt %, and DPPTTTFeCl₃ − 84 wt %, respectively. Pristine DPPTTT film is composed of continuous agglomerates with the size of ~ 50 × 50 nm (Figure 2d). After being doped by FeCl₃, the agglomerates aggregate as shown in the SEM images of DPPTTTFeCl₃ − 21 wt % (Figure 2e) and DPPTTTFeCl₃ − 84 wt % (Figure 2f). The gaps between the agglomerates increase because of the aggregation (inserted images in Figures 2d–2f), which might be one of the main reasons for the decrease of electrical conductivity from FeCl₃ concentration of 21 wt % in Figure 2a. Atomic force microscopy (AFM) was performed to identify the roughness of the film. As shown in Supporting Information Figure S2, the root mean square (RMS) values obtained for pristine DPPTTT, DPPTTTFeCl₃ − 21 wt %, and DPPTTTFeCl₃ − 84 wt % were 2.95, 4.47, and 36.6 nm, respectively (Supporting Information Figure S3). It further confirmed that the aggregation of DPPTTT agglomerates at high FeCl₃ concentration over 21 wt %. Temperature dependence of the electrical conductivity of DPPTTTFeCl₃ − 21 wt % and DPPTTTFeCl₃ − 84 wt % at the temperature range of 150–300 K was performed as shown in Supporting Information Figure S3. The electrical conductivities increased with increased temperature, indicating that the charge transport in DPPTTTFeCl₃ fitted the variable range hopping model as reported for most of the conducting polymers. The activation energies calculated from the plots were 43.64 and 81.44 meV for DPPTTTFeCl₃ − 21 wt % and DPPTTTFeCl₃ − 84 wt %, respectively. The larger activation energy should be due to the larger gaps between the agglomerates, leading to the lower electrical conductivity of DPPTTTFeCl₃ − 84 wt %.

Figure 2b shows the Seebeck coefficient of DPPTTTFeCl₃ as a function of the FeCl₃ concentration. It is interesting to note that the Seebeck coefficient of DPPTTTFeCl₃, switching from p- to n-type. Pristine DPPTTT is a p-type material, according to previous works. The Seebeck coefficient of DPPTTTFeCl₃ − 10 wt % was +223 μV/K, which indicated that it is still p-type at low FeCl₃ concentration. The Seebeck coefficient decreased while more FeCl₃ was added due to an increase in the carrier concentration at a higher p-type doping level. However, the Seebeck coefficient of DPPTTTFeCl₃ became negative after the FeCl₃ concentration was over 47 wt %. Further increasing the FeCl₃...
concentration led to more negativity of the Seebeck coefficient. The negative Seebeck coefficient of DPPTTTFeCl3 revealed that it became an n-type material. The maximum n-type electrical conductivity and the maximum Seebeck coefficient were 14.2 S/cm (DPPTTTFeCl3−47 wt%) and −78.9 μV/K (DPPTTTFeCl3−84 wt%), respectively.

The maximum p- and n-type electrical conductivities of DPPTTTFeCl3 were compared with those of previously reported solution-processable D-A copolymers as shown in Supporting Information Tables S1 and S2. Very rare examples were reported to have bipolar electrical conductivities for bulk-doped conducting polymers without the assistant of the gate voltage.19,24 High electrical conductivities over 2 S/cm for both p- and n-type in a single conducting polymer have never been reported in previous literature. Figure 2c compares the maximum p- and n-type electrical conductivities of DPPTTTFeCl3 with those of solution-processable D-A copolymers. As far as we know, the maximum p- and n-type electrical conductivities achieved were the highest for p- and n-type solution doped ambipolar D-A polymers. A few post-doped solution-processable D-A polymers were reported recently to have higher electrical conductivities. Therefore, compared to all the solution-processable D-A polymers, the maximum p-type electrical conductivity of 130.6 S/cm achieved by the DPPTTTFeCl3 film was among the top seven values of solution-processable state-of-the-art D-A copolymers, revealed by previous literature reports (including unipolar and ambipolar D-A polymers) (Supporting Information Table S1). Likewise, the maximum n-type electrical conductivity of 14.2 S/cm for DPPTTTFeCl3 was one of the best among n-type electrical conductivities, as only one example is available in previous reports, with a higher n-type electrical conductivity of over 14.2 S/cm (Supporting Information Table S2). Compared with previously reported ambipolar D-A copolymers, the maximum bipolar electrical conductivities were ~4–5 orders of magnitude higher than previously reported values. The high bipolar electrical conductivities indicated a potential to make p- and n-type modules for modern organic electronics with a single conducting polymer, which might promote a revolution in the field of semiconducting polymers.

The electrical conductivity and Seebeck coefficient of FeCl3-doped P3HT were measured at room temperature for comparison, as shown in Figure 2. The electrical conductivity increased with an increase in FeCl3 concentration, reaching its maximum of 63 S/cm at the FeCl3 concentration of 47 wt % (Figure 2a), after which it started to drop when the FeCl3 concentration was increased further. The Seebeck coefficient of P3HT at the FeCl3 concentration of 10 wt % was +157 μV/K, which decreased with the rising FeCl3 concentration. Unlike FeCl3-doped DPPTTT, no switching from p- to n-type was observed (Figure 2b). All the Seebeck coefficients for P3HTFeCl3 samples were positive. Ultraviolet-visible–near-infrared (UV–vis–NIR) spectrophotometry was performed to monitor the doping process of DPPTTT and P3HT. Figure 3a shows the UV–vis–NIR spectra of DPPTTTFeCl3 films at different FeCl3 concentrations. A major peak appeared at 810 nm for pristine DPPTTT film, assigned to the π–π* transition of the diketopyrrolo-pyrrole (DPP) unit.32–34 This prominent peak decreased together with an increase in a new broad peak at the NIR region when the FeCl3 concentration was increased, ascribed to the reduction in the neutral state of the DPP units since they were converted into the polaron state or bipolaron state,34 resulting in the emergence and increase of a new peak (>1000 nm) in the NIR region. Figure 3d shows a clear conversion process of P3HT between the neutral, the polaron, and the bipolaron states. The neutral state of P3HT could be converted to the polaron state, which might be converted further to the bipolaron state.35,36 At low FeCl3 concentration, the neutral state of P3HT was converted into the polaron and bipolaron states, leading to a decrease in the neutral state peak at 532 nm, an increase of the polaron state peak at 832 nm, and an increase in the bipolaron state peak in the NIR region (>1100 nm). At high FeCl3 concentration, the decrease in the polaron state peak at 832 nm indicated that the rate of the polaron state P3HT conversion to the bipolaron state was higher than the rate of the generation of the polaron state P3HT. The band gaps obtained from the UV–vis–NIR spectra of pristine DPPTTT and P3HT were 1.28 and 1.9 eV, respectively (Supporting Information Figure S4), consistent with previous reports.37–42

The highest occupied molecular orbitals (HOMOs) of DPPTTT and P3HT were estimated using the cyclic voltammetry (CV) method with a three-electrode electrochemical system. Ferrocene was used as the internal reference (see detailed description in the Supporting Information). Figures 3b and 3e show that the oxidation peak edges (Eox) were 0.97 and 0.94 V for DPPTTT and P3HT, respectively. Therefore, the HOMOs (E1/2ferrocene + Eox) were −5.19 and −5.16 eV for DPPTTT and P3HT, respectively, according to the following equation37:

$$E_{\text{HOMO}} = -(4.8 - E_{1/2}\text{ferrocene} + \phi_{\text{ox}})$$

where $E_{1/2}\text{ferrocene}$ is the difference between the average oxidation peak potential and the reduction peak of the internal reference, ferrocene (shown in Supporting Information Figure S5). The HOMO values obtained were similar to those previously reported, −5.2 eV for P3HT,37,38 and −5.2 eV for DPPTTT.40–42 Based on the CV results and the optical band gap values, the LUMO values for DPPTTT and P3HT were calculated to be −3.91 and −3.26 eV, respectively.

Ultraviolet photoelectron spectroscopy (UPS) was performed to provide the work function (WF) changes of DPPTTT and P3HT during the FeCl3 doping process. Figure 3c shows UPS results of pristine DPPTTT,
DPPTTT$_{\text{FeCl}_3-21 \text{ wt} \%}$ and DPPTTT$_{\text{FeCl}_3-84 \text{ wt} \%}$ along with that of gold as a reference. Their WFs can be obtained from the below equation 6:

$$WF = h\nu + |E_f| - |E_{\text{cutoff}}|$$  \hspace{1cm} (4)

where $E_f$ and $E_{\text{cutoff}}$ are high and low kinetic energy cutoff, respectively, and $h\nu$ is the photon energy of the used Helium I (He I) source (21.2 eV). The WF achieved for pristine DPPTTT was 4.58 eV. After being doped with FeCl$_3$ at a concentration of 21 wt %, the WF became larger ($\approx$5.09 eV), indicating p-type doping of DPPTTT. It further increased to 5.4 eV when the FeCl$_3$ concentration was increased to 84 wt %. Also, the WF of P3HT increased after FeCl$_3$ doping, as shown in Figure 3f, as follows: The WFs for pristine P3HT, P3HT$_{\text{FeCl}_3-21 \text{ wt} \%}$, and P3HT$_{\text{FeCl}_3-84 \text{ wt} \%}$ were in the order of $WF_{\text{P3HT}}$ (4.14 eV) < $WF_{\text{P3HT-FeCl}_3-21 \text{ wt} \%}$ (4.39 eV) < $WF_{\text{P3HT-FeCl}_3-84 \text{ wt} \%}$ (4.95 eV). As a comparison, the WF of pure gold was measured, obtaining a value of 5.27 eV (Supporting Information Figure S6), which is in the range of previously reported values, 5.0–5.4 eV.63–45

The electronic band diagrams of DPPTTT and P3HT during the FeCl$_3$ doping process are shown in Figures 3g and 3h, respectively. The Fermi level was
obtained from the above work function, $WF = E_{vac} - E_F$, where $E_{vac}$ is the vacuum level, which typically equals zero since the WF represents the energy barrier required for an electron to move at the Fermi level to the free space.\(^{46}\) The Fermi level of pristine DPPTTT, derived from the UPS results, was $-4.58$ eV, close to the middle of HOMO and LUMO of pristine DPPTTT ($-4.55$ eV). The slight differences between these two values could be ascribed to oxygen doping or other contaminants in the air. After being doped by FeCl$_3$, the Fermi level shifted to $E_F = -5.09$ eV for DPPTTT$_{FeCl_3} - 21$ wt%, close to the HOMO of DPPTTT ($-5.19$ eV), indicating massive p-type doping of DPPTTT (Figure 3g). Meanwhile, the Fermi level for P3HT$_{FeCl_3}$ was $-4.39$ eV, which was still far from its HOMO of $-5.16$ eV. These results indicated that it was easier to dope DPPTTT than P3HT at the same FeCl$_3$ concentration. This trend was consistent with the theoretically calculated IP for DPPTTT ($5.9$ eV) and P3HT ($8.1$ eV). The lower IP suggested a better electron-giving ability,\(^{26,47}\) leading to a lower Fermi level at the same FeCl$_3$ concentration. When the FeCl$_3$ was $84$ wt %, the Fermi level for DPPTTT$_{FeCl_3} - 84$ wt% shifted to $-5.40$ eV, which was below the HOMO of DPPTTT, while the Fermi level for P3HT$_{FeCl_3} - 84$ wt% was $-4.95$ eV, which was still above the HOMO of P3HT (Figure 3h).

Based on these results, we believe that the polarity switching of DPPTTT films from p- to n-type was due to crossing the Fermi level ($E_F$) from above the HOMO (valence band, $E_v$) to below HOMO. The hopping model reported by Fritzsch was typically used to describe the charge carrier transport in conducting polymers.\(^{48}\) For a p-type material, the Seebeck coefficient is defined as:

$$S = \frac{k_B}{q} \left( \frac{E_F - E_V}{k_B T} \right)$$

where $k_B$, $q$, and $T$ are the Boltzmann constant, the elementary charge, and the absolute temperature.

For a neutral conducting polymer, the $E_F$ localizes in the middle of LUMO and HOMO. As shown in Figures 3g and 3h, the $E_F$ of pristine DPPTTT and P3HT lied close to the middle of the HOMO and LUMO. When they were doped by the p-type dopant, FeCl$_3$, the $E_F$ shifted toward HOMO. For example, the $E_F$ for DPPTTT$_{FeCl_3} - 21$ wt% shifted $0.51$ eV toward HOMO and the $E_F$ for P3HT$_{FeCl_3} - 21$ wt% shifted $0.25$ eV toward HOMO. The shift in $E_F$ led to a reduced distance between the $E_F$ and $E_V$, which subsequently resulted in a decrease of the Seebeck coefficient, according to eq 5 (Figure 2b). The Seebeck coefficients for DPPTTT$_{FeCl_3} - 21$ wt% and P3HT$_{FeCl_3} - 21$ wt% were positive because $q$ was positive and $E_F - E_V > 0$. For DPPTTT$_{FeCl_3} - 84$ wt%, the $E_F$ shifted below the HOMO ($E_F - E_V < 0$), which resulted in a negative Seebeck coefficient of $-78.92$ $\mu$V/K. This polarity switching is rare for conducting polymers; however, it has been observed in several other polymer semiconductors, such as D–A copolymer poly([2,7-bis(2,2/(2-ethoxyethoxy)ethoxy)ethyl])-1,2,3,6,7,8-hexahydro-1,3,6,8-tetraoxobenzo[llmn][3,8]phenan-throline-4,9-diy1][3,3’-bis(dodecyloxy)[2,2’-bithio- phene]-5,5’-diyl] (PNDI2T2G-2T)\(^{49}\) and poly([2,5-bis(2-octyldodecyl)-3,6-di(pyridin-2-yl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dionealt-(E)-2,2’-(ethene-1,2-diylbis(thio- phene-5,2-diyl))) (PDPH).\(^{48}\) Such behavior is often observed for p-type devices.

Further work is ongoing in our laboratory.

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The oxidation of DPPTTT led to a color change of the films. As shown in Figure 4c, the color change from purple to gray was observed as the concentration of FeCl₃ was increased. Likewise, the color of the P3HT film was dark gold, which changed gradually to dark grey, as shown in Supporting Information Figure S9. A free-standing DPPTTTFeCl₃⁻84 wt% film was achieved by peeling off the thick film from the glass substrate. Figure 4b shows that the film obtained had good flexibility, which demonstrated the potential application of this material in flexible organic electronics.

The n-typeDPPTTTFeCl₃ exhibited modest stability in the glovebox (O₂ < 0.2 ppm and H₂O < 0.02 ppm). Figure 5a shows that the electrical conductivity and the Seebeck coefficient of DPPTTTFeCl₃⁻84 wt% changed with time. The Seebeck coefficient could be maintained after 25 days, while the electrical conductivity could only be retained for 7 days and dropped to half of the electrical conductivity of freshly prepared DPPTTTFeCl₃⁻84 wt% after 15 days.

The sample preparation and testing environment were varied to study the effect of oxygen and water on its thermoelectric properties for DPPTTTFeCl₃⁻84 wt%. The samples, dried in a glovebox under the protection of N₂, were labeled as “N₂ (RH~0%)” (Figure 5b). The samples, dried in a vacuum bucket filled with N₂ and O₂ with an
RH ≈ 15%, were labeled as “N2 (RH ≈ 15%)” and “O2 (RH ≈ 15%)”, respectively. A high Seebeck coefficient of −78.9 μV/K was obtained for samples prepared under N2 (RH ≈ 0%) while samples prepared under N2 (RH ≈ 15%) and O2 (RH ≈ 15%) showed poor Seebeck coefficients of −5.69 and −5.87 μV/K, respectively. These results indicated that water played a major role in the dropping of the n-type Seebeck coefficient. According to previous literature, both water and oxygen might affect the doping efficiency since not many FeCl3 can penetrate the DPPTTT film. A post-treatment method was also used to prepare DPPTTTFeCl3 samples. The pristine DPPTTT samples were immersed in 84 wt % FeCl3 solution. The electrical conductivities and Seebeck coefficients of DPPTTT as a function of the soaking time are shown in Supporting Information Figure S10. Surprisingly, no n-type Seebeck coefficient was obtained. The reason could be ascribed to insufficient FeCl2 generation inside the DPPTTT film since not many FeCl3 can penetrate the DPPTTT films.

To identify the dominant carriers in the n-type DPPTTTFeCl3, the frequency-dependent (1−106 Hz) alternating current (AC) impedance was performed to distinguish electronic and ionic current. The n-type DPPTTTFeCl3 sample exhibited a deviation from a very high frequency (−106 Hz; Figure 5c), which was even higher than the deviation frequency of the pristine DPPTTT (101 Hz). Typically, the deviation frequency for ionic conduction is ∼ 0.3 Hz. These results suggested that electronic transport was dominant in the n-type material other than the ionic effect. Figure 5d shows a p–n junction made by p-type DPPTTTFeCl3 and n-type DPPTTTFeCl3 related to the probe tip. The transient and steady-state current of the organic diode is shown in Figure 5d. The transient and steady-state current of the organic diode is shown in Figure 5d. A composite film sample was prepared by drop-casting p-type DPPTTTFeCl3 on half of the glass substrate first, and then drop-casting n-type DPPTTTFeCl3 on the other half of the glass substrate after drying the p-type film (see Supporting Information Figure S11). The current density was measured at room temperature, as a function of the bias voltage in the range of −5 to 5 V with a scan rate of 0.05 V/s. A high Seebeck coefficient and n-type Seebeck coefficient of DPPTTTFeCl3 as a function of bias voltage (Figure 5d) was even higher than the deviation frequency of the pristine DPPTTT (101 Hz). The deviation frequency for ionic conduction is ∼ 0.3 Hz. These results suggested that electronic transport was dominant in the n-type material other than the ionic effect. To identify the dominant carriers in the n-type DPPTTTFeCl3, the frequency-dependent (1−106 Hz) alternating current (AC) impedance was performed to distinguish electronic and ionic current.6 The n-type DPPTTTFeCl3 sample exhibited a deviation from a very high frequency (∼106 Hz; Figure 5c), which was even higher than the deviation frequency of the pristine DPPTTT (101 Hz). Typically, the deviation frequency for ionic conduction is ∼ 0.3 Hz. These results suggested that electronic transport was dominant in the n-type material other than the ionic effect.
0.5 V/s for DPPTTTFeCl3−84 wt%. The rectification was observed when a current was passed from the p-type side to the n-type side, as shown in the inserted image and Figure 5d (1) (reverse bias). The forward bias [Figure 5d (2)] current density of the organic diode is 3.0 A/cm² at 5 V. The high rectification ratio (current density at 5 V divided by that of −5 V) obtained was ~2 × 10², which met the requirement for high-frequency R-ID tags of rectification ratio >100 at ~5 V. The current–voltage relations of single p-type DPPTTTFeCl3−21 wt% and single n-type DPPTTTFeCl3−84 wt% were measured for comparison. No rectification was obtained, as shown in Supporting Information Figure S12.

The responses of a transient and steady-state current of the organic diode were measured while alternating the input voltage of ±5 V (Figure 5e). The reverse bias current was quickly recovered in <5 s, reaching a steady-state by switching the bias polarity. The relaxation behavior was ascribed to the capacitive effects that might derive from the high resistance of the films and dissociated ions by moisturization. The quick response further indicated that this organic diode was electronic dominant since the typical ion-based organic diode barely maintained a steady current and took a much longer time to reach a stationary current.53,54

Kelvin probe (KP) techniques were performed to identify the WF difference between the p-type DPPTTTFeCl3−21 wt% side and the n-type DPPTTTFeCl3−84 wt% side. Figure 5f shows the WF differences between the two sides of the sample (WFsample) and the probe tip (WFtip), which is also called a contact potential difference (CPD): WFsample = WFtip − CPD. Assuming the WF of the used tip was 5.1 eV, the estimated WFs for the p-type DPPTTTFeCl3−21 wt% side and the n-type DPPTTTFeCl3−84 wt% were 5.14 and 5.39 eV, respectively. These results matched well with those values obtained by UPS, as shown in Figure 3c, which further demonstrated the p- to n-type switching of DPPTTT by FeCl3 doping.

**Conclusion**

We have demonstrated that solution-processable D–A copolymers could exhibit both high p- and n-type electrical conductivities over 10 S/cm during a p-type doping process. The polarity switching from p- to n-type was attributable to the crossing of Fermi level from the position above the HOMO to the position below HOMO of the polymer, demonstrated by UPS, CV, KP, and UV–vis–NIR techniques. The high bipolar electrical conductivities were four to five orders of magnitude higher than those of previously reported ambipolar D–A copolymers and resulted in four to five orders of magnitude enhancement in the bipolar power factors among the solution-processable ambipolar D–A copolymers. These are also among the top values of nowadays state-of-the-art solution-processable D–A copolymers, including both unipolar and ambipolar D–A copolymers. A fully organic p-n junction was created with the p- and n-type material exhibiting a high rectification ratio of over 2 × 10² at ±5 V with a high current density of 3 A/cm², which met the requirement for high-frequency R-ID tags. Collectively, our results open up an opportunity of making p- and n-type modules with a single conducting polymer for modern organic electronics in the future.

**Supporting Information**

Supporting Information is available and includes materials, instrumentation, experimental procedures, AFM, the resistance change below room temperature, UV–vis–NIR, CV, UPS of Au, XPS spectra, images of the color change of P3HT, post-treatment thermoelectric properties of P3HT, P-N junction images, current density versus bias voltage, and thermoelectric properties of P- and N-type solution-processable D–A polymer.

**Conflicts of Interest**

There are no conflicts of interest to declare.

**Preprint Acknowledgment**

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