Proquinoidal-Conjugated Polymer as an Effective Strategy for the Enhancement of Electrical Conductivity and Thermoelectric Properties

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Supporting Information

**ABSTRACT:** P-doping of conjugated polymers requires electron transfer from the conjugated polymer to the p-dopant. This implies that the highest occupied molecular orbital (HOMO) of the conjugated polymer has to be higher than the lowest unoccupied molecular orbital (LUMO) of the p-dopant. Although commonly used p-dopants such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) have a low LUMO of −5.24 eV, most conjugated polymers used in high-performance field-effect transistors are donor–acceptor-type polymers with deep HOMO values, making them difficult to be effectively doped by F4TCNQ. Here, we utilized the proquinoidal 2,6-dialkyl-benzo[1,2-d:4,5-d’]-bistriazole (BBTa26) moiety in conjugated polymers to destabilize HOMO, allowing effective p-doping using very dilute F4TCNQ solutions. The extent of the quinoidal character and hence their intrinsic conductivities and the ability to be doped are dependent on the dihedral angles and aromaticity of the aryl spacer groups along the polymer backbone. Intrinsically, conductivities as high as 10−2 S cm−1 were achieved. Upon doping using F4TCNQ, highly delocalized polarons were observed. As such, electrical conductivities of over 100 S cm−1 and an enhancement of the Seebeck coefficient from carrier-induced softening can be achieved. A maximum power factor of 11.8 μW m−1 K−2 was achieved in thin-film thermoelectric devices. These results are among the highest for solution-phase p-doping using F4TCNQ without additional processing.

**INTRODUCTION**

Conjugated polymers have shown promising results in thin-film field effect transistors (FETs) with the hole and electron mobilities greater than and approaching 10 cm2 V−1 s−1, respectively. Such high mobilities, together with low thermal conductivities, set good prerequisites for thermoelectric (TE) materials. No doubt, doped conjugated polymers have demonstrated great potential in TE applications. For p-type polymeric materials, TE has been dominated by poly(3,4-ethylenedioxythiophene) (PEDOT)-based conducting polymers, with the TE figure-of-merit ZT value as high as 0.42. Other traditional conducting polymers such as polypyrrole, polyaniline, and polyacetylene have also been tested for TE but are inferior in comparison to PEDOT-based polymers. These traditional conducting polymers generally have poor process-ability, hence hindering the development of printed TE devices. For nontraditional p-type solution-processable conjugated polymers, the most commonly used p-dopant is F4TCNQ. Apart from the low solubility of F4TCNQ in organic solvents, gelation often occurs during solution-phase doping. Hence, conjugated polymers are usually doped with F4TCNQ by sequential solution-phase doping of the...
polymeric films or by thermal evaporation.\textsuperscript{10} Comparatively, solution-phase doping using F4TCNQ often results in TE properties very much inferior to vapor-phase doping.\textsuperscript{11}

Most conjugated polymers used in high-performance FETs are donor–acceptor-type polymers with deep highest occupied molecular orbital (HOMO) values,\textsuperscript{12} making them difficult to be effectively doped by F4TCNQ [lowest unoccupied molecular orbital (LUMO) = \(-5.24\) eV].\textsuperscript{7} Thus, most examples of conducting polymers using F4TCNQ as p-dopant are primarily based on polythiophenes.\textsuperscript{8–11,13–17} In this regard, conjugated polymers based on proquinoidal structures also make excellent candidates for p-doping using F4TCNQ. This is because quinoidal structures often result in higher HOMO levels because of the disruption of aromaticity in the polymer.\textsuperscript{1}

Herein, we synthesized a series of polymers using the proquinoid 2,6-dialkyl-benzo[1,2-d:4,5-d’]bistriazole (BBTa26) moiety. According to density functional theory (DFT) calculations, the BBTa26 moiety is a weak acceptor with proquinoidal structure that can form highly coplanar geometry with thiophene \(\pi\)-spacer groups\textsuperscript{18–22} and can be made highly soluble by the incorporation of solubilizing groups. Single-crystal X-ray diffraction of 2,6-dihexyl-4,8-bis(2-thienyl)-BBTa26 also revealed a small dihedral angle of 4.9° and a short C–C bond of 1.446 Å between the BBTa26 core and thiophene.\textsuperscript{21} The newly synthesized BBTa26 polymers exhibited low band gaps and intrinsic electrical conductivities (\(\sigma\)) as high as \(10^{-2}\) S cm\(^{-1}\), which is among the highest for neutral conjugated polymers.\textsuperscript{23–26} Their large intrinsic \(\sigma\) and ease of doping are related to the dihedral angles/aromaticity of the \(\pi\)-spacer groups along the polymer backbone. By doping with F4TCNQ, \(\sigma\) of over 100 S cm\(^{-1}\) and power factor as high as 11.8 \(\mu\)W m\(^{-1}\) K\(^{-2}\) could be achieved in solution-phase processed thin-film TE devices. These values are highly respectable for solution-phase doping of conjugated polymers using F4TCNQ.\textsuperscript{11,13,14,16,27}

\section*{EXPERIMENTAL SECTION}

\textbf{Materials.} All commercially available reagents were purchased from Sigma-Aldrich Corp. unless otherwise stated. 7-(Bromomethyl)-pentadecane, tetrakis(triphenylphosphine)palladium(0), and F4TCNQ were purchased from Tokyo Chemical Industry Co. (4,4'-Di-n-dodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) was purchased from Luminescence Technology Corp. Tetraamino-benzene tetrahydrobromide was purchased from Hangzhou Trylead Chemical Technology. 1 was synthesized according to the literature.\textsuperscript{19,28}
Table 1. Gel Permeation Chromatography, Electrochemical, Photophysical Data, and Electrical Conductivity of the BBTa26 Polymers

<table>
<thead>
<tr>
<th>polymer</th>
<th>$M_w$ (kDa)</th>
<th>PDI</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{gCV}$ (eV)</th>
<th>$E_{gap}$ (eV)</th>
<th>$\sigma_{intrinsic}$ (S cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pBBTa26-2T</td>
<td>242</td>
<td>8.47</td>
<td>−5.01</td>
<td>−3.60</td>
<td>1.41</td>
<td>1.22</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>pBBTa26-4T</td>
<td>140</td>
<td>8.20</td>
<td>−4.82</td>
<td>−3.60</td>
<td>1.56</td>
<td>1.38</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>pBBTa26-TT</td>
<td>283</td>
<td>6.05</td>
<td>−5.16</td>
<td>−3.60</td>
<td>1.56</td>
<td>1.38</td>
<td>$10^{-1}$</td>
</tr>
<tr>
<td>pBBTa26-BDT</td>
<td>220</td>
<td>2.15</td>
<td>−5.02</td>
<td>−3.50</td>
<td>1.52</td>
<td>1.26</td>
<td>$10^{-1}$</td>
</tr>
</tbody>
</table>

“Reduction not observed.

**DFT Calculations.** All theoretical calculations were carried out using Gaussian 09 package. Gas-phase B3LYP 6-31+G(d) was used for all calculations. The alkyl groups were all reduced to methyl groups. UHF/6-31G(d) was used to calculate % $\sigma$ for all calculations. The alkyl groups were all reduced to methyl using Gaussian 09 package. Gas-phase B3LYP 6-31+G(d) was used to calculate % $\sigma$ for all calculations. The alkyl groups were all reduced to methyl using Gaussian 09 package.

**FET Device Fabrication and Measurement.** Bottom gate–bottom contact (BGBC) FETs were fabricated using a source- and drain-patterned SiO$_2$ wafer by electron beam lithography. The heavily doped Si wafer was used as a gate and the thickness of the SiO$_2$ layer was 230 nm. The source-and-drain electrode consisted of 30 nm Au on a 10 nm ITO adhesion layer. The channel width ($W$) and length ($L$) were 2000 and 20 $\mu$m, respectively. To improve the surface property, the substrate was immersed in 0.2 wt % octadecyltri-chlorosilane (ODTS) solution (toluene as the solvent) for 10 min, followed by rinsing with toluene to remove the extra ODTS. The substrate was subsequently baked at 80 $^\circ$C for 30 min. The polymers were dissolved in chlorobenzene at a concentration of 8 mg/mL. The polymer films were spin-cast at 1500 rpm for 60 s under N$_2$ atmosphere and vacuum-annealed for 60 min. The hole mobility was calculated based on the saturation regime equation for pBBTa26-2T and based on the linear regime equation for pBBTa26-TT and pBBTa26-4T ($\mu_H = −60 $ V, $V_G = −50$ to $−60$ V). The output and transfer characteristics of the FETs were measured under N$_2$ using a custom-made setup with a Peltier heater (298 K $±$ 100 $^\circ$C) were spin-coated onto the gold-patterned glass slides at 2000 rpm. The spin-coated glass slides were immersed in F4TCNQ solution (concentration of 10 mg/mL in anhydrous chlorobenzene, stirred at 200 rpm). The spin-coated glass slides were immersed in F4TCNQ solution (concentration of 0.2, 0.4, 0.6, or 0.8 mg/mL in acetonitrile) for 24 h. The doped polymer films were dried, and electrical resistance ($R$) was measured across the gold contacts at room temperature. The doped polymer films have thicknesses ($t$) around 30 nm. Electrical conductivity ($\sigma$) was obtained from the device using the formula $W (R \times t \times L)$, where $W$ = width of the channel between the gold electrodes (0.2 cm), $R$ = measured resistance, $t$ = thickness of the film, and $L$ = length of the electrode (1.7 cm). The Seebeck coefficient was measured by a custom-made setup with a Peltier heater (298 K + $\Delta T$), and the Peltier cooler (298 K) used to vary the temperature gradient across the two ends of the coated thin film and induce a thermal voltage. Two K-type thermocouples, with a diameter of 0.20 mm, were placed on the coated thin film alongside two electrical probes which were connected to a Keithley 2400 source meter (Figure S12 in the Supporting Information for schematics). The Seebeck coefficient value was then derived from a linear fit of the measured $\Delta V$ versus $\Delta T$ graph. Five devices were fabricated and measured for each polymer and F4TCNQ concentration.

**RESULTS AND DISCUSSION**

Syntheses of the BBTa26 polymers are shown in Scheme 1. Compound 1 was synthesized according to the literature. Subsequent alkylation using different alkyl bromides afforded 2. Stille coupling of 2 with 2-(trimethylstannyl)thiophene followed by bromination afforded 3 and 4, respectively. The BBTa26 polymers were polymerized using Stille coupling. The characterization data of these polymers are tabulated in Table 1 and their thin-film ultraviolet–visible–near infrared (UV–vis–NIR) absorption spectra are shown in Figure 1. Their

![Image](Image 354x486 to 534x574)

**Figure 1.** Thin-film UV–vis–NIR absorption spectra of pristine BBTa26 polymers.

HOMO and LUMO values were calculated using the onset of the first oxidation and reduction potentials from their thin-film cyclic voltammetry (CV) measurements (external reference: ferrocene; onset of HOMO = +4.4 eV) in 0.1 M tetrabutylammonium hexafluorophosphate solution in dry acetonitrile (Figure S1, Supporting Information). The resulting low band gap polymers had very high molecular weights ($M_w$) of 140–283 kDa, with the exception of pBBTa26-4T ($M_w$ = 46 kDa), probably because of the constraint on the purity of the distannyl precursor. Intrinsic $\sigma$ of conjugated polymers is usually in the range of $10^{-10}$ to $10^{-5}$ S cm$^{-1}$. Because of the quinoid structure of the BBTa26 moiety, all polymers showed high intrinsic $\sigma$ from $10^{-5}$ to $10^{-2}$ S cm$^{-1}$.

The low band gap ($E_g$) HOMO values and intrinsic $\sigma$ of the BBTa26 polymers can be rationalized according to their resonance structures (Figure 2) and DFT calculations of their pentamers (Figure 3). The dihedral angles between BBTa26 and the $x$-spacer groups are generally small, with values around 0.5° or less. For pBBTa26-TT, the dihedral angles between BBTa26 and TT are even smaller (0.1°–0.2°), and this allows pBBTa26-TT to take a highly coplanar conformation with extensive quinoidal character along the polymer backbone. Apart from the HOMO $→$ LUMO transition with $\lambda_{max}$ at 1060 nm, a background NIR absorption that extended from 1500 to 3200 nm and beyond was observed. Fourier transform infrared (FTIR) measurement of pBBTa26-TT also showed a significantly higher background absorption as compared to the other BBTa26 polymers (Figure S2, Supporting Information). Such NIR absorption has been observed in doped thiophenes as a result of polaron/bipolaron absorption, commonly depicted as quasi-quinoidal in their chemical character, which also led to a higher HOMO value, as well as a high intrinsic $\sigma$ of $10^{-2}$ S cm$^{-1}$. This, to the best of our
knowledge, is on par with some of the highest reported intrinsic $\sigma$ values for neutral conjugated polymers.\textsuperscript{23} For $p\text{BBTa26-2T}$ and $p\text{BBTa26-4T}$, the dihedral angles between the thiophene moieties are significant, ranging from 1.2° to 9.6°. This caused their polymer backbones to be twisted and thus perturbed the quinoidal structure, resulting in slightly higher $E_g$, deeper HOMO values, and lower intrinsic $\sigma$. For $p\text{BBTa26-BDT}$, because of the very small dihedral angles between BBTa26 and BDT, its backbone is also very coplanar. However, the strong aromaticity of the benzene ring in the BDT moiety prevents the extensive quinoidal character along the polymer backbone, leading to the highest $E_g$, deepest HOMO value, and lowest intrinsic $\sigma$ among the BBTa26 polymers. The extent of the quinoidal character is also verified by the bond order of the BBTa26$-\pi$-spacer bond (Figure 3), with $p\text{BBTa26-TT} > p\text{BBTa26-2T} > p\text{BBTa26-4T} > p\text{BBTa26-BDT}$.

To elucidate the electronic structure and the intrinsic $\sigma$ of the BBTa26 polymers, the radical character ($\gamma_0$), a consequence of the re-aromatization of the quinoidal structure to the biradical structure (see Figure 2), of the BBTa26 polymers with five repeating units was calculated according to the Yamaguchi scheme\textsuperscript{32}

$$\gamma_0 = 1 - \frac{2T}{1 + T}$$

where $T = \frac{E_{\text{HOMO}} - E_{\text{LUMO}}}{2}$ and $n$ = occupancy number calculated using UHF/6-31G(d). The radicals often display intrinsic $\sigma$ because of the presence of half-filled orbitals. The calculated $\gamma_0$ values are 3.6, 5.3, 2.0, and 1.2% for $p\text{BBTa26-2T}$, $p\text{BBTa26-TT}$, $p\text{BBTa26-BDT}$, and $p\text{BBTa26-4T}$, respectively. These results agree well with the trend of their electron paramagnetic resonance (EPR) signal intensity, as well as their intrinsic $\sigma$, with the exception of $p\text{BBTa26-4T}$ (vide infra). As expected, $p\text{BBTa26-TT}$ has the highest $\gamma_0$ because of its very planar backbone. Even though $p\text{BBTa26-BDT}$ has a very planar backbone, the high aromaticity of the benzene ring in the BDT moiety renders it to have a lower $\gamma_0$ than $p\text{BBTa26-2T}$. $p\text{BBTa26-4T}$ was found to have the lowest $\gamma_0$. In a recent theoretical study on the curvature effect of quinoidal
cycloparaphenylenes, a larger bent angle was found to lower \( y_0 \). Hence, the lowest \( y_0 \) of \( \text{pBBTa}26-4T \) is highly likely because of the large curvature in its backbone (Figure S7, Supporting Information) induced by the large dihedral angles between the thiophenes with the methyl group. Planarization of the polymer backbone is often known to occur in the solid state.\(^{34,35}\) Hence, it is likely that \( y_0 \) of \( \text{pBBTa}26-4T \) in the solid state is higher than that of \( \text{pBBTa}26-\text{BDT} \) to account for its higher intrinsic \( \sigma \).

Figure 4 shows the line cuts for grazing-incidence small-angle and wide-angle X-ray scattering (GISAXS and GIWAXS), which were utilized to investigate the morphology of the BBTa26 polymer thin films on SiO\(_2\) without any surface treatment. In general, the BBTa26 polymers are predominantly amorphous in nature with a face-on orientation. The peaks at \( q = 1.45-1.65 \) \( \text{Å}^{-1} \) in the out-of-plane line cuts were assigned to the (010) \( \pi-\pi \) stacking. The peaks between \( q = 0.25-0.60 \) \( \text{Å}^{-1} \) and \( q = 1.30-1.45 \) \( \text{Å}^{-1} \) in the in-plane line cuts were assigned to the (h00) lamellar stacking and alkyl interaction, respectively. We note that the \( \pi-\pi \) stacking distance follows the order: \( \text{pBBTa}26-\text{TT} \) (4.28 \( \text{Å} \)) > \( \text{pBBTa}26-2T \) (3.96 \( \text{Å} \)) > \( \text{pBBTa}26-4T \) (3.91 \( \text{Å} \)) > \( \text{pBBTa}26-\text{BDT} \) (3.82 \( \text{Å} \)). BGBF FETs were fabricated to determine the hole mobility (\( \mu_h \)) of \( \text{pBBTa}26-2T \), \( \text{pBBTa}26-\text{TT} \), and \( \text{pBBTa}26-4T \). \( \mu_h \) of \( \text{pBBTa}26-\text{BDT} \) was not measured because we were unable to determine its TE performance because of its very low \( \sigma \) even after doping (infra vide). The BGBF FET configuration is chosen because it mimics the TE device configuration (polymer spin-coated onto glass substrates with thermally evaporated gold electrodes), and thus the measured \( \mu_h \) will give a good representation of the charge transport in the TE devices. The FET mobilities of \( \text{pBBTa}26-2T \), \( \text{pBBTa}26-\text{TT} \), and \( \text{pBBTa}26-4T \) were measured to be 0.092, 0.0011, and 0.13 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \), respectively (Figure S8, Supporting Information). Their \( \mu_h \) values correlate well with their \( \pi-\pi \) stacking distances and are considered relatively low as compared to the high-performance FET polymers reported in recent years.\(^{7}\) We attribute this to their predominantly amorphous nature and face-on orientation.

The on/off ratios of the \( \text{pBBTa}26-2T \), \( \text{pBBTa}26-\text{TT} \), and \( \text{pBBTa}26-4T \) BGBF FETs were determined to be 651, 2, and 30, respectively (Figure S8, Supporting Information). As the on/off ratio is characterized by the ratio of the on-state current and off-state current, the observed small on/off ratios and high intrinsic \( \sigma \) for \( \text{pBBTa}26-2T \), \( \text{pBBTa}26-\text{TT} \), and \( \text{pBBTa}26-4T \) strongly suggest that there are significant amounts of free charge carriers present in their pristine form. This again strongly supports the presence of quinoidal structures along their polymer backbone as the quinoidal form is likely to be in equilibrium with the biradical form, which can act as free charge carriers (Figure 2).

The BBTa26 polymers were doped by immersing their spin-coated thin films in F4TCNQ solution in acetonitrile. After doping a very dilute F4TCNQ solution (0.1 mg/mL, equivalent to 0.36 mM), their UV–vis–NIR absorption showed an increase in NIR absorption and a decrease in HOMO \( \rightarrow \) LUMO transition absorption (Figures 5a and S9 in Supporting Information). From the UV–vis–NIR absorption spectra of the doped thin films, a strong polaron absorption can be observed for \( \text{pBBTa}26-2T \), \( \text{pBBTa}26-\text{TT} \), and \( \text{pBBTa}26-4T \). The huge change in the UV–vis–NIR absorption of their thin films doped by the very dilute F4TCNQ solution suggests that these polymers can be very efficiently doped because of their strong quinoidal character. In contrast, the absorption profile of the doped \( \text{pBBTa}26-\text{BDT} \) only showed a weak polaron absorption because of the strong aromaticity of the BDT moiety and hence a weak quinoidal character in the polymer. The polaron absorption peaks at longer and shorter wavelengths are assigned to the P1 and P2 transitions of lightly doped conjugated polymers, respec-
The backbone for the extensive polaron delocalization along the polymer backbone with minimum interchain delocalization, and this is made possible only by the proquinoidal character of the BBTa26 core and the high $M_w$ of the polymers.

The $\sigma$ values of the BBTa26 polymers were found to increase by 4–5 orders of magnitude after doping in different concentrations of F4TCNQ solutions, with the highest $\sigma$ achieved for pBBTa26-2T, pBBTa26-TT, and pBBTa26-4T to be 43.1, 102.1, and 1.41 S cm$^{-1}$, respectively (Figure 5b). Exception was found for pBBTa26-BDT whose $\sigma$ remained $\sim 10^{-5}$ S cm$^{-1}$ even after doping. Because of its very low $\sigma$, we were not able to measure the TE performance of pBBTa26-BDT, and hence it is excluded from the later discussion on TE properties. The trend of the measured $\sigma$ is in agreement with the extent of the quinoidal character and polaron delocalization along the polymer backbone, and it is among the highest reported for solution-phase F4TCNQ-doped conjugated polymers without additional processing.10,11,14,15,17,27,38 It has been demonstrated that conjugated polymers can achieve a higher level of doping and a higher $\sigma$ value via vapor-phase doping.11,13,29 The higher $\sigma$ achieved via vapor-phase doping as compared to solution-phase doping is often accredited to the disruption of the polymer thin-film morphology necessary for good charge transport by the solvent molecules in the latter.59,60 Recall that from the GIWAXS measurements, these BBTa26 polymers are predominantly amorphous in nature with face-on orientation that does not permit high $\mu_e$. To determine if the doping process affects the morphology of the polymer film, we used atomic force microscopy (AFM) to image the morphology of the pristine and doped polymer films (Figure S11). From the height profile in the AFM images, there was a slight increase in surface roughness after doping for all BBTa26 polymers. The phase images showed little changes for pBBTa26-2T, whereas pBBTa26-TT and pBBTa26-4T showed the formation of fibrillar networks that should promote charge transport. However, it seems that there is no clear trend between the morphology and $\sigma$ of the polymer films. Recently, a dopant-induced ordering of the amorphous region of regiorandom P3HT has been reported,41 and this may play an important role in the increase in $\sigma$ for the predominantly amorphous BBTa26 polymers. However, there is also a report that the exposure of regioregular P3HT to a poor solvent like methanol (in our case, acetonitrile used to dissolve F4TCNQ is a poor solvent for BBTa26 polymers) can lead to nanostructured P3HT aggregates that favor charge transport.42 The effects the doping process have on the morphology of the polymers are extremely complex and beyond the scope of this paper. Regardless, the high $\sigma$ achieved by these BBTa26 polymers using solution-phase doping highlights the importance of the extensive polaron delocalization along the polymer backbone for $\sigma$,43 which we believe can only be made possible using highly planar proquinoidal structures with high molecular weights. Even higher $\sigma$ may be achieved for these BBTa26 polymers with additional processing (solution shearing, thermal annealing, etc.) and by using vapor-phase doping. In general, $\sigma$ increases with an increasing [F4TCNQ] from 0.2 to 0.6 mg/mL for pBBTa26-2T, pBBTa26-TT, and pBBTa26-4T because of increasing polaron formation. At [F4TCNQ] of 0.8 mg/mL, $\sigma$ decreases. This is likely caused by polaron compression upon excessive polaron formation at higher [F4TCNQ], leading to lower polaron delocalization.53

The Seebeck coefficient of pBBTa26-2T, pBBTa26-TT, and pBBTa26-4T thin films doped by F4TCNQ at different concentrations was measured, and the results are shown in Figure 5c. In general, the Seebeck coefficient is in the following order: pBBTa26-2T > pBBTa26-4T > pBBTa26-TT. We elucidate the trend of the Seebeck coefficient using carrier concentration ($\eta$) and polaron size. On the basis of their FET mobilities, we estimate the $\eta$ values of doped BBTa26 polymers using the formula $\sigma = \eta \mu_e$, where $\epsilon$ is the elementary charge. Accordingly, the $\eta$ values are estimated to be $4.0 \times 10^{23}$ cm$^{-3}$ for pBBTa26-TT, $1.7 \times 10^{21}$ cm$^{-3}$ for pBBTa26-2T, and $3.1 \times 10^{20}$ cm$^{-3}$ for pBBTa26-4T. The trend of their $\eta$ is in agreement with the UV–vis–NIR absorption of their doped films, where the intensity ratio of the P1 transition to HOMO → LUMO transition is in the order pBBTa26-TT > pBBTa26-2T > pBBTa26-4T. Although it is well-known that the Seebeck coefficient is inversely related to $\eta$, significant enhancements of the Seebeck coefficient from carrier-induced softening are expected when the carriers are in molecular orbitals encompassing many atomic sites,44 that is, delocalized polarons. Such delocalization carrier-induced softening has been observed in several doped PCBM-blended conjugated polymers.45 Hence, although pBBTa26-TT would have the most well-delocalized polaron because of its strongest quinoidal character along the polymer backbone, a very large number of carriers render its Seebeck coefficient to be the lowest. For pBBTa26-2T, although its $\eta$ is higher than that of pBBTa26-4T by 1 order of magnitude, it possesses more well-delocalized polarons than pBBTa26-4T because of its stronger quinoidal character along the polymer backbone, resulting in a higher Seebeck coefficient. Together with the measured $\sigma$, the power factor of the BBTa26 polymers is shown in Figure 5d. The power factor was the highest for pBBTa26-2T among the BBTa26 polymers, with a maximum value of 11.8 $\mu W m^{-1} K^{-2}$ when doped with the F4TCNQ solution at a concentration of 0.2 mg/mL. This is a result of its high Seebeck coefficient and relatively high $\sigma$. pBBTa26-TT has the second highest power factor because of its very high $\eta$ but low Seebeck coefficient, with a value of 6.8 $\mu W m^{-1} K^{-2}$ when doped with the F4TCNQ solution at a concentration of 0.6 mg/mL. pBBTa26-4T suffers from a lower power factor of about 1.2 $\mu W m^{-1} K^{-2}$ because of its low $\sigma$ and a less than desirable Seebeck coefficient. Even though these power factors are not the best results in polymer TE, they are among the highest for solution-phase doping using F4TCNQ.31,43,44,56,27

### CONCLUSIONS

Here, we have demonstrated that effective p-doping of conjugated polymers using very dilute F4TCNQ solutions can be easily achieved by incorporating proquinoidal moieties such as BBTa26 into conjugated polymers. By varying the dihedral angles/aromaticity of the $\pi$-spacer groups systematically, we are able to control the extent of the quinoidal
character along the polymer backbone. Even without doping, intrinsic $\sigma$ as high as $10^{-2}$ S cm$^{-1}$ can be achieved for pristine $\text{pBBTa26-TT}$. Upon doping with F4TCNQ, these polymers possess highly delocalized polarons, according to their P1 transitions. GISAXS and GIWAXS measurements suggest that these polymers are predominantly amorphous in nature which does not possess an extensive long-range order. Hence, their highly delocalized polarons can be considered to be highly intrachain-delocalized with minimum interchain delocalization. Even as such, we were able to achieve a very high $\sigma$ of over 100 S cm$^{-1}$ (for $\text{pBBTa26-TT}$). The highly delocalized polarons also allow the enhancement of the Seebeck coefficient via carrier-induced softening. As a result, a maximum power factor of 11.8 $\mu$W m$^{-1}$ K$^{-2}$ was achieved for $\text{pBBTa26-2T}$ by sequential solution-phase doping using a very dilute F4TCNQ solution. Our results are among the highest for solution-phase p-doping using F4TCNQ. Hence, we believe this can be a general design strategy toward fully solution-processed conducting polymers for high-performance TE materials.

**ASSOCIATED CONTENT**

2 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.9b03684.

Synthetic procedures and characterization of the intermediates and polymers, thin-film CV, thin-film FTIR (reflectance mode), gel permeation chromatography traces, solid-state EPR, DFT calculations, FET characterization, evolution of the solution and thin-film UV−vis−NIR absorption spectra of the BBTA26 polymers upon F4TCNQ doping, AFM images, schematic of the TE measurement setup, and representative Seebeck measurements of the F4TCNQ-doped BBTa26 polymers (PDF)

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Notes

The authors declare no competing financial interest.

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