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Effect of Backbone Regiochemistry on Conductivity, Charge Density, and Polaron Structure of n-Doped Donor–Acceptor Polymers

Suhao Wang, Daniele Fazzi, Yuttapoom Puttisong, Mohammad J. Jafari, Zhihua Chen, Thomas Ederth, Jens W. Andreasen, Weimin M. Chen, Antonio Facchetti, and Simone Fabiano

ABSTRACT: We investigated the influence of backbone regiochemistry on the conductivity, charge density, and polaron structure in the widely studied n-doped donor–acceptor polymer poly[N,N′-bis(2-octyldodecyl)-1,4,5,8-naphthalenediimide-2,6-diyl-alt-5,5′-(2,2′-bithiophene) [P-(NDI2OD-T2)]. In contrast to classic semicrystalline polymers such as poly(3-hexylthiophene) (P3HT), the regioregular (RR) structure of the naphthalenediimide (NDI)-bithiophene (T2) backbone does not alter the intramolecular steric demand of the chain versus the regi irregular (RI) polymer, yielding RI-P(NDI2OD-T2) with similar energetics and optical features as its RR counterpart. By combining the electrical, UV–vis/infrared, X-ray diffraction, and electron paramagnetic resonance data and density functional theory calculations, we quantitatively characterized the conductivity, aggregation, crystallinity, and charge density, and simulated the polaron structures, molecular vibrations, and spin density distribution of RR-/RI-P(NDI2OD-T2). Importantly, we observed that RI-P(NDI2OD-T2) can be doped to a greater extent compared to its RR counterpart. This finding is remarkable and contrasts benchmark P3HT, allowing us to uniquely study the role of regiochemistry on the charge-transport properties of n-doped donor–acceptor polymers.

INTRODUCTION

Tuning the charge carrier density of \( \pi \)-conjugated polymers is a viable route to control their electronic and electrical properties. Among several chemical strategies, this goal can be conveniently achieved either by blending a molecular dopant guest with the conjugated polymeric host via solution processing using a common organic solvent or by sequential doping upon exposure of the polymer film to the dopant vapors or a dopant solution in an orthogonal solvent. The dopant molecules, having appropriate electronic properties, operate by removing electrons from the highest occupied molecular orbital (HOMO) level of the polymer for p-type doping or donating electrons to the lowest unoccupied molecular orbital (LUMO) level for n-type doping. The simplicity of forming a doped film on the substrate of interest and without the need of electrolyte/electrochemical apparatus is one of the intrinsic advantages of molecular doping over other doping strategies, such as the electrochemical one, facilitating implementation in optoelectronic devices. Moderately doped conjugated polymers have been used in several applications such as to minimize Ohmic losses in organic solar cells (OSCs), organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs), whereas highly doped conducting polymers have found applications in numerous emerging energy-related technologies, such as unconventional batteries and organic thermoelectrics.
regiochemistry, and short-range (i.e., aggregation) character-
response compared to RR-P(NDI2OD-T2). Despite this,”

“has been shown that regioregular (RR) poly-
N electron conductivity lower than 0.01 S/cm. For example, it
only ∼ were attributed to the limited solubility of the organic dopant
mer,

“depending on the dopant,26,27 most n-doped polymers have
localization,33 which is typical of donor
T2) might be ascribed to the strong charge carrier intrachain
interactions. Thus, RR-P(NDI2OD-T2) with the more electron-de
− stackings
− acceptor character as well
35.0 kDa and
2.1, ActivInk N2200). The RI-P(NDI2OD-T2) sample was
obtained from Flexterra Inc. (Mn = 29.5 kDa and D = Mn/Mw =
2.1, ActivInk N2200). The RI-P(NDI2OD-T2) sample was
synthesized according to the procedure reported in ref 44 (Mn =
35.0 kDa and D = 1.8), where a mixture of NDI2OD-2,6Br2 and
NDI2OD-2,7Br2 (77:23 mol/mol) is reacted with 5,5- bis-
(trimethylstannyl)-2,2′-dithiophene using Pd(PPh3)4Cl2 as the
catalyst (Stille coupling, Figure S1). Note that this RI batch has a
content of 2,6- and 2,7-NDI-T2 linkages in the backbone of

In addition, because Tz2 has a far lower intrachain steric demand than T2, it planarizes the polymer
backbone and thus enhances the intermolecular π→π stacking
interactions. Thus, RR-P(NDI2OD-T2) exhibited a higher σ
value (up to ∼0.1 S/cm) and enhanced thermoelectric response compared to RR-P(NDI2OD-T2). Despite this
progress, the role of polymer backbone conformation, regiochemistry, and short-range (i.e., aggregation) character-
istics on the doping efficiency remains unexplored and poorly
understood. Note that ref 34 compares RR-P(NDI2OD-T2) to
regioirregular (RI) perylenediimide-based polymers also
having different donor units, which makes it difficult to
decouple the effect of regiochemistry from that of the chemical
structure/donor→acceptor character on charge density and
conductivity.

Here, we investigate the influence of backbone regio-
chemistry on the electronic structure and charge transport of n-
doped donor→acceptor P(NDI2OD-T2) polymers. In contrast
to polythiophenes such as poly(3-hexylthiophene) (P3HT,
Figure 1), the regioirregular backbone in RI-P(NDI2OD-T2)
does not alter the intramolecular steric demand of the chain
versus the RR polymer, allowing RI-P(NDI2OD-T2) to show
similar energetics and optical features as its RR counterpart.
Importantly, we observed that RI-P(NDI2OD-T2) can be
doped to a far greater extent compared to RR-P(NDI2OD-
T2). These data are corroborated by complementary measure-
ments such as electrical conductivity, electron paramagnetic
resonance (EPR), UV−vis, and infrared (IR) spectroscopies, as
well as by density functional theory (DFT) calculations.
This results in striking contrasts to homopolymers such as P3HT,
where the RI linkage leads to a low doping level, a reduced
charge carrier mobility, and thus a low electrical conductivity.40
This allows us to uniquely study the role of regioregularity
on the charge-transport properties of n-doped donor→acceptor
polymers.

EXPERIMENTAL SECTION
Polymer Samples. The RR-P(NDI2OD-T2) polymer was
obtained from Flexterra Inc. (Mn = 29.5 kDa and D = Mn/Mw =
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catalyst (Stille coupling, Figure S1). Note that this RI batch has a
content of 2,6- and 2,7-NDI-T2 linkages in the backbone of ~75 and
25%, respectively, as accessed by high-temperature 1H NMR
spectroscopy (Figure S2). Considering the similarity of monomer
steric/electronic characteristics, thus reactivity, the similarity between
the monomer feed and incorporation molar ratios, and NMR
assignment, the RI-P(NDI2OD-T2) sample should be randomized.

Film Preparation and Doping. All substrates were cleaned
sequentially in water, acetone, and isopropanol for 10 min each and

Figure 1. Chemical structures of typical donor−acceptor polymers such as RR-P(NDI2OD-T2), RI-P(NDI2OD-T2), RR-P(NDI2OD-Tz2), as
well as homopolymers such as RR-P3HT and RI-P3HT. Chemical structures of typical n-dopants used in this study.

The chemical and intrinsic electronic structure of the polymer has a critical impact on the charge transport and on
the extent of the doping process. Thus, understanding the
factors limiting the doping efficiency and charge transport in n-
doped polymers is critical to guide the rational design of new
high-conductivity conjugated polymers. With the exception of
halo-substituted benzodifuranodionehenphenylenvinylene poly-
mers, which can reach σ values as high as 0.6−14 S/cm
depending on the dopant,26,27 most n-doped polymers have
electron conductivity lower than 0.01 S/cm. The introduction of polar side chains 29,30 or
comonomers 31 in naphthalene-based polymers

The RR-P(NDI2OD-T2) polymer was
prepared via palladium-catalyzed Stille coupling of NDI2OD-2,6Br2 (77:23 mol/mol) with
5,5′-bis(dicarboximide)-2,6-diylo]-alt-S,S′-(2,2′-bithiophene) [RR-P(NDI2OD-T2), Figure 1], a high field-effect/space-charge-limited
electron mobility polymer extensively studied in the OFET/OSC literature.32
here, we investigate the influence of backbone regio-
chemistry on the electronic structure and charge transport of n-
doped donor→acceptor P(NDI2OD-T2) polymers. In contrast
to polythiophenes such as poly(3-hexylthiophene) (P3HT,
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similar energetics and optical features as its RR counterpart.
Importantly, we observed that RI-P(NDI2OD-T2) can be
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ments such as electrical conductivity, electron paramagnetic
resonance (EPR), UV−vis, and infrared (IR) spectroscopies, as
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25%, respectively, as accessed by high-temperature 1H NMR
spectroscopy (Figure S2). Considering the similarity of monomer
steric/electronic characteristics, thus reactivity, the similarity between
the monomer feed and incorporation molar ratios, and NMR
assignment, the RI-P(NDI2OD-T2) sample should be randomized.

Film Preparation and Doping. All substrates were cleaned
sequentially in water, acetone, and isopropanol for 10 min each and
then dried by nitrogen blowing. RR-P(NDI2OD-T2) (5 mg/mL) and RI-P(NDI2OD-T2) (5 mg/mL) were obtained by dissolving the polymer in 1,2-dichlorobenzene under stirring at 70 °C for at least 1 h to ensure complete dissolution of the polymers. The pristine films were obtained by spin-coating 5 mg/mL of P(NDI2OD-T2) at 1000 rpm for 30 s. Then, the films were thermally annealed at 110 °C under nitrogen atmosphere for 30 min and cooled down to room temperature naturally.

For tetraakis(dimethylamino)ethylene (TDAE) vapor doping, the polymer films, spin-coated on glass substrates, were exposed to the TDAE vapor inside a 20 mL airtight glass bottle filled with approximately 1 mL of TDAE, following a procedure reported earlier. The exposure was stopped at the required time by removing approximately 1 mL of TDAE, following a procedure reported earlier. Then, the two abovementioned solutions were mixed in volume ratios. Prior to doping, each blend solution was stirred and thermally annealed at 70 °C for at least 1 h. After stirring, the solutions were spin-coated onto the glass substrates at 1000 rpm for 30 s. Then, the films were thermally annealed at 110 °C under nitrogen atmosphere for 30 min and cooled down to room temperature naturally.

**Optical and Electrical Characterization.** Optical absorption spectra were recorded using a UV–vis-NIR spectrophotometer (Varian, Cary-5000). All the electrical characteristics were measured using a Keithley 4200-SCS in a glove box under N2 atmosphere.

Reflection–absorption IR spectroscopy (RAIRS) was carried out at grazing angle (86°) reflection in a Bruker PMA 50 accessory, with a LN2-cooled mercury cadmium telluride detector, using a Bruker VERTEX 70 as the light source. A photoelastic modulator (Hinds: ZnSe 50 kHz) was used to modulate the polarization of the light, and demodulation of signals was accomplished with a lock-in amplifier (Stanford Research SR830). All spectra were acquired at 4 cm⁻¹ resolution by 100 scans between 4000 and 800 cm⁻¹.

For conductivity measurements, Au electrodes with a Ti adhesion layer (L/W = 30 μm/1000 μm) were deposited on the glass substrates prior to the deposition of the active layers. Electrical conductivity measurements were performed inside a N2-filled glove box using a semiconductor parameter analyzer (Keithley 4200-SCS). For top-gate bottom-contact OFETs fabrication, the dielectric polymer poly(methyl methacrylate) (PMMA) was dissolved in 2-butanol to form a 70 mg/mL solution and then spin-coated on top of the pristine RR-/RI-P(NDI2OD-T2) films at 1500 rpm. The films were subsequently baked at 80 °C under a nitrogen atmosphere for 3 h and cooled down to room temperature. Finally, all the devices were completed by evaporating Al gate electrodes (~70 nm) through a metal shadow mask on top of the dielectric layers.

**EPR Measurements.** EPR measurements were performed in a standard X-band Bruker ELEXYS E500 spectrometer. The microwaves were used in the experiment was kept below the signal saturation limit. All EPR spectra were obtained in dark at room temperature and are normalized to film detection volume.

**Thin-Film Morphology Characterization.** Atomic force microscopy (Digital Instruments) was performed in tapping mode using a silicon cantilever having a spring constant of 40 N/m. For the grazing incidence wide-angle X-ray scattering, the silicon substrate surface was aligned at a grazing incident angle of 0.18° with respect to the incoming X-ray beam, supplied by a rotating Cu anode operated at 50 kV, 200 mA in point focus mode. The Cu Kα radiation [wavelength (λ) = 1.542 Å] was collimated and monochromatized with a one-dimensional multilayer optic. The scattered radiation was recorded in vacuum on photostimulable imaging plates 121.5 mm from the sample. The data integration and conversion to reciprocal space coordinates was done with MATLAB scripts.

**RESULTS AND DISCUSSION**

**Polymer Sample Preparation and Doping Procedure.** RR- and RI-P(NDI2OD-T2) were synthesized following a procedure previously reported. The LUMO energies of RR- and RI-P(NDI2OD-T2) are nearly invariant (≈−3.95 eV) despite the different regiochemistry. This datum is not surprising because in this donor–acceptor polymer, the LUMO is predominantly localized on the NDI unit, while the HOMO delocalizes between the NDI and the T2 units.

In stark contrast, the backbone regiochemistry is known to greatly influence the molecular orbital energetics of polythiophenes such as P3HT, with the HOMO energy level varying by ~0.4 eV (~−4.30 eV for RR-P3HT and ~−4.70 eV for RI-P3HT). In addition, the NDI-based polymer samples used in this study have comparable number-average molecular weights and polydispersity indexes: Mₙ = 35.0 kg/mol, D = 1.8 for RR-P(NDI2OD-T2), and Mₙ = 29.5 kg/mol, D = 2.1 for RI-P(NDI2OD-T2).

As both RR- and RI-P(NDI2OD-T2) have similar electron affinities and molecular weights, we conclude that the difference in electrical conductivity and charge density observed for the two doped polymers is due to different energetics and degree of polymerization (vide infra).
TDAE was used as the n-type dopant, unless specified otherwise. TDAE has a strong reducing character with an oxidation potential (∼−0.6 V vs SCE) that is comparable to the reduction potential of both RR- and RI-P(NDI2OD-T2) (∼−0.5 V vs SCE).48 Hence, the doping process occurs through an electron transfer from the dopant to the semiconducting polymer. The polymer films were exposed to the TDAE vapor inside a nitrogen-filled glove box (more details of the device preparation and doping procedure are reported in the Experimental Section).

**Electrical Measurements.** The electrical properties of both RR- and RI-P(NDI2OD-T2) films were investigated before and after exposure to the TDAE vapors in an inert environment. The conductivity data are summarized in Figure 2a as a function of the exposure time. Before exposure, both RR- and RI-P(NDI2OD-T2) are in their undoped pristine state and show σ values as low as ∼10−12 S/cm. After exposure to the dopant vapors (after just 60 s of exposure, at room temperature), the σ of both polymers steeply increases, reaching a maximum value of ∼1.8 ±0.5 × 10−9 and ∼2.6 ±0.3 × 10−9 S/cm for RR- and RI-P(NDI2OD-T2), respectively. These values are almost 5 orders of magnitude higher than those of the pristine polymer films. The conductivity of both polymers eventually decreases for longer exposure times. The maximum σ values and trends are in agreement with previous reports for RR-P(NDI2OD-T2),33,39 assuring that the films investigated in this study are representative of the high-performance polymer samples. Note also that these σ values are independent of the nature of the dopant because the molecular dopant 4-(1,3-dimethyl-2,3-dihydro-IH-benzoimidazol-2-yl)-N,N-dimethylaniline (N-DMBMI) affords comparable results (Figure 2b). Benzimidazole derivatives such as N-DMBMI are air-stable base dopants that allow for n-doping of organic semiconductors through hydride (H−) transfer.59 As shown in Figure 2b, the conductivity of both N-DMBMI-doped RR- and RI-P(NDI2OD-T2) rapidly increases by 5 orders of magnitude and saturates to ∼2.7 ±0.3 × 10−9 S/cm for RR-P(NDI2OD-T2) at an N-DMBMI molar ratio of 1.5 mol % (maximum conductivity not greater than ∼5 × 10−9 S/cm) and ∼3.3 ±0.4 × 10−9 S/cm for RI-P(NDI2OD-T2) (maximum conductivity not greater than ∼5 × 10−9 S/cm) at an N-DMBMI molar ratio of 9 mol %. For dopant molar ratio larger than 25 mol % for RR-P(NDI2OD-T2) and 15 mol % for RI-P(NDI2OD-T2), the conductivity of both samples starts to decrease. These values are comparable to those of TDAE-doped samples and consistent with previous reports.28 When compared to doped RR and regiorandom P3HT, charge transport in doped P(NDI2OD-T2) appears to be more tolerant to the regiochemistry. Indeed, the σ of doped RR-P3HT (σmax ≈ 10 S/cm) is orders of magnitude higher than that of the regiorandom counterpart (σmax ≈ 0.01 S/cm).40 It is also noteworthy that for P(NDI2OD-T2), two different doping processes lead to maximum electrical conductivity similar for all doped samples. In addition, similar conductivity values have been reported for RR-P(NDI2OD-T2) doped with dimer dopants reacting quantitatively by electron transfer.50 Thus, we believe that the electrical conductivity saturation observed in Figure 2 for both RR- and RI-P(NDI2OD-T2) is not due to inefficiencies of the dopant but rather linked to intrinsic limitations of the polymer, as also suggested recently.39

To identify any correlations between conductivity of the doped films and mobility of the pristine polymers, we tested the electron-transport properties of pristine RR- and RI-P(NDI2OD-T2) polymers by field-effect mobility measurements. Top-gate bottom-contact OFETs were fabricated using PMMA as the gate insulator. First, the semiconducting thin films were spin-coated on untreated gold source–drain electrodes/glass substrates from solution (5 mg/mL in 1,2-dichlorobenzene). The films were then thermally annealed at 110 °C under nitrogen atmosphere for 30 min and cooled down to room temperature. Next, the polymeric dielectric PMMA layer (70 mg/mL in 2-butanol) was spin-coated. These films were annealed at 80 °C prior to thermal evaporation of the aluminum gate electrode (further details about OFET fabrication and characterizations are reported in the Experimental Section). The transfer characteristics of these OFETs are reported in the Supporting Information (Figure S3), and the saturation mobility (μ) values are summarized in Table 1. RR- and RI-P(NDI2OD-T2) show a rather moderate difference in mobility (μRR/μRI ≈ 6), with RI-P(NDI2OD-T2) having an average μRI = 0.020 cm2/V s, which is only 6 times lower than that of RR-P(NDI2OD-T2) (μRR = 0.13 cm2/V s). This transport trend is in agreement with recent mobility values measured for these polymers by space-charge-limited currents measurements in unipolar diodes54 and for other NDl-based polymers in OFETs.51 Very notably, RI-P(NDI2OD-T2) shows a remarkably high charge carrier mobility compared with other RI polymers such as P3HT (μRR/μRI ≈ 1000),52 pyridial[2,1,3]thiadiazole-based polymers (μRR/μRI ≈ 120),12 and poly(dithienyl-benzol[1,2-b:4,5-b]di thiophene-co-S-fluoro-2,1,3-benzothiadiazole) (μRR/μRI ≈ 70). Qualitatively, by assuming the field-effect mobility (μEFT) as an estimation for the electron mobility in our doped films,58 we estimate the maximum carrier concentration in our RI-P(NDI2OD-T2) films (∼9.4 × 1017 cm−3) to be about 5-fold that of RR-P(NDI2OD-T2) (∼2.0 × 1017 cm−3), taking into account that σ = nμEFT, where e is the fundamental charge. We also attempted to measure the mobility of the doped films, up to doping levels where this measurement could be meaningful, observing that, even for low doping levels, the charge density in RI-P(NDI2OD-T2) is larger (∼2×) than that of RR-P(NDI2OD-T2) (see Figure S4 for further details).

**Optical Absorption Spectroscopy.** To monitor the changes in the electronic structure of the polymer upon doping, UV−vis−NIR spectroscopy was performed on thin polymer films for different TDAE exposure times. Figure 3 shows the absorption spectra of both RR- and RI-P(NDI2OD-T2) films before and after exposure (15 h) to the TDAE vapor. Similar to literature reports,55 undoped RR-P(NDI2OD-T2) shows an intense absorption band at ∼390 nm, which is assigned to a high-energy π−π* transition and a broad
structured low-energy band centered at ∼705 nm. This latter band results from an intramolecular charge-transfer (CT) transition between the NDI and the bithiophene units (705 nm) and from an intermolecular transition (∼800 nm) between chain segments, representing a spectrscopic fingerprint of the formation of aggregate species (∼30% aggregate content). In contrast, undoped RI-P(NDI2OD-T2) films exhibit a less structured CT absorption band (∼700 nm) and a less intense 800 nm band, indicative of reduced aggregation. This is in agreement with previous observations and shows that, despite significant structural modification of the polymer backbone, RI-P(NDI2OD-T2) films retain a substantial fraction of aggregates. TDAE treatment of both RR- and RI-P(NDI2OD-T2) films decreases the band intensity at ∼390 and ∼700/705 nm, together with the appearance of two new absorption bands at ∼500 and ∼820 nm. Note that TDAE absorbs at 205 and 273 nm in the UV spectrum. In addition, the bands at ∼390 and ∼700/705 nm shift to shorter wavelengths as the n-doping level increases (Figures 3 and S5). These optical spectra are consistent with the formation of negative polarons, as also recently supported by TDDFT calculations.

Film Microstructure and Molecular Packing. Grazing-incidence wide-angle X-ray scattering (GIWAXS) of spin-coated thin films allows us to investigate the impact of TDAE doping on the solid-state microstructure of RR- and RI-P(NDI2OD-T2) (Figures 4 and S6 and Table 2). For both pristine and doped RR-P(NDI2OD-T2), the majority of the crystalline regions have a π-face-on orientation of the polymer chains. GIWAXS diffractograms (Figure 4) indicate that the π-stacking distance of neat RR-P(NDI2OD-T2) shifts from \(d_{\text{010}} = 4.0\) (undoped) to 3.5–3.8 Å upon doping (Figure 4 and Table 2). The lamellar stacking of neat RR-P(NDI2OD-T2) is oriented in-plane and the distance also decreases from \(d_{\text{010}} = 25.5\) (undoped) to 25.1–24.4 Å in the doped samples. This behavior is consistent with previous literature for doped RR-P(NDI2OD-T2) and suggests that optimal doping (3 min) densifies crystalline aggregates likely via planarization of the π-conjugated backbone. Relative crystallinity of the RR-P(NDI2OD-T2) samples for the 001/010 crystal directions, as evaluated by the integrated reflection intensities, generally increases for optimal doping time \([1.5/1.0 \rightarrow 3.3/2.4]\), whereas crystallite dimensions are far less affected. Further doping strongly depresses 001 crystallinity, whereas along the 010 direction, it remains close to the weekly doped sample. Similarly, the RI-P(NDI2OD-T2) polymer exhibits preferential face-on π-stacking of the crystalline domains with the \(d_{\text{010}}\) and \(d_{\text{100}}\) periodicities exhibiting a far less dependence upon doping and remaining in a close range of 3.8–3.6 and 24.0–22.7 Å, respectively. Both the relative crystallinity and the coherence length of the doped RI-P(NDI2OD-T2) samples are far lower than those of the RR counterpart and generally less affected or slightly enhanced for a short doping period. Thus, overall, RR-P(NDI2OD-T2) adopts a substantially more ordered structure than the RI one, but both polymers exhibit, after doping, similar stacking/lamellar geometrical parameters.

EPR Analysis. To shed light on the origin of the unprecedented enhanced conductivity of the RI polymer, TDAE-doped RR- and RI-P(NDI2OD-T2) films were investigated via EPR. EPR allows for a direct observation of the radical anions formed upon electron transfer and were performed at room temperature in an oxygen-free environment. The results are reported in Figure 6. Both pristine RR- and RI-P(NDI2OD-T2) films do not exhibit any EPR signals. However, TDAE-doped RR- and RI-P(NDI2OD-T2) show the presence of paramagnetic species with a characteristic electron g-factor of about 2.0041 and 2.0040, respectively (Figure 5a). These values are slightly larger than that of a free electron \((g = 2.0023)\) but within the range commonly reported for organic radicals. Remarkably, the EPR spectra indicate that doped RI-P(NDI2OD-T2) possesses a significantly larger amount (up to four times) of paramagnetic species than doped RR-P(NDI2OD-T2), supporting the observation that higher charge carrier density is attained in doped RI-P(NDI2OD-T2) than RR-P(NDI2OD-T2) films. Note that a similar trend is observed when N-DMBI is used as the n-dopant (Figure S7). This observation is in stark contrast to p-doping of P3HT with different regioregularity, where RR-P3HT was reported to possess a significantly larger amount of paramagnetic species compared to RI-P3HT. In addition to this observation, the EPR signal of the doped RI-P(NDI2OD-T2) exhibits a spectral line width of 0.15 mT, whereas for doped RR-P(NDI2OD-T2), the line width becomes broader with a spectral line width of 0.30 mT (Figures Sb and S8). The narrowing of the EPR line width is consistent with a higher

Figure 3. Normalized UV−visible absorption spectra of RR- and RI-P(NDI2OD-T2) thin films before and after TDAE exposure. The new peaks at 500 and 805 nm appear after TDAE exposure for 15 h, indicating the formation of polaronic species.

Figure 4. GIWAXS two-dimensional scattering patterns of RR- and RI-P(NDI2OD-T2) before and after overnight (15 h) exposure to TDAE vapor.
Doping level for RI-P(NDI2OD-T2) as compared to the RR counterpart.59

DFT Calculations.

We performed extensive DFT calculations for both the neutral and charged species to get insights into the molecular and electronic structures describing the pristine and doped RR- and RI-P(NDI2OD-T2), respectively, and thus rationalize the experimental observations. RR and RI polymers are modeled considering the NDI2OD-T2 linkage at the NDI 2,6-(meta-) and 2,7-(para-) positions. RR-P-(NDI2OD-T2) shows the linkage between the NDI2OD and T2 units in 2,7-(para) position, whereas RI-P(NDI2OD-T2) shows a mixture of both 2,6-(meta) and 2,7-(para) positions. For each case, we investigated the NDI2OD-T2 repeat unit (here called \(n_1\), Figure 6) and up to a five-member oligomer (\(n_5\), Figure 7), the latter as a representative of the polymer limit. A first attempt to explore whether the EPR signal correlates with the polymer regiochemistry consisted in analyzing the molecular property variation induced by the RR- and the RI-substitution. As already documented by Neher et al.44 and Gierschner at al.,60 the electronic structure of RR- and RI-P(NDI2OD-T2) is quite similar despite the different ground-state cross-conjugation via the meta connection. This result was rationalized by the fact that the meta linkage does not alter the intramolecular steric demand of the polymer backbone versus the para substitution, allowing RI-P-(NDI2OD-T2) to display similar electronic properties, such as electronic transitions and HOMO–LUMO gap, as its RR counterpart.

Starting from these observations, we tackled the problem from a different perspective that is more related to the polaronic properties. Thus, we analyzed the single occupied molecular orbital (SOMO) distributions and the spin density of the negatively charged species. As reported in Figure 6, the meta or para substitutions in the NDI2OD-T2 unit do not cause any perturbation or asymmetric distribution into the spatial extension of the SOMO. For both \(n_1\)-RR and \(n_1\)-RI, SOMO\(_{\alpha}\) and SOMO\(_{\beta}\) are symmetric with respect to the local \(D_{2h}\) point group of the NDI02D unit and thus cannot provide any a priori chemical reason which would justify a different spin density for the two species, as instead experimentally observed. However, a monomer (or a short-length oligomer) cannot be a representative for the polymer properties.

Exploring the polymer limit, we computed the structural and electronic properties of long oligomers, up to five-member units (\(n_5\)), for both the neutral and the charged (i.e., anionic) electronic states. Dealing with extended \(\pi\)-conjugated systems, and based on our previous experience in investigating the electronic properties of another high electron mobility organic polymer (namely BBL),33 we carefully checked the stability of the computed UDFT-pseudo-wave function, through the BS formalism.61,62 In fact, the UDFT solution might become unstable by increasing the extension of the \(\pi\)-conjugated core, thus being incapable of describing the properties of charged (or excited) states properly.58 We already demonstrated how, by increasing the oligomer lengths—as for the case of BBL—

| \(P(\text{NDI2OD-T2})\) doping time | \(d\)-spacing [Å] | relative crystallinity [Å] | coherence length [Å] | \(d\)-spacing [Å] | relative crystallinity [Å] | coherence length [Å] |
|-----------------------------------|------------------|----------------------------|---------------------|------------------|----------------------------|---------------------|
| RR none                           | 25.5             | 1.5                        | 151                 | 4.0             | 1.0                        | 17                  |
| 3 min                             | 25.1             | 3.3                        | 156                 | 3.5             | 2.4                        | 11                  |
| 15 h                              | 24.4             | 0.4                        | 108                 | 3.8             | 2.9                        | 12                  |
| RI none                           | 24.5             | 0.3                        | 104                 | 3.6             | 0.5                        | 10                  |
| 3 min                             | 24.7             | 0.4                        | 111                 | 3.7             | 0.7                        | 10                  |
| 15 h                              | 24.0             | 0.1                        | 71                  | 3.8             | 0.3                        | 10                  |

Figure 5. (A) EPR spectra of doped RR- and RI-P(NDI2OD-T2) films (TDAE exposure for 15 h), indicating that doped RI-P(NDI2OD-T2) possesses a significantly larger amount of paramagnetic species than RR-P(NDI2OD-T2) under the same doping conditions. (B) Corresponding EPR line widths.

Figure 6. Molecular structure and SOMO of the charged (i.e., anionic) species for RR and RI monomers (\(n = 1\)). Calculations are at the U\(\omega\)B97X-D/6-311G* level of theory.

Figure 7. Equilibrium molecular structures and SOMOs of the charged (i.e., anionic) species for RR and RI oligomers (\(n = 5\)). Calculations are at the U\(\omega\)B97X-D/6-311G* level for the RR and at the BS-U\(\omega\)B97X-D/6-311G* level for the RI.
the UDFT-BS solution become more stable than the UDFT one, leading to different electronic structures (e.g., electronic-transition energies or spin density distribution). Thus, $n_1$ RR-P(NDI2OD-T2) does not show any instability of the charged state UDFT wave function. However, the UDFT wave function of $n_1$ RI-P(NDI2OD-T2) is unstable, leading to a more stable UDFT BS solution. The stabilization energy, evaluated as $\Delta E = E_{\text{UDFT-BS}} - E_{\text{UDFT}}$, is $-0.22$ eV. This is a remarkable result because it indicates that in a more extended \(\pi\)-conjugated system, the \(\text{meta}\) substitution (or the RI structure, as named here) affects the description of the electronic structure of the charged (i.e., polaronic) species, requiring an unrestricted BS approach (UDFT-BS), rather than UDFT. In practical terms, in analogy to biradicaloid systems, this case can be related to a multiconfigurational character of the wave function. A fully satisfactory description of the charged (polaron) electronic structure in RI-P(NDI2OD-T2) would require multiconfigurational wave function methods or hybrid approaches (e.g., multiconfigurational pair-DFT), still nonpractical for such extended systems with the current state-of-the-art computational resources.

With enhanced accurate description of the ground state of the charged electronic structure (within the UDFT framework), we can now analyze the differences between RR- and RI-P(NDI2OD-T2). As reported in Figure 7, the equilibrium molecular structures of charged RR- and RI-chains differ, being the first linear and the latter distorted, with a kinked structure as induced by the \(\text{meta}\) substitution. The different single-chain structures also reflect, on a large scale, different packing and order/disorder film morphologies (as discussed in the GIWAXS section and commented in the following RAIRS section). Analyzing the electronic structure of charged species and their molecular orbitals, SOMO$_\alpha$ and SOMO$_\beta$ of the two species differ, with the RR-structure maintaining the local $D_{2h}$ symmetry distribution of the molecular orbitals while the RI does not. In particular, the SOMO$_\beta$ of the RI-P(NDI2OD-T2) presents an asymmetric distribution with respect to the NDI2OD unit. This asymmetric distribution leads to a spin density distribution which is asymmetric too, being unbalanced toward one bithiophene unit rather than being equally distributed on both sides of the NDI2OD moiety [as for the case of RR-P(NDI2OD-T2)]. The different stabilities in the UDFT solutions of the charged state, as well as the asymmetric distribution of the SOMO and spin density, are the only molecular-based features (i.e., at the single chain level) differentiating the RR- from the RI-P(NDI2OD-T2), and we believe that they might be at the origin of the different EPR signals. The asymmetric spin density distribution of the RI polymer, together with a more distorted chain structure (Figure 7), can result, at the macroscopic level, in a larger amount of paramagnetic species (i.e., charge density) present with respect to the RR one. The distorted chain structure of RI-P(NDI2OD-T2) induces a higher structural and energetic disorder, favoring a deeper percolation of the dopant molecules within the film, thus leading to higher doping level and polaron density than the RR-polymer. In this way, the combination of an extended \(\pi\)-conjugated system and the presence of a \(\text{meta}\) substitution in the chain both induce a different molecular structure, energetic disorder, and spatial...

**Figure 8.** Comparison between experimental RAIRS spectra and the theoretical calculations for the RR (left panel) and RI (right panel) species. RAIRS were recorded for the pristine species (cyan), after 3 min and 15 h of doping with TDAE (purple and green) and doping with DMBI (blue). DFT IR calculated spectra (scaling factor 0.95) are reported for the neutral species ($\omega$B97X-D/6-311G*, red) and for the negatively charged species ($\omega$B97X-D/6-311G*, black). The IR spectrum of the charged RI-P(NDI2OD-T2) was computed with UDFT BS calculations. Sketches of the normal modes III and IV (displacements are indicated via green arrows) and spin density for the polaronic species (isosurfaces 0.0001 Å$^3$, gray for both $\alpha$ and $\beta$) are reported.
localization of the polaron spin density with respect to the para substitution, possibly resulting in different EPR spectra.

**Vibrational Spectroscopy Characterization: Experiments Versus Theory.** As reported by Fazzi et al., RAIRS combined with quantum-chemical calculations is a powerful tool to investigate the vibrational, structural, and molecular orientation properties of polymer chains with respect to a refractive substrate. For the case of RR-P(NDI2OD-T2), we demonstrated the effectiveness of using a combined experimental/theoretical (i.e., RAIRS/DFT) approach, being able to derive the structure and orientations of RR-P(NDI2OD-T2) chains with respect to a gold substrate. The methodology required the assignment of specific IR-active normal modes and their transition dipole moment orientations (acting as vibrational/structural fingerprints), together with the selection rules governing the RAIRS band activities. As previously reported, the IR and RAIRS bands used for the vibrational and structural assignment of RR-P(NDI2OD-T2) are as follows:

- **band I** (∼1720 cm⁻¹), that is, the IR-active C==O symmetric stretching localized on the NDI2OD unit and polarized perpendicular to the polymer chain, namely, along the long axis of the NDI2OD plane;
- **band II** (∼1680 cm⁻¹), that is, the IR-active C==O antisymmetric stretching localized on the NDI2OD unit and polarized parallel to the polymer chain, namely, along the short axis of the NDI2OD plane;

On the basis of these assignments, the analysis of RAIRS spectra revealed that the polymer chains of a spin-coated RR- and RI-P(NDI2OD-T2) film run parallel to the substrate, featuring the T2 units parallel to it and the NDI2OD units tilted by an angle of 42°. Here, we adopted a similar approach to get insights for both RR- and RI-P(NDI2OD-T2) into the doping process and the polymer/doping structure. Figure 8 shows the RAIRS spectra of RR and RI species in their pristine (undoped) state (cyan line), after 3 min (purple line) and 15 h of doping time with TDAE (green line) and doped with N-DMBI (blue line). In Figure 8, we also report the computed IR spectra of the neutral and charged species for both RR and RI cases (see also Figures S9 and S10). The RAIRS spectrum of pristine RR P(NDI2OD-T2) (Figure 8, left side) reproduces the spectral shape reported previously for spin-coated P(NDI2OD-T2) films. Accordingly, the intensity ratio of bands I and II (I_{band I}/I_{band II}) indicates that the polymer chains are parallel to the substrate, with the NDI2OD units tilted by 42° and the T2 units parallel with respect to the substrate. This is in agreement with a preferential face-on chain orientation observed by GIWAXS. The RAIRS of pristine RI-P(NDI2OD-T2) (Figure 8, right side) is similar to the that of the RR case, however showing a I_{band I}/I_{band II} slightly higher than the RR case. This would suggest that the polymer chains (on average) are pointing slightly out of the substrate, being tilted or more distorted than those of RR. According to DFT structural calculations, because of the meta substitution, RI chains do show a more distorted structure than the RR ones, again consistent with the GIWAXS data reported in the previous section.

Upon doping, two additional RAIRS bands appear in the 1700–1600 cm⁻¹ region (bands III and IV). Comparison of the DFT-computed IR spectra of the neutral and charged species (Figure 8, red and black lines) reveals that such bands are the result of the polymer chain doping process. In particular, **band III** and **band IV**, assigned for the first time here by DFT calculations (Figure 8), represent the IR-active C==O symmetric and antisymmetric stretching oscillations of charged species (green arrows in Figure 8), respectively, as localized prevalently on one monomer unit of the chain. In detail, DFT calculations reveal that the normal modes related to bands III and IV are localized on the unit over which the polaron mainly relaxes, as visible in Figure 8 from the comparison between the sketches of the normal modes and the spin density maps. Bands III and IV are, consequently, the IR vibrational fingerprints of the P(NDI2OD-T2) polaron. They represent the IR-active C==O symmetric and antisymmetric stretching modes, as bands I and II do, but their transition energies are red-shifted with respect to bands I and II. The energy shift can be explained by the removal of degeneracy, as induced by the break in the translational symmetry of the polymer because of polaron relaxations.

Having clarified the assignment of the bands, we can interpret the RAIRS spectra. At first, we can observe that doping affects the RAIRS spectra (Figure 8), suggesting different orientations of the polymer chains with respect to the substrate and, eventually, different polymer/dopant morphologies (as also observed by GIWAXS). For both the RR- and RI-P(NDI2OD-T2) polymers, doping with TDAE induces the appearance of **band III** as registered after 3 min of exposure to the dopant, whose RAIRS intensity increases further as recorded at 15 h of doping. For RI-P(NDI2OD-T2), the RAIRS intensity of **band III** is higher than that of the RR polymer after 15 h of doping and also **band IV** is further enhanced. According to the DFT band assignments, the RAIRS spectra reveal (i) the presence of a localized charge on the polymer chains and (ii) RI-P(NDI2OD-T2) chains being more tilted than the RR-P(NDI2OD-T2) ones, also featuring the NDI2OD units oriented more perpendicularly to the substrate than the RR polymer. Moreover, the enhanced RAIRS intensity of the polaron **band III** of RI-P(NDI2OD-T2) might suggest not only a more tilted orientation of the NDI2OD units but also a higher charge density than the RR species. We can assume that I_{band I}/I_{band II} is representative for the backbone structural reorientation while I_{band III}/I_{band II} for the polaron formation. At 15 h of doping, the I_{band III}/I_{band II} is the same (∼1) for both polymers. Assuming the polymer chain reorientation effects and the dopant diffusion processes as completed, the intensity ratio I_{band III}/I_{band II} at 15 h should correlate with the doping level (or charge density) of the polymer chains. The I_{band III}/I_{band II} for RR- and RI-P(NDI2OD-T2) at 15 h, calculated from a Lorentzian deconvolution of the areas, is 1.3 and 3.9, respectively, thus ∼3× larger for the RI polymer. This result could be related to a higher doping level for RI- with respect to RR-P(NDI2OD-T2). Similarly, a factor of 2 is present in the EPR spectral line width values (Figure 5), namely, 0.30 and 0.15 mT for the RR and RI polymers, respectively, thus leading to a higher doping level for the latter. Considering our above assumptions valid, and accounting for the intrinsic error in decoupling the structural and doping contributions in the RAIRS signals, we could suggest that also from a quantitative analysis of the RAIRS intensities, RI-P(NDI2OD-T2) can be doped more efficiently (∼3×) than RR-P(NDI2OD-T2), further supporting the EPR findings. Further in-depth and systematic investigations in this direction are required to better analyze the differences in the RAIRS spectra for various doping agents/
levels and film morphologies. Nevertheless, for the first time, we report here the effects of the doping process of P(NDI2OD-T2) polymer on the corresponding RAIRS spectra.

■ CONCLUSIONS

In conclusion, we investigated the impact of polymer backbone regiochemistry on the conductivity, charge density, and polaronic structure for n-doped RR and RI donor–acceptor P(NDI2OD-T2)s. Interestingly, we found that the maximum electrical conductivity of doped RI-P(NDI2OD-T2) is statistically larger than that of RR-P(NDI2OD-T2), despite the considerably lower charge carrier mobility and the far less textured film microstructure of the former polymer. EPR measurements indicate that doped RI-P(NDI2OD-T2) possesses a significantly larger amount of paramagnetic species compared to the doped RR counterpart and thus can support a greater electron density as measured experimentally from combined conductivity/mobility data. This phenomenon arises from a different molecular chain structure, polaron structure, and spin density distribution in the RI polymer backbone, as suggested by DFT calculations. All of these data are in striking contrast to homopolymers such as P3HT and other π-conjugated polymers, where regioirregularity leads to a lower doping level, reduced charge carrier mobility, and thus far lower electrical conductivity. We attributed this to an increased tolerance of P(NDI2OD-T2) backbone to disorder. The RI structure in, for example, P3HT greatly impacts the planarization of the backbone because of steric constraints, which lock the undoped/doped polymer chains in severely twisted conformations. This prevents the P3HT chains from aggregating/crystallizing, reduces the conjugation length, and dramatically affects the energetic structure of the RI-P3HT films. In contrast, the mixed 2,6- and 2,7- NDI-T2 linkages in the RI-P(NDI2OD-T2) do not affect the intrachain steric demand of the backbone, yielding RI-P(NDI2OD-T2) with a similar conformational structure and LUMO energy as its RR counterpart. In comparison to homopolymers such as P3HT, negative polarons in P(NDI2OD-T2) are prevalently localized over mostly one repeating unit, as confirmed here by DFT computations and the comparison between theoretical and experimental IR/RAIRS spectra, thus providing a higher baseline for charge-transport tolerance to disorder regardless of the film microstructure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmate.9b00558.

Additional characterization data, such as NMR, OFETs, UV−vis, EPR, GIWAXS, computed (DFT) IR spectra for oligomer \( n_1 \) RR and RI (both neutral and charged states), together with the computed IR spectra of TDAE and N-DMBI anions, and DFT-optimized geometries for oligomer \( n_2 \) and \( n_3 \), considering both RR and RI substitutions (PDF).

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Notes

The authors declare no competing financial interest.

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