

# Intrachain Charge Transport through Conjugated Donor–Acceptor Oligomers

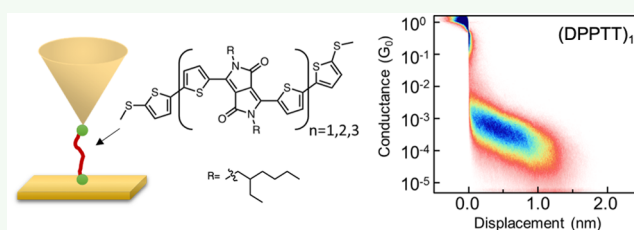
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## Supporting Information

**ABSTRACT:** Donor–acceptor (D–A) polymers are promising materials for organic electronics because of high charge carrier mobilities and narrow band gaps. Despite recent progress, there is incomplete understanding of the mechanisms underlying charge transport in these materials. In this work, we use single molecule techniques to study intrachain charge transport in D–A oligomers containing alternating diketopyrrolopyrrole (DPP) acceptor and bithiophene donor units. Interestingly, at high applied bias, longer DPPTT oligomers exhibit substantially higher conductance compared to shorter oligomers, which is interpreted using density functional theory (DFT) simulations. Overall, this work provides an increased understanding of intrachain charge transport along D–A oligomers.

**KEYWORDS:** donor–acceptor oligomers, intrachain charge transport, organic semiconductors, single molecule, scanning tunneling microscope break-junction (STM-BJ)



A major challenge in the field of organic electronics lies in the design and development of high-performance conducting polymers.<sup>1,2</sup> In recent years, donor–acceptor (D–A) polymers have been shown to exhibit high charge carrier mobilities,<sup>3,4</sup> which makes them ideal candidates as active layers in flexible electronic devices.<sup>5</sup> D–A molecules are composed of a polymeric backbone with alternating electron-rich and electron-deficient moieties, yielding a combination of high-lying HOMO levels (residing on the donor units) and low-lying LUMO levels (residing on the acceptor units), thereby providing a narrow band gap for high performance.<sup>6,7</sup>

Two distinct mechanisms are thought to govern charge transport in  $\pi$ -conjugated materials: (1) intrachain charge transport, which refers to charge transport along conjugated polymer backbones because of  $\pi$ -electron delocalization, and (2) interchain charge transport, which refers to charge transport between nearby molecules mediated by  $\pi$ - $\pi$ -stacking.<sup>8,9</sup>

In general, interchain charge transport is thought to limit the overall charge carrier mobility in conjugated polymer films.<sup>10,11</sup> To this end, prior work has largely focused on improving interchain charge transport in conjugated polymer thin films using a wide array of postsynthetic processing techniques, including different material deposition methods and annealing procedures as well as tuning substrate–polymer interactions.<sup>12</sup> On the other hand, it has been shown that high charge carrier mobilities are achieved at the device scale because of efficient intrachain charge transport complemented by short-range

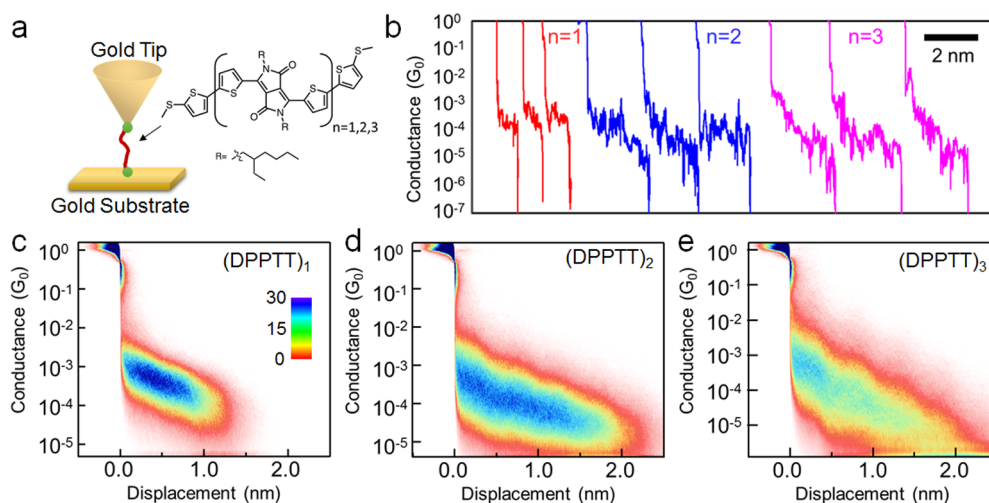
intermolecular aggregation.<sup>13</sup> Together, these results suggest that achieving large-area crystallinity in semiconductor polymer films may not be necessary to optimize interchain charge transport. Indeed, high-performance wearable and stretchable organic electronic devices have recently been developed with high charge carrier mobilities facilitated by efficient intrachain charge transport within nanofibril networks of D–A polymers.<sup>14</sup>

Despite recent progress in the development of integrated devices based on D–A polymers, we still lack a full understanding of intrachain charge transport in D–A polymers at the molecular level. Prior work focusing on molecular junctions has shown that off-resonant tunneling dominates intrachain charge transport at short distances. The exponential decay constant  $\beta$  describing conductance as a function of molecular extension for common  $\pi$ -conjugated molecules (such as oligothiophene or oligophenylene) is generally around  $\sim 2$ – $3 \text{ nm}^{-1}$ .<sup>15–17</sup> On the other hand, multistep charge hopping dominates over longer distances (generally  $> 4 \text{ nm}$ ), and molecular conductance is observed to follow Ohm's law.<sup>18</sup> Prior single molecule studies of ladder-type D–A oligomers have shown that the experimentally measured molecular extensions over which conductance is observed are unexpectedly short ( $< 1 \text{ nm}$ ).<sup>19</sup> Recent single molecule conductance

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**Figure 1.** Single molecule conductance of DPPTT oligomers determined using the STM-BJ technique. (a) Schematic illustration of a DPPTT oligomer junction in the STM-BJ experiment, with molecular structures shown for DPPTT oligomers. (b) Characteristic single molecule traces of conductance–displacement for (DPPTT)<sub>*n*</sub>, where *n* = 1, 2, or 3 at a bias of 250 mV. (c–e) 2D conductance–displacement histograms for (c) (DPPTT)<sub>1</sub>, (d) (DPPTT)<sub>2</sub>, and (e) (DPPTT)<sub>3</sub> over an ensemble of ~15 000 individual molecules.

measurements revealed high levels of conductance for D–A polymers, which supports the observation of efficient charge transport over long distances for these materials.<sup>20</sup> Moving forward, there is a strong need for an improved understanding of the mechanisms underlying charge transport D–A molecules.

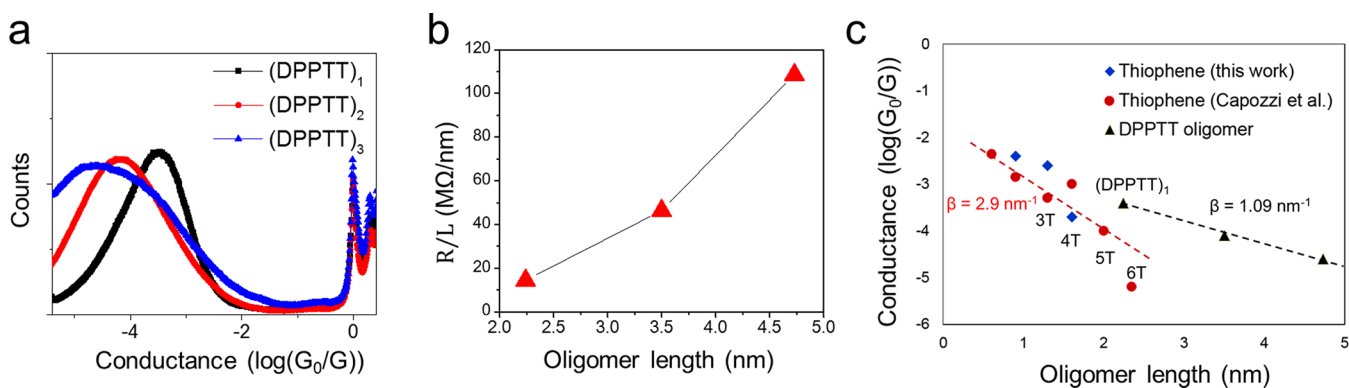
In this work, we study the intrachain charge transport properties of D–A oligomers consisting of alternating diketopyrrolopyrrole (DPP) acceptor units and bithiophene donor units using a combination of single molecule conductance experiments, bulk electrochemical methods, and computational modeling. In particular, we use a scanning tunneling microscope break-junction technique (STM-BJ)<sup>21,22</sup> to directly measure intrachain charge transport for D–A polymers at the single molecule level. Unlike bulk-scale measurements where intermolecular interactions may obscure the role of intrachain transport in determining emergent electronic properties, single molecule methods such as STM-BJ enable direct characterization of electron transport through a molecular backbone.<sup>23</sup> Using this technique, the conductance of single D–A oligomers is measured as a function of applied voltage and nanoscale separation between electrodes (Supporting Information). Single molecule traces of conductance versus molecular displacement show that D–A oligomers are conductive over large distances >2 nm. At low applied bias (250 mV), our results show that the resistivity of D–A oligomers generally increases with molecular length. At high applied bias, however, we unexpectedly observe high levels of conductance for longer D–A oligomers, which is interpreted in the context of electron transport through additional pathways and molecular energy levels using density functional theory (DFT) simulations.

Sequence-defined oligomers containing thiophene as donor and DPP as an acceptor were synthesized by a palladium-catalyzed Suzuki cross-coupling reaction in the presence of Pd(PPh<sub>3</sub>)<sub>4</sub> and K<sub>2</sub>CO<sub>3</sub>, thereby yielding three distinct D–A oligomers known as (DPPTT)<sub>*n*</sub>, where *n* = 1, 2, or 3, as shown in Scheme S1 and Figure 1a. All three sequence-defined D–A oligomers (Scheme S1) were end-capped with methylthio groups to facilitate single molecule conductance measure-

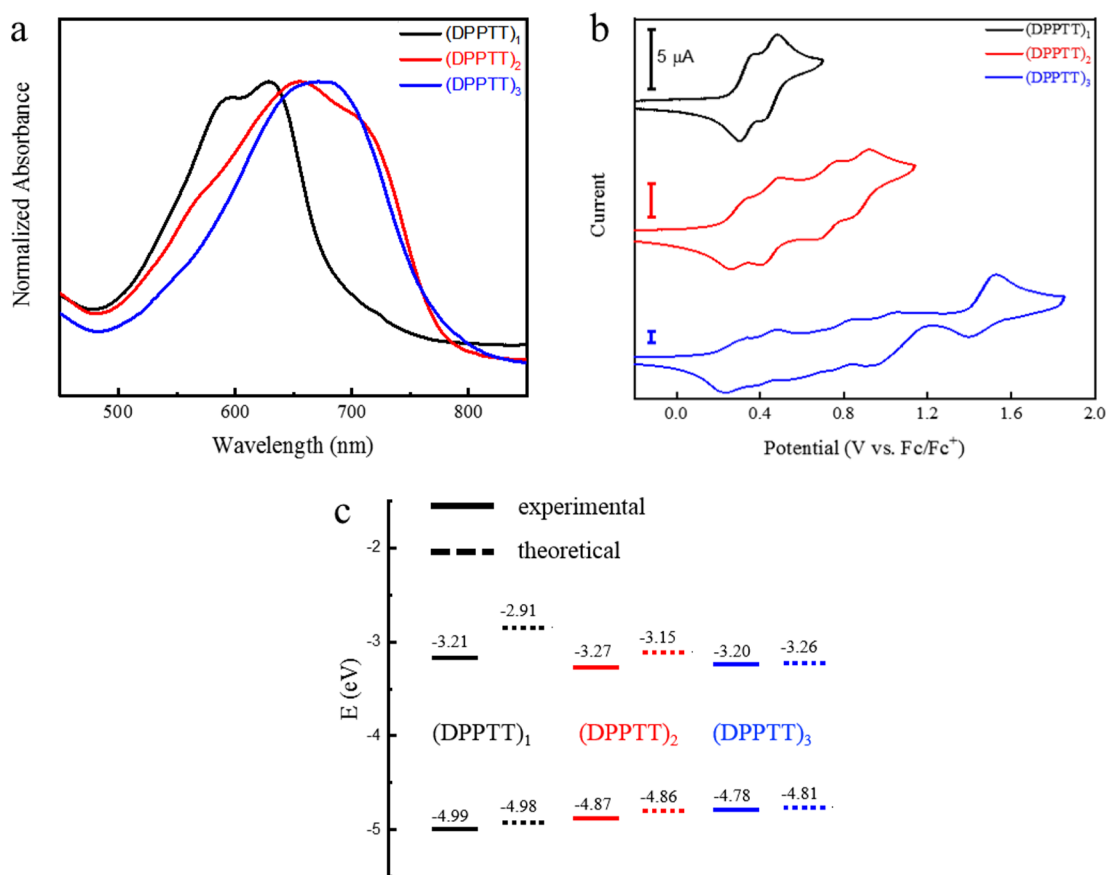
ments. Following synthesis, crude oligomers were precipitated in methanol and purified through Soxhlet extraction in hot methanol and acetone, and molecular structures were characterized by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies and mass spectrometry (Figures S1–S18). Following synthesis and chemical characterization, DPPTT oligomers were studied using single molecule methods based on STM-BJ and bulk electrochemical methods including cyclic voltammetry (Supporting Information).

We first measured the conductance of individual (DPPTT)<sub>*n*</sub> oligomers using STM-BJ. Using this method, single DPPTT oligomers are bound to a gold tip and a supporting gold substrate through two methylthio linker groups (Figure 1a). Characteristic single molecule conductance–displacement traces for oligomers (DPPTT)<sub>1</sub>, (DPPTT)<sub>2</sub>, and (DPPTT)<sub>3</sub> are shown in Figure 1b. Unless otherwise noted, conductance is measured under an applied bias of 250 mV with a tip pulling rate of 15 nm/s. In all cases, single molecule conductance is determined over a large ensemble of ~15 000 measurements, thereby enabling robust statistical analysis of experimental data. Single molecule conductance data are further analyzed to generate two-dimensional (2D) histograms of conductance versus displacement, as shown in Figure 1c–e. The molecular ensemble data for (DPPTT)<sub>1</sub> conductance falls in a relatively narrow range between ~10<sup>-3</sup>–10<sup>-4</sup> G<sub>0</sub>, but (DPPTT)<sub>2</sub> and (DPPTT)<sub>3</sub> oligomers generally exhibit a much wider range of conductance, where G<sub>0</sub> is the quantum unit of conductance such that the quantum unit of conductance is  $G_0 = 2e^2/h = 77.4 \mu\text{S}$ , where *e* is the electron charge, and *h* is Planck's constant.

Characteristic single molecule conductance traces for (DPPTT)<sub>1</sub> (Figure 1b, red traces) generally show that the conductance exhibits a plateau as the tip is pulled away from the surface. In contrast, characteristic traces for the single molecule conductance of (DPPTT)<sub>3</sub> (Figure 1b, violet traces) generally show a continual decrease from a value of ~10<sup>-2</sup> G<sub>0</sub> when the tip–substrate displacement is small (<0.5 nm) to a conductance value of ~10<sup>-6</sup> G<sub>0</sub> when the molecular junction is disrupted (~2 nm). Theoretical calculations using the extended Hückel method show that molecular conductance



**Figure 2.** Average molecular conductance and molecular length-dependent conductance for DPPTT oligomers. (a) 1D conductance histograms for DPPTT oligomers over  $\sim 15\,000$  single molecule measurements at 250 mV bias. (b) Resistivity (defined as resistance per unit length,  $R/L$ ) of DPPTT oligomers as a function of molecular length. (c) Average single molecule conductance of DPPTT oligomers and oligothiophenes as a function of molecular length. Dashed lines are fits to the experimental data.

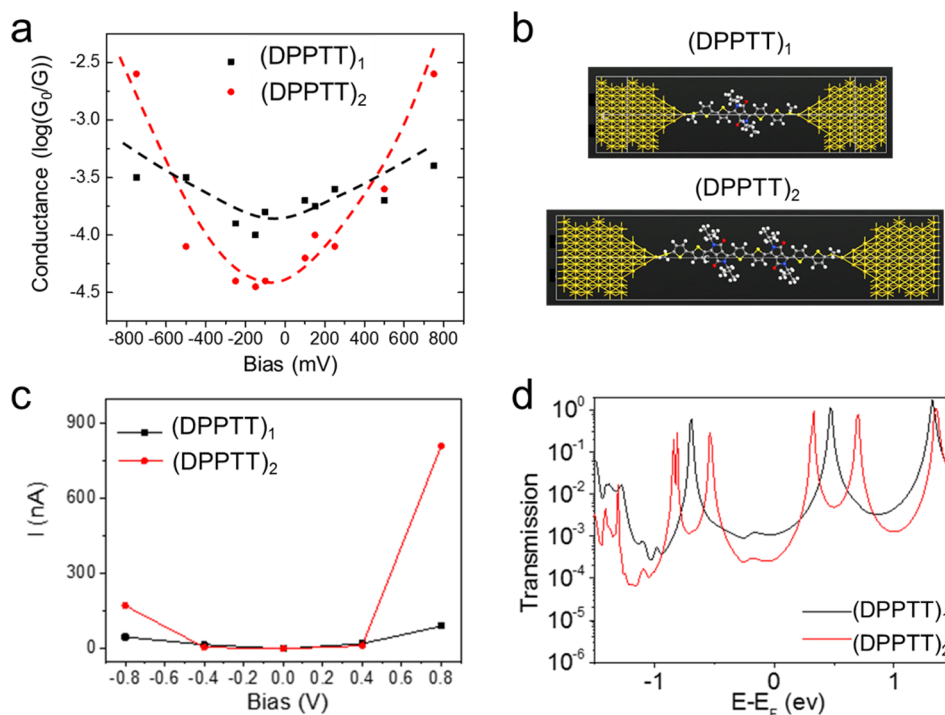


**Figure 3.** Electronic property characterization of DPPTT oligomers. (a) Absorption spectra of three DPPTT oligomers in CHCl<sub>3</sub>. (b) Cyclic voltammetry of three DPPTT oligomers in CH<sub>2</sub>Cl<sub>2</sub>. (c) HOMO and LUMO energies obtained from DFT calculations and experiments.

decreases exponentially under stretching because of molecular conformational changes.<sup>24</sup> On the basis of these observations, we conjecture that the intrachain charge transport pathway remains unchanged during molecular pulling for (DPPTT)<sub>1</sub>, suggesting minimal intramolecular conformational changes for (DPPTT)<sub>1</sub>. On the other hand, (DPPTT)<sub>2</sub> and (DPPTT)<sub>3</sub> appear to show evidence of molecular conformational changes during molecular pulling, likely a result of the conformational unfolding of larger  $\pi$ -conjugated oligomeric structures during pulling events. Moreover, (DPPTT)<sub>3</sub> shows appreciable conductance at molecular extensions  $>2$  nm, which corre-

sponds to a relatively large molecular extension, at which conductance has been observed compared to other  $\pi$ -conjugated molecules.<sup>19,25,26</sup>

Single molecule conductance data are further analyzed as one-dimensional (1D) conductance histograms as shown in Figure 2a, which enables determination of the maximum average molecular conductance by fitting the histogrammed data to a Gaussian function. For cases in which molecular conductance is dominated by multistep hopping, the resistivity remains constant as molecular length increases, with the conductance behavior described by Ohm's law.<sup>18,27</sup> However,



**Figure 4.** Effect of applied bias on molecular conductance and corresponding DFT simulation results for DPPTT oligomers. (a) Single molecule conductance of DPPTT oligomers, determined by Gaussian fits to histogram peaks (corresponding 2D histogram shown in Figures S23 and S24) at different bias. (b) DPPTT molecular junction for DFT-based simulation of transmission functions. (c) Current–voltage relationships of (DPPTT)<sub>1</sub> and (DPPTT)<sub>2</sub> calculated by nonequilibrium Green’s function/DFT simulations (NEGF-DFT) (d) Transmission probabilities,  $T(E)$ , of (DPPTT)<sub>1</sub> and (DPPTT)<sub>2</sub> as a function of energy relative to the Fermi level.

our results show that the resistivity of DPPTT oligomers increases by a factor of  $\sim 7$  (from 1.5 to 10.5 M $\Omega$ /nm) as molecular length increases (Figure 2b), where molecular lengths are determined using density functional theory (DFT) calculations (Figure S19). Taken together, these results suggest that conductance in DPPTT oligomers is not governed by multistep hopping, at least for oligomers up to the trimer (DPPTT)<sub>3</sub>, corresponding to a molecular length of  $\sim 5$  nm.

The conductance–length relationship for DPPTT oligomers is plotted on a semilog scale in Figure 2c. Our results show that the conductance of DPPTT oligomers is well described by a single decaying exponential as a function of molecular length, which is consistent with a coherent tunneling model such that  $G \sim e^{-\beta L}$ . In this way, we determined a decay constant  $\beta = 1.1$  nm<sup>-1</sup> for DPPTT oligomers, which is significantly lower compared to other  $\pi$ -conjugated molecules ( $\beta = 2.9$  nm<sup>-1</sup> for oligothiophenes, as determined in our experiments and consistent with prior work).<sup>28</sup> We attribute these observations to the narrow energy band gap in D–A molecules, as discussed below. Importantly, the conductance–length relationship for DPPTT oligomers is linear, which suggests that the intrachain charge transport mechanism in DPPTT oligomers is governed by electron tunneling, at least for oligomers up to the trimer. Prior work has reported that the intrachain charge transport mechanism for  $\pi$ -conjugated molecules switches from tunneling to multistep hopping for distances  $>4$  nm,<sup>18</sup> though this transition is not observed in our experiments.

To further explore the role of molecular structure on single molecule conductance, we sought to compare the charge transport properties of DPPTT oligomers to oligothiophenes. Here, we synthesized bithiophene (2T) and DPPT, where DPPT contains only a single thiophene unit linked to the DPP

core (instead of two thiophene units for DPPTT), and we determined the single molecule conductance for both molecules (Figure S20). We found that DPPT and 2T exhibit similar levels of conductance, around  $\sim 10^{-2.6} G_0$ , though the conductance of quaterthiophene (4T) decreases to  $\sim 10^{-4} G_0$  upon addition of two thiophene groups. In the context of oligothiophene molecules (2T and 4T), these results can be rationalized by considering the length-dependent exponential decay of conductance for electron tunneling. However, upon inserting the acceptor group DPP in between two thiophene groups 2T to yield the oligomer DPPT, quite remarkably, the conductance remains nearly unchanged while molecular length increases from 0.3 to 0.6 nm. These results suggest that electron transport is enhanced for the D–A structured oligomer. Interestingly, these trends also hold for the case for 4T and (DPPTT)<sub>1</sub> (Figures 1 and S21). In this case, the conductance of (DPPTT)<sub>1</sub> is slightly higher than that of 4T, despite the fact that (DPPTT)<sub>1</sub> has a longer molecular length than 4T. The higher conductance of the DPPTT oligomer can be attributed to the reduced band gap in the donor–acceptor structure compared to oligothiophenes.

Because molecular conductance is closely related to the frontier energy levels,<sup>28</sup> we investigated the orbital energies of three well-defined oligomers using UV–visible spectroscopy and cyclic voltammetry (CV) (Figures 3 and S22). The energy of highest occupied molecular orbital (HOMO) was calculated from the onset oxidation potential from CV, whereas the energy of the lowest unoccupied molecular orbital (LUMO) was determined from the HOMO energy and the optical bandgap calculated from UV–vis spectra. Our results show that the extended conjugation length further narrowed the energy bandgap of the three oligomers, thereby resulting in a

lower tunneling barrier and higher molecular conductance.<sup>19</sup> In all cases, experimental results generally showed good agreement with DFT simulations (B3LYP/6-31G\*\*) (Figure 3).

We further investigated the effect of applied bias on the molecular conductance for DPPTT oligomers (Figure 4). In Figure 4a, each data point is determined as the peak conductance value based on  $\sim 10\,000$  single molecule conductance traces, with the respective 2D histogram data shown in Figures S23 and S24. At low applied bias, the conductance of (DPPTT)<sub>2</sub> is smaller than (DPPTT)<sub>1</sub> because of a longer molecular length for the dimer. According to the Simmons model,<sup>29</sup> a lower bias generally results in a lower probability for electron tunneling through a molecule, thereby resulting in smaller conductance values. Indeed, this behavior is generally observed for both (DPPTT)<sub>1</sub> and (DPPTT)<sub>2</sub> but only at low applied biases. Remarkably, at high applied bias (750 mV), the conductance of (DPPTT)<sub>2</sub> is an order of magnitude larger than that of (DPPTT)<sub>1</sub>. This result is unexpected and directly reveals the voltage-dependent response of D–A oligomers. In addition, we further explored the voltage-dependent conductance trends for (DPPTT)<sub>3</sub> (Figure S25). Interestingly, similar to the dimer, we observe an increase in the conductance of (DPPTT)<sub>3</sub> at high bias (>750 mV) compared to conductance at low bias. However, the average conductance of (DPPTT)<sub>3</sub> at an applied bias of 750 mV is comparable to that of the monomer DPPTT but less than that of the dimer (DPPTT)<sub>2</sub> at the same bias. Remarkably, our results show a further increase of in the conductance of the trimer (DPPTT)<sub>3</sub> at an even higher applied bias of 1000 mV.

To understand the voltage-dependent conductance response of DPPTT oligomers, we determined the Landauer transmission function for Au–molecule–Au junctions using nonequilibrium Green's function/DFT simulations (NEGF-DFT) (Supporting Information). The transmission as a function of energy relative to the Fermi energy (between  $-1.5$  to  $1.5$  eV) and local transmission at the Fermi energy level of both molecules are shown in Figure 4d. In particular, the transmission of (DPPTT)<sub>1</sub> near the Fermi energy level is 1 order of magnitude higher than that of (DPPTT)<sub>2</sub>, suggesting a higher conductance of (DPPTT)<sub>1</sub>, which is consistent with the experimental data shown in Figure 4a. For (DPPTT)<sub>1</sub>, the peaks in the transmission function around  $-0.7$  and  $+0.5$  eV represent charge transport through the HOMO and LUMO levels, respectively. However, the transmission function for (DPPTT)<sub>2</sub> exhibits multiple peaks around  $-0.8$ ,  $-0.5$ ,  $0.4$ , and  $0.7$  eV, which correspond to charge transport through the HOMO–1, HOMO, LUMO, and LUMO+1 energy levels, respectively.

The voltage-dependent conductance experiments reveal several interesting results for DPPTT oligomers. In general, single molecule conductance increases upon increasing applied bias for these materials. However, our results show unexpected voltage-dependent behavior for D–A oligomers. At low applied bias (<500 mV), the conductance of (DPPTT)<sub>2</sub> is smaller than that of (DPPTT)<sub>1</sub>. However, at high applied bias (750 mV), the conductance of (DPPTT)<sub>2</sub> is an order of magnitude larger than that of the shorter oligomer (DPPTT)<sub>1</sub>. Moreover, the conductance of the trimer (DPPTT)<sub>3</sub> is larger than the conductances of the shorter oligomers. These results can be understood using molecular modeling by considering the energy-dependent Landauer transmission function obtained from DFT simulations. The relatively high conductance

of (DPPTT)<sub>2</sub> at high bias can be attributed to charge transport through HOMO–1/LUMO+1 levels, as evidenced by the additional peaks in the transmission function for (DPPTT)<sub>2</sub> compared to the shorter oligomer (DPPTT)<sub>1</sub>. Recent single molecule conductance experiments on similar but chemically distinct D–A oligomers also observed a bias-dependent conductance,<sup>20</sup> suggesting that enhanced conductance at high bias could be attributed to resonant transport in these materials. Taken together, these results reveal that intrachain charge transport can be controlled by modulating the applied bias in D–A oligomers, which can be understood in the context of an energy-dependent transmission probability.

In this work, we studied the intrachain charge transport of sequence-defined D–A oligomers. Our results show that DPPTT oligomers are conductive over relatively long molecular extensions >2 nm using an STM-BJ technique. The intrachain charge transport mechanism in DPPTT oligomers (up to the trimer) occurs by tunneling with a conductance decay constant of  $1.1\text{ nm}^{-1}$ , which is generally smaller compared to other conventional  $\pi$ -conjugated molecules such as oligothiophenes. Indeed, our single molecule experiments do not show evidence of a tunneling to charge hopping transition, at least for oligomers of DPPTT up to the trimer. Optical and electrical measurements provide further evidence that DPPTT oligomers have a narrow band gap, which can be attributed to the donor–acceptor molecular structure in the polymer backbones. Remarkably, DPPTT oligomers were found to exhibit a strong voltage-dependent conductance response. The voltage-dependent response for D–A oligomers was unexpected but can be understood in the context of multiple electron transport pathways using molecular modeling and DFT simulations. Overall, this work advances our fundamental understanding of intrachain charge transport through D–A molecules based on DPP acceptor moieties, which may be useful for future design of D–A materials.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b00050.

Description of chemical synthesis, chemical and physical characterization of DPPTT oligomers, experimental details on STM-BJ, NEGF/DFT simulation methods, electrochemical characterization, supporting text, supporting figures (PDF)

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### Author Contributions

All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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