Synthesis of Anthradithiophene Containing Conjugated Polymers via a Cross-coupling Strategy

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New conjugated polymers that incorporate dihexylanthradithiophene (DHADT) in the main chain were prepared by Stille and Sonogashira cross-coupling polymerization reactions. The polymerization chemistry is enabled by a soluble 5,11-dibromodihexylanthradithiophene monomer that is capable of cross-coupling reactions. Four readily soluble DHADT containing co-polymers were prepared and characterized experimentally and computationally. These polymers possess HOMO energies of -5.18 eV to -5.43 eV and LUMO energies of -3.0 eV to -2.82 eV. The notable optical features include broad absorption and band gaps ranging from 1.62 eV to 2.15 eV.

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Synthesis of Anthradithiophene Containing Conjugated Polymers via a Cross-coupling Strategy

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ABSTRACT
New conjugated polymers that incorporate dihexylanthradithiophene (DHADT) in the main chain were prepared by Stille and Sonogashira cross-coupling polymerization reactions. The polymerization chemistry is enabled by a soluble 5,11-dibromodihexylanthradithiophene monomer that is capable of cross-coupling reactions. Four readily soluble DHADT containing co-polymers were prepared and characterized experimentally and computationally. These polymers possess HOMO energies of -5.18 eV to -5.43 eV and LUMO energies of -3.0 eV to -2.82 eV. The notable optical features include broad absorption and band gaps ranging from 1.62 eV to 2.15 eV.

INTRODUCTION
Pentacenes and their isoelectronic heteroacene analogues have long been investigated for their applications as optoelectronic materials in organic field effect transistors, organic photovoltaics and organic light emitting diodes.\(^1\)\(^-\)\(^3\) Despite pentacene-based materials having high hole carrier mobilities, their poor photostability and solution processability have limited their applications in conjugated polymer materials and have led to the investigation of alternative thiophene-fused polycyclic aromatic hydrocarbons. Anthradithiophenes (ADTs) in particular have been developed for their isoelectronic character with pentacenes.\(^4\)\(^-\)\(^6\) ADTs have shown promise owing to their higher stability and solubility compared to pentacenes.\(^7\) The lowered HOMO levels are owed to the peripherally fused thiophene rings that impart greater stability in ADT systems by inducing loss of aromaticity that hinders endo-peroxide formation at the central 5,11 positions of ADT.\(^4\)\(^,\)\(^8\) ADT derivatives with hydrocarbon side chains\(^4\)\(^,\)\(^9\) have imparted even more solubility and provide a potential building block for conjugated polymers. However, in
relation to pentacene-based polymers, \textsuperscript{10-12} even fewer conjugated polymers containing the more stable ADT derivatives have been prepared. \textsuperscript{13-17}

Here we report the synthesis of a new series of conjugated copolymers (1-4, Figure 1) that are accessible through a metal catalyzed cross-coupling reaction at the 5 and 11 positions of dihexylantrathadiophene (DHADT). This strategy is different than the traditional method to create 5,11-functionalized ADT polymers, which rely on nucleophilic substitutions on anthradithiophenequinones. \textsuperscript{18,19} Co-polymers 1 and 2 were prepared by a Sonogashira cross-coupling polymerization while copolymers 3 and 4 were prepared using Stille cross-coupling reactions of stannanes. These metal catalyzed transformations were possible owing to our recent report of a soluble and isomerically pure 5,11-dibromodihexylanthradithiophene 5 (Scheme 1). \textsuperscript{20} The halogenated ADT monomer provides alternative reaction pathways to enlarge the library of possible coupling partners and to expand the possible aryl substituents (e.g., ester groups) that would not be compatible with the traditional nucleophilic substitutions pathway. An initial version of this work was deposited to ChemRxiv on July 23, 2020. \textsuperscript{21}

RESULTS AND DISCUSSIONS

Two new ethynylene containing polymers were prepared via a Sonogashira cross-coupling polymerization between 5 and two bis-ethynylene containing monomers, 1,4-bis((2-ethylhexyl)oxy)-2,5-diethynylbenzene 6 and 9,9-didodecyl-2,7-diethynyl-9H-fluorene 7 (Scheme 1). The polymerization employed the catalyst system of Pd(PPh\textsubscript{3})\textsubscript{4} and CuI in toluene and diisopropyl amine. Precipitates of sharp purple and dark maroon colored materials were obtained for polymers 1 and 2, respectively. We found that long reaction times of up to five days were required to access reasonable molecular weight polymers (M\textsubscript{n} = 9-16 kDa, Table 1). Polymers 3 and 4 were synthesized with commercially available stannane monomers by the employment of Stille coupling reaction conditions. The catalyst system employed Pd\textsubscript{2}(dba)\textsubscript{3} with P(o-Tol)\textsubscript{3} in toluene at 100 °C under argon for five days. The polymers were precipitated and filtered to afford 3 and 4 as brick red colored solids with molecular weights (M\textsubscript{n} \sim 4 kDa) that were less than the ethynylene containing derivatives.
The diffused reflectance absorption spectra of polymer (1-4) are shown in Figure 2. The optical gaps of the Sonogashira cross-coupled copolymers (1 and 2) were lower than the Stille cross-coupled copolymers (3 and 4). While 1 and 2 had optical gaps of 1.62 eV and 1.84 eV; polymers 3 and 4 possessed optical gaps of 2.13 and 2.15 eV, respectively. This considerable difference suggests better interchain delocalization between monomers in 1 and 2. The steric encumbrance of the aryl-aryl linkages of 3 and 4 limits the coplanarity of the aromatic residues more so than the ethynylene containing polymers 1 and 2. Overall, these band gap values are smaller than the isoelectronic pentacene containing conjugated polymeric analogues\textsuperscript{10} and similar to other reported ADT containing polymers.\textsuperscript{13,14}

Cyclic voltammetry (CV) of polymer films coated on a glassy carbon working electrode were measured in acetonitrile (Figure 3). All oxidation and reduction transitions were irreversible for all polymers. Using the onset of oxidation and reduction in the CV, the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular (LUMO) orbitals were calculated using ferrocene as an internal standard (Table 1). The HOMO energies were found to vary between -5.14 eV and 5.45 eV. The LUMO energies were found to vary between -2.7 eV and -2.82 eV.

![Figure 2. Diffused reflectance absorption spectra of polymers 1-4.](image)

![Figure 3. Cyclic voltammograms of thin films of polymer 1-4 in 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF\textsubscript{6}) in acetonitrile with glassy carbon working electrode, platinum counter electrode and Ag/AgCl reference electrode. Scan rate of 100 mV/s. Ferrocene was used as internal standard and referenced to 0 V.](image)

Table 1. Summary of Molecular Weights and Optoelectronic Properties of Polymers 1-4\textsuperscript{a}

|   | M\textsubscript{n} | M\textsubscript{w} | PDI | E\textsubscript{ox/onset} (V) | E\textsubscript{red/onset} (V) | HOMO (eV) | LUMO (eV) | E-chem gap (eV) | Optical gap (eV) |
|---|-----------------|-----------------|-----|-----------------|-----------------|------------|------------|----------------|-----------------|
| 1 | 15,800          | 56,400          | 3.6 | 0.38            | -1.80           | -5.18      | -3.00      | 2.18           | 1.62            |
| 2 | 8,600           | 29,400          | 3.4 | 0.34            | -1.80           | -5.14      | -3.00      | 2.14           | 1.84            |
| 3 | 4,200           | 6,900           | 1.7 | 0.65            | -2.09           | -5.45      | -2.71      | 2.74           | 2.13            |
| 4 | 4,000           | 7,700           | 1.9 | 0.63            | -1.98           | -5.43      | -2.82      | 2.61           | 2.15            |

\textsuperscript{a}Potentials are measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Figure 3). E\textsubscript{ox/onset} is the oxidation onset potential and E\textsubscript{red/onset} is the reduction potential onset. The redox potential onsets were used to calculate HOMO and LUMO via ferrocene standard in vacuum (4.8 eV). The Mn, Mw and Polydispersity PDI values were measured with GPC with THF as eluent and polystyrene standard.
The geometries of the copolymer repeat units of 1-4 were optimized using density functional theory with the B3LYP functional and 6-311G(d,p) basis set (Figure 4). Solvent free default convergence criteria were used to calculate the energy minimized structures. The optimized geometries suggest the HOMO and LUMO contours are largely concentrated on the DHADT unit with some delocalization at the adjoining monomers in the ethynylene containing polymers 1 and 2. Negligible probability for the HOMO or LUMO contours was found on the dithiophene monomers in copolymers 3 and 4. The minimized geometries confirm that the ethynylene containing polymers 1 and 2 can possess a more planarized structure and therefore enable significant overlapping of the frontier molecular orbitals (FMOs). In contrast, the monomers in the Stille copolymers 3 and 4 exhibit orthogonal geometry inhibiting the overlap of FMOs and lead to weak delocalization of the electronic cloud. These findings are substantiated by the diffused reflectance spectra (Figure 2) of copolymer 1-4 showing low energy absorption onsets and broad band absorption for copolymer 1-2 and relatively higher energy onsets for copolymer 3 and 4. The structural optimization of copolymer units 1-4 was followed by the UV-Vis spectra determination utilizing CAM-B3LYP/6-311G(d,p) (Supporting Information). The calculated $\lambda_{max}$ values for the UV-vis spectra generally corroborated the experimental results. Copolymers 1 and 2 were found to be red-shifted in relation to copolymers 3 and 4.

In conclusion, we have synthesized two new classes of conjugated co-polymers incorporating DHADT. The dibrominated ADT monomer provides an alternative synthetic route to make soluble conjugated polymers. The readily soluble behavior of these polymers in almost all the organic solvents make them strong candidates for solution processable device applications.

![Figure 4. B3LYP/6-311g(d,p) calculated HOMO and LUMO contours polymers 1-4.](image-url)
Acknowledgments.

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Figure SI1. The B3LYP/6-311g(d,p) DFT minimized structures of polymers 1-4 (with methyl substituents replacing alkyl chains and polymeric connectivity).
Figure S2. UV-Vis of polymers 1-4 in dichloromethane.

Figure S3. Calculated absorption spectra of polymers 1-4 using Cam-B3LYP/6-311G(d,p).
**Polymer 1.** In a glove box were combined 5 (16 mg, 0.025 mmol), 6 (9 mg, 0.025 mmol), Pd(PPh₃)₄ (2.6 mg, 2.2 µmol), CuI (.49 mg, 2.6 µmol), diisopropylamine (240 µl) in toluene (1 ml) in a pressure sealed tube. The contents of the sealed tube were stirred at 80 °C for five days in the absence of light. The reaction mixture was cooled to room temperature and poured in cold methanol (10 ml). The precipitates were filtered and washed with methanol (10 ml) to give 1 as a purple solid (19 mg 76%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.57 – 8.14 (m, 4H), 6.64 (m, J = 93.5, 85.8 Hz, 6H), 3.36 (m, J = 66.2 Hz, 4H), 2.19 (s, 4H), 1.37 (s, 1H), 0.85 (s, 36H), 0.57 (s, 6H), 0.12 (s, 12H). Mn: 15,800 Da; PDI: 3.56.

**Polymer 2.** In a glove box were combined 5 (10 mg, 0.017 mmol), 7 (9 mg, 0.017 mmol), Pd(PPh₃)₄ (1.968 mg, 1.707 µmol), CuI (0.32 mg, 1.7 µmol), diisopropylamine (240 µl) in toluene (1 ml) in a pressure sealed tube. The contents of the sealed tube were stirred at 80 °C for five days in the absence of light. The reaction mixture was cooled to room temperature and poured in cold methanol (10 ml). The precipitates were filtered and washed with methanol (10 ml) to give 2 as a maroon solid (13 mg 68%). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.37 (s, 2H), 8.23 (s, 2H), 7.05 – 6.92 (m, 22H), 6.88 – 6.73 (m, 28H), 6.53 (s, 2H), 2.34 – 2.18 (m, 8H), 1.04 (s, 88H), 0.57 (m, J = 24.1 Hz, 136H), 0.25 (d, J = 12.4 Hz, 61H). Mw: 8,600 Da; PDI: 3.41.

**Polymer 3.** In a glove box were combined 5 (10 mg, 0.016 mmol), 8 (14 mg, 0.016 mmol), Pd₂(dba)₃ (1.5 mg, 1.6 µmol) and p(o-Tol)₃ (1.5 mg, 4.9 µmol) in 2 mL toluene in a sealable tube. This mixture was stirred at 100 °C for 5 days in the absence of light. The reaction mixture was cooled down to room temperature and precipitation was carried out in methanol. The precipitates were filtered and washed with methanol and hexane and gave 3 and a brick red solid (20 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.09
Polymer 4. In a glove box were combined 5 (10 mg, 0.016 mmol), 9 (14 mg, 0.016 mmol), \( \text{Pd}_2(\text{dba})_3 \) (1.5 mg, 1.6 \( \mu \)mol) and \( \text{p(o-Tol)}_3 \) (1.5 mg, 4.9 \( \mu \)mol) in 2 mL toluene in a sealable tube. This mixture was stirred at 100 °C for 5 days in the absence of light. The reaction mixture was cooled down to room temperature and precipitation was carried out in methanol. The precipitates were filtered and washed with methanol and hexane and gave 4 and a brick red solid (19 mg, 73%). \(^1\)H NMR (400 MHz, \( \text{CD}_2\text{Cl}_2 \) δ 6.56 (m, 4H), 6.43 (m, 2H), 6.28 (m, 6H), 1.98 (m, 8H), 0.71 (s, 32H), 0.37 (s, 14H), -0.00 (s, 12H). Mw: 4000 g/mol; PDI: 1.93.
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| C       | 2.99997195| -0.19664051|  3.73868009 |
| C       | 3.37715567|  0.46289104|  4.94389571 |
| C       | 4.13680759|  1.58100692|  4.74631208 |
| S       | 4.40007288|  1.83983826|  3.03914791 |
| H       | 2.40563132| -1.10036704|  3.70744477 |
| H       | 3.09460017|  0.11561208|  5.92995904 |
| C       | 4.70260802|  2.51684472|  5.77082581 |
| H       | 5.79438091|  2.56769967|  5.71860416 |
| H       | 4.31908566|  3.53429679|  5.64875467 |
| H       | 4.43039607|  2.17455060|  6.77130604 |
| C       | 1.30949228| -3.18274973| -6.13284824 |
| H       | 1.69903427| -4.19867466| -6.01733631 |
| H       | 0.21833760| -3.23971517| -6.07558512 |
|   |   |   |   |
|---|---|---|---|
| H | 1.57510729 | -2.83402502 | -7.13289248 |
| C | -3.70459614 | 3.98572414 | -0.72279570 |
| C | -4.51482032 | 2.91775349 | -0.41549375 |
| C | -3.97915383 | 1.62376657 | -0.14181710 |
| C | -2.53486668 | 1.46082385 | -0.17830170 |
| C | -1.71311163 | 2.57972083 | -0.51050275 |
| C | -2.28279561 | 3.79194117 | -0.77262262 |
| C | -4.80400648 | 0.51802461 | 0.16766311 |
| C | -1.96090910 | 0.20624274 | 0.11234970 |
| C | -2.77887989 | -0.88899155 | 0.45912411 |
| C | -4.22052575 | -0.72807901 | 0.49447367 |
| C | -5.01608944 | -1.84931755 | 0.87290740 |
| H | -6.09140292 | -1.75047077 | 0.93015989 |
| C | -4.44844373 | -3.06283112 | 1.18712298 |
| C | -3.02633333 | -3.20081898 | 1.12626011 |
| C | -2.21046249 | -2.15859554 | 0.77706321 |
| H | -5.58233520 | 3.08087226 | -0.36860546 |
| H | -0.64017374 | 2.44898071 | -0.54750788 |
| H | -1.13609727 | -2.27687724 | 0.73751984 |
| C | -5.08413422 | -4.29403294 | 1.58997169 |
| C | -4.22471535 | -5.31232827 | 1.82145375 |
| S | -2.53181293 | -4.84118560 | 1.56223098 |
| H | -6.15687876 | -4.39897834 | 1.69768331 |
| C | -3.01236121 | 6.15643494 | -1.28945442 |
| C | -4.06511639 | 5.35062134 | -1.02282986 |
| S | -1.46035166 | 5.29756312 | -1.19210251 |
| H | -5.08918233 | 5.70350467 | -1.03599591 |
| C | -3.02485498 | 7.61059798 | -1.63726803 |
| H | -2.45930887 | 8.20067650 | -0.90928978 |
| H | -2.57867370 | 7.79058164 | -2.62039315 |
| H | -4.05035139 | 7.98416553 | -1.65526206 |
| C | -4.53992511 | -6.71065174 | 2.24703975 |

SI16
Coordinates for DFT Calculated Structure of 4
Job type: Geometry optimization
Method: B3LYP
Basis set: 6-311G(d,p)
Number of basis functions: 1216
Multiplicity: 1
Total Energy: -4957.1153304
Imaginary Frequencies: 0
|   |    X    |    Y    |    Z    |
|---|--------|--------|--------|
| H | -7.53809350 | 2.23631653 | -0.82834163 |
| H | -2.55876976 | 2.22101391 | -1.10029741 |
| H | -2.47078051 | -2.59003227 | -0.05750510 |
| C | -6.13168521 | -5.10290037 | 0.75686891 |
| C | -5.15300683 | -6.02148220 | 0.92173666 |
| S | -3.53371951 | -5.34055110 | 0.65650611 |
| H | -7.18174517 | -5.33974505 | 0.87804230 |
| C | -5.37193591 | 5.64787163 | -1.61858386 |
| C | -6.31574798 | 4.70878242 | -1.38091189 |
| S | -3.72714407 | 4.97828599 | -1.58519174 |
| H | -7.37474294 | 4.93596527 | -1.36335702 |
| C | -5.56490881 | 7.10537442 | -1.89104743 |
| H | -5.05918791 | 7.72266090 | -1.14193940 |
| H | -5.16343480 | 7.38585069 | -2.86988654 |
| H | -6.62781333 | 7.35333418 | -1.87528593 |
| C | -5.29071133 | -7.46608523 | 1.28207871 |
| H | -4.87265674 | -8.11373352 | 0.50506057 |
| H | -4.76783614 | -7.69701565 | 2.21549024 |
| H | -6.34391873 | -7.72314986 | 1.40924795 |
| C | -7.96364319 | -0.23697700 | -0.42099813 |
| H | -8.36111896 | 0.07020345 | 0.55361774 |
| H | -8.37324739 | 0.44158691 | -1.16952408 |
| H | -8.36754572 | -1.22239929 | -0.64466118 |
| C | 3.76505876 | 0.42420120 | 1.43899005 |
| C | 4.54633972 | 0.16103808 | 0.27453371 |
| C | 3.90712030 | -0.15000821 | -0.94115810 |
| C | 2.51264979 | -0.18618725 | -0.93736912 |
| C | 1.73240751 | 0.07659569 | 0.22699680 |
| C | 2.37116506 | 0.38809806 | 1.44277889 |
| C | 6.21566686 | 0.57228315 | 1.90257582 |
| C | 5.94380125 | 0.26264190 | 0.58543577 |
| C | 0.33314520 | -0.02453446 | -0.08158497 |
|   |      |      |      |
|---|------|------|------|
| H | 8.00116313 | 0.89817299 | 3.18830253 |
| C | 9.88255764 | 0.42953300 | 1.04321857 |
| H | 10.27729894 | -0.54365851 | 0.73563218 |
| H | 10.25057025 | 1.17433133 | 0.33092355 |
| H | 10.30161776 | 0.66688057 | 2.02302670 |
