Conjugated Ladder Polymers by a Cyclopentannulation Polymerization

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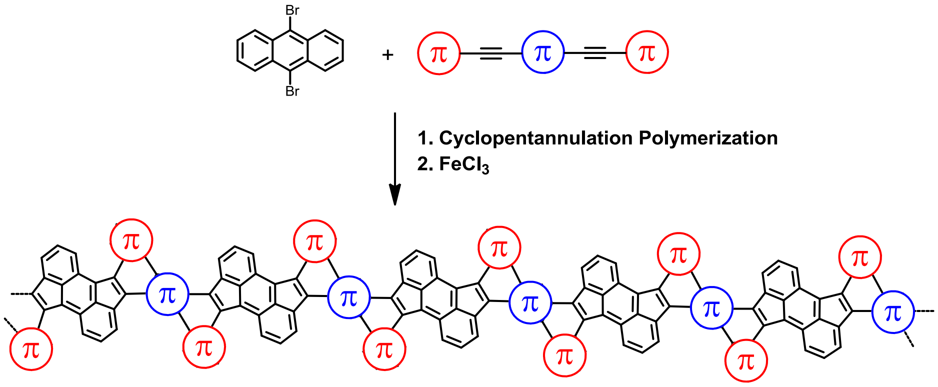
ABSTRACT: We report a non-traditional synthesis of cyclopentafused-polycyclic aromatic hydrocarbon embedded ladder polymers using a palladium catalyzed cyclopentannulation polymerization followed by a cyclodehydrogenation reaction. Donor-acceptor type polymers containing a cyclopenta[hi]aceanthrylene acceptor groups can be synthesized by a palladium catalyzed copolymerization between 9,10-dibromoanthracene and a variety of bis(arylethynyl)arenes to give polymers with molecular weights (M_n) of 9-22 kDa. The bis(arylethynyl)arenes were composed of benzene, thiophene, or thieno[3,2-b]thiophene moeities, which provided access to a series of four donor-acceptor copolymers. The polymers were subjected to cyclodehydrogenation with $FeCl_3$ to access rigid ladder type polymers with the conversion investigated by ^{13}C NMR of isotopically labelled polymers.. The ladder polymers possess broad UV-Vis absorptions, narrow optical band gaps of 1.17 – 1.29 eV, and are p-type semiconductors in organic field effect transistors.

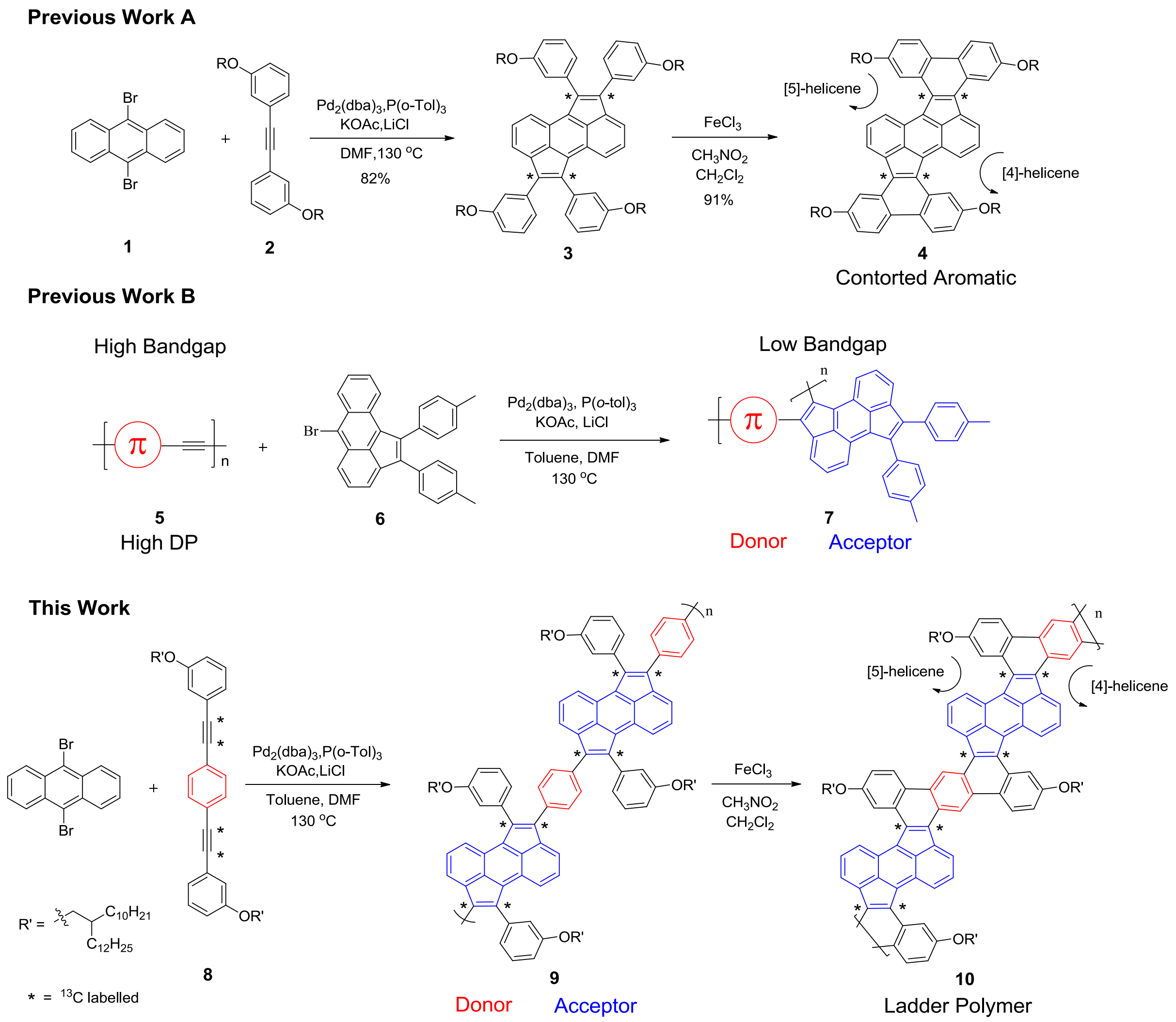


Introduction

Conjugated polymers (CPs) are attractive components for organic electronic devices owing to their broad light absorption, tunable emission, and charge transport capabilities.[1,2] Among conjugated polymers, ladder-type polymers that contain annulated π-conjugated frameworks provide opportunities for enhanced conjugation and useful properties due to their rigid coplanar structures.[3–7] The doubly fused linkages eliminate bond rotations between adjoined aryl groups and often provide increased thermal stability and enhanced π–π stacking interactions.[8–23] This feature can lead to advantageous properties such as narrow band gaps and high charge carrier mobilities.[24–29] Therefore, CP ladder polymers are prime targets for organic electronic devices including organic thin film transistors (OTFTs), organic light emitting diodes (OLEDs), and optically pumped lasers.[30–34] Unique methods to create new materials based on ladder polymers are therefore of considerable interest in an effort to seek out improved device stabilities and performance.

Here we report a method to synthesize rigid ladder-type polymers via a cyclodehydrogenation reaction of donor – acceptor (D-A) polymers that are initially prepared by a distinctive palladium catalyzed cyclopentannulation polymerization.[35] The new polymerization conditions diverge from traditional synthetic methods for donor-acceptor polymers that involve transition metal-catalyzed cross-couplings of metalated (Sn, Zn, Mg, boronate, etc) and halogenated monomers.[36,37] In this contribution, the strategy is reminiscent of direct arylation polymerizations (DARP) that utilize C-H activation chemistries to synthesize CPs in an atom-economical manner while producing minimal metal-containing byproducts.[38–42] In contrast to C-H activation, the present work utilizes palladium catalyzed addition across an ethynylene bond. Metal-catalyzed annulation chemistry applied to build up polymeric materials in a single step are less common with more recent annulation-based examples being shown to access polynorboranes[43], nanographenes,[23] as well as new poly(tetraarylethene)s.[44–46]

We have recently investigated new methods to synthesize cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) through adaptation of previous palladium-catalyzed cyclopentannulation chemistries.[47–51] Our new methodologies have been applied to give both small molecule derivatives as well as donor-acceptor copolymers from poly(arylene ethynylene) polymer precursors (Scheme 1).[35,52–54] As an example, the reaction of 9,10-dibromoanthracene **1** with a diarylethynylene **2** in presence of $Pd_2(dba)_3$, P(o-



Scheme 1: Previous methodologies to contorted aromatics and donor-acceptor copolymers using cyclopentannulation reactions (top). Combination of those methodologies lead to the current work that can access ladder-type polymers (bottom).

Tol)$_3$, KOAc and LiCl in DMF at 130 °C gives 1,2,6,7-tetraarylcyclopenta[*hi*]aceanthrylenes **3** that can be cyclodehydrogenated with $FeCl_3$ to give tetrabenzo[*f*,*h*,*r*,*t*]rubicenes **4**. Owing to the helicene-like character in **4**, the compounds are contorted and provide considerably more soluble materials than similar sized, flat PAH molecules.[35] With these results, we had interest in applying the cyclopentannulation conditions to access polymeric systems and recognized that poly(arylene ethynylene) polymers **5** are essentially repeating units of **2** and should react in a similar fashion. Utilizing 6-bromo-1,2-di-p-tolylaceanthrylene **6**, which is a partially formed cyclopenta[hi]aceanthrylene, to react with the ethynylene polymer backbone provided access to a variety of donor-acceptor copolymers **7** with a repeating cyclopenta[hi]aceanthrylene acceptor units. Unfortunately, owing to the kinked nature of the polymer and the steric congestion between adjacent aryl groups, little conjugation along the backbone is possible.[54] Looking for systems that would provide extended conjugation, we considered reacting difunctional **1** with difunctional ethynylene units to give extended polymeric structures. The novelty of this research direction lies in the fact the resulting materials should provide solubility benefits owing to the contortion of the aromatic units along the backbone. Furthermore, new synthetic routes to polymeric materials with novel architectures is of fundamental interest. Thus, in this work we have first employed 1,4-bis((3-((2-decyltetradecyl)oxy)phenyl)ethynyl)benzene **8** as a difunctional monomer to copolymerize with **1** to give a repeating donor-acceptor copolymer **9**. For the polymerization, the reaction conditions were similar to our previous examples except for an extended reaction time of 3 days and toluene was mixed with DMF in a 1:1 solvent ratio to help maintain polymer solubility during the reaction. This solvent ratio was determined to be optimal after screening a variety of solvent mixtures containing the polar DMF component to find polymers with the highest molecular weights. The resulting polymer **9** has a main-chain repeating structure of phenylene and cyclopenta[hi]aceanthrylene units with appendage alkoxyphenyl groups. Owing to the lack of differentiation between the aryl substituents on the ethynylene, it should be pointed out that two regiosomers at each linkage could be formed (Supporting Information). The alkoxy groups of **9**, similar to **3**, are properly arranged *para* to a desirable ring closure to promote successful Scholl cyclodehydrogenation reactions.[35,55] Using a traditional $FeCl_3$ catalyzed Scholl reaction, we accessed the final ladder polymer structure with doubly fused aromatic linkages along the polymer backbone. The final polymer **10** is considerably less soluble than the precursor polymer **9**. This is expected as the polymer has been converted from a system that does not favor pi-pi stacking, owing to the perpendicular arrangement of the benzene rings to the cyclopenta[hi]aceanthrylene unit, to a contorted aromatic backbone that does allow pi-pi stacking albeit not as severely as a completely planar ribbon.[35]

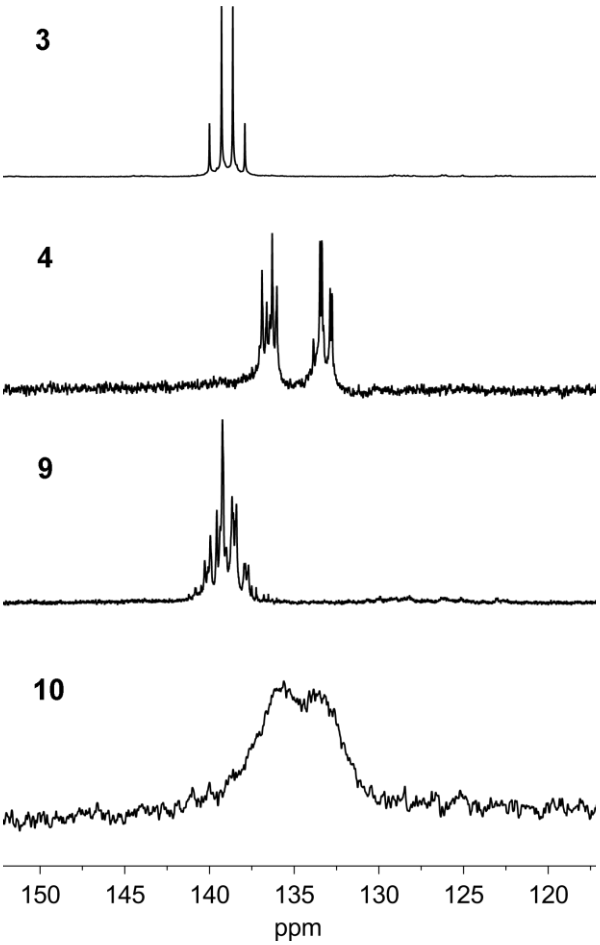


Figure 1: ^{13}C-labeled small molecules (**3** and **4**) and polymers **9** and **10**. The up-field shift in the spectra of **4** and **10**is attributed to the change in chemical environment when the labelled carbons are included in a new 6-membered ring. Difference in signal-to-noise is a result of the decreased relative solubility of **10**.

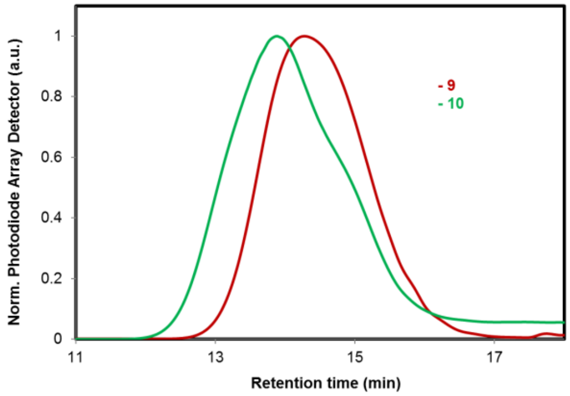
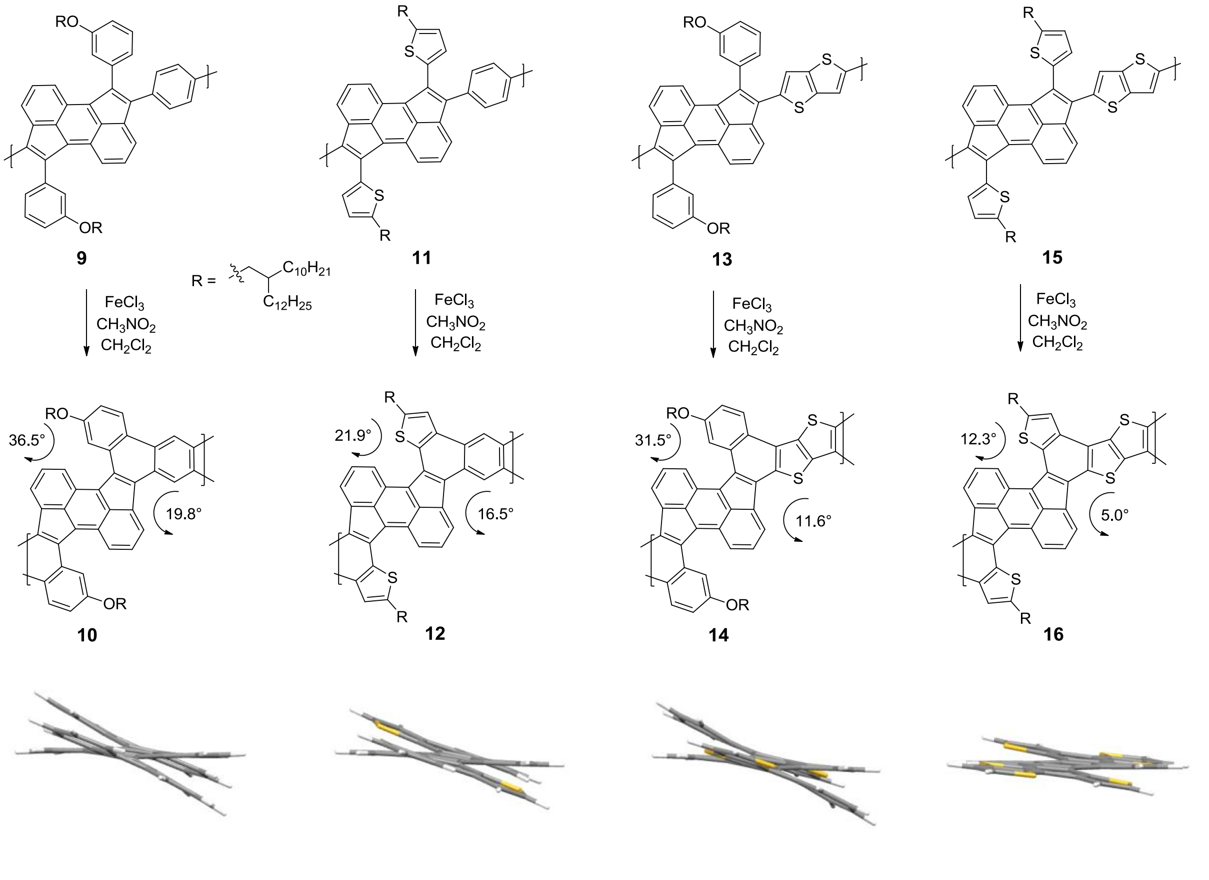


Figure 2: Room temperature GPC comparison of precursor polymer **9** (red) and ladder polymer **10** (Green). An apparent increase in molecular weight (vs. polystyrene standard) is attributed to planarization of the polymer backbone that leads to higher hydrodynamic volume or aggregated species. High temperature GPC measurements can be found in Supporting Information.

To track the polymerization and to provide evidence for the desired Scholl cyclodehydrogenation reactions, compound **8** with ^{13}C enrichment on the ethynylene carbons was prepared and incorporated into polymer **9**. The ^{13}C labels reside on the five-membered rings of the polymer (Scheme 1) and are included into a newly formed 6-membered ring in **10** after the Scholl cyclodehydrogenation. We also prepared ^{13}C enriched model compounds **3** and **4** to provide chemical shift references and to help determine conversion. Figure 1 shows the ^{13}C NMR spectra of both the model compounds (**3** and **4**) and polymeric compounds (**9** and **10**). A set of signals centered at 139.4 ppm of polymer **9** represents the unsymmetrically substituted alkene linkages in the polymer backbone. After the Scholl cyclodehydrogenation, the ^{13}C signals are broadened and shifted up-field to around 134.8 ppm. The magnitude of the chemical shift matches that of the model compound **4** upon cyclodehydrogenation and also matches the general two-signal trend. We attribute the observed peak shift to the new chemical environment in the 6-membered ring structure. Although it is difficult to definitively provide a conversion owing to the broad nature of the signal of **10**, it is apparent that most, if not all, of the ring closures have occurred in the polymer backbone. The broadening of the signal and the dramatic change in signal-to-noise between the spectra of **9** and **10** arise owing to the reduced solubility and conformational flexibility of ladder polymer **10**.

A comparison of the room temperature gel permeation chromatography (GPC) results of **9** and **10** further infer significant structural changes upon cyclodehydrogenation (Figure 2). Precursor polymer **9**



Scheme 2: Synthesis of ladder polymers with varying composition. Splay angle of helicene segments in ladder polymers **10**, **12**, **14**, and **16** obtained from the DFT-calculated (B3LYP/6-31G**) repeat unit structures (bottom). Alternative regioisomer splay angles and structures can be found in supporting information.

gave a peak retention time coinciding with an estimated molecular weight (Mn) of 13,685 g/mol versus a polystyrene standard. Upon cyclization of the polymer backbone, the retention time was lowered and gave an estimated molecular weight of 19,735 g/mol for **10**. One possibility is that the hydrodynamic volumes (measured by GPC) increase for more rigid polymer backbones,[56] which would be consistent with planarization and rigidification in the ladder polymer structure. However, an alternative and possibly more plausible explanation is the new rigid polymers are more prone to aggregation in solution. To address these questions, the polymer set was measured in a high-temperature GPC apparatus using trichlorobenzene at 160° C. The results (supporting information) gave no clear trends in polymer molecular weight before and after cyclodehydrogenation for each of the polymer pairs tested. Although the results did not give definitive answers to the changes in GPC elution times, the results did provide further evidence for attainment of reasonable molecular weights with the polymerization strategy.

The polymerization strategy can be extended to build a library of polymer structures through variation of both the side-chain aromatic group as well as the main-chain aromatic groups attached to the cyclopenta[*hi*]aceanthrylene core. These structural changes can be accessed through modifications to the bis(arylethynyl)arene monomer at the terminal aromatic groups or the internal aromatic group, respectively. In this work, the internal aromatic group has been varied between benzene and thieno[3,2-b]thiophene and the external aromatic group between 3-((2-decyltetradecyl)oxy)benzene and 5-(2-decyltetradecyl)thiophene (Supporting Information). The four resulting polymers obtained upon polymerization of all combinations of bis(arylethynyl)arene monomers with 9,10-dibromoanthracene are shown in Scheme 2. The polymerizations give donor-acceptor polymers (**9**, **11**, **13**, **15**) with molecular weights (M_n) in the range of ~10-20 KDa. The molecular weights obtained in the thieno[3,2-b]thiophene cases were consistently higher in a series of repeated polymerizations and the thieno[3,2-b]thiophene/ thiophene functionalized polymers **15** gave the highest molecular weights. The smaller internal angles of the five-membered thiophene rings provides greater overlap between adjacent aromatic groups (than six-membered rings) and is presumably more reactive in the polymerization owing to less steric encumberment. The Scholl cyclodehydrogenation conditions were applied to the full set of polymers to give ladder polymers **10**, **12**, **14**, and **16**. Similar to **10**, all polymers showed considerably lower solubilities when converted into the ladder polymers. In fact, **16** was found to be almost completely insoluble, with minimal dissolved color only through extended heating in high boiling chlorinated solvents. The DFT calculated structure of the polymer **16** repeat unit shows a considerably more flat arrangement in comparison to benzene-containing polymers **10**, **12**, and **14** (Scheme 2). While the splay angles of the repeat unit of **10** are 36.5° and 19.8° for the 5-helicene and 4-helicene like arrangements, **16** has splay angles of 12.3° and 5.0° and represent a much flatter arrangement. Polymers **12** and **14** possess intermediary splay angles and have similar solubilities to **10**. A series of possible splay angles for a variety of regiosomers for the polymer repeat units were also calculated (Supporting Information). As expected, isomers that place the smaller thiophene or thieno[3,2-b]thiophene in the 5-helicene like arrangements give more planar arrangements.

Table 1. Summary of molecular weight and optoelectronic properties of polymers **9-16**.[a]

Polymer	M_n[a]	M_w[a]	Đ[a]	$E_{ox,onset}$ (V)[b]	$E_{red,onset}$ (V)[b]	HOMO (eV)	LUMO (eV)	λ_{onset} (nm)[c]	E_{gap}^{opt} (eV)[c]
9	13,685	22,196	1.6	0.70	-1.35	-5.50	-3.45	798	1.55
10	19,735	37,307	1.9	0.61	-1.30	-5.41	-3.50	960	1.29
11	8,600	11,891	1.4	0.50	-1.30	-5.30	-3.50	888	1.40
12	13,376	25,699	1.9	0.47	-1.07	-5.27	-3.73	897	1.38
13	15,685	28,214	1.8	0.45	-1.16	-5.25	-3.64	1015	1.22
14	17,988	42,598	2.3	0.38	-0.95	-5.18	-3.85	1056	1.17
15	21,197	72,861	3.4	0.65	-1.22	-5.45	-3.58	1040	1.19
16	-	-	-	0.56	-1.07	-5.36	-3.73	1030[c]	1.20[d]

[a] Obtained from room temperature GPC measurements. High temperature GPC can be found in supporting information). [b] Potentials are measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Figure 04). $E_{ox/onset}$ is the onset of oxidation potential, $E_{red/onset}$ is the onset of reduction potential and were used to calculate the HOMO and LUMO via ferrocene reference in vacuum (4.8 eV). [c] Optical gap obtained from film (supporting information). [d] Optical gap obtained from solution.

Although the control of the repeat unit regiochemistry would be beneficial, for example to tune the contortion along the backbone, the current methodology does not provide such abilities. Future directions that can control the regioselective additions at the metal center would be a benefit for future polymer design.

The optical and electronic properties of polymers **9-16** were significantly modulated with changing of both the backbone aromatic groups as well as the side-chain group aromatics. For example, switching of the side-chain aromatic from benzene to thiophene in **9** (798 nm) to **11** (888 nm) led to a 90 nm bathochromic shift (Table 1) in the onset of the longest wavelength absorption (λ_{onset}) in solution (Figure 3). Even more significant bathochromic shifts were found when switching the backbone aromatic group from benzene to thieno[3,2-b]thiophene. Polymer **13** (1015 nm) was shifted 217 nm relative to **9** and the all-thiophene/thieno[3,2-b]thiophene containing polymer **15** had the largest λ_{onset} at 1040 nm. Polymer films were prepared (Supporting Information) and the λ_{onset} values of the varied aromatic substituents give materials with optical band gaps of 1.19-1.44 eV (Table 1). These gaps are consistent with traditional donor-acceptor copolymers[57] that give smaller gaps with more electron rich donors or electron poor acceptors. The thieno[3,2-b]thiophene system is not only more electron rich than a simple benzene but also allows for a more coplanar arrangement between donor and acceptor owing to the smaller internal angle of the five-membered rings. Upon cyclodehydrogenation to form ladder polymers **10**, **12**, **14**, and **16** the

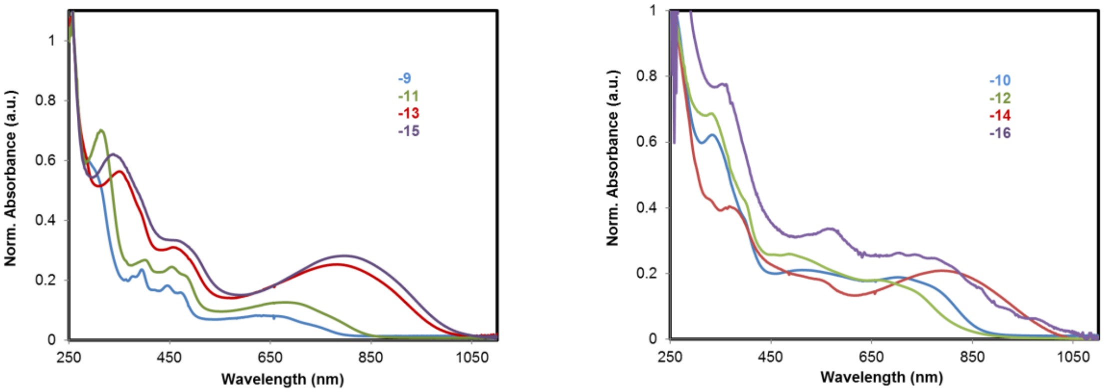


Figure 3: Solution absorption of D-A type polymers 9, 11, 13, 15 (left) and ladder polymers 10, 12, 14 16 (right).

optical band gaps were also modulated slightly in solution and in the film (Polymer **16** was too insoluble to prepare a consistent film and the solution-based λ_{onset} was used). The largest change was found for the transformation of the all benzene **9** (798 nm) to **10** (960 nm). The other ladder polymer systems showed smaller changes in the optical band gaps. Such small changes were on par with the optical changes seen in small molecule transformations as in converting **3** to **4**.[35]

Cyclic voltammetry of the polymers were obtained from spin-coated thin films on indium titanium oxide (ITO) substrates (Supporting Information). Owing to the CP-PAH character and the ability to form reduced cyclopentadienyl anions, all polymers gave relatively low-lying lowest unoccupied molecular orbitals (LUMO) of -3.45 to -3.85 eV (Table 1). As found in the absorption spectra, some modulation of the electronic properties of the polymers were found when converting the donor-acceptor copolymers into the ladder polymers, albeit small. For all the rigid ladder polymers the highest occupied molecular orbital (HOMO) was higher in energy and the LUMO was lower compared to the corresponding D-A type polymer. The resulting film-based electrochemical band gaps are considerably higher than the optical band gaps obtained. We have previously seen similar discrepancies with small molecule CP-PAHs based on cyclopenta[hi[aceanthrylenes[58,59] and believe it involves substantial differences in the exciton binding energy of these systems.[60] These energy discrepancies point to the significant influence of the five-member rings to the electronic properties in these systems.[61] For all polymer regioisomeric repeat units, the DFT-calculated HOMO and LUMO contours (Supporting Information) reside mostly on atoms that are positioned along a diagonal with inclusion of the five-membered rings. There are little contributions to the atoms outside of those rings. Higher HOMO energy levels are found for isomers that include the more electron rich thiophene or thienothiophene substituents in this diagonal arrangement. The LUMO energy levels remain mostly constant with the contour remaining on the inner cyclopenta[hi]aceanthrylene core. The modulation of the electronic properties, as well as the optical properties, between the donor-acceptor copolymers, and the ladder polymers, demonstrate the ability to modulate function through varying aromatic substitution strategies.

To investigate the molecular packing of the ladder polymers, we carried out grazing incidence wide-angle X-ray scattering (GIWAXS) measurements (Supporting Information). The 2D GIWAXS patterns of these polymers show an isotropic halo at $q \approx 1.5$ Å−1, indicating they are randomly oriented amorphous structures. The d spacing of this ring is calculated to be around 0.4 nm using the equation $d = 2\pi/q$. We assume this d spacing is from the disordered alkyl side chains instead of π-π stacking of these polymers.[62] To have a better understanding about the packing of these three polymers, we plotted in-plane 1D WAXS curve (Supporting Information). The average peak positions for **10**, **12**, and **14** are 1.43 Å^{-1} (or 0.44 nm d spacing), 1.43 Å^{-1} (or 0.44 nm d spacing) and 1.5 Å^{-1} (or 0.4 nm d spacing), respectively. Clearly, **14** has a smaller d spacing than the other two polymers. In addition, from GIWAXS images we observed another weak broad ring highlighted by red arrows for polymers **10** and **12**. By carefully looking at 1D WAXS curve, the peak position is around 0.5 Å^{-1} and 0.75 Å^{-1}, respectively, corresponding to the d spacing of ~ 1.2 nm and ~ 0.75 nm for these two polymers, which is assumed to be the size of one monomer unit. Overall, these ladder polymers showed amorphous phases similar to other known ladder polymer systems.[9] In addition, atomic force microscopy (AFM) of the case polymer films were found to be relatively rough with root-mean squared (RMS) surface roughness of **10**, **12**, and **14** to be 3.2 nm, 3.6 nm, and 3.4 nm, respectively (Supporting Information).

To tested the ladder polymers (**10**, **12**, and **14**) as active components for charge transport, we fabricated organic field effect transistors (OFETs) in a bottom-gate top-contact devices by spin coating the polymers from chloroform onto trichloro(phenethyl)silane coated silicon wafers (Supporting Information). The OFETs measured in air showed the ladder polymers to be p-type semiconductors with typical mobilities ranging from 5.1X10^{-6} cm^{2}V^{-1}s^{-1} to a maximum of 2.0X10^{-5} cm^{2}V^{-1}s^{-1}. The highest mobilities measured were found for polymer **10**. The output plots also showed diode like behavior at low gate voltage, which suggests possible ambipolar transfer characteristics; however, n-type behavior was not found at positive gate and source potentials under our experimental conditions. Overall, the mobilities were quite low, and is most likely indicative of the amorphous packing in the film.

In conclusion, we have presented a non-conventional synthetic pathway to access complex rigid ladder type polymers from simple, easily accessible, and non-metallated monomers. The palladium catalyzed annulations chemistry produces complex donor-acceptor type polymers with reasonably high molecular weights that can be further modified into rigid ladder type polymers through a $FeCl_3$ promoted Scholl cyclodehydrogenation. The resulting polymers have low optical gaps, possess low lying LUMO levels owing to the CP-PAH character, and are p-type semiconductors in OFETs. These results demonstrate that efficient annulation chemistries offer new opportunities to access complex and unique carbon frameworks that are otherwise difficult to achieve.

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