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Cyclopentannulation and cyclodehydrogenation of isomerically pure 5,11-dibromo-anthradithiophenes leading to contorted aromatics†

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Isomerically pure 5,11-dibromo-2,8-dihexylanthra[2,3-*b*:76-*b*′]dithiophene, a brominated analog of anthracenedithiophene (ADT), was prepared and utilized for a palladium catalyzed cyclopentannulation reaction with 3,3′-dimethoxy-phenylacetylene to give cyclopentannulated ADT (CP-ADTs). A further Scholl cyclodehydrogenation reaction gave contorted aromatics with large splay angles, low optical gaps, and low LUMOs.

Contorted aromatics are a class of polycyclic aromatic hydrocarbons (PAH) that contain extended pi networks yet twist out of planarity owing to intramolecular steric congestion.[1] These aromatics are rooted in the decades of research involving twisted aromatics such as helicene-based molecules.[2] Over the past decade, a re-emergence of extended pi-molecules with contorted natures have been described.[3] The major benefits of the contorted character of these compounds is that they possess a unique shape and that the non-planarity provides significant increases in solubility in comparison to similarly sized flat aromatics, therefore allowing easier characterization and processability. While the unique shapes and contortion help increase solubility, these factors do not always limit pi–pi stacking in the solid state[4] or performance in organic electronics.[5] In fact, the unique three-dimensional shapes may provide value added properties in organic electronics as non-fullerene based electron acceptors in organic photovoltaics.[6]

We recently became interested in utilizing a palladium-catalyzed cyclopentannulation to create cyclopenta-fused polycyclic aromatic hydrocarbons (*e.g.*, **1**) that could be cyclodehydrogenated to build up contorted aromatics such as 1,2,6,7-tetraarylcyclopenta[*hi*]aceanthrylenes (**2**, Fig. 1).[7] The contorted compounds contain [4]helicene-like and [5]helicene-like moieties[8] that impart contortion and splay angles of 14.3° and 36.8°, respectively. The compounds were found to be quite soluble, even with methoxy substituents, yet displayed concentration dependent aggregation in solution, and lock-and-key pi–pi stacking in the solid state.[7] We had interest in extending this methodology to elongated aromatics, and attempted to create similar contorted aromatics from our recently described 1,2,8,9-tetraaryldicyclopenta[*fg*,*qr*]pentacenes (**3**).[9] Unfortunately, we were not successful in applying a variety of well-known cyclodehydrogenation conditions to facilitate the oxidative C–C bond formation of **3** to give the desired contorted aromatics. Although we noted the cyclopenta-fused pentacene cores of **3** was more photo-oxidatively stabilized in comparison to traditional pentacenes, we feared their inherent instability may be limiting the preparation of the expanded contorted aromatics based on this strategy. To address this instability, we turned our focus from pentacene based materials to thienoacene-based materials that have also shown promise as active materials in OFETs.[10]

Anthradithiophene (ADT) is a thienoacene that is isoelectronic to pentacene, with five linearly-fused aromatic rings, yet considerably more stable to oxidative degradation.[11] ADTs were originally

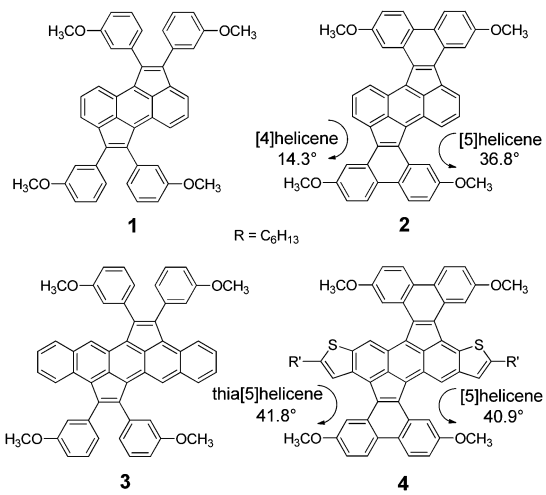

Fig. 1 Chemical structures of cyclopentannulated 'acenes' prepared previously **1–3** and in the contribution (**4**).

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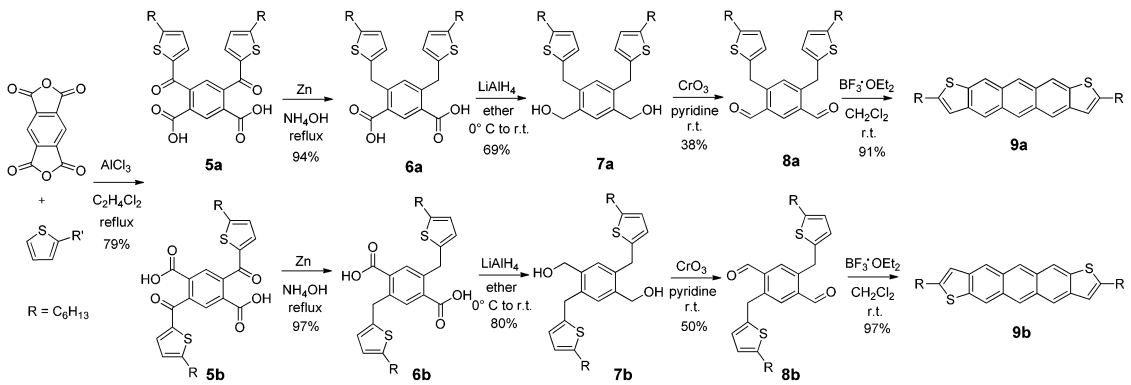
synthesized from regiorandom ADT-quinones and utilized as a mixture of *syn* and *anti*-isomers owing to the difficulties in separating the generated isomers.[11a] However, recent reports have shown that isomerically pure *syn* and *anti*-ADT derivatives can be obtained through new synthetic strategies.[12] Unfortunately, 5,11-dihalogenated ADTs, which would be useful for our desired metal-catalyzed transformations were not known at the undertaking of this project. In this contribution, we have expanded on these recent synthetic advances and have prepared isomerically pure ADT that contain two hexyl solubilizing chains. The additional solubility added to the system by the hexyl chains was then exploited to create the first known 5,11-dibromo-ADT derivatives. We then utilized these new 5,11-di-bromo-ADT derivatives as a substrate for a palladium-catalyzed cyclopentannulation that gives cyclopentafused-ADTs (CP-ADTs). Lastly, these CP-ADTs were found to successfully undergo cyclodehydrogenation to give tetraaryl[4,5:6,7:11,12:13,14]-rubiceno[2,3-*b*:10,9-*b*′]dithiophene (**4**) that is considerably contorted in structure owing to helicene-like arrangements (Scheme 1).

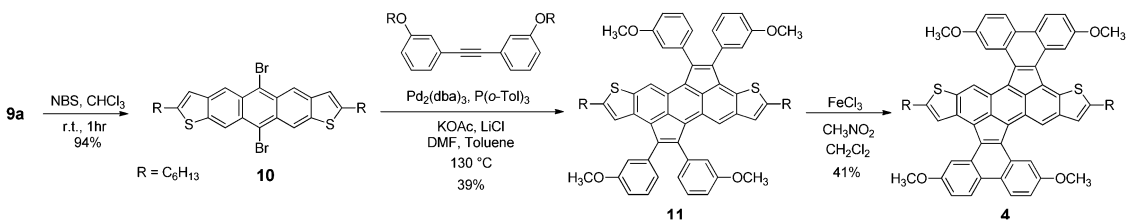
The synthesis of isomerically pure *syn*- and *anti*-2,8-dihexyl-anthradithiophene (DHADT) (**9a**, **9b**) was achieved through modification of a recently described strategy.[12d] We used 2-hexylthiophene instead of thiophene or methyl-thiophene to give access to more soluble materials *via* the more flexible hexyl chain. The initial step was a Friedel–Crafts acylation between 2-hexylthiophene and 1,2,4,5-benzenetetracarboxylic dianhydride to give a mixture of 4,6-di(5-hexylthiophene-2-carbonyl)isophthalic acid (**5a**) and 2,5-di(5-hexylthiophene-2-carbonyl)terephthalic acid (**5b**). These two isomers were separated in 79% overall yield *via* recrystallizing in 80% acetic acid by taking advantage of solubility difference between the *syn*- and *anti*-isomer. Reduction of ketone **5a,b** using Zn and NH_4OH gave **6a,b** in high yields. $LiAlH_4$ reduction of compounds **6a,b** lead to the corresponding alcohols **7a,b** that were oxidized to aldehydes **8a,b** using Collins reagent in considerably lower yields of 38% and 50%, respectively. Dehydrative cyclization and aromatization of the aldehydes using $BF_3{\cdot}OEt_2$ in dichloromethane gave the final DHADTs **9a,b**.

The synthesis of 5,11-dibromo-2,8-dihexylanthra[2,3-*b*:7,6-*b*′]-dithiophene (**10**) was initially challenging owing to the relative low solubility, even with the added solubilizing chains, and reactive nature of ADTs (*e.g.*, bromination with Br_2 was not selective). However, the desired transformation was achieved by bromination with *N*-bromosuccinimide (NBS) in highly diluted chloroform at room temperature (Scheme 2). A key preliminary step was the prolonged sonication in a large amount of solvent for complete dissolution of **9a** before functionalization.

Our recently developed palladium-catalyzed cyclopentannulation conditions were applied to the reaction between **10** and 3,3′-dimethoxyphenylacetylene. Our previous small-molecule optimized conditions[7] utilizing the catalyst system of $Pd_2(dba)_3$, $P(o\text{-Tol})_3$, and LiCl with KOAc as base in DMF solvent only led to trace amounts of product. However, using a more solubility-favorable mixture of 1 : 1 toluene : DMF as a solvent system[13] yielded 4,10-dihexyl-1,2,7,8-tetrakis(3-methoxyphenyl)cyclopenta-[6,7]aceanthryleno[4,3-*b*:8,9-*b*′]dithiophene (**11**) in 39% yield. This compound is considerably more soluble than **9a** or **10** owing to the perpendicular arrangement of the attached aryl groups. This compound (**11**) was subjected to Scholl cyclodehydrogenation conditions using $FeCl_3$ to fuse the flanking aryl rings and we were happy to find the fully ring-closed product 2,14-dihexyl-5,10,17,22-tetramethoxytetrabenzo[4,5:6,7:11,12:13,14]rubiceno[2,3-*b*:10,9-*b*′]-dithiophene (**4**) was readily formed. Compound **4** possessed good



Scheme 1 Synthesis of *syn*- and *anti*-2,8-dihexylanthradithiophene.



Scheme 2 Cyclopentannulation and Scholl cyclodehydrogenation to make contorted PAHs.

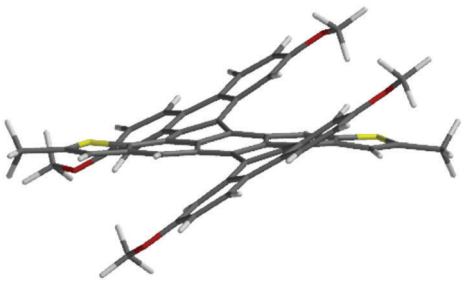


Fig. 2 The B3LYP/6-311g(d,p) DFT minimized structure of **4** (with methyl substituents on thiophene rings for clarity).

solubility in common organic solvents owing to the hexyl side-chain on thiophene rings and the contorted aromatic structure. The success of this reaction with the ADT system contrasted with our inability to form the final ring-closed structure using $FeCl_3$ in previously prepared pentacene based compounds (*e.g.*, **3**). Although, we were unable to obtain suitable crystals for single crystal analysis, we previously found that the DFT calculated structure of **2** was consistent with its crystal structure.[7] Owing to the similarities of these systems, we employed DFT to analyze the structure of **4**.

The DFT minimized structure of **4** (Fig. 2) shows that it is highly contorted owing to the interactions between the central ADT core and the outer phenanthrene units. The arrangement of fused rings gives rise to a total of four [5]helicene-like fragments[8] (Fig. 1). These bonding arrangements generate large splay angles of 41.8° and 40.9° in the coves, respectively, and are considerably larger than the splay angles in the anthracene-based contorted aromatic (**2**) that possess splay angles of 14.3° and 36.8°, respectively (Fig. 1). This higher contortion is attributed to the inclusion of two additional [5]helicene-like arrangements compared to that of **2**.

The photophysical and electrochemical properties of compounds **11** and **4** were intermediate between CP-pentacene **3** and CP-anthracene analogues **1** and **2**. One observation of note was that upon ring closure, **4** ($\lambda_{max,onset}$ ~ 830 nm) was significantly red-shifted compared to **11** ($\lambda_{max,onset}$ ~ 670 nm) (Fig. 3), while very little change in the optical gap was observed

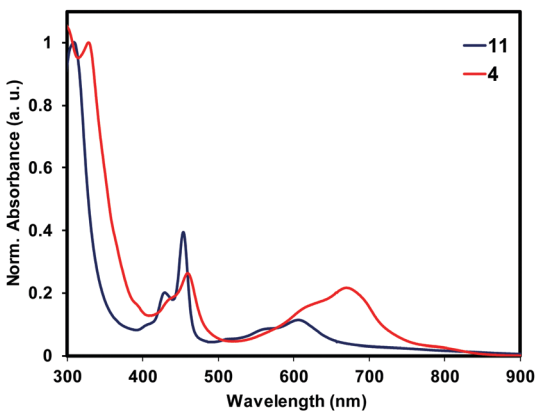


Fig. 3 UV-vis spectra of **11** (blue), and **4** (red) in chloroform.

Table 1 Summary of optoelectronic properties of **1–4**, **11**[a]

Cmpd	$E_{ox/onset}$ (V)	$E_{red/onset}$ (V)	HOMO (eV)	LUMO (eV)	E-chem gap (eV)	Optical gap (eV)
1	0.66	−1.32	−5.46	−3.48	1.98	1.63
2	0.52	−1.24	−5.32	−3.56	1.76	1.67
3	0.51	−0.99	−5.31	−3.81	1.50	1.22
11	0.43	−1.36	−5.23	−3.44	1.79	1.85
4	0.50	−1.10	−5.30	−3.70	1.60	1.50

[a] Measurements taken at sample concentration of 0.2 mM and potentials measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Fig. 4). $E_{ox/onset}$ is the onset of oxidation potential, $E_{red/onset}$ is the onset of reduction potential. HOMO and LUMO values calculated on the basis of the oxidation of the ferrocene reference in vacuum (4.8 eV).

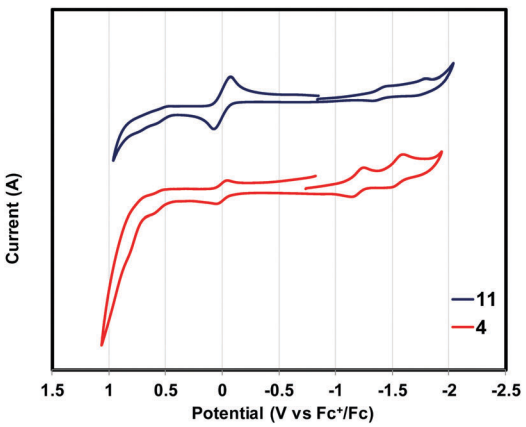


Fig. 4 Cyclic voltammetry of **11** (blue) and **4** (red) in 0.1 M tetrabutylammonium hexafluorophosphate in THF with glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 50 mV s^{-1}. Ferrocene added as internal standard and referenced to 0 V.

going from **1** to **2** (Table 1).[7] The cyclic voltammograms show that these compounds give two reversible reductions and quasi-reversible or irreversibly oxidations (Fig. 4). The redox properties were significantly modulated after the cyclodehydrogenation reactions with **4** being significantly easier to reduce (−1.10 eV) compared to non-cyclized **11** (−1.36 eV). A comparison to a ferrocene standard gave lowest unoccupied molecular orbital (LUMO) energies of −3.70 eV for **4** and −3.44 eV for **11**. In contrast the highest occupied molecular orbital (HOMO) energies were not significantly different with the HOMO energy of −5.30 eV for **4** and −5.23 eV for **11**. The photostabilities of CP-ADTs **11** and **4** were tested in comparison to TIPS-pentacene and cyclopentannulated pentacene **3** by photodegradation in an oxygenated THF solution under ambient light (ESI). We previously showed that **3** was more stable[9] than TIPS-pentacene and wanted to compare the effects of ring closure to photostability. The decomposition half-lives for each compound were obtained by monitoring the disappearance of the prominent absorption band in each compound. We found that CP-ADT **11** ($\tau_{half\text{-}life}$ = 1572 min) was more stable than our previously synthesized pentacene derivative **3** ($\tau_{half\text{-}life}$ = 824 min). This result agrees with previous stability studies of ADT compared to pentacenes.[11a]

However, upon ring closure of **11** to **4** the stability of the CP-ADT system was significantly lowered ($\tau_{\text{half-life}}$ = 367 min), which was similar to TIPS-pentacene ($\tau_{\text{half-life}}$ = 286 min). This result suggests a cause for our previous inability to isolate the Scholl cyclodehydrogenated product of **3**. Our current hypothesis is that the ring-closed product of the **3** is even more reactive than **4** and was therefore not capable of isolation. These results further demonstrate the stabilizing effect of ADT in comparison to pentacene backbones.

In conclusion, we have shown that the synthesis of hexyl-containing ADT compounds can be successfully brominated to create isomerically pure 5,11-dibromo-2,8-dihexylanthra[2,3-*b*:7,6-*b*′]dithiophene **10** that can be modified by palladium-catalyzed reactions. These dibrominated ADT compounds could provide access to newly functionalized ADTs that are incompatible with traditional nucleophilic addition reactions to ADT quinones (*e.g.*, ester functionalized nucleophiles). In this contribution, we showed that a palladium-catalyzed cyclopentannulation can lead to more stabilized CP-PAHs than the isoelectronic pentacene derivatives and that can be further modified to create significantly contorted PAH structures with reduced optical gaps and low LUMO energies.

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Conflicts of interest

There are no conflicts to declare.

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