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Orthogonal Functionalization of Cyclopenta[*hi*]aceanthrylenes

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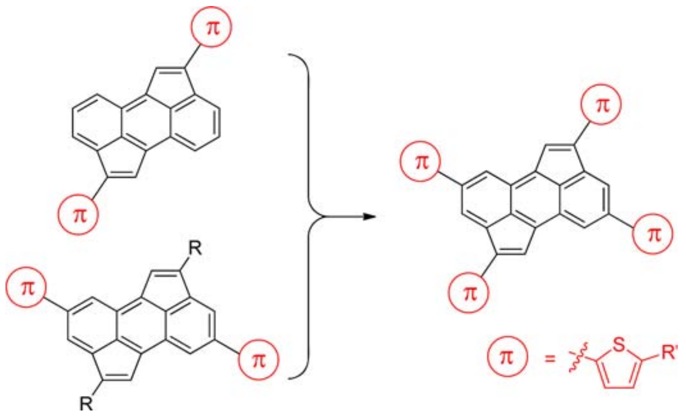
ABSTRACT



A synthetic strategy to prepare 2,7- or 4,9-functionalized cyclopenta[*hi*]aceanthrylenes that are capable of Suzuki cross-coupling reactions is demonstrated. This method has been utilized to create a series of thiophene derivatized compounds that were subsequently used to investigate the role of substitution pattern on the photophysical and electronic properties of cyclopenta[*hi*]aceanthrylenes. The orthogonal functionalization provides access to unique substitution patterns (e.g., cruciform-like architectures) and materials with small optical band gaps (1.22–1.97 eV).

Cyclopentafused-polycyclic aromatic hydrocarbons (CP-PAHs) possess unique properties including high electron affinities and interesting photophysical properties that have utility for organic electronic devices.[1] However, successful postmodification strategies that provide access to small-molecule CP-PAH conjugates have only recently been developed. New synthetic advances have led to functional CP-PAH scaffolds based on indenofluorenes,[2] corannulene,[3] pentalenes,[4] emeraldicene,[5] and cyclopenta[*hi*]aceanthrylene[6] scaffolds to name a few. Some of these systems have recently been incorporated into devices and behave as ambipolar semiconductors[6f,7] in field-effect transistors or electron acceptors (and fullerene substitutes) in organic photovoltaics.[8] There is still a critical need, however, to develop chemistry that can facilitate the creation of

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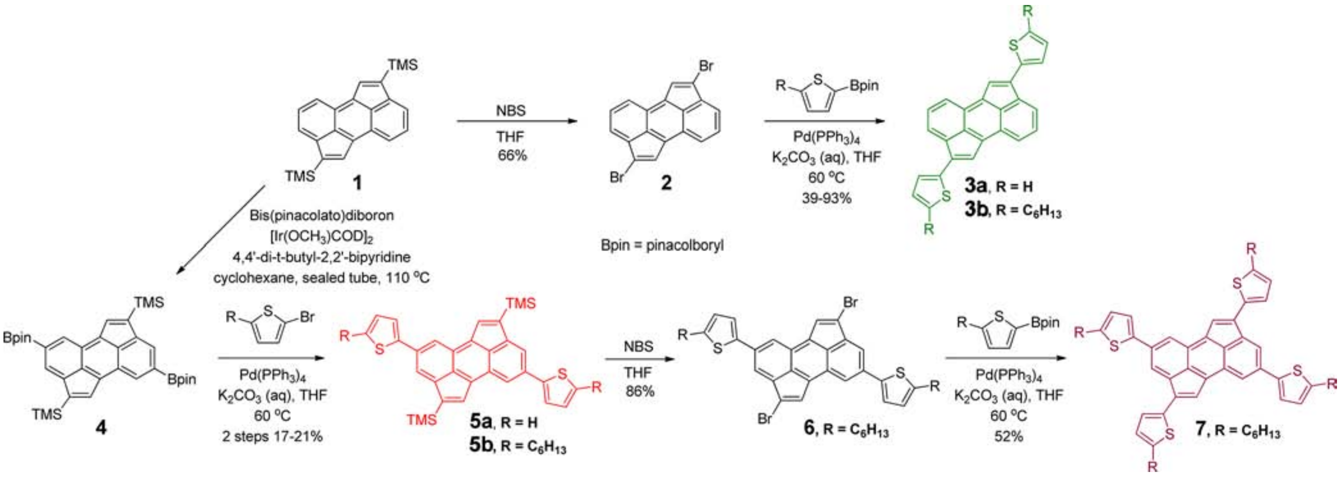
Scheme 1. Synthesis of Thiophene-Conjugated CP-PAHs



libraries of compounds for the screening of materials properties. With the apparent utility of the cyclopenta[*hi*]aceanthrylene scaffold for electronic applications, we set out to create a series of analogs based on thiophene conjugates. In this report, we demonstrate an orthogonal functionalization strategy to selectively modify a cyclopenta[*hi*]aceanthrylene core on either the five-membered rings (2- and 7-positions), six-membered rings (4- and 9-positions), or both positions in series. We further show that the resulting optical and electrochemical properties of the CP-PAH are greatly influenced by the location of substitution.

As demonstrated previously, the formation of the core 2,7-bis(trimethylsilyl)cyclopenta[*hi*]aceanthrylene (**1**) can be accomplished through a palladium-catalyzed cyclopentenalation reaction between 9,10-dibromoanthracene and (trimethylsilyl)acetylene (TMS-acetylene).[6b,c,9] Mild bromination with *N*-bromosuccinimide (NBS) at the ipso-position of the TMS group creates a universal cross-coupling partner (**2**) for functionalization on the five-membered rings (Scheme 1). We have previously shown that a simple Sonogashira cross-coupling reaction at these locations could create both low band gap small molecules[9] and donor−acceptor copolymers[10] that behave as electron acceptors. In this work, we show the bromide can be utilized for a Suzuki cross-coupling reaction to create thiophene-containing analogs (**3a,b**), which are functionalized at the five-membered rings, in moderate yields. The reduced yields for these compounds, as well as others in this work, are due to slow decomposition on silica gel during purification.[11]

A secondary modification strategy, which leads to orthogonally functionalized CP-PAHs, has also been developed.

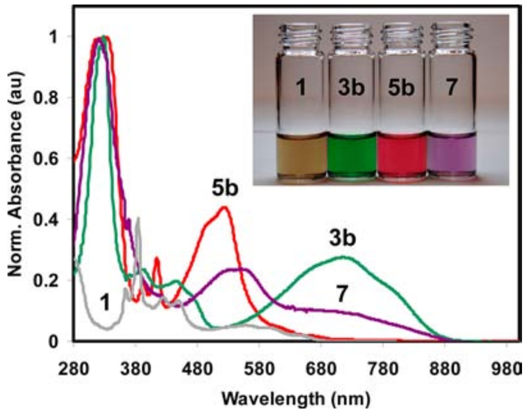


Figure 1. Normalized absorbance of **1** (gray), **3b** (green), **5b** (red), and **7** (purple) in THF.

Using C−H activation with an iridium catalyst,[12] boronate esters have been installed at the two least sterically hindered carbons of **1** to produce a cyclopenta[*hi*]aceanthrylene that can be further functionalized at the six-membered rings (**4**). We utilized the Suzuki cross-coupling conditions to create the comparable thiophene-containing analogs (**5a,b**) in tolerable yields for a two-step borylation/Suzuki cross-coupling procedure. The residual TMS groups on these compounds provided an opportunity to create a cruciform-like structure with functionalization at both the six- and five-membered ring locations. Ipso bromination of the TMS group with NBS provided the brominated species (**6**), which was carried forward with one last Suzuki cross-coupling

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to provide the tetrathiophene substituted cyclopenta[*hi*]aceanthrylene cruciform (**7**).

The optical and electrochemical properties of the thiophene-conjugated cyclopenta[*hi*]aceanthrylenes are greatly influenced by the functionalization location. Substitution at the five-membered rings (**3a,b**) creates dark green materials with relatively small band gaps as demonstrated by the absorption spectrum in solution (Figure 1) and in thin film (Supporting Information). The saturated green color is due to the simultaneous absorption of both blue (below 500 nm) and red (above 600 nm) light. For **3b**, the thin film absorbance onset is 1008 nm, which represents an optical band gap of 1.23 eV (Table 1). Although the structures of **3a,b** are very similar to that of emeraldicene,[5a] which is a fused thiophene analog of cyclopenta[*hi*]aceanthrylene, the band gaps of the materials presented here are considerably lower. When the thiophene substitution is switched to the six-membered rings (**5a,b**), the materials are visibly different and produce dark red solids with a much larger band gap. For **5b**, the thin-film absorbance onset is 632 nm (Supporting Information), which represents an optical band gap of 1.96 eV, and is ~370 nm larger (~0.7 eV) than that for **3b**. Cyclic voltammetry (CV) of each compound provided some insight into the dramatic difference in energies. The voltammograms (Supporting Information) showed little change in the reduction potential among each of the compounds (Table 1) with all LUMO energies occurring between −3.53 and −3.57 eV. The Density Functional Theory (DFT) calculated structures support this result with the LUMO frontier orbitals of each compound identical and localized on the cyclopenta[*hi*]aceanthrylene core (Figure 2). The oxidation potentials, however, were dramatically affected by the substitution location. The DFT calculated HOMO contours for **3** and **5** show the molecular orbitals distributed through each of the cores and out onto the thiophene appendages. The HOMO for **3b**, however, was −5.03 eV while the six-membered ring substituted **5b** HOMO was much more stabilized at −5.49 eV.

Table 1. Summary of Electrochemical and Optical Properties[a]

compd	HOMO (eV)	LUMO (eV)	E_{gap} (eV) e-chem	E_{gap} (eV) optical[b]	Φ[c]
3a	−5.12	−3.57	1.55	1.23	–
3b	−5.03	−3.55	1.48	1.23	–
5a	−5.66	−3.53	2.13	1.97	0.033
5b	−5.49	−3.53	1.96	1.96	0.013
7	−5.08	−3.60	1.48	1.22	0.0014

[a] HOMO and LUMO values calculated from the cyclic voltammograms (Supporting Information) on the basis of the oxidation of the ferrocene reference in vacuum (4.8 eV). [b] Optical band gap calculated from the onset of absorption in thin film (Supporting Information). [c] Quantum yields were calculated relative to anthracene in ethanol (Φ = 0.27).

The cruciform-like tetrathiophene **7** possesses a combination of the electronic properties of the simpler dithiophene-substituted analogs (e.g., **3b** and **5b**) as evident by the absorption spectra (Figure 1). For **7**, the absorption band centered at 550 nm is similar in energy to the major long-wave absorption of **5b** (530 nm) while the longest wavelength absorption matches the absorption of **3b** (720 nm). The DFT calculated structure is in agreement with these observations with the LUMO contour remaining localized on the core much like the LUMOs of **3** and **5**. The HOMO of **7** is visually and energetically similar to **3** while the HOMO−1 is similar to the HOMO of **5**. This combination of absorption transitions leads to a dark purple material. The fluorescence emission properties of cruciform **7** were also intermediate between those of **3a,b** and **5a,b**. The fluorescence quantum yield was found to be heavily influenced by substitution location. CP-PAHs often have reduced or absent fluorescence,[6c,9,13] and we

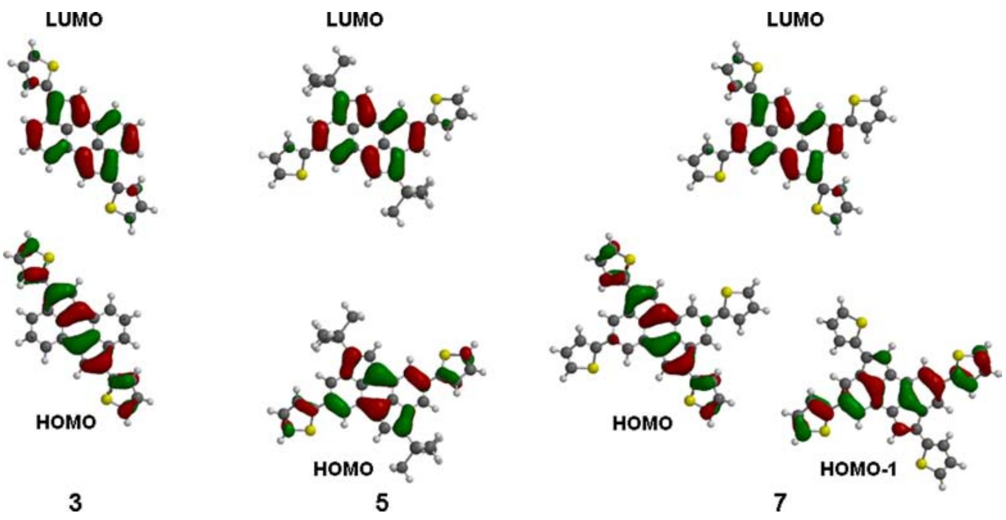

Figure 2. DFT calculated HOMO (bottom) and LUMO (top) contours of **3**, **5**, and **7** calculated at the B3LYP/6-31G** level.

found that the five-member ring substituted **3a,b** showed no measurable fluorescence. However, when the substitution was moved to the six-membered ring, we were able to measure a small, yet noticeable fluorescence quantum yield (Φ) of 0.033 and 0.013 for compounds **5a** and **5b**, respectively. The cruciform **7**, with substitutions on both the five- and six-membered rings, had a small, intermediate quantum yield of 0.0014.

In conclusion, we have demonstrated an orthogonal synthetic strategy for the discrete functionalization of cyclopenta[*hi*]aceanthrylene. Using this method, we have created a series of thiophene-substituted analogs that demonstrate the importance of functionalization location on the CP-PAH core. These strategies should provide access to a variety of well-defined small molecules, as well as polymeric materials, for utility in organic electronic applications.

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Supporting Information Available. Experimental details, NMR spectra, cyclic voltammetry, and UV−vis of all compounds in solution and thin film. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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