

# Electron Acceptors Based on Functionalizable Cyclopenta[*hi*]aceanthrylenes and Dicyclopenta[*de,mn*]tetracenes

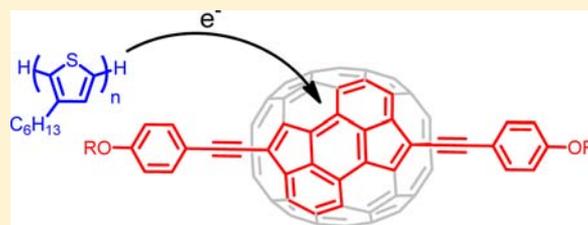
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**S** Supporting Information

**ABSTRACT:** We report the synthesis and selective functionalization of two externally fused cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) and demonstrate their electron accepting behavior. 2,7-Bis(trimethylsilyl)cyclopenta[*hi*]aceanthrylene (1) and 2,8-bis(trimethylsilyl)dicyclopenta[*de,mn*]tetracene (4) were prepared in a one-pot, palladium-catalyzed cross-coupling of (trimethylsilyl)acetylene and either 9,10-dibromoanthracene or 5,11-dibromotetracene, respectively. The trimethylsilyl groups were selectively converted into bromides via substitution with *N*-bromosuccinimide to create universal partners (2 and 6) for metal-catalyzed cross-coupling reactions. To demonstrate the utility of the halogenated CP-PAHs, we successfully employed a Sonogashira cross-coupling between the CP-PAHs and a phenylacetylene derivative. The resulting compounds (3 and 7) were found to be highly conjugated between the CP-PAH core and the substituents, as demonstrated by large bathochromic shifts in the absorption spectra as well as density functional theory calculations. Ethynylated CP-PAHs 3 and 7 were found to possess low optical bandgaps (1.52 and 1.51 eV, respectively) and displayed two reversible reductions. We further demonstrated the fullerene-like electron-accepting behavior of 3 through solution-phase fluorescence quenching of the prototypical electron donor, poly(3-hexylthiophene).



## INTRODUCTION

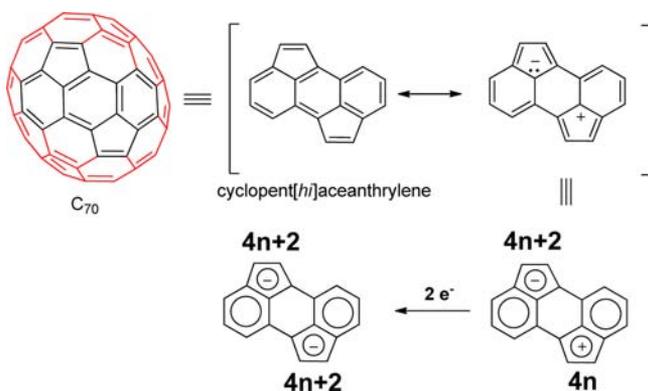
Fullerene derivatives are currently the most widely employed electron acceptor material because of their stability, their disposition to create charge percolation pathways through crystallization, and their generous capacity to accept electrons.<sup>1–3</sup> Unfortunately, they are not conducive to chemical modification that would lead to dramatically new morphological or electronic properties. Fullerenes can only be modified through addition reactions, which limit the interactions between the substituents and the fullerene to inductive effects that are in general weak and fall off exponentially with distance.<sup>4</sup> More importantly, fullerenes are not able to undergo substitution reactions that lead to new fully conjugated species. It is therefore difficult to appreciably change the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) due to a lack of resonance effects.<sup>4</sup> To accomplish such control, and to create new acceptor materials that can be electronically and/or morphologically tailored, we envision creating conjugated species with the desirable cyclopenta-fused polycyclic aromatic hydrocarbon (CP-PAH) character of fullerenes and universal  $\pi$ -donating or  $\pi$ -withdrawing aromatics. Using this strategy, small-molecule variants that behave similarly to fullerenes but can have their electronic properties systematically adjusted through chemical synthesis will be prepared. This article describes our initial work in creating such systems.

Traditional interest in CP-PAH synthesis has predominantly focused on fragments of C<sub>60</sub> that have bowl-like structures (i.e.,

corannulene).<sup>5–10</sup> The synthetic methods<sup>8,11,12</sup> used to create these five-membered ring-containing compounds are typically laborious, not conducive to scaled up procedures, and often too harsh to maintain functionality for subsequent chemical transformations. Recent advances have led to new scalable syntheses<sup>13</sup> and new CP-PAHs such as indenofluorenes,<sup>14–17</sup> dibenzopentalenes,<sup>18–20</sup> emeraldicenes,<sup>21,22</sup> and cyclopenta[*hi*]aceanthrylenes<sup>23</sup> that show promise for functionalization and possess relatively low bandgaps and good stability. However, comparison studies of the electron acceptor behavior of CP-PAHs have shown that externally fused CP-PAHs are often more capable electron acceptors than their internally fused counterparts.<sup>24</sup> We were therefore interested in creating acceptors based on externally fused CP-PAHs. We were encouraged by the serendipitous discovery by Garcia-Garibay and co-workers that externally fused aceanthrylenes (one five-membered ring) and cyclopenta[*hi*]aceanthrylenes (two five-membered rings) could be obtained in one step from the palladium-catalyzed cross-coupling of bromoanthracene derivatives and a few terminal acetylenes.<sup>25,26</sup> The resulting compounds were found to have fullerene-like electron affinity, in that they could be reversibly reduced twice at low potentials. This observation is justifiable as the cyclopenta[*hi*]aceanthrylene<sup>27–29</sup> subunit is a unique fragment in the oval-shaped C<sub>70</sub> fullerene (Figure 1). A resonance structure of

Received: May 11, 2012

Published: August 31, 2012



**Figure 1.** Cyclopenta[hi]aceanthrylene is a fragment of C<sub>70</sub> and can accept two electrons through aromatic 4n+2 stabilization.

cyclopenta[hi]aceanthrylene details the chemical means for reduction by forming a 4n+2 aromatic, benzocyclopentadienyl anion (favorable) and a 4n anti-aromatic, benzocyclopentadienyl cation (unfavorable). The addition of two electrons creates a reduced structure with two stabilized aromatic, benzocyclopentadienyl anions. These unique properties, as well as the ability to scale up the synthesis, suggested new electron-accepting compounds based on the cyclopenta[hi]aceanthrylene or other similar CP-PAHs scaffolds<sup>4</sup> would be of utility.

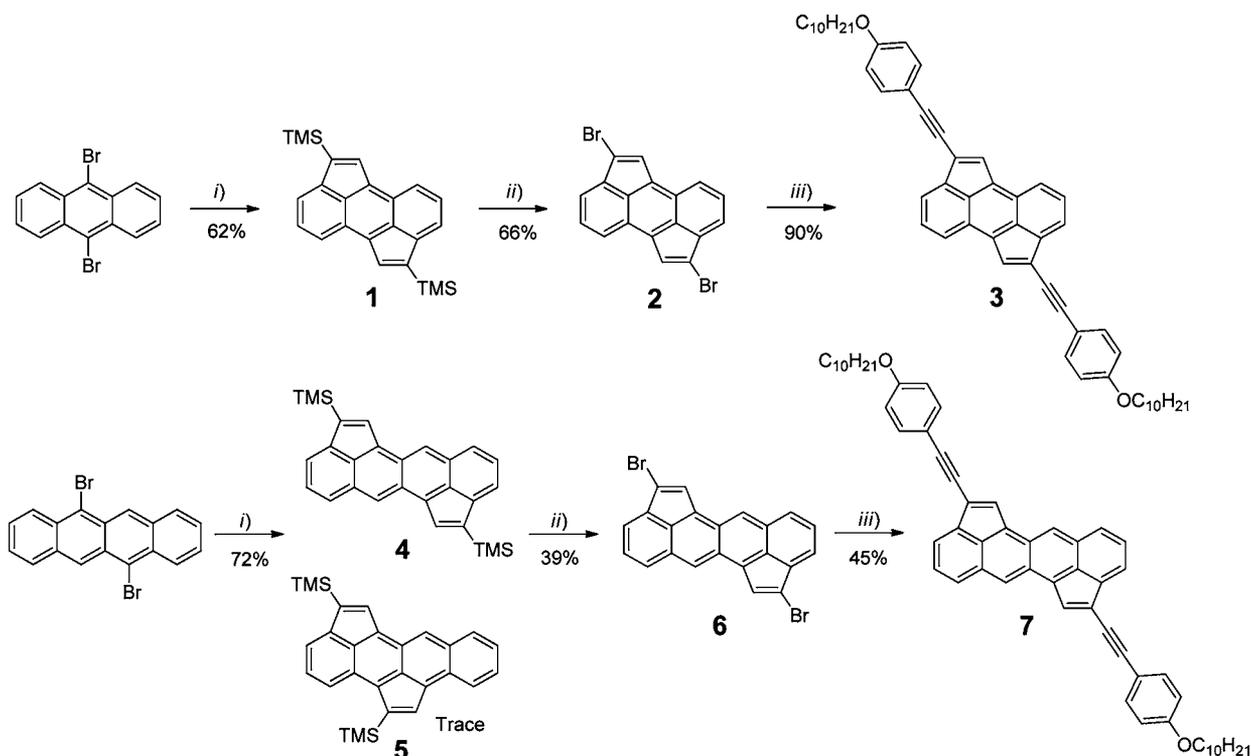
## RESULTS AND DISCUSSION

In this work, we have developed a methodology to create two new CP-PAH scaffolds that are capable of discrete functionalization via transition metal-catalyzed cross-couplings. The

resulting compounds are fully conjugated, and therefore systematic modulation of peripheral groups should readily affect the frontier orbitals of the electron acceptor CP-PAH core. We have prepared the previously unknown 2,7-bis(trimethylsilyl)cyclopenta[hi]aceanthrylene<sup>30</sup> (**1**) via a one-pot, Pd-catalyzed cross-coupling between 9,10-dibromoanthracene and (trimethylsilyl)acetylene (TMS-acetylene, Scheme 1). As formerly demonstrated,<sup>26</sup> heating the reaction in a sealed tube at 110 °C in the absence of copper iodide minimizes the typical Sonogashira cross-coupling product and promotes the formation of a thermally stable alkenylpalladium intermediate.<sup>25</sup> This intermediate is capable of undergoing an intramolecular alkene insertion into the anthracene core to form a five-membered ring. The reaction proceeds in high yield, and multiple grams of product can be easily obtained. To create a universal partner for metal-catalyzed cross-coupling reactions, the resulting vinylic-TMS groups were substituted with *N*-bromosuccinimide (NBS) to give 2,7-dibromocyclopenta[hi]aceanthrylene (**2**). The silyl-substitution strategy is preferable because its *ipso*-selectivity is in contrast to simple electrophilic bromination. Dibromide **2** was easily converted to the  $\pi$ -extended, diethynyl CP-PAH derivative **3** by modified Sonogashira cross-coupling with 1-(decyloxy)-4-ethynylbenzene. The cross-coupling reaction was carried out at room temperature using Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> and P<sup>t</sup>Bu<sub>3</sub> in toluene and diisopropylamine to give **3** in 90% yield. The resulting CP-PAH conjugate shows remarkable properties, including low bandgaps and electron-accepting behavior that will be discussed shortly.

We also became interested in extending the described ring-closure and bromination methodology to other polycyclic aromatic hydrocarbons such as tetracene. We felt this new

**Scheme 1.** Synthesis of Brominated CP-PAHs **2** and **6** and Conjugated Analogues **3** and **7**<sup>a</sup>



<sup>a</sup>Reagents: (i) TMS-acetylene, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, PPh<sub>3</sub>, benzene, triethylamine, 110 °C; (ii) NBS, THF; (iii) 1-(decyloxy)-4-ethynylbenzene, Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>, P<sup>t</sup>Bu<sub>3</sub>, CuI, toluene, diisopropylamine.

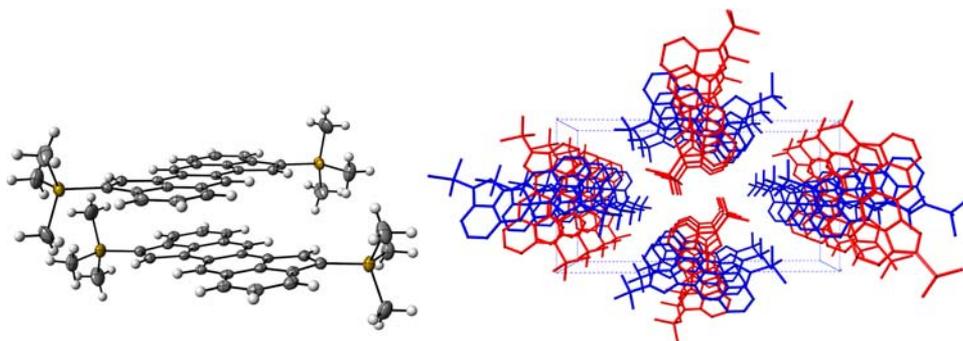


Figure 2. Crystal structure and columnar packing (looking down *a*-axis) of 4.

strategy would provide quick access to dicyclopenta[*de,mn*]-tetracene<sup>31</sup> scaffolds and provide opportunities for their selective functionalization. Starting with 5,11-dibromotetracene, we carried out the one-pot Pd-catalyzed cross-coupling with TMS-acetylene and expected to find a mixture of 4 and 5 owing to the central location of the bromides (Scheme 1). Interestingly, we found 2,8-bis(trimethylsilyl)dicyclopenta[*de,mn*]tetracene (4) as the major product from the reaction, with 5 present only in trace amounts. Crystals of 4 suitable for X-ray analysis, grown from slow evaporation of CDCl<sub>3</sub> solution, confirmed the regioselectivity (Figure 2). The solid-state packing shows  $\pi$ -stacked dimers propagating down the *a*-axis and the column orientation along the *c*-axis offset by  $\sim 90^\circ$ . The TMS groups appear to enforce  $\pi$ -stacking by blocking a more typical “herringbone” interaction.<sup>32</sup> The face-to-face arrangement is similar to other trialkylsilane-pentacene derivatives.<sup>33</sup> Bromination of 4 with NBS was also successfully employed to create 2,8-dibromodicyclopenta[*de,mn*]tetracene (6). Unfortunately, the reaction is not as straightforward as for 2 because prolonged reaction times in the presence of NBS led to a variety of side products that were not immediately identified. However, we were able to successfully obtain a reasonable yield of 6 by monitoring the reaction via NMR and then filtering the precipitated product straight from the reaction mixture. Upon purification, the product was air- and solution-stable and could be carried forward with an analogous Sonogashira cross-coupling of 1-(decyloxy)-4-ethynylbenzene to give 7.

It is immediately obvious by visual inspection that the photophysical properties of the  $\pi$ -extended compounds 3 and 7 are dramatically altered from those of the TMS-functionalized CP-PAHs 1 and 4. While 1 is a black solid that creates a tan-colored solution, 3 is a dark green/black solid and forms a dark green solution (Figure 3). Similarly, the tetracene derivative transforms from an aqua-blue to a dark green solution upon extending the conjugation from 4 to 7. The absorption spectra for compounds 1, 3, 4, and 7 can be found in Figure 3. Similar to a previous analogue,<sup>26</sup> 1 possessed three sets of absorption bands: a prominent band centered at 248 nm, a medium range band with fine structure from 340 to 480 nm, and a broad transition centered at 560 nm with an absorbance onset of 682 nm. Upon the formation of the  $\pi$ -extended 3, a prominent fourth transition emerged at 327 nm, and all other transitions were slightly (or largely) bathochromically shifted. The most striking change occurred to the longest wavelength transition that dramatically red-shifted and grew in intensity at 680 nm with an absorbance onset of 815 nm. The tetracene derivative demonstrated a similar bathochromic shift, with the lowest energy transition shifting from an absorbance onset of 693 nm for 4 to an absorption onset of 822 nm for 7. Although the

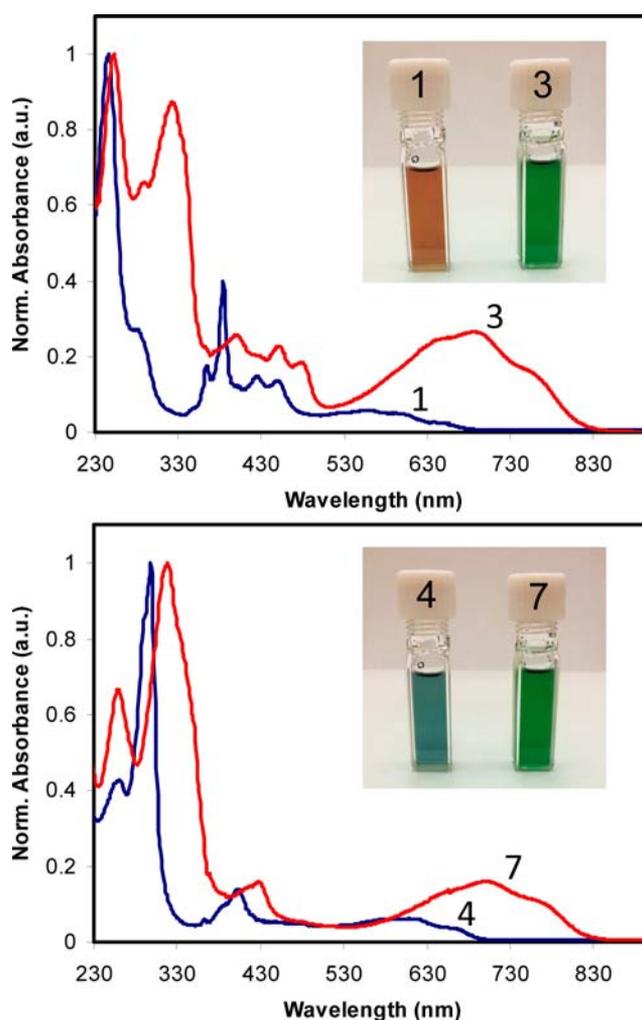


Figure 3. Absorbance of anthracene-based 1 and 3 (top) and of tetracene-based 4 and 7 (bottom).

spectra of 3 and 7 are not shown on the same plot, it is apparent that the absorption spectra and optical bandgaps (1.52 and 1.51 eV, respectively) are very similar. The overall bathochromic shifts upon functionalization suggest highly delocalized states with communication between the central CP-PAH core and the phenylacetylene substituents. To confirm the delocalized character of 3 and 7, we explored their electronic structure further with density functional theory (DFT) calculations. Calculations were carried out using the Becke's three-parameter exchange functional with the Lee–

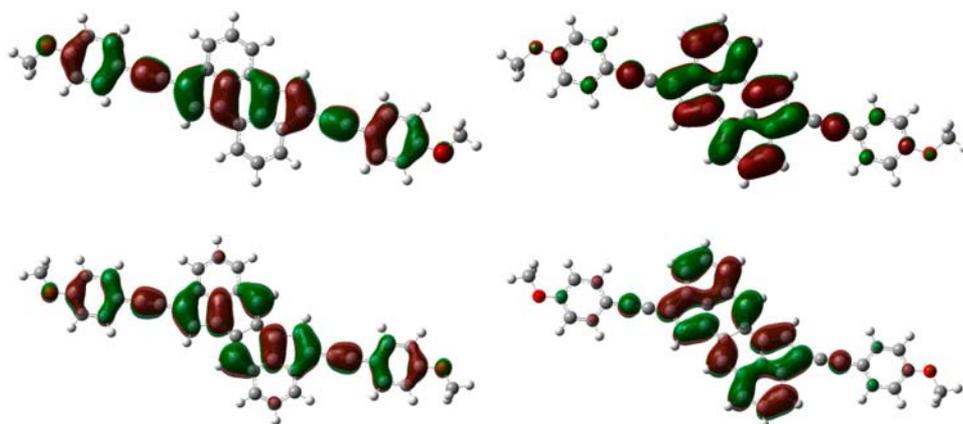


Figure 4. DFT-calculated HOMO (left) and LUMO contours of 3 (top) and 7 (bottom).

Yang–Parr correlation functional (B3LYP)<sup>34–36</sup> with a 6-311G(d,p) basis set, which was shown to be sufficiently accurate from our previous calculations.<sup>37,38</sup> As shown in Figure 4, the HOMO contours of 3 and 7 illustrate the delocalized character that extends from the CP-PAH core to the phenylacetylene substituents. Further analysis of the time-dependent DFT suggests the excitation from HOMO to LUMO undergoes partial charge transfer. In this type of excitation, DFT calculations typically do not provide accurate absorption spectra simulation. However, the current calculations predicted the first absorptions for 3 and 7 to occur at 821 and 856 nm, respectively. These values agree reasonably well with the experimental measurement of absorbance onset of 815 and 822 nm, respectively.

Cyclic voltammetry of the four CP-PAH compounds was utilized to further elucidate the electronic structure and assign energy levels to the frontier orbitals (Figure 5). Each compound showed two reduction steps that can be assigned to the two-step reduction process described in Figure 1. Upon conversion of 1→3 and 4→7, the onset of the first reduction wave was lowered by 0.23 and 0.17 V, respectively, suggesting the reduced CP-PAH structures are further stabilized through

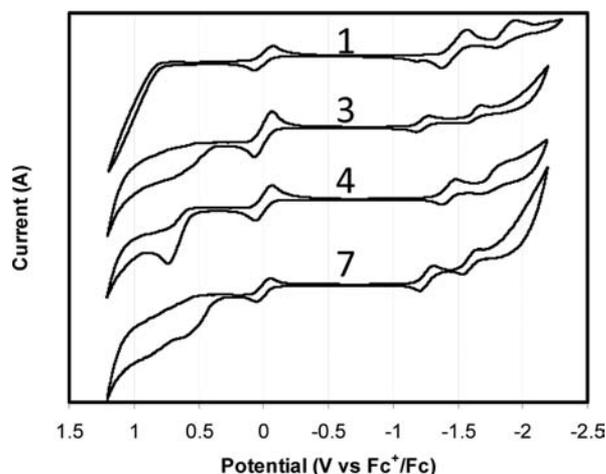


Figure 5. Cyclic voltammograms of 1, 3, 4, and 7 in THF with 0.1 M tetrabutylammonium hexafluorophosphate, glassy carbon electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 50 mV/s. Ferrocene added as internal standard and referenced to 0 V.

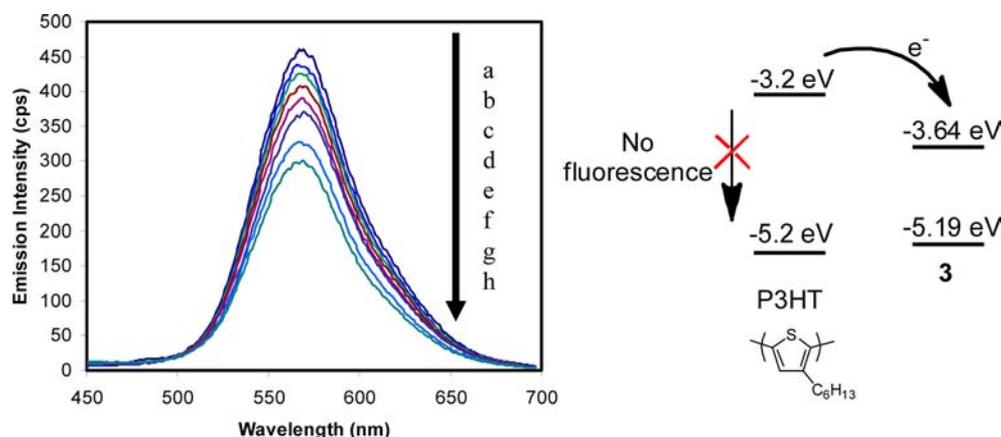
conjugation to the periphery substituents (Table 1). Each of the compounds 1, 3, 4, and 7 showed irreversible oxidation

Table 1. Summary of Electrochemical and Optical Properties<sup>a</sup>

compd	$E_{\text{ox/onset}}$ (V)	$E_{\text{red/onset}}$ (V)	HOMO (eV)	LUMO (eV)	$E_{\text{gap}}$ (eV)	
					e-chem	optical
1	0.79	-1.39	-5.59	-3.41	2.18	1.82
3	0.39	-1.16	-5.19	-3.64	1.55	1.52
4	0.56	-1.35	-5.36	-3.45	1.91	1.79
7	0.39	-1.18	-5.19	-3.62	1.57	1.51
anthracene	0.69	–	-5.49	-2.25 <sup>b</sup>	–	3.24
tetracene	0.38	–	-5.18	-2.61 <sup>b</sup>	–	2.57
perylene	0.54	–	-5.34	-2.55 <sup>b</sup>	–	2.79

<sup>a</sup>Potentials are measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Figure 5 or Supporting Information).  $E_{\text{ox/onset}}$  is the onset of oxidation potential,  $E_{\text{red/onset}}$  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). <sup>b</sup>From optical bandgap (Supporting Information).

steps that were modulated through substitution. Using an internal ferrocene reference, the HOMO and LUMO levels of each compound were calculated (Table 1). As demonstrated from the optical bandgaps in the absorption spectra, the experimentally obtained frontier orbitals of 3 (HOMO = -5.19 eV, LUMO = -3.64 eV) and 7 (HOMO = -5.19 eV, LUMO = -3.62 eV) are surprisingly similar, even though they are based on two separate acenes. This peculiarity may be rationalized by noting the similarities of the chromophore length and structure in the calculated frontier orbitals of 3 and 7 (Figure 4). An interesting discrepancy between the optical bandgap and the electrochemical bandgap is found for 1 and 4, while 3 and 7 are relatively similar. Although we do not fully understand this discrepancy at this time, the data suggest a substantial difference between the exciton binding energy of these two classes (TMS vs ethynylated) of compounds.<sup>39</sup> These results highlight the electronic ramifications of externally fused CP-PAHs and how the five-membered ring can greatly influence the electronic properties of PAHs.<sup>24</sup> We have included the electrochemical properties of anthracene, tetracene, and perylene in Table 1. Perylene possesses a fused ring structure similar to that of cyclopent[hi]acanthrylene 1 with the exception of substitution of five-membered rings for six-



**Figure 6.** Emission spectrum of P3HT ( $1.0 \times 10^{-5}$  M) in chloroform with varying concentrations of the electron acceptor 3: (a) 0, (b)  $1.00 \times 10^{-6}$ , (c)  $2.50 \times 10^{-6}$ , (d)  $5.00 \times 10^{-6}$ , (e)  $7.50 \times 10^{-6}$  M, (f)  $1.00 \times 10^{-5}$ , (g)  $1.50 \times 10^{-5}$ , and (h)  $2.00 \times 10^{-5}$  M. The spectra were corrected for the inner filter effect due to the absorbance of 3 at the excitation and emission wavelengths (Supporting Information).

membered rings. As can be seen in Table 1, the CP-PAH analogues have LUMOs that are  $\sim 1$  eV lower in energy than those of the parent PAHs (Supporting Information). The B3LYP calculated energy levels of 3 (HOMO =  $-5.14$  eV, LUMO =  $-3.27$  eV) and 7 (HOMO =  $-5.09$  eV, LUMO =  $-3.26$  eV) as well as the calculated absorption spectra (Supporting Information) agreed reasonably well with the experimental results. As a final comparison, the low-lying LUMOs described here are similar to the literature reported values for PCBM- $C_{60}$  (LUMO =  $-3.7$  eV)<sup>40</sup> and other small-molecule acceptors such as perylene bisimide (LUMO =  $-3.8$  eV).<sup>41</sup>

None of the CP-PAH compounds prepared in this work produce easily measured fluorescence, a property that is consistent with the extremely small fluorescent quantum yields found for other small-molecule CP-PAHs<sup>26,42</sup> and fullerenes.<sup>43,44</sup> However, the lack of fluorescence was beneficial in our attempt to further illustrate the similarity of the electron-accepting behavior of the described compounds to fullerenes. We performed fluorescence quenching experiments of a prototypical donor material, poly(3-hexylthiophene) (P3HT), with varying concentrations of 3 (Figure 6). We found that 3 was an excellent quencher for P3HT, as the observed fluorescence intensity was markedly reduced upon addition of the electron acceptor. Analysis of the quenching data using the Stern–Volmer equation showed a linear trend and gave a quenching constant  $K_{SV} = 2.7 \times 10^4$  M $^{-1}$ , which was similar to that of  $C_{60}$ . A general electron-transfer scheme is summarized in Figure 6 and shows the energetically favorable transfer from the P3HT LUMO ( $-3.2$  eV) to the LUMO of 3 ( $-3.64$  eV). The electron transfer described here is analogous to the well-known P3HT/fullerene donor–acceptor pairing used in high-efficiency photovoltaic cells.<sup>3</sup> Although the energy difference between the LUMOs of 3 and P3HT is not optimal for high open-circuit voltages in photovoltaic cells,<sup>45</sup> the described system provides ample opportunities for tuning the frontier orbitals through conjugation with the correct choice of aromatic substituent added to 2 or 6.

## CONCLUSIONS

We have presented a unique synthetic pathway to access externally fused CP-PAHs (2 and 6) that can be further modified through metal-catalyzed cross-coupling reactions. We have prepared two such modified analogues, 3 and 7, that share

several favorable traits with fullerenes. They possess low-lying LUMOs, exhibit minimal fluorescence, and act as electron acceptors. Additionally, the structures are fully conjugated, absorb broadly over the visible spectrum, and have remarkably low bandgaps. We have also demonstrated that the electronic properties of the CP-PAHs can be controlled via substitution of the brominated compounds 2 and 6 and have recently utilized 2 as a monomer in the preparation of donor–acceptor copolymers.<sup>46</sup> Finally, electronic and morphological control through side-chain variation presents opportunities to create new functional materials that may have utility in organic photovoltaics and field effect transistors, topics we are currently pursuing.

## EXPERIMENTAL SECTION

Unless otherwise noted, all reagents were used as received, and all reactions were carried out under an argon atmosphere. Column chromatography was performed on a CombiFlash Rf system with Rediseq normal phase silica columns (Teledyne ISCO Inc., Lincoln, NE). Millipore filtrations were accomplished with a 47 mm Millipore vacuum filter.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on a Varian 400 MHz NMR station at room temperature, unless otherwise noted. Cyclic voltammetry was performed on a CH-Instruments 700D potentiostat with a 0.1 M tetrabutylammonium hexafluorophosphate solution (in THF) using a glassy carbon electrode, a platinum counter electrode, and a Ag/AgCl reference electrode. Mass spectra and X-ray crystallography were obtained from the University of Illinois Mass Spectrometry Laboratory and the George L. Clark X-ray Facility, respectively.

**2,7-Bis(trimethylsilyl)cyclopenta[hi]aceanthrylene (1).** In a glovebox, 9,10-dibromoanthracene (2.0 g, 6.0 mmol), TMS-acetylene (2.34 g, 3.30 mL, 23.8 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (190 mg, 0.27 mmol), triphenylphosphine (370 mg, 1.4 mmol), benzene (15 mL), and triethylamine (6 mL) were combined in a sealed tube. The reaction mixture was stirred overnight at 110 °C. The reaction was cooled to room temperature and filtered. The white solid was washed with hexane, and the collected filtrate was concentrated. The residue was purified by silica gel chromatography ( $R_f = 0.3$ , 100% hexane) followed by recrystallization in ethanol to give 1.37 g (62%) of a black crystalline material. Alternatively, the reaction can also be carried out without the use of a glovebox. In a sealed tube, 9,10-dibromoanthracene and triphenylphosphine were dissolved in benzene and triethylamine and bubbled with argon for 10 min. To this solution was added the palladium followed by the TMS-acetylene, and the tube was sealed. Similar yields can be achieved with this method.  $^1\text{H}$  NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d,  $J = 8.5$  Hz, 2H), 7.82 (d,  $J = 6.5$  Hz, 2H), 7.73 (s, 2H), 7.66 (dd,  $J = 8.5, 6.6$  Hz, 2H), 0.45 (s, 18H).  $^{13}\text{C}$  NMR

(101 MHz, CDCl<sub>3</sub>)  $\delta$  144.4, 142.8, 138.5, 135.7, 130.7, 129.0, 136.2, 125.0, 124.0, 0.06. LRMS (EI+) 370.0; HRMS  $m/z$  for C<sub>24</sub>H<sub>26</sub>Si<sub>2</sub> calcd 370.1573, found 370.1558.

**2,7-Dibromocyclopenta[hi]aceanthrylene (2).** To a 500 mL round-bottom flask were added **1** (1.87 g, 5.05 mmol) and THF (200 mL). The solution was cooled to 0 °C, and NBS (1.96 g, 11.1 mmol) was added all at once. The reaction was allowed to warm to room temperature and stirred for 3 h. The solvent was removed, and the residue was dispersed in 300 mL of hot ethanol and then filtered. The solid was washed with ethanol and collected to give 1.27 g (66%) of a black/green solid. Further purification could be accomplished via recrystallization with chloroform. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16 (d,  $J$  = 8.4 Hz, 2H), 7.80 (d,  $J$  = 6.7 Hz, 2H), 7.72 (dd,  $J$  = 8.4, 6.7 Hz, 2H), 7.58 (s, 2H). <sup>13</sup>C was difficult due to solubility. LRMS (EI+) 383.8; HRMS  $m/z$  for C<sub>18</sub>H<sub>8</sub>Br<sub>2</sub> calcd 381.8993, found 381.9002.

**2,7-Bis((4-(decyloxy)phenyl)ethynyl)cyclopenta[hi]aceanthrylene (3).** In a glovebox were combined **2** (50 mg, 0.13 mmol), Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (3.0 mg, 0.0078 mmol), and CuI (1.5 mg, 0.0078 mmol) in a small vial. To these solids were added toluene (2 mL), diisopropylamine (0.33 mL), and P<sup>t</sup>Bu<sub>3</sub> (3.2 mg, 32 mg of a 10% solution). The mixture was stirred for 2 min, and then a solution of 1-(decyloxy)-4-ethynylbenzene (74 mg, 0.29 mmol) in toluene (1 mL) was added. The vial was capped and stirred for 6 h at room temperature. The solvent was removed, and the crude solid was dissolved in a minimal amount of THF and precipitated into cold methanol. The green/black solid was filtered to give 86 mg (90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d,  $J$  = 8.5 Hz, 2H), 8.00 (d,  $J$  = 6.7 Hz, 2H), 7.72 (dd,  $J$  = 8.5, 6.7 Hz, 2H), 7.69 (s, 2H), 7.56 (d,  $J$  = 8.9 Hz, 4H), 6.92 (d,  $J$  = 8.9 Hz, 4H), 4.00 (t,  $J$  = 6.6 Hz, 4H), 1.86–1.76 (m, 4H), 1.29–1.47 (m, 28H), 0.89 (t,  $J$  = 6.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.4, 140.5, 138.0, 134.0, 133.1, 129.4, 129.1, 128.0, 126.2, 124.2, 123.4, 115.3, 114.7, 97.5, 84.5, 68.1, 31.9, 29.6, 29.6, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1. LRMS (MALDI) 738.5; HRMS  $m/z$  for C<sub>54</sub>H<sub>58</sub>O<sub>2</sub> calcd 738.4437, found 738.446

**2,8-Bis(trimethylsilyl)dicyclopenta[de,mn]tetracene (4).** In a glovebox, 5,11-dibromotetracene (600 mg, 1.55 mmol), TMS-acetylene (763 mg, 7.77 mmol), bis(triphenylphosphine)palladium(II) chloride (54.7 mg, 0.077 mmol), triphenylphosphine (94.0 mg, 0.360 mmol), triethylamine (630 mg, 77.0 mmol), and benzene (15 mL) were combined in a sealed tube. The solution was stirred at 110 °C overnight. After cooling to room temperature, solvent was removed and the resulting residue was purified via silica gel chromatography ( $R_f$  = 0.28, 100% hexane) to give 471 mg (72%) of a dark blue/black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.99 (s, 2H), 8.02 (d,  $J$  = 8.5 Hz, 2H), 7.97 (s, 2H), 7.84 (d,  $J$  = 6.4 Hz, 2H), 7.59 (dd,  $J$  = 8.5, 6.5 Hz, 2H), 0.48 (s, 18H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.8, 140.2, 138.0, 137.2, 130.0, 128.4, 128.2, 128.1, 127.7, 127.0, 124.2, 29.9. LRMS (EI+) 420.2; HRMS  $m/z$  for C<sub>28</sub>H<sub>28</sub>Si<sub>2</sub> calcd 420.1730, found 420.1729.

**2,8-Dibromodicyclopenta[de,mn]tetracene (6).** In a NMR tube were dissolved **4** (27 mg, 0.064 mmol) and NBS (57 mg, 0.32 mmol) in 0.6 mL of THF-*d*<sub>8</sub>. The tube was heated to 45 °C for 45 min while being monitored for reaction progress via NMR. The solid was filtered and washed with methanol to give 11.0 mg (39%) of a green/black solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.82 (s, 2H), 8.08 (d,  $J$  = 8.6 Hz, 2H), 7.80 (d,  $J$  = 6.5 Hz, 2H), 7.79 (s, 2H), 7.64 (dd,  $J$  = 8.5, 6.6 Hz, 2H). <sup>13</sup>C NMR, too insoluble. LRMS (EI+) 433.9; HRMS  $m/z$  for C<sub>22</sub>H<sub>10</sub>Br<sub>2</sub> calcd 431.9149, found 431.9139.

**2,8-Bis((4-(decyloxy)phenyl)ethynyl)dicyclopenta[de,mn]tetracene (7).** In a glovebox were combined **6** (11.0 mg, 0.025 mmol), Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (1.0 mg, 0.0026 mmol), and CuI (1.0 mg, 0.0053 mmol) in a small vial. To these solids were added toluene (2 mL), diisopropylamine (0.33 mL), and P<sup>t</sup>Bu<sub>3</sub> (1.1 mg, 11 mg of a 10% solution). The mixture was stirred for 2 min, and then a solution of 1-(decyloxy)-4-ethynylbenzene (14.4 mg, 0.055 mmol) in toluene (1 mL) was added. The vial was capped and stirred for 6 h at room temperature. The solvent was removed, and the crude solid was dissolved in a minimal amount of THF and precipitated into cold methanol. The green/black solid was filtered to give 9 mg (45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.84 (s, 2H), 8.01 (d,  $J$  = 8.5 Hz, 2H), 7.93 (d,  $J$  = 6.5 Hz, 2H), 7.84 (s, 2H), 7.58 (dd,  $J$  = 8.5, 6.5 Hz, 2H),

7.51 (d,  $J$  = 8.7 Hz, 4H), 6.86 (d,  $J$  = 8.8 Hz, 4H), 3.94 (t,  $J$  = 6.6 Hz, 4H), 1.79–1.70 (m, 4H), 1.2–1.4 (m, 28H), 0.82 (t,  $J$  = 6.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, THF-*d*<sub>8</sub>)  $\delta$  161.4, 142.5, 138.9, 134.6, 132.3, 131.9, 130.9, 129.9, 129.5, 127.3, 126.6, 126.4, 123.5, 117.3, 116.3, 98.0, 85.6, 55.7, 33.7, 31.4, 31.4, 31.2, 31.1, 31.1, 27.9, 24.4, 15.3. LRMS (MALDI) 788.51; HRMS  $m/z$  for C<sub>58</sub>H<sub>60</sub>O<sub>2</sub> calcd 788.4593, found 788.458.

## ■ ASSOCIATED CONTENT

### ☞ Supporting Information

Synthesis and characterization of precursor compounds, inner filter effect correction, NMR spectra, computational methods and spectra, molar absorption of compounds, electrochemistry of acenes, and X-ray crystallography data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

K.N.P. thanks Southern Illinois University for startup funds and a seed grant. The authors thank Danielle Gray for help with the crystallography. She is a part of The Materials Chemistry Laboratory at the University of Illinois, which was supported in part by grants NSF CHE 95-03145 and NSF CHE 03-43032 from the National Science Foundation.

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