Electron Acceptors Based on Cyclopentannulated Tetracenes

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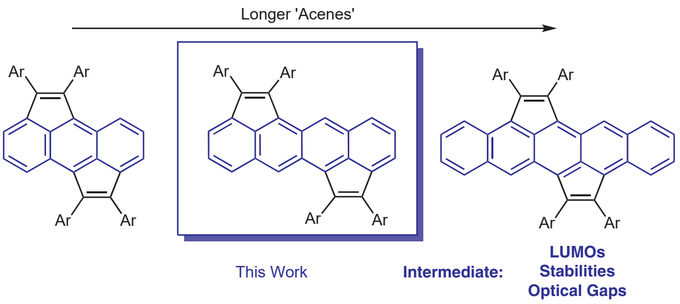
Published as part of the Cluster *Synthesis of Materials*



Received: 01.08.2018
Accepted after revision: 19.08.2018

DOI: 10.1055/s-0037-1609949; Art ID: st-2018-v0489-c

Abstract New cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) based on tetracene have been prepared by a palladium-catalyzed cyclopentannulation reaction. The new compounds have low-energy lowest unoccupied molecular orbitals (LUMOs) and relatively small band gaps. The photooxidative stability was intermediate to previously prepared CP-PAHs based on anthracene and pentacene as found in traditional acene stabilities. Scholl cyclodehydrogenation of pendant aryl groups led to materials that quickly formed endoperoxide products.

Key words cyclopenta-fused polycyclic aromatic hydrocarbons, electron acceptors, acenes, palladium-catalyzed annulation

Cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) based on extended acene backbones are a relatively new class of electron-accepting molecules.[1–19] In strict definition, acenes are linearly fused benzene rings with no additional annulated rings. However, we have recently suggested that the annulation of five-membered rings to an acene backbone could provide a pseudo-acene structure that is more representative of the reactivity of acenes in comparison to six-membered ring annulated derivatives.[15] We proposed this trait by considering the maintained ability to possess a migrating π-sextet defined by Klar.[20,21] In general, extended acenes are reactive and unstable in the presence of light and oxygen, sensitizing their own destruction through the formation of dimers or endoperoxides.[22,23] In regard to cyclopentannulated structures, recent work from our lab has shown that the modification of anthracene (**1**) and pentacene (**2**) cores (Figure 1) can lead to low-energy lowest unoccupied molecular orbitals (LUMO) and small band-gap materials.[15,16] These properties are appealing for electron acceptors in organic photovoltaics where broad absorption would be beneficial in the acceptor region.[24] Central to the design criteria, the five-member ring inclusion in the PAHs allows for the formation of cyclopentadienyl anion-like structures that are Hückel aromatics in the reduced state.[18] While we previously demonstrated that the cyclopentannulation of a pentacene core **2**[15] led to more stable structures than the well-known, and relatively stable, TIPS-pentacene, the stabilities were found to be less than desirable.

In this work, we looked to address the relative instability of the cyclopentannulated pentacenes by reducing the acene portion of the molecule to a tetracene backbone. Furthermore, the new tetracene structures provides a bridge in structure from pentacenes **2** to shorter anthracene derivatives **1** previously prepared. As traditional acene stabilities decrease with increasing ring fusion,[25] we believed that a

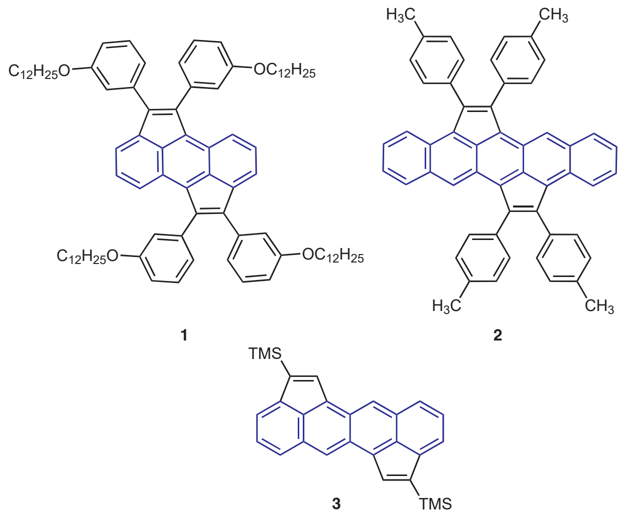


Figure 1 Previously reported cyclopenta-fused acenes based on anthracene (**1**), pentacene (**2**), and tetracene (**3**) prepared by a palladium-catalyzed cyclopentannulation

tetracene core could provide additional stability in relation to the pentacene derivatives. Here, we have applied a palladium-catalyzed cyclopentannulation[3–5,16] between 5,11-dibromotetracene and two diarylethynylene compounds to make two new CP-PAHs with modestly low band gaps and reduced LUMO levels. In addition, we investigated the ability to form contorted aromatic structures from these compounds through the Scholl cyclodehydrogenation reaction of the pendant aryl groups. Interestingly, the resulting cyclodehydrogenated structure was found to be even more photooxidatively reactive and was not successfully isolated.

The palladium-catalyzed cyclopentannulation reaction between 5,11-dibromotetracene **4** and 1,2-bis(3-(dodecyloxy)phenyl)ethyne **5** was carried out with a catalyst system composed of Pd_2dba_3, P(*o*-Tol)$_3$, LiCl, and KOAc in DMF at 130 °C (Scheme 1).[26] Although we previously showed that 2,8-bis(trimethylsilyl)dicyclopenta[*de*,*mn*]tetracene[17] **3** could be made as a single isomer from 5,11-dibromotetracene and trimethylsilylacetylene, it was presumed that steric interactions between the acene rings and the TMS group provided its selectivity. Therefore, we were initially concerned that the current chemistry may lead to two isomers owing to the symmetry of the diarylethynylene reactant. However, we were happy to find that a single dicyclopenta[*de*,*mn*]tetracene isomer **6** was formed during the reaction and none of the dicyclopenta[*de*,*op*]tetracene isomer was formed. Of importance, the relative positions of the five-membered rings of **6** differ from the previously synthesized **1** and **2**, as well as other CP-tetracenes,[8,9] with the five-membered rings being pushed further apart in space. We similarly found that the reaction of 5,11-dibromotetracene with 1,2-bis(5-methylthiophen-3-yl)ethyne **7** formed the single isomer **8** during a parallel reaction.

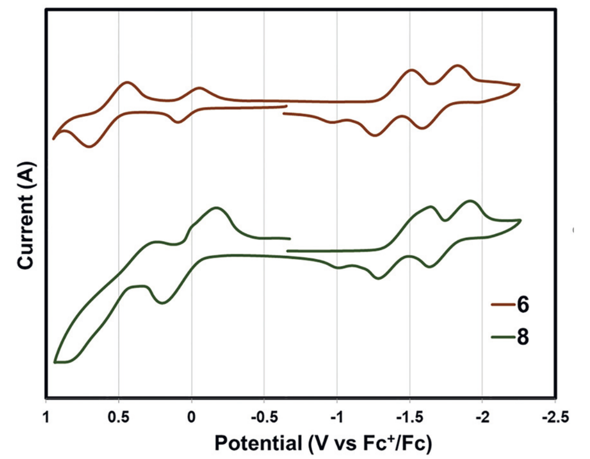
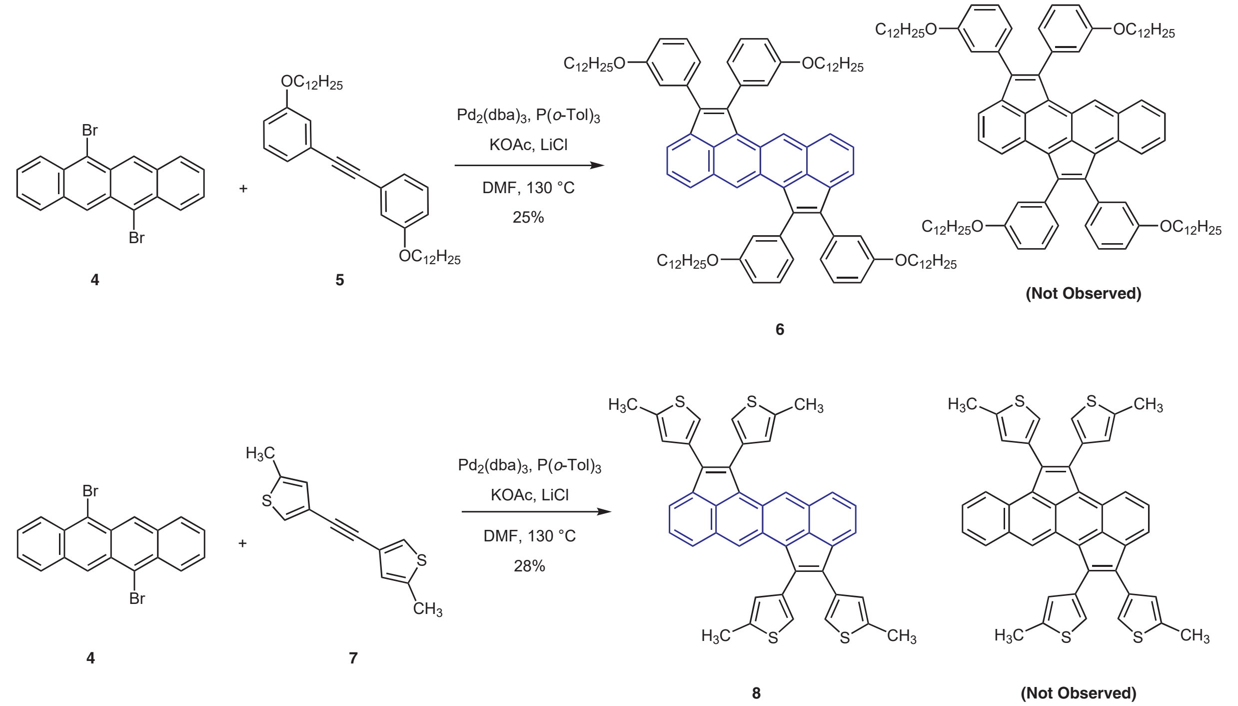


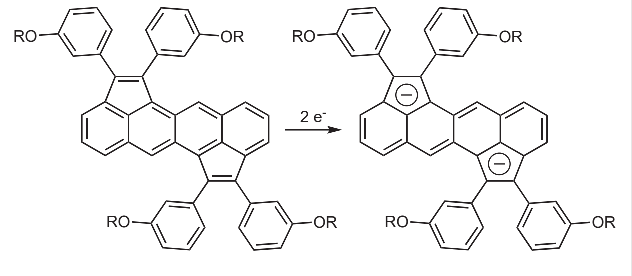
Figure 2 Cyclic voltammetry of **6** and **8** in 0.1 M tetrabutylammonium hexafluorophosphate in THF with glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 50 mV/sec. Ferrocene added as internal standard and referenced to 0 V.

We investigated the electronic and optical properties of these new CP-tetracene derivatives using cyclic voltammetry and UV/Vis spectroscopy. The cyclic voltammograms of



Scheme 1 Synthesis of cyclopenta-fused tetracene derivatives **6** and **8**. A single isomer was found for the palladium-catalyzed cyclopentannulation

6 and **8** are shown in Figure 2. As found in previous cyclopentannulated derivatives,[15–17] the new compounds gave two reversible reduction waves. The two-electron reduction is imparted to the molecule because of the ability to form cyclopentadienyl anion-like structures in the reduced state (Figure 3).



6

Figure 3 Reduction of **6** leads to two new cyclopentadienyl anions that are stabilized as Hückel aromatics leading to the electron-accepting behavior

For **6**, the oxidation was reversible, whereas for **8** the oxidative process was pseudo-reversible. A ferrocene redox couple was utilized as an internal standard and provided the highest occupied molecular orbital (HOMO) and LUMO energies (Table 1). The LUMO value was similar, albeit a little higher than the previously synthesized anthracene derivative and considerably higher in energy than previously synthesized pentacene derivatives. The destabilization of the tetracene derivative LUMOs could be due to the separation of the five-membered rings in relation to the previous compounds or simple extension of the acene core. The DFT minimized structure of **6** shows the perpendicular arrangement of the appendage aryl rings and the HOMO and LUMO contours do not reach onto these rings (Figure 4). The HOMO contour is isolated along a trajectory involving the two five-membered rings and the two inner six-membered rings of the tetracene. Alternatively, the LUMO is distributed onto all rings of the CP-tetracene core.

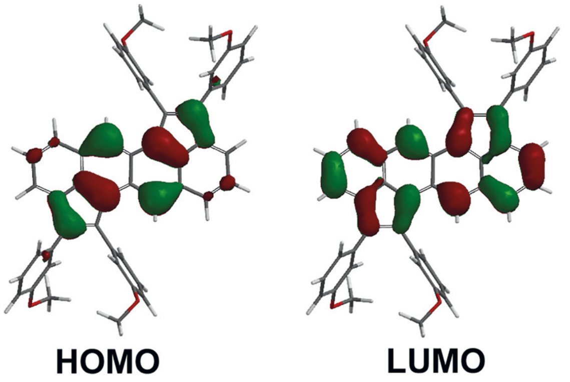


Figure 4 The B3LYP/6-311g(d,p) DFT calculated HOMO and LUMO contours of compound **6**

Table 1 Summary of Optoelectronic Properties of **1–3**, **6**, and **8**[a]

Cmpd	$E_{\mathrm{ox/onset}}$ (V)	$E_{\mathrm{red/onset}}$ (V)	HOMO (eV)	LUMO (eV)	E-chem gap (eV)	Optical gap (eV)	$\tau_{\mathrm{half-life}}$ (min)
1	0.66	−1.32	−5.46	−3.48	1.98	1.63	1119
2	0.55	−0.98	−5.35	−3.82	1.53	1.20	192
3	0.56	−1.35	−5.36	−3.45	1.91	1.79	–
6	0.49	−1.31	−5.29	−3.49	1.79	1.59	502
8	0.41	−1.32	−5.21	−3.48	1.73	1.53	753

[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 (Figure 2). $E_{\mathrm{ox/onset}}$ is the onset of oxidation potential, $E_{\mathrm{red/onset}}$ is the onset of reduction potential. HOMO and LUMO values calculated based on the oxidation of the ferrocene reference in vacuum (4.8 eV).

The absorption properties of **6** and **8** are shown in Figure 5. The high-energy absorptions dominate the spectra, but a middle-energy absorption and a broad, charge-transfer band centered at ca. 650 nm with an onset wavelength of 780 nm and 810 nm, respectively, are also present. The optical band gaps from these absorption profiles give values of 1.59 and 1.53 eV, respectively. These band gaps are intermediary to those found for anthracene **1** (1.63 eV) and pentacene **2** (1.20 eV) derivatives and are consistent with the elongation of the acene backbone. We also investigated the photostability of **6** and **8** in the presence of oxygenated THF. The absorption intensity was monitored over time under ambient light to give decomposition profiles (see the Supporting Information) that were compared to the decomposition rates of **1** and **2**. Similar to the trends found for traditional acenes,[25] the tetracene decomposition half-lives (Table 1) were between the more stable anthracene and the less stable pentacene derivatives.

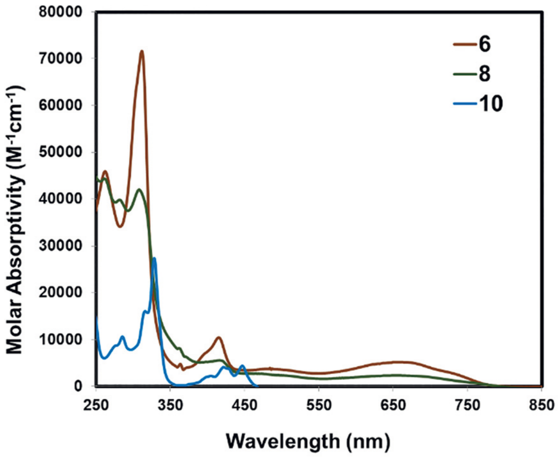
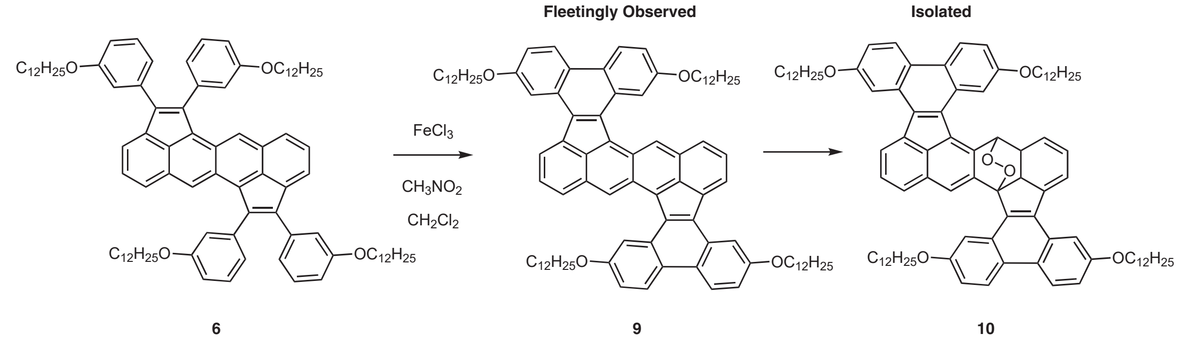


Figure 5 UV/Vis spectra of **6**, **8**, and **10**. The oxidized derivative **10** shows the loss of the long wavelength absorption of the tetracene backbone.



Scheme 2 Scholl cyclodehydrogenation reaction of **6**. The oxidized product **10** was isolated instead of the desired compound **9**.

The arrangement of the attached aryl groups of **6** provided opportunities to create extended π-networks through the Scholl cyclodehydrogenation reaction, as previously employed for anthracene and pyrene derivatives to make contorted aromatics.[16,27] While it became evident by NMR and mass spectrometry that the two ring closures were successful upon addition of $FeCl_3$, we were unable to isolate compound **9** (Scheme 2). Instead, we isolated the *endo*-peroxide-containing derivative **10**. The oxidation process was fast, and the desired green color of the **9**, which was observed in the precipitated product, was quickly eroded to the yellow color of the oxidized product **10** during filtration. Attempts to control the oxidation process were unsuccessful and we propose the fully ring-closed **9** is even more susceptible to oxidation than the precursor **6**. The UV/Vis of **10** can also be found in Figure 5 and shows that the spectra of the oxidized product are blueshifted with the loss of the long-wave absorption band. The longest wavelength absorption was reduced to 460 nm, which clearly demonstrates the loss of conjugation along the acene backbone. The reduced photooxidative stability is consistent with our previous work on pentacene derivatives in which we were not able to isolate the Scholl cyclodehydrogenation product because of rapid oxidation.[28]

In conclusion, we have prepared new CP-PAHs based on a tetracene scaffold. The palladium-catalyzed cyclopentannulation reaction was regioselective and provided a slightly different bonding motif to previous CP-PAH based acenes with the five-member rings being further separated in space. The new compounds provide low LUMO levels and broad absorption profiles. The stability of **6** and **8** are less than anthracene derivatives but they are more stable than pentacene derivatives, which mirrors traditional acene stability trends.

Funding Information

We are grateful to the National Science Foundation (NSF CAREER CHE-#1352431) for financial support. J.L.M.-C. was supported by NSF REU grant DMR-#1757954

Acknowledgment

G.C.K. thanks Dr. Akshita Patel for valuable discussions and support.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609949.

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(26) **1,2,7,8-Tetrakis(3-(dodecyloxy)phenyl)dicyclopenta[*de*,*mn*]tetracene (6)**: In a glove box, **4** (0.127 g, 0.328 mmol), **5** (0.430 g, 0.786 mmol), $Pd_2(dba)_3$ (30.0 mg, 0.0328 mmol), P(*o*-Tol)$_3$ (15.1 mg, 0.0495 mmol), KOAc (0.161 g, 1.64 mmol), LiCl (27.8 mg, 0.657 mmol) and DMF (7.67 mL) were combined in a sealed tube and stirred overnight at 130 °C. The reaction mixture was cooled to room temperature and poured dropwise into methanol (50 mL) and filtered. The solid was washed with methanol and acetone to give **5** (0.164 g, 25.0%) as a green solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.62 (s, 2 H), 7.87 (d, *J* = 6.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 7.57 (dd, *J* = 8.4, 6.6 Hz, 2 H), 7.50 (t, *J* = 7.7 Hz, 2 H), 7.29 (t, *J* = 7.9 Hz, 2 H), 7.24 (d, *J* = 7.4 Hz, 2 H), 7.16 (s, 2 H), 7.13–7.09 (m, 4 H), 6.98 (s, 2 H), 6.84 (dd, *J* = 8.1, 2.1 Hz, 2 H), 4.00 (t, *J* = 6.6 Hz, 4 H), 3.83 (t, *J* = 6.6 Hz, 4 H), 1.80–1.71 (m, 8 H), 1.48–1.19 (m, 72 H), 0.91 (q, *J* = 7.0 Hz, 12 H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 159.38, 158.92, 141.12, 139.74, 139.39, 136.67, 136.33, 136.08, 131.06, 129.60, 129.00, 128.89, 127.69, 126.93, 126.68, 125.64, 124.20, 122.93, 122.43, 116.58, 115.65, 114.27, 113.69, 68.15, 67.93, 31.93, 31.91, 29.71, 29.65, 29.60, 29.41, 29.38, 29.35, 29.22, 29.16, 26.01, 22.70, 22.68, 13.88. HRMS: *m*/*z* calcd for $C_{94}H_{124}O_4$: 1316.9500; found: 1316.9111.
4,4′,4″,4‴-(Dicyclopenta[*de*,*mn*]tetracene-1,2,7,8-tetrayl)tetrakis(2-methylthiophene) (8): In a glove box, **4** (41.3 mg, 0.107 mmol), **7** (56.0 mg, 0.257 mmol), $Pd_2(dba)_3$ (9.80 mg, 0.0107 mmol), P(*o*-Tol)$_3$ (4.92 mg, 0.0162 mmol), KOAc (52.6 mg, 0.536 mmol), LiCl (9.12 mg, 0.215 mmol) and DMF (10.7 mL) were combined in a sealed tube and stirred overnight at 130 °C. The reaction mixture was cooled to room temperature and poured dropwise into methanol (50 mL) and filtered. The solid was washed with methanol and acetone to give **7** (20.2 mg, 28.3%) as a green solid. ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 8.47 (s, 2 H), 7.84 (d, *J* = 6.5 Hz, 2 H), 7.67 (d, *J* = 8.5 Hz, 2 H), 7.47 (dd, *J* = 8.4, 6.6 Hz, 2 H), 7.10 (d, *J* = 1.1 Hz, 2 H), 7.04 (d, *J* = 1.1 Hz, 2 H), 6.91 (s, 2 H), 6.76 (s, 2 H), 2.59 (s, 6 H), 2.40 (s, 6 H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 140.67, 139.63, 139.20, 137.89, 136.50, 135.69, 135.64, 132.68, 130.89, 128.97, 128.03, 127.55, 126.92, 126.90, 126.34, 125.12, 124.11, 122.34, 121.46, 15.27, 15.09. HRMS: *m*/*z* calcd for $C_{42}H_{28}S_4$: 660.1074; found: 659.926.

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