

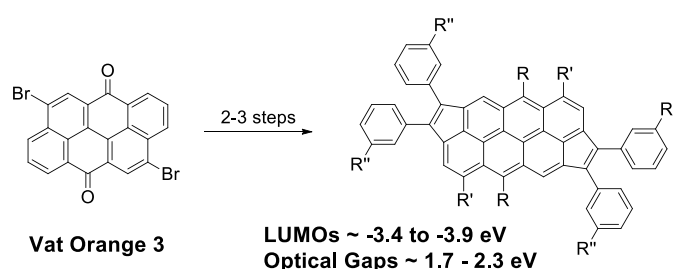
# Electron Acceptors Based on Cyclopentannulated Anthanthrenes

Yachu Du,<sup>a</sup> Hope B. Lovell,<sup>a</sup> Frédéric Lirette,<sup>b</sup> Jean-François Morin,<sup>b,\*</sup> and Kyle N. Plunkett<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL USA

<sup>b</sup>Département de Chimie and Centre de Recherche sur les Matériaux Avancés (CERMA), Université Laval, 1045 Ave de la Médecine, Québec QC,

[jean-francois.morin@chm.ulaval.ca](mailto:jean-francois.morin@chm.ulaval.ca), [kplunkett@chem.siu.edu](mailto:kplunkett@chem.siu.edu)

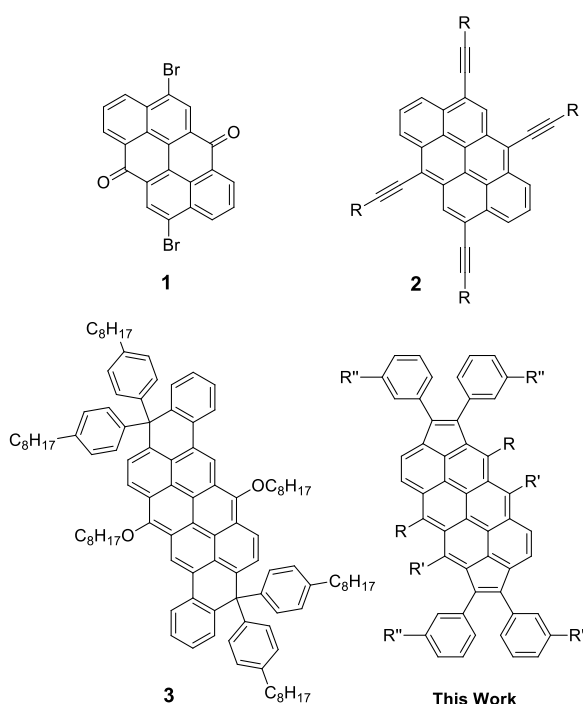


## Abstract

We demonstrate the preparation of anthanthrene derivatives with fused five-membered rings. These new derivatives are prepared by a palladium catalyzed cyclopentannulation reaction from precursors derived from the low-cost dye Vat Orange 3 (4,10-dibromoanthanthrene). The new cyclopenta-anthanthrene compounds possess reduced optical and electrochemical gaps (~0.9 eV) compared to anthanthrene derivatives and are electron acceptors with lowest unoccupied molecular orbital energies of ~ -3.4 eV to -3.9 eV.

## Introduction

Polycyclic aromatic hydrocarbons (PAHs) are intensely studied owing to their potential application as organic semiconductors in organic electronic devices.<sup>1,2</sup> Their extended pi surfaces, large variety of edge topologies, and ability to include heteroatom substitutions have allowed the preparation of small molecules and polymers with a wide range of band gaps and electronic properties.<sup>3,4</sup> Moreover, their flat surfaces lead to strong  $\pi$ - $\pi$  interactions in the solid state, which improves charge transport. We have

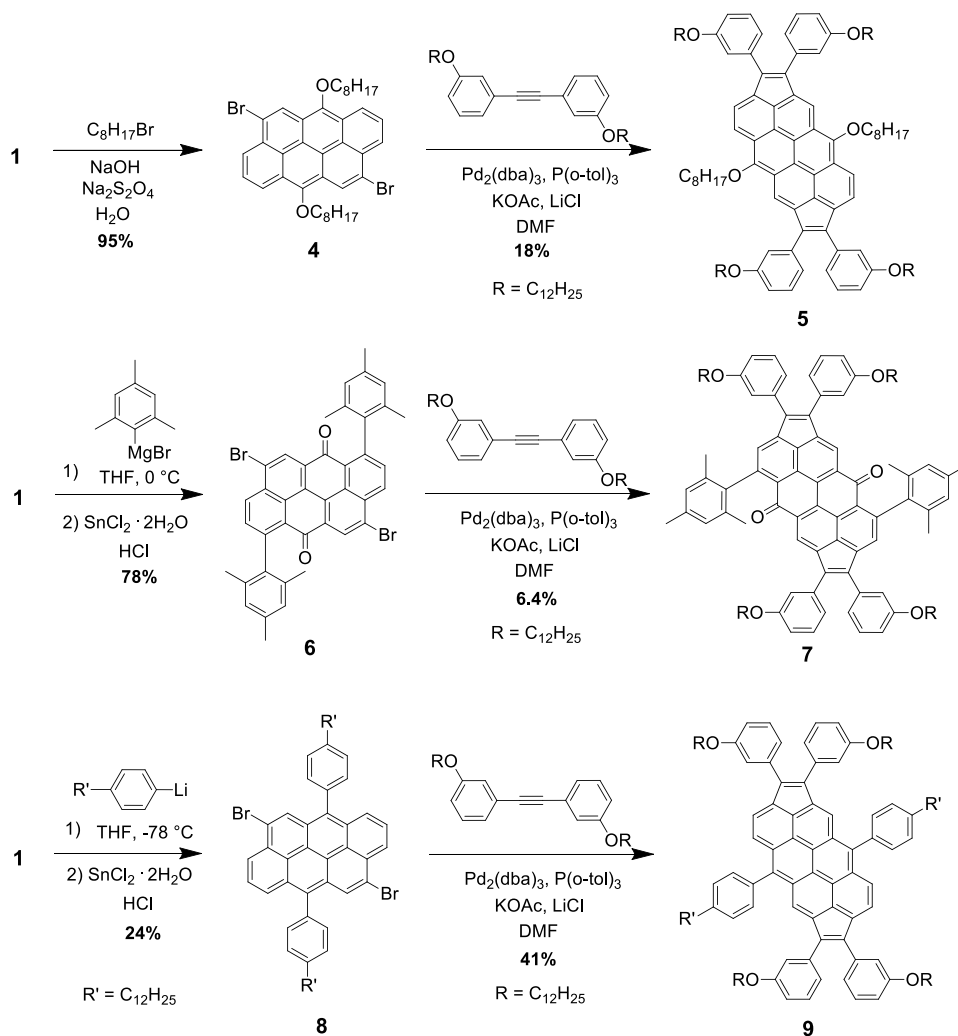


**Figure 1.** Vat Orange 3 (**1**) precursor and examples of anthanthrene based compounds.

interest in utilizing new PAH scaffolds to elucidate structure-property relationships in cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) to create new electron accepting materials. (refs) These materials have potential applications as negative channels in organic field effect transistors or acceptor materials in non-fullerene organic photovoltaics.<sup>5,6</sup>

In this manuscript, we have employed a low-cost dye, 4,10-dibromoanthanthrone (**1**, vat orange 3), as a precursor to new CP-PAHs (Figure 1). This inexpensive dye has already been utilized to prepare a multitude of functionalized anthanthrenes (e.g. **2** and **3**)<sup>7,8</sup> and can be easily functionalized at the ketone (6,12) and bromine (4,10) positions.<sup>9,10</sup> Several anthanthrene derivatives have been synthesized and tested as p-type semiconductors in OFETs and OSCs with charge mobilities up to  $0.078 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and solar power conversion efficiencies (PCE) up to 2.4%, respectively.<sup>7</sup> Among the challenges for these anthanthrene derivatives is ability to access planar yet soluble anthanthrene derivatives owing to the steric congestion at the periphery of the molecule. Recent strategies to maintain planarity include

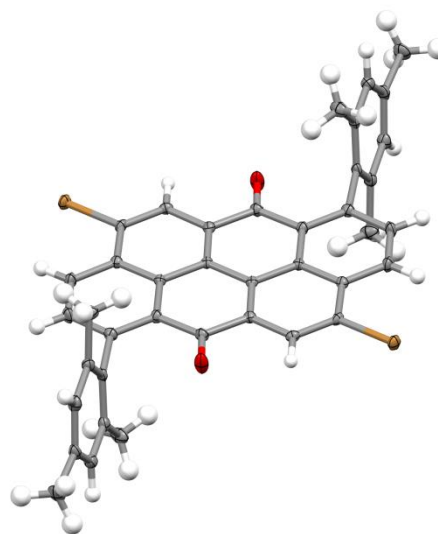
**Scheme 1.** Synthesis of anthanthrene based CP-PAHs from 4,10-dibromoanthanthrone **1**.



the formation of intramolecular H-bonding system<sup>11</sup> or the addition of alkyne spacers that help reduce the steric hindrance.<sup>12</sup> Herein, we demonstrate that a series of cyclopenta-fused anthanthrene derivatives (Figure 1) can be prepared via a palladium catalyzed cyclopentannulation reaction and the resulting materials are stable chromophores. Cyclopentene bridges were installed between the 3, 4 and 9, 10 positions of anthanthrene to extend the  $\pi$  surface, while keeping the backbone rigid. The resulting CP-PAHs were characterized by UV-Vis spectroscopy, cyclic voltammetry, and DFT calculations.

## Result and discussion

Substitution effects and their impact on the electronics around the anthanthrene core were investigated through the utilization of three different precursors based on **1**. Electron rich alkoxy and aryl derivatives, as well as electron poor diketone derivatives, were prepared. In the first route, **1** was reacted with 1-bromooctane under reducing conditions with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to give **4** in 95% yield.<sup>9</sup> The palladium catalyzed cyclopentannulation was then achieved by using Pd<sub>2</sub>(dba)<sub>3</sub>, P(*o*-tol)<sub>3</sub>, KOAc, LiCl in DMF to give the final the electron-rich alkoxy containing CP-PAH **5** in 18 % yield. The low yield is attributed to several byproducts that were difficult to separate.<sup>13</sup> In a second route aimed at preparing an aryl substituted derivative, 2-mesitylmagnesium bromide was added to **1** in hopes of addition to the carbonyl functionality to prepare anthanthrenes with mesityl groups at the 6 and 12 positions. However, we found that the Grignard reagent added via Michael addition to the 1 and 7 positions to give **6** in 78% yield. This was confirmed by single x-ray crystallography (Figure 2). This Michael addition chemistry has been recently witnessed in other PAH systems.<sup>14</sup> Attempts at reducing **6** with a series of reducing agents including NaBH<sub>4</sub>, LiAlH<sub>4</sub> and Zn/HCl were unsuccessful to obtain an aryl-functionalized anthanthrene core. Nevertheless, we performed the cyclopentannulation reaction on **6** to give the CP-PAH **7** that maintains the electron poor diketone functionality in 6.4% yield. This product was again accompanied by byproducts that made complete purification tedious. In a final



**Figure 2.** Crystal structure of **6** with thermal ellipsoids drawn at 50% probability.

route to access the aryl functionalized anthanthrene, we first reacted **1** with the organo-lithium species prepared from 1-bromo-4-dodecylbenzene to give **8** in 24% yield. Here, the organolithium species added to the carbonyl carbons to finally prepare the 6 and 12 functionalized derivative. The palladium catalyzed cyclopentannulation was then applied and product **9** was isolated in a much higher 41% yield. The new cyclopentene ring along with the two aryl groups, provided an opportunity to extent the planarized backbone of these

derivatives through cyclodehydrogenation reactions.<sup>15-17</sup> However, Scholl cyclodehydrogenation of the new derivatives with FeCl<sub>3</sub> or DDQ in TFA were unsuccessful in completing the ring closure of the new appended benzene rings.

The UV-Vis spectra of CP-PAH compounds **4**, **5**, **7**, **9** and **10** are found in Figure 3. The results show that the longest wavelength transitions of the new CP-PAHs were significantly bathochromic shifted comparing to **4**. The completely reduced anthanthrene based materials (**5** and **9**) were shifted to even lower wavelengths in comparison to diketone **7**. The onset absorption shifted from 470 nm for **4**, to ~710 nm for **5** and **9** (Table 1). This modulation of the absorption results in a ~0.9 eV reduction in the optical gaps after cyclopentannulation with the derivatives possessing optical gaps of around ~1.8 eV. Alternatively, the optical gap of **7** was minimally changed after the same cyclopentannulation reaction. This small change in optical properties owes to the aromatic isolation of the two CP-PAH units compared to the fully aromatized anthanthrene based derivatives.

The cyclic voltammetry spectra for **4**, **5**, **7**, and **9** are shown in Figure 4. On the reduction side of the spectra, the two new CP-PAH based materials with the reduced anthanthrene core (**5** and **9**) showed two reversible reduction waves and were more readily reduced than anthanthrene **4**. The compounds gave irreversible or pseudo-reversible oxidation transitions. The highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) were estimated in reference to an added ferrocene standard

(Table 1). The HOMO energies for **5** and **9** were calculated to be -5.11 eV and -5.19 eV, respectively and coincide with the higher HOMO energy being with the more electron-rich alkoxy-derived **5**. The LUMO energies were more similar and were found to be -3.41 eV

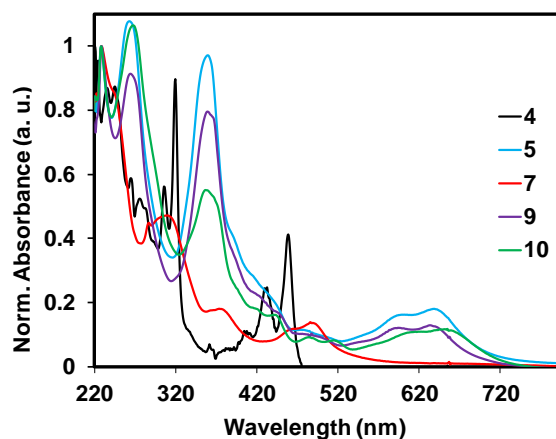


Figure 3. Absorption spectra **4**, **5**, **7**, **9**, and **10**.

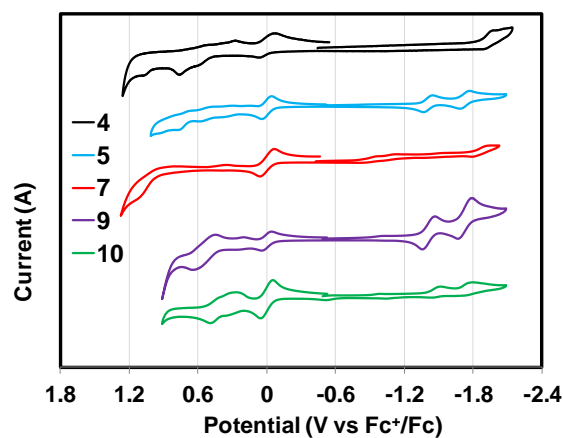


Figure 4. Cyclic voltammetry of 0.2 mM **4**, **5**, **7**, **9**, and **10** in dichloromethane with 0.1 M tetrabutyl ammonium hexafluorophosphate, glassy carbon working electrode, platinum counter electrode, and an Ag/AgCl reference electrode. Scan rate = 100 mV/s. Ferrocene added as internal standard and referenced to 0 V.

Table 1. Summary of optical and electronic properties of **4**, **5**, **7**, **9** and **10**<sup>a</sup>

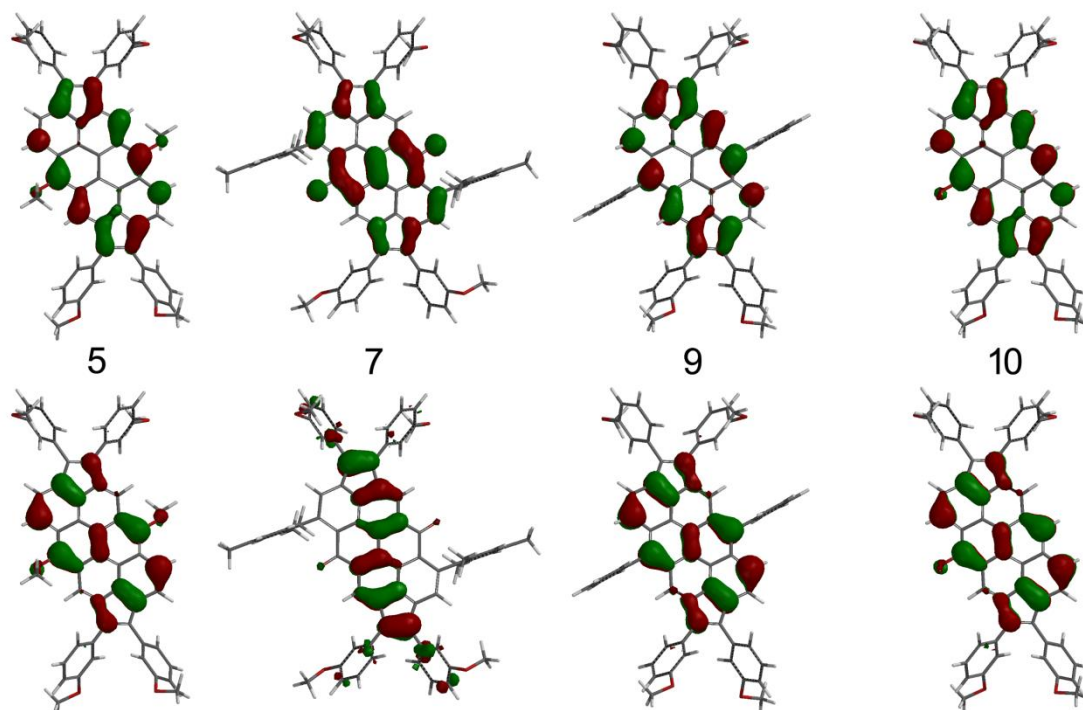
Cmpd	E <sub>ox/onset</sub> (V)	E <sub>red/onset</sub> (V)	HOMO (eV)	LUMO (eV)	E-chem gap (eV)	Optical gap (eV)
<b>4</b>	0.46	-1.90	-5.26	-2.90	2.36	2.64
<b>5</b>	0.31	-1.39	-5.11	-3.41	1.70	1.76
<b>7</b>	0.98	-0.88	-5.78	-3.92	1.86	2.29
<b>9</b>	0.39	-1.38	-5.19	-3.42	1.77	1.78
<b>10</b>	0.26	-1.39	-5.06	-3.41	1.65	1.71

<sup>a</sup>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 4). E<sub>ox/onset</sub> is the onset of oxidation potential, E<sub>red/onset</sub> 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).

and -3.42 eV, respectively. These LUMO energies were found to be not as low as other CP-PAHs we have recently developed.<sup>18,19,17,20</sup> The CV spectrum of diketone **7** was considerably different than the other two CP-PAHs, with the LUMO energy being considerably lower at -3.92 eV and the HOMO energy being significantly lower at -5.78 eV. The considerably lower LUMO energy arises owing to the reducibility of the electron-poor diketone functionality in addition to the cyclopentene functionality.

DFT calculations using the B3LYP/6-31G\*\* level of theory were performed on the new derivatives and the HOMO and LUMO contours can be found in Figure 5. Here the considerable differences in the optical and electronic properties of **5** and **9** in comparison to **7** are visualized in terms of differences in the frontier orbital contours. CP-PAHs **5** and **9** were quite similar in their distribution of both the HOMO and LUMO contours with the electron probabilities distributed around the anthanthrene core as well as the five-membered rings. Alternatively, diketone **7** was considerably different with the HOMO contour transcending through the middle of the molecule between the five membered rings and the LUMO heavily distributed out onto the ketone functionality. These results show that while these derivatives have similar cyclopentene ring structures their physical properties are heavily influenced by the core ring structure.

Lastly, we attempted to reduce the diketone functionality of CP-PAH **7** with NaBH<sub>4</sub> followed by re-aromatization with SnCl<sub>2</sub> in HCl (Scheme 2). Interestingly, a new intermediate species that maintains oxygen content was obtained and we assign to the structure **10**. The completely reduced anthanthrene-based compound was never isolated despite multiple conditions employed to carry **10** to a completely reduced structure. In all

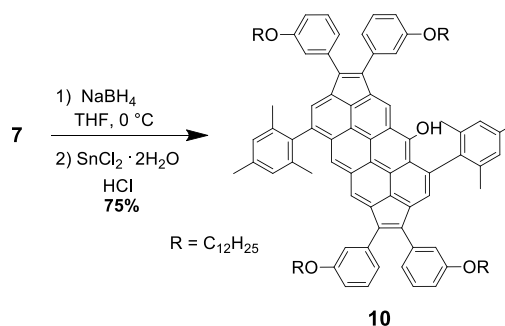


**Figure 5.** The B3LYP/6-311g DFT calculated HOMO (bottom) and LUMO (top) contours of **5**, **7**, **9**, and **10**.

attempts, the reactions conditions gave either **10**, or reverted to diketone **7**. The structure assignment of **10** was given owing to the NMR and MS analysis, as well as the similar DFT, UV-Vis, and CV spectra compared to **5** and **9**. These results and comparisons suggest the CP-PAH anthanthrene unit is present yet maintains oxygen content. In addition, **10** was found to be not as photostable as the other CP-PAH derivatives. The oxidation of **10** was observed using UV-Vis spectroscopy over several days with complete oxidation obtained in ~ 4 days (supporting information).

In conclusion, a series of new CP-PAHs based on an anthanthrene core were prepared from an inexpensive dye. Owing to the five-member ring inclusion, the anthanthrene based compounds absorbed significantly more light across the visible spectrum and were better electron acceptors. While the compounds were successfully prepared, the cyclopentannulation yields were low owing to difficulties removing byproducts from the reaction mixtures. The optical and electronic properties of these cyclopentannulated derivatives were heavily influenced by the core PAH. While the fully aromatized anthanthrene derivatives gave lower optical gaps the anthanthrene derivative gave considerably lower LUMO energies.

**Scheme 2.** Reduction of diketone **7**



## Acknowledgments

This work was supported by a National Science Foundation CAREER grant (CHE-1352431) and REU grant (DMR-1757954).

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