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Tunable electron acceptors based on cyclopenta[hi]aceanthrylenes

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ABSTRACT

A series of substituted cyclopenta[*hi*]aceanthrylene derivatives with electron donating (NH₂, OCH₃), neutral (H), and electron withdrawing (COOH, CF₃, CN, NO₂) substituents were prepared. A room-temperature Sonogashira cross-coupling reaction between 2,7-dibromocyclopenta[*hi*]aceanthrylene and an appropriately functionalized phenylene ethynylene precursor was utilized to access the materials that were characterized by Nuclear Magnetic Resonance Spectroscopy (NMR), cyclic voltammetry (CV), and UV–Vis spectroscopy. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were systematically varied when proceeding from electron donating to electron withdrawing substituents. The optical band gap was significantly altered for the most electron donating species, while little change was observed between different electron withdrawing substituents. This study demonstrates the ability to control the frontier orbital energies of this class of cyclopenta-fused polycyclic aromatic hydrocarbon materials through selective substitution.

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Introduction

Cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) are effective electron acceptors owing to their ability to form aromatic cyclopentadienyl anion-like structures in their reduced state.¹ Over the past several years, new CP-PAH scaffolds that allow systematic variation in substituent structure have been reported.^{2–7} These substitution strategies provide opportunities to tune frontier orbitals, such as the Lowest Unoccupied Molecular Level (LUMO), to beneficially interface with donor materials in organic photovoltaics^{8–10} or to access stable ambipolar or n-type organic field-effect transistors (OFETs).^{11–15} Here we demonstrate that the electronic properties of cyclopenta[hi]aceanthrylenes (CPAA) based materials can be systematically varied depending on the substituent constant of an attached arylene ethynylene.

We have previously utilized the CPAA scaffold to make both small molecule^{16–18} and polymeric materials¹⁹ with relatively stabilized LUMOs (\sim -3.6 eV). In this contribution, we show that by varying the electronic structure on the substituent rings, we can tune the HOMO and LUMO as well as the optical band gap of the material in a controlled fashion. We have employed phenylene ethynylene substitution of the CPAA core to facilitate electronic coupling via the alkyne linker. The synthetic strategy employs a Sonogashira cross-coupling reaction²⁰ between 2,7-dibromocy-

clopenta[*hi*]aceanthrylene¹⁶ and phenylene ethynylenes²¹ with varying electron withdrawing or donating substituents in the *para* position (Scheme 1). We have utilized the catalyst system of Pd(PhCN)₂Cl₂ and P(^tBu)₃ to perform these cross-couplings reactions and the purification of the resulting materials is straight forward via a simple precipitation and filtration to give high yields of the substituted compounds.

All substituted CPAA compounds are dark green in the solid state, produce emerald green solutions, and share similar absorption profiles (Fig. 1). Each UV–Vis trace shows a characteristic high energy absorption (280–380 nm, ε ~30,000 M⁻¹ cm⁻¹) and low energy absorption (530–880 nm, ε ~10,000 M⁻¹ cm⁻¹) with some variation depending on substituent composition. The onset of the longest wavelength absorption, which is related to the electronic band gap, can be influenced by the nature of the phenyl substituent. While, strongly withdrawing para-substituents (NO₂, CN, CF₃, COOH) do not appreciably change the onset of this band, the more electron rich unsubstituted (H) and electron donating substituents (OCH₃ and NH₂) do significantly red-shift the absorption band in accordance with the strength of the donor substituent. These observations are in agreement with known donor-acceptor diads and triads that show reduced band gaps with stronger donor and/or acceptor strengths.²²⁻²⁵ The optical band gap ranges from 1.43 eV to 1.61 eV for the most electron rich to the most electron poor substituent, respectively (Table 1). As found with previous 2,7-difunctionalized CPAAs, as well as other CP-PAHs, 4,26,27 1-7 are not fluorescent. The crystal structure of **4** shows the aryl groups are orthogonal to the plane of the CPAA core (Fig. 3). This arrangement could help explain the lack of optical gap variation for





Tetrahedror Letters

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Scheme 1. Sonogashira cross-coupling conditions to prepare tunable cyclopenta [*hi*]aceanthrylenes. ^aObtained from ethyl ester via saponification.



Figure 1. Absorbance of phenylene-ethynylene substituted cyclopenta[*hi*] aceanthrylenes.

Table 1			
Summary of electrocl	nemical and	optical	properties ^a

Cmpd	Substituent	E _{ox/onset} (V)	E _{red/onset} (V)	HOMO (eV)	LUMO (eV)	Optical E _{gap} (eV)
1	NH ₂	0.14	-1.20	-4.94	-3.60	1.43
2	OCH ₃	0.39	-1.18	-5.19	-3.62	1.52
3	Н	0.41	-1.13	-5.21	-3.67	1.57
4	COOH	0.54	-1.07	-5.34	-3.73	1.59
5	CF ₃	0.57	-1.04	-5.37	-3.76	1.60
6	CN	0.59	-1.02	-5.39	-3.78	1.60
7	NO ₂	0.62	-1.00	-5.42	-3.80	1.61

^a Potentials are measured relative to a ferrocenium/ferrocene redox couple used as an internal standard (Fig. 2). $E_{\text{ox/onset}}$ 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).

electron accepting substituents. Although we were unable to grow suitable crystals of more electron rich substituents, we hypothesize the aryl rings are more coplanar with the CPAA core, which would facilitate the observable bathochromic shifts.

The cyclic voltammograms (CV) of each substituted CPAA can be found in Figure 2. While the UV–Vis spectra (Fig. 1) show variation only with the most electron rich substituents, the CV traces show that both the highest occupied molecular level (HOMO) and LUMO are systematically varied across the entire range of



Potential (V vs Fc+/Fc)

Figure 2. Cyclic voltammograms of 1–7 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 0V.



Figure 3. Crystal structure of 4²⁹.

electron withdrawing to electron donating substituents. All derivatives show irreversible oxidations and at least two reversible reductions. The onset of the first oxidation wave shows a step-wise cathodic shift going from electron withdrawing (7, NO₂) to electron donating (1, NH₂) substituents (Table 1), which demonstrates that stronger electron donating groups make the compounds easier to oxidize. The range in HOMO energies vary from -4.94 eV to -5.42 eV for **1** to **7**, respectively, and shows the destabilization of the HOMO with increasing donating character. The onset of the first reduction wave shows a step-wise anodic shift going from electron donating to electron withdrawing substituents. The range in LUMO energies vary from -3.60 eV to -3.80 eV for 1 to 7, respectively and confirm that stronger withdrawing groups make the structures easier to reduce. The LUMO values of the 1-7 can be analyzed via a Hammett Plot (Fig. 4) that shows the variation of LUMO energy versus the known substituent constants.²⁸ A linear relationship between the LUMO values and the substituent



Figure 4. Hammett plot of LUMO level (eV) versus substituent constant (σ) as it relates to aryl substitution. $R^2 = 0.973$.

constant is found and demonstrates the ability to systematically vary the frontier orbitals in this system. The band gap energies do not follow a linear trend when subjected to a Hammett plot owing to the plateau with electron withdrawing groups.

In conclusion, we have shown that systematic variation of the aryl substituent of a CPAA scaffold can efficiently tune the HOMO and LUMO energy over a 0.5 V and 0.2 V window, respectively. The work demonstrates a rational design for electron accepting materials based on cyclopenta-fused polycyclic aromatic hydrocarbons and provides opportunities to efficiently match energy levels for applications such as OPV devices.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.11. 022.

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- 20. Synthesis of 2,7-substituted cyclopenta[*hi*]aceanthrylenes. In a glovebox were combined 2,7-dibromocyclopenta[*hi*]aceanthrylene (1 equiv), aryl ethynylene (3 equiv), Pd(PhCN)₂Cl₂ (6 mol %), and Cul (6 mol %) in a small vial. To these solids were added toluene (4 mL), diisopropylamine (0.8 mL), and PtBu3 (12 mol %). The vial was capped and stirred for 48 h at 50 °C. The solvent was removed, and the crude solid was dissolved in a minimal amount of THF and precipitated into cold methanol.
- 21. Synthesis of aryl ethynylenes. In a glovebox were combined aryl bromide, Pd (PPh₃)2Cl₂ (5 mol %), triphenylphosphine (10 mol %), THF (50 mL), and triethylamine (10 mL). After stirring 3 min, Cul (5 mol %) was added and the solution was stirred another 1 min. TMS-acetylene (1.5 equiv) was then added and the reaction vessel was sealed and heated to 60 °C for 18 h. The reaction mixture was cooled, concentrated, and the residue was purified by silica gel chromatography. The obtained intermediate was then dissolved in THF (50 mL), methanol (25 mL), and a 20% KOH solution (aq, 15 mL) in 250 mL round bottom flask and stirred overnight at room temperature. The solution was diluted with ethyl ether (150 mL) and extracted twice with brine (50 mL). The organic layer was collected and concentrated to give a residue that was purified by silica gel chromatography.
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