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Synthesis and Optical Properties of Phenylene-Containing Oligoacenes (POAs)

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Supporting Information Placeholder

ABSTRACT: The synthesis of a new class of fully unsaturated ladder structures, phenylene-containing oligoacenes (POAs), using 3,4-Bis(methylene)cyclobutene as a building block for sequential Diels-Alder reactions is described. Analysis of the electronic effects of strain and antiaromaticity demonstrates stable, extended structures in which neighboring chromophores are partially electronically isolated while still undergoing a reduction in the HOMO-LUMO gap.

Introduction

The promise of organic electronics to enable the creation of inexpensive, flexible, and multifunctional devices¹ is presently limited by access to stable high performance materials. One strategy to develop such materials is to create extended rigid aromatic systems that promote delocalization and minimize energetic disorder in the electronic states. Among the polycyclic aromatic hydrocarbons (PAHs), acenes, defined as linearly annelated arenes with the fewest number of rings containing Clar sextets,² are considered one of the most important candidates for high performance organic semiconductors (Figure 1a).

A natural strategy to create higher charge mobilities in an organic material is to increase the spatial electronic delocalization in the constituent molecular building blocks. However, as the length of the acene increases, the reduction in aromaticity also causes a rapid decrease in the HOMO-LUMO gap, and the chemical stability of these materials becomes problematic. The higher acene homologs do appear to have improved electronic properties, such as increasing charge mobility, decreasing reorganization energy, and a predicted decrease in exciton binding energy. This final property is appealing for solar cell applications, where recently the unique ability of acenes to undergo singlet fission has been of interest as a method of creating two dissociated charge carriers from a single photon.³

A close relative to the acenes are the [N]phenylenes, a family of PAHs wherein benzene rings are fused together by four-membered rings, resulting in a ladder structure with alternating aromatic and antiaromatic character (Figure 1b).⁴ Molecules of this family have classically been synthesized *via* the [2+2+2] cycloaddition methodology developed largely by Vollhardt *et al.* It has been demonstrated both experimentally and theoretically that the π -bonds in these systems tend to localize within the six-membered rings so as to minimize the 4π antiaromatic character of the cyclobutadiene linkage.⁵ Recently, a dibenzannulated biphenylene framework served as key intermediate in the synthesis of the first example of [4]circulene.⁶ We report herein that antiaromatic phenylene-linkages can be used in conjunction with oligoacene units to create high stability extended, shape-persistent phenylene-

containing oligoacenes (POAs) with interesting electronic properties.

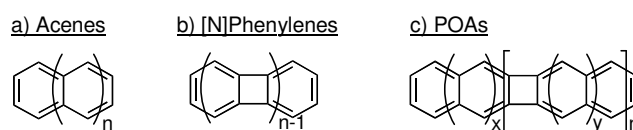


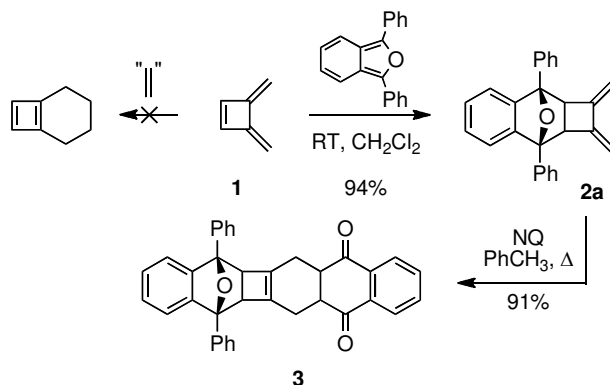
FIGURE 1. General structure of (a) acenes, (b) [N]phenylenes, and (c) phenylene-containing oligoacenes (POAs).

Results and Discussion

Diels-Alder Reactivity of 3,4-Bismethylenecyclobutene.

The synthesis reported herein relies on the unique Diels-Alder reactivity of 3,4-bis(methylenecyclobutene) (**1**) (Scheme 1).⁷ Although the exocyclic methylene groups are locked in the desired *s-cis* conformation, **1** is not reactive as a Diels-Alder diene as the resulting product would contain cyclobutadiene. However, we have shown that initial reaction of the endocyclic double bond with a diene such as 1,3-diphenylisobenzofuran (Scheme 1) is facile and selective. This reaction, in turn, generates a single isomer of **2**, which is reactive as a Diels-Alder diene. A second Diels-Alder reaction with 1,4-naphthoquinone yields a single isomer of polycyclic **3**.

SCHEME 1. Sequential Diels-Alder reactions to yield **3**.



The stereoselectivity of each Diels-Alder reaction has been confirmed by both 2D NMR of **2** (Figures S11-S13, Supporting Information) and X-ray crystallography of **3** (Figure 2a). Although Diels-Alder reactions of isobenzofurans tend to result in a mixture of isomers,⁸ the initial reaction in this case is selective for the *exo* product, consistent with previous reports by Kaupp *et al.*⁹

Examining the calculated LUMO of **1** (B3LYP/6-31g**, Figure 2b), secondary orbital interactions (SOI) of the orbitals on C3/4 with the diene HOMO would favor the *endo* transition state, however the coefficients at this position are significantly smaller than those at C5/C6. Additionally, the geometry of the highly strained ring brings the C5/C6 molecular orbitals closer to the reaction site, causing instead an anti-bonding interaction in the *endo* transition state. In the second Diels-Alder reaction, the product results from approach of the dienophile to the less hindered side of diene **2**.

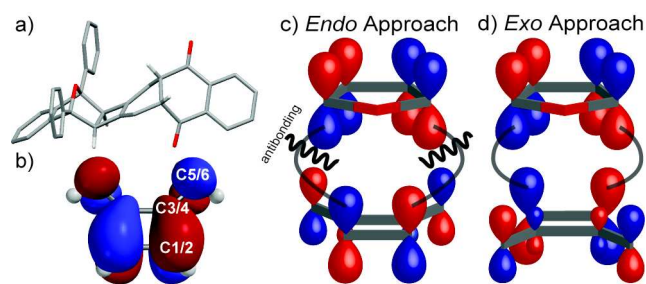
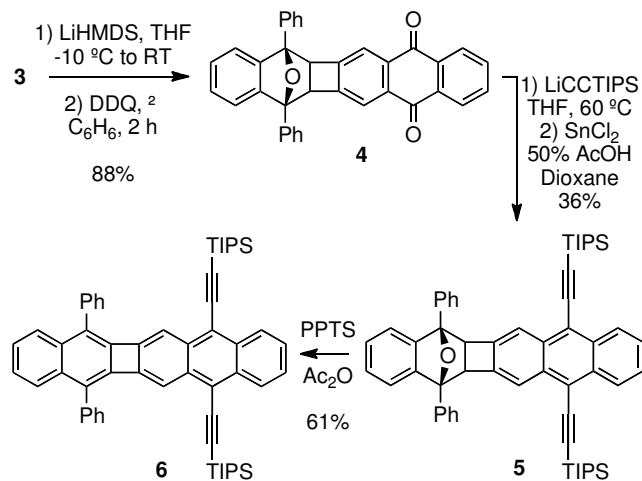


FIGURE 2. (a) X-Ray crystal structure of **3**. (b) LUMO of **1** (B3LYP/6-31g**). (c) *Endo* and (d) *exo* approaches of **1** to a furan diene.

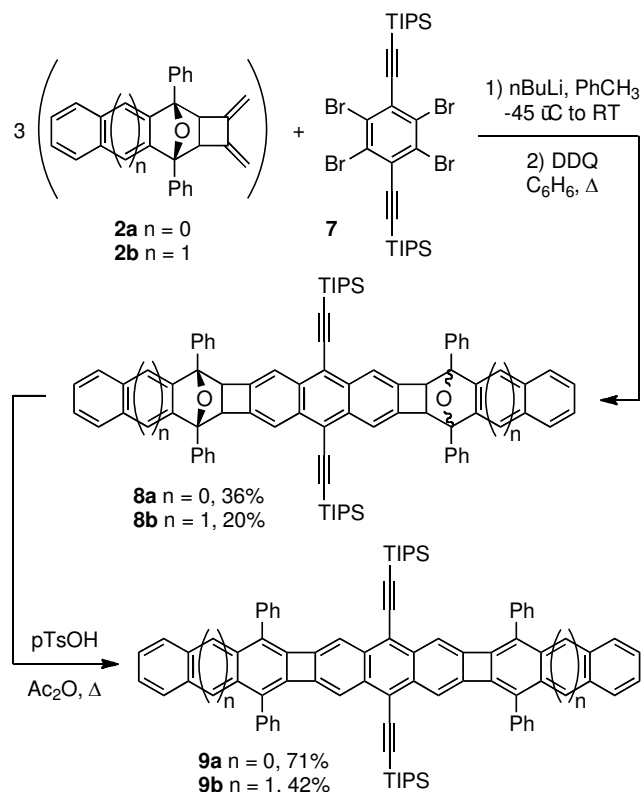
Synthesis of POAs. With **3** in hand, its fully-unsaturated counterpart, compound **6**, is readily available through a series of synthetic transformations (Scheme 2). Addition of a strong base such as LiHMDS generates the high-energy bis-enolate, which then oxidizes to the 1,4-quinone, presumably by action of air introduced during the work-up. DDQ is then used to aromatize the neighboring ring giving compound **4** in an 88% yield over two steps (for X-Ray crystal structure of **4** see Figure S5-S6, Supporting Information). Nucleophilic addition of TIPS-protected lithium acetylide followed by reductive deoxygenation yields the TIPS-anthracene containing **5**. Finally, **5** is dehydrated to give **6**. Analysis by differential scanning calorimetry (DSC) indicates the high thermal stability of POA **6** (Figure S1, Supporting Information).

SCHEME 2. Synthesis of POA **6** from compound **3**.



Based on the synthetic methodology demonstrated above, molecules of this family can be extended into even larger structures (Scheme 3). 1,3-Diphenylisobenzofuran¹⁰ can be used to generate diene **2b**. Reacting a bis-functionalized dienophile with **2** results in symmetrical structures. As a bisaryne precursor, we chose to use 1,2,4,5-tetrabromo-1,6-bis(triisopropylsilyl)ethynylbenzene (**7**), synthesized *via* the procedure previously reported by our laboratory.¹¹ Products from the bisaryne Diels-Alder addition of **2** with **7** were taken on to aromatization step without further purification to yield isomeric mixtures of precursors **8a/b**. Dehydration was then carried out with *p*TsOH in acetic anhydride to give the desired POAs **9a/b**.

SCHEME 3. Bisaryne Diels-Alder reaction and aromatization to yield POAs **9a/b**.



Optical and Electrochemical Properties. Analysis of the optical properties of **6** and **9a/b** as compared to those of TIPS-anthracene (**TIPS-Anth**)¹² is shown in Figure 3. The absorbance curve of **5** is almost identical to that of **TIPS-anth** with the exception of a slightly lower energy absorption around 260 nm corresponding to the phenyl substituents (Figure S2, Supporting Information). In the case of **6**, there are two distinct absorbances; a higher energy absorption due to the diphenylnaphthalene chromophore and lower energy absorption

($\lambda_{\max} = 464$ nm) due to the diethynyl-anthracene chromophore. The 21 nm bathochromic shift between TIPS-anthracene and compound **6** demonstrates that although the phenylene-linkage limits delocalization between the two chromophores there is still sufficient communication to cause a reduction in the bandgap of about 0.17 eV. A similar pattern is evident in the absorbance curves of **9a/b**, with a reduction in the band gap with each increase in the length of the POA.

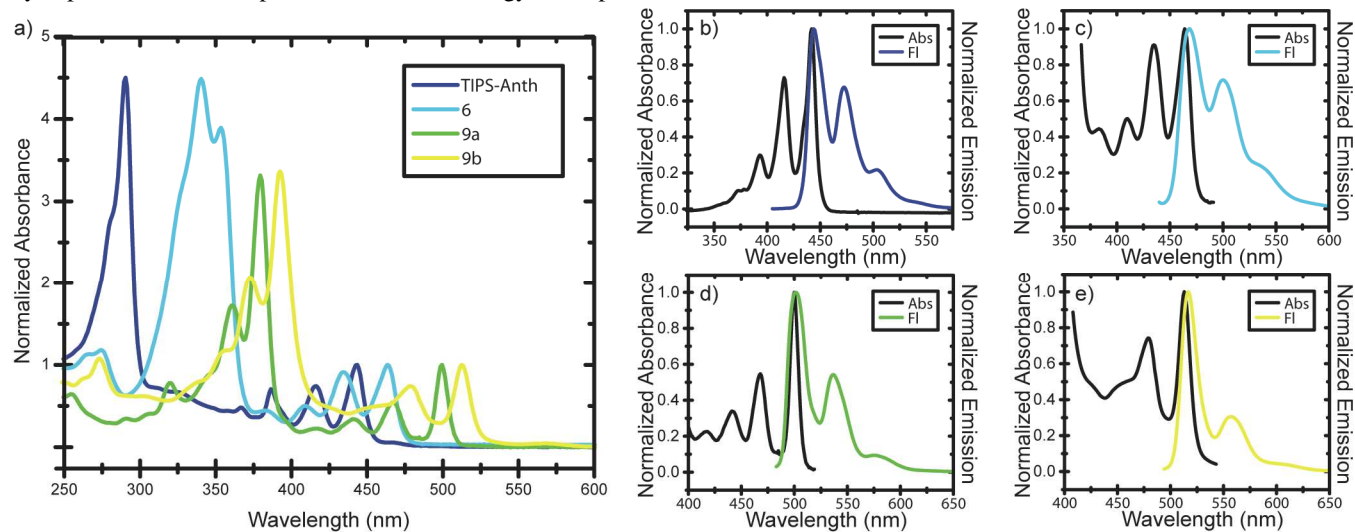


Figure 3. (a) Overlay of the absorbance curves of **TIPS-Anth**, **6**, and **9a/b**. Absorbance and Emission of (b) **TIPS-Anth**, $\lambda_{\max} = 442$ nm, $\lambda_{\text{em}} = 444$ nm, $\phi_{\text{em}} = 0.97$, $\tau = 5.04$ ns; (c) **6**, $\lambda_{\max} = 464$ nm, $\lambda_{\text{em}} = 469$ nm, $\phi_{\text{em}} = 0.69$, $\tau = 7.72$ ns (d) **9a**, $\lambda_{\max} = 500$ nm, $\lambda_{\text{em}} = 502$ nm, $\phi_{\text{em}} = 0.45$, $\tau = 5.60$ ns, and (e) **9b**, $\lambda_{\max} = 513$ nm, $\lambda_{\text{em}} = 517$ nm, $\phi_{\text{em}} = 0.26$, $\tau = 6.71$ ns. All experiments were performed in CHCl_3 .

There is a corresponding bathochromic shift in the emission curve of each POA. The emission quantum yields decrease within the series from **TIPS-Anth** ($\phi_{\text{em}} = 0.94$) to **9b** ($\phi_{\text{em}} = 0.26$). In each case the Stokes shifts are small, ranging from 2–5 nm, consistent with the rigid, shape-persistent nature of these materials.

The ionization potential and stability of the oxidized forms of the POAs were analyzed by cyclic voltammetry (CV) (Table 1 and Figure S3, Supporting Information). The difference in the potential of the first oxidation peak (E_{ox} vs. Fc/Fc^+) of **TIPS-Anth**, **6**, and **9a** is quite small decreasing from 710 mV for **TIPS-Anth** to 678 mV for **9a**. Therefore, the reduction in the band gap for these three species can primarily be attributed to a decreasing LUMO level, confirming oxidative stability. Although **TIPS-Anth** and **6** both undergo only one reversible oxidation, compound **9a** displays a second oxidation peak within the window studied. Compound **9b**, alternatively, exhibits three reversible oxidation peaks, with the first two shifted to significantly lower potentials than those previously discussed. Consistent with these findings, **9b** appears to be susceptible to slow oxidative degradation in the solution state.

TABLE 1. Electrochemical Data for POAs.

Compound	E_{ox} (mV) ^a vs. Fc/Fc^+	HOMO (eV)	LUMO (eV)	E_g (optical) ^b (eV)
TIPS-Anth	710	-5.42	-2.68	2.74

6	702	-5.41	-2.84	2.57
9a	678	-5.39	-2.96	2.43
9b	527	-5.24	-2.87	2.37

^aPerformed in a 0.1 M solution of TBAPF₆ in CH_2Cl_2 , Pt button electrode, scan rate 150 mV/s, ferrocene as an external standard. ^bDetermined from λ_{onset} in CHCl_3 .

Structural Analysis. Compounds **6** and **9a** were both analyzed by X-ray crystallography (Figure 5). Examination of the bond lengths around the phenylene-linkage confirms the increased localization of π -bonds, with bonds lengths alternating between 1.46 Å exocyclic and 1.34 Å endocyclic to the four-membered ring. Although theoretical studies have shown [N]phenylenes to be planar in the lowest energy conformation, strain and antiaromaticity are also known to impart additional flexibility to [N]phenylenes in the solid state.¹³ In the case of **6** and **9a** there are small torsion angles around the phenylene-linkage (5.60°/1.31° and 1.58°/0.05°, respectively), however the molecules are very close to planar.

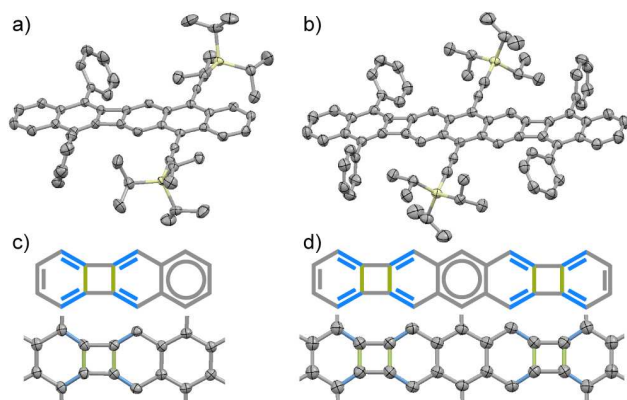


FIGURE 4. X-ray crystal structures of (a) **6** and (b) **9a**. Localization of \bullet -bonds in (c) **6** and (d) **9a**.

Summary

In conclusion, we have reported the design and synthesis of new class of non-benzenoid PAHs, phenylene-containing oligoacenes. The unique reactivity of 3,4-bismethylene-cyclobutene was exploited to build ladder structures *via* sequential Diels-Alder reactions. The resulting POAs represent stable, shape-persistent chromophores, with band gap and quantum efficiencies that decrease as length increases. Studies on the ability of this class of molecules to participate in singlet fission are underway.

ASSOCIATED CONTENT

Supporting Information. Experimental data including synthetic procedures, characterization data for all compounds, and additional figures. 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.

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