

Synthesis and Electronic Properties of Extended, Fused-Ring Aromatic Systems Containing Multiple Pentalene Units

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Abstract: A series of elongated dibenzopentalenes were synthesized via a Pd-catalyzed cyclization followed by an Fe-mediated cyclodehydrogenation. Structural geometries varying from linear to extremely bent are shown to drastically influence solubility properties as well as reduction potentials. Comparisons are made to monopentalenes and related diindenoindacenes. UV–vis absorption spectra and cyclic voltammetry measurements indicate a strong modulation of the electronic structure of these compounds mediated by the strength of interactions between pentalene centers.

Fused polycyclic aromatic hydrocarbons displaying extended π -conjugation, particularly linear polyacenes, have become a primary focus in the field of organic electronics. While pentacene derivatives are considered to be among the most promising organic semiconductors, they are commonly susceptible to oxidative degradation and often suffer from poor solubility. Extended pentalene derivatives^{1,2} and related polyindenoindenes,³ though scarcely studied, represent an interesting alternative to classic polyacenes. Until recently,^{4a–f} synthetic methodologies for accessing indenoindenes, dibenzopentalenes, and other five-membered ring acene analogues were quite limited. This contribution describes a series of extended dibenzopentalene derivatives (Figure 1, 1–4) with varying structural geometries, obtained by

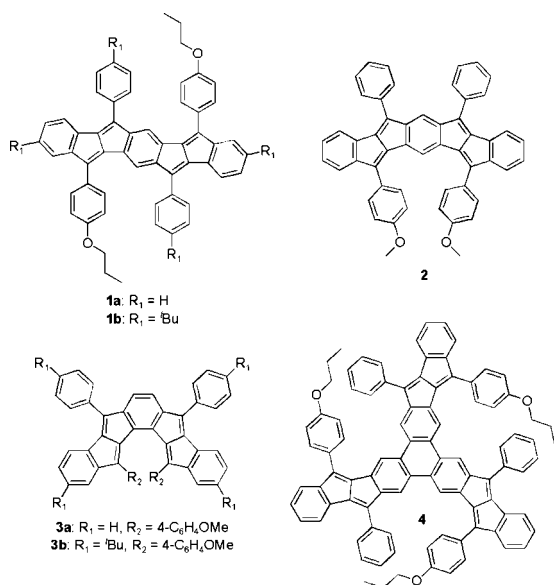


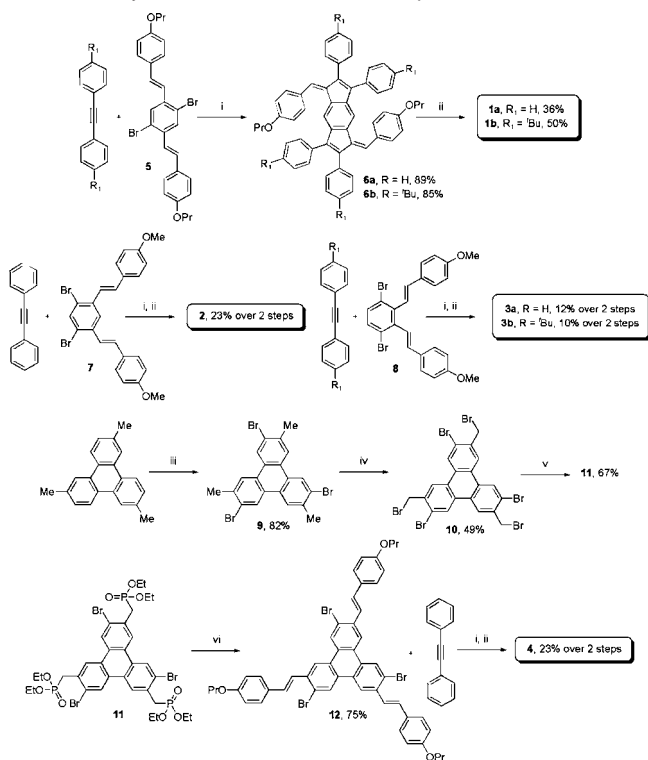
Figure 1. Highly extended dibenzopentalene derivatives 1–4.

utilization of a two-step reaction sequence that allows for the controlled cross-coupling of a bromostilbene with a diarylalkyne.^{4d} Through spectroscopic and electrochemical measurements, the geometric arrangement of pentalene moieties is shown to influence electronic

structure, reduction chemistry, and solubility properties. This class of materials, centered around multiple electroactive pentalene units, displays extended conjugation while benefiting from air and moisture stability and exhibiting solubility properties that are readily modulated. Although many extended ladder π -conjugated compounds have been prepared,⁵ only one report describes elongated dibenzopentalene derivatives with more than one pentalene moiety in a single molecule,⁶ obtained as a mixture of minor products upon reaction of $PtCl_4$ with 1,2,4,5-tetrakis(phenylethynyl)benzene.

The synthesis of multipentalene based compounds 1–4 is outlined in Scheme 1. Bromostilbene derivatives 5, 7, and 8 were

Scheme 1. Synthesis of Extended Dibenzopentalenes 1–4^a



^a Conditions: (i) *N,N*-diisopropylethylamine, PPh_3 , $Pd(OAc)_2$, 135 °C; (ii) $FeCl_3$, $MeNO_2$, CH_2Cl_2 , CS_2 , RT; (iii) Fe , Br_2 , $MeNO_2$, 80 °C, in the dark, RT, 82%; (iv) *N*-bromosuccinimide, benzoyl peroxide, 1,2-dichlorobenzene, 180 °C, 49%; (v) $P(OEt)_3$, 170 °C, 67%; (vi) (a) NaH , THF, 0 °C; (b) 4-propoxybenzaldehyde, 60 °C, 75%.

prepared with use of established Horner–Wadsworth–Emmons (HWE) chemistry starting from commercially available *para*-, *meta*-, and *ortho*-xylene, respectively; alkoxy substituents were included to aid the solubility of the final products. Under standard Heck conditions ($Pd(OAc)_2$, PPh_3 , DIPEA, DMF, 135 °C),^{4d} 5 reacted with an excess of the appropriate diarylacetylene to afford the *s*-indacenes 6a and 6b, which precipitate from solution as light

maroon solids. Related palladium chemistry has recently been used to construct indacendiide ligands,⁷ and the formation of **6a/b** likely occurs through a similar mechanism. Oxidative cyclodehydrogenation of **6a/b** with FeCl₃ affords the linear dipentalenes **1a** and **1b** as dark purple solids. While **1a/b** have exceedingly low solubilities in common organic solvents, carbon disulfide (CS₂) is an excellent solvent for both chromatographic purification and structural characterization.

Dipentalenes **2** and **3a/b** were prepared by an identical two-step reaction sequence. However, the high solubility of the corresponding indacenes made purification of these intermediates difficult. Thus, these indacenes were used in subsequent cyclodehydrogenations with minimal purification. The resulting dipentalenes **2** and **3a/b** are readily soluble in common organic solvents and easily purified by column chromatography; in the case of **3a/b**, a helical twist along the molecular framework is likely responsible for the heightened solubility relative to **1a/b**.

To extend this chemistry beyond dipentalene derivatives, the triphenylene tribromide **12** was synthesized. Trimethyltriphenylene was prepared according to the literature procedure⁸ and subjected to electrophilic bromination conditions to afford 2,6,10-tribromo-3,7,11-trimethyltriphenylene in high yield (82%). A 3-fold benzylic bromination followed by an Arbuzov reaction with excess triethylphosphite afforded the triphosphonate **11**. Subsequent reaction of **11** under HWE conditions with 4-propoxybenzaldehyde furnished the necessary tribromotrialkene **12** in good yield (75%). Treatment of this bromoarene under standard Heck conditions with excess diphenylacetylene followed by a 3-fold cyclodehydrogenation afforded the dark-red tripentalene **4**.

The electronic spectra (Figure 2) and electrochemical behavior (Figure 3) of the extended pentalenenes differ significantly from the monopentalenes prepared to date.⁴ The lowest energy absorption band displays a large bathochromic shift of 100 nm with a 4.8-fold increase in the extinction coefficient upon extending the conjugation from monopentalene **A** to the linear dipentalene **1b**. The linear dipentalenes also differ markedly from **2** to **4**; consistent with the linear dipentalenes having the longest effective conjugation length, **1b** also exhibits the lowest energy λ_{\max} value (Table 1) while having extinction coefficients that are comparable to those of the tripentalene **4**. Preliminary optical characterization indicates that these materials are nonfluorescent.

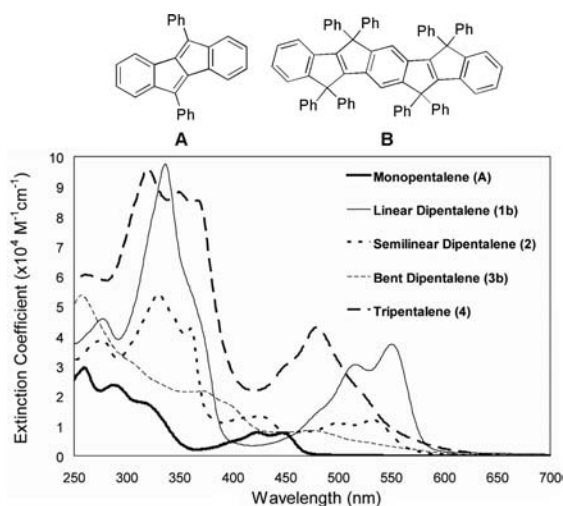


Figure 2. Absorption spectra of **1–4** in CH₂Cl₂ (10⁻⁵ M).

While monopentalenes (MPs) typically display one to two reductions to form the corresponding dianion, up to four reductions

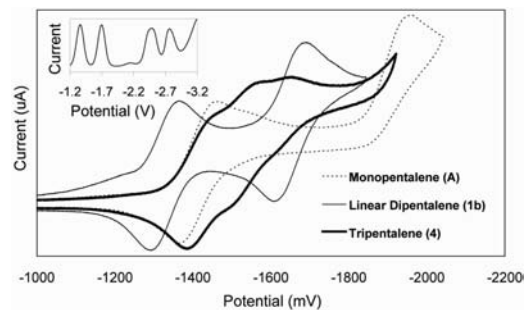


Figure 3. Cyclic voltammograms of **A**, **1b**, and **4** in CH₂Cl₂: V versus Fc/Fc⁺ in 0.1 M nBu₄NPF₆/CH₂Cl₂ at 100 mV/s scan rate; Fc/Fc⁺ = 0.19 V; Inset: Square wave voltammogram of **1b** in 0.3 M Bu₄NClO₄/THF.

Table 1. Comparisons of Mono-, Di-, and Tripentalenes

Compound	^{red} E _{1,1/2} [V]	^{red} E _{2,1/2} [V]	(E _{1,1/2} - E _{2,1/2}) [V]	λ_{\max} (nm)
Monopentalene A ^a	-1.41 (-1.58)	-1.96 (-2.13)	0.55	447
Linear Dipentalene 1b	-1.33	-1.65	0.32	550
Semilinear Dipentalene 2	-1.34	-1.71	0.37	534
Bent Dipentalene 3b	-1.56	-1.89	0.33	476
Tripentalene 4	-1.64	-2.19	0.55	479
Diindenoindacene B	-2.75	—	—	419

^a Literature average of single dibenzopentalenes in parantheses.⁴

can be observed for the dipentalenes (Figure 3, Inset). These reductions occur at significantly more positive potentials for the dipentalenes versus the monopentalenes (Table 1); that is, the formation of **1b**⁻¹ occurs at a potential ca. 80 mV (240 mV) more positive than that for **A**⁻¹ (lit average for MP⁻¹), and the formation of **1b**⁻² occurs at a potential ca. 310 mV (480 mV) more positive than that for **A**⁻² (lit average for MP⁻²). Furthermore, tripentalene **4** displays three distinct reductions centered around the first reduction potential for typical MPs (-1.4 to -1.6 V). Thus, the absorption spectra and distinctive cyclic voltammetric behavior suggest a strong modulation of the electronic structure of these compounds mediated by the strength of interactions between pentalene centers. In the case of **1**, and to a lesser extent **2** and **3**, strong coupling across the π -framework results in extended conjugation, more positive reduction potentials, and delocalized anions. In stark contrast, the triphenylene core in **4** imparts weak coupling across the structure resulting in three nearly independent pentalene moieties. In addition, a noteworthy comparison can be made to the recently prepared diindenoindacene **B**,⁹ which, lacking a pentalene moiety, exhibits only a single reduction at -2.75 V.

This work demonstrates the versatile synthesis of elongated dibenzopentalene derivatives containing for the first time up to three pentalene units in a single molecule. In addition, the low reduction potentials of the dipentalenes suggest a delocalized diradicaloid structure for the corresponding dianions. The reduction chemistry and enhanced optical absorption combined with air and moisture stability make these extended materials promising candidates for use in organic electronic devices.

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Supporting Information Available: Experimental details, UV-vis absorption spectra, and cyclic voltammograms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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