Larger Acenes

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Heptacene and Beyond: The Longest Characterized Acenes**

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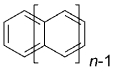
acenes · heptacene · HOMO–LUMO gap · molecular electronics · nonacene

Acenes (**1**) are polycyclic aromatic hydrocarbons consisting of linearly fused benzene rings.[1] The smallest acenes, benzene, naphthalene, and anthracene, are among the most studied organic molecules, while pentacene has received much attention as an active semiconducting material in organic field-effect transistors (OFETs)[2] owing to its high charge-carrier mobility.[3] Since increased conjugation length is expected to be beneficial for some applications in organic electronics, interest in the synthesis of acenes larger than pentacene has been increased in the last decade, and significant efforts have been devoted to the development of appropriate synthetic methods.[3] However, the synthesis of larger stable acenes is a difficult and challenging task because of their very low solubility, poor light and oxygen stability, and tendency to dimerize, as well as the difficult multistep synthetic approaches required. Consequently, successful experimental studies on larger acenes are very limited. An excellent review by Anthony covered the literature on larger acenes up to 2007.[3c] In recent years and, particularly, in the last one and a half years, significant progress has been made in the synthesis of larger acenes, and stable and fully characterized heptacene derivatives were obtained.[4–7]



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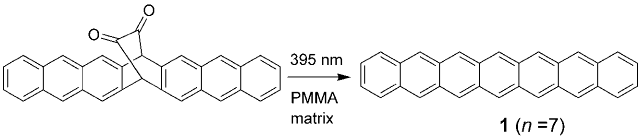
Larger acenes can be considered to be the building blocks of carbon nanotubes and graphene, and studies on larger acenes may increase understanding of their properties. For example, the chirality of carbon nanotubes can be described as arising from different arrangements of the acene chains that are responsible for its electronic properties (metallic or semiconducting). Although the electronic properties of larger acenes have been examined extensively using computational techniques,[3a] their electronic structure, aromaticity, and HOMO–LUMO gaps are still not completely understood. A singlet disjoint biradical character in the ground states of larger acenes is predicted based on UB3LYP/6-31G(d) calculations.[8] Using spin-polarized DFT, Jiang and Dai predict antiferromagnetic ground states for larger acenes ($n > 7$) and polyacenes.[9] As the number of rings increases, acenes become increasingly reactive, with the central ring being the most reactive.[10–12] Photooxidation with molecular oxygen and dimerization of the longer acenes are the major degradation pathways.[11]

Although the synthesis of heptacene (**1**, $n = 7$) was claimed in 1942,[13a] later reports in 1943[13b] and 1955[13c] questioned this synthesis and it was withdrawn[13d] in 1957. No significant progress in this area was made until 1986, when the synthesis of larger acenes was reported in the PhD dissertation of Fang which was written under the supervision of Chapman.[14] Thermolysis of the heptacene dimer was reported to produce heptacene.[14] However, pure heptacene was not obtained, since it was always contaminated with heptacene dimer and dihydroheptacene. Heptacene formation was confirmed by accurate mass measurement (using mass spectrometry) and by the λ_{max} value for the highest wavelength absorption band in the sublimed film (968 nm) and in 1-methylnaphthalene solution (at 220 °C, 752 nm).[14]

Twenty years later, Neckers and co-workers obtained unsubstituted (parent) heptacene in a poly(methyl methacrylate) (PMMA) matrix by photodecarbonylation of a dione precursor at 395 nm (Scheme 1).[4] The λ_{max} value (roughly 760 nm, for the central vibronic peak) recorded in the PMMA matrix concurred with Fang's report[14] on unsubstituted



Scheme 1. Synthesis of heptacene in a poly(methyl methacrylate) (PMMA) matrix.[4]

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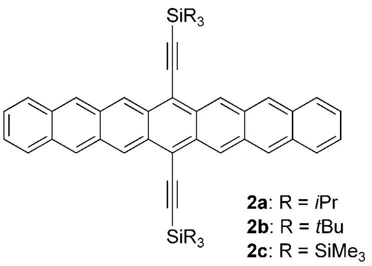
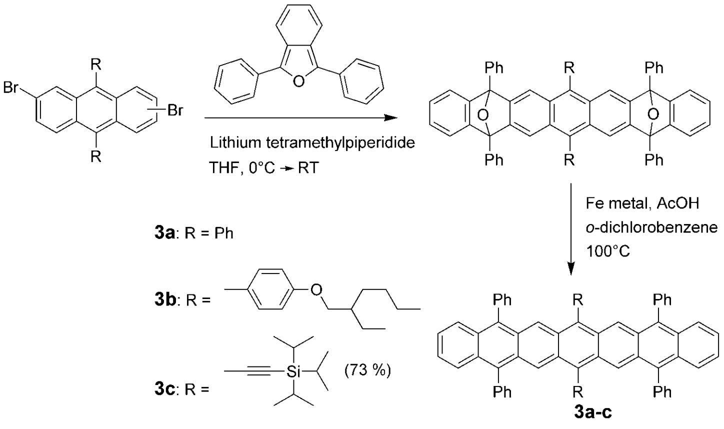
heptacene. Heptacene was found to be stable for only 4 h in the PMMA matrix, also confirming the reactivity of this compound. In solution, it immediately converts into the oxygen adduct in the presence of air. Heptacene that lacks protecting groups is highly unstable at room temperature[15] and, therefore, protecting groups are required to stabilize the larger acenes.

Anthony and co-workers, in pioneering work, synthesized 7,16-silylethynylheptacenes **2a**–**c**.[5] The λ_{max} value (852 nm in CH_2Cl_2) for **2c** is red-shifted by about 92 nm relative to that of the unsubstituted heptacene.[4] Compound **2c**, with bulky protecting groups and optical and electrochemical gaps (measured from the onsets) of 1.36 and 1.30 eV, respectively, was sufficiently stable to enable chromatographic purification, spectroscopic characterization, and a single-crystal X-ray study. Tris(trimethylsilyl)silylethynyl groups, whose diameter is 40 % of the length of heptacene, provide sufficient protection, mostly through steric effects. Heptacene **2c** is very soluble and is stable in the solid state for a week; however, it decomposes within a few hours when exposed to air.[5] This work by Anthony's group[5] shows that heptacene is a stable and synthetically accessible molecule if it is protected by significantly bulky groups.



New and exciting progress in the synthesis of heptacenes has been made in the last year by groups led by Wudl[6] and Miller.[7] The most common synthetic route to functionalized acenes is through the nucleophilic addition of organometallic reagents to an acene quinone, followed by reduction.[3] Wudl et al. have explored different synthetic methods to functionalized heptacenes through double Diels–Alder cycloaddition between a lateral "bisanthracyne" and dienes, followed by reduction to give stable substituted heptacene derivatives (Scheme 2).[6] Although the alkoxy side chains significantly improved its solubility, **3b** was too reactive to be isolated or characterized completely. To further improve its stability, the aryl groups in the central ring were replaced by triisopropylethynyl groups, so creating **3c**. Compound **3c** is stable for over 21 days to the atmosphere and light when coated in mineral oil and for 41 h when stored in degassed toluene solution. Dimer and polymer formation is not observed even after recrystallization over three weeks, which indicates the effectiveness of bulky substituents in preventing dimerization.

The single-crystal X-ray structure of **3c** (Figure 1) exhibits edge-to-face herringbone packing in the solid state; however, there are no π–π interactions between the acene backbones.



Scheme 2. Synthesis of heptacene derivatives **3a–c**.[6]

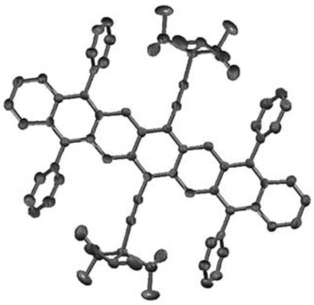
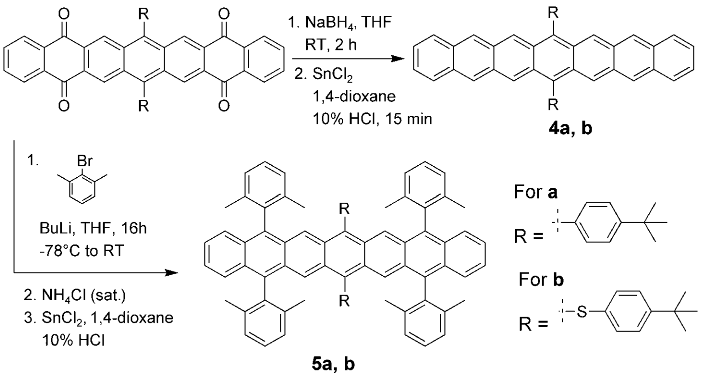


Figure 1. X-ray crystal structure of **3c**.[6] Hydrogen atoms are omitted for clarity.

Although the heptacene derivatives are very reactive, which may support a singlet diradical character in the ground state,[8] this is not detectable spectroscopically (^{1}H NMR signals show sharp splitting and narrow linewidths).[5,6] These reports by the Anthony[5] and Wudl[6] groups support the proposed empirical model for engineering crystalline derivatives using trialkylsilylethynyl groups, which must have a diameter of 35–50 % of the length of the acene to exert a significant stabilizing effect. Also, trialkylsilylethynyl groups red-shift the NIR absorption by approximately 20 nm for **3c** (863 nm in toluene) relative to **3b**. The optical HOMO–LUMO gap of **3c** (1.35 eV, onset at 917 nm) matches the electrochemical HOMO–LUMO gap (1.38 eV) very well.[6] This report by the Wudl group[6] significantly expands the synthetic methodologies available for the synthesis of large acenes and describes a material that is sufficiently stable to potentially enable electronic applications.

Additional significant progress was achieved recently by Miller's group.[7] On studying a substituent effect for a large series of pentacene derivatives, they concluded that steric effects, electronic effects, and the position of the substituents are all important factors for determining photooxidative resistances and HOMO–LUMO gaps.[16] *ortho*-Alkyl-substituted phenyl groups are superior to phenyl substituents in enhancing photooxidative resistance by providing better steric hindrance: the *ortho*-alkyl groups lie directly over and under acene's π system. Thioalkyl and thioaryl substituents enhance photooxidative resistance more than silylethynyl substituents.[16] Using 2,6-dimethylphenyl and thioaryl substituents, Miller et al. prepared persistent heptacene derivatives (Scheme 3).[7] In line with the impressive substituent effects of arylthio substituents, heptacene derivative **4b** is even longer lived than **5a**. Derivative **5b** was obtained as an especially persistent heptacene derivative with a small HOMO–LUMO gap (1.37 eV) comparable with those of **2** and **3**.[7] Heptacene derivative **5b** is soluble in a variety of solvents and stable for weeks as a solid, for 1–2 days in solution if protected from light, and for several hours in solution when directly exposed to both light and air. All solids **4a**,**b** and **5a**,**b** are dark green in color. The longest wavelength absorption maxima for **5b** is 865 nm (in CH_2Cl_2), which is comparable with **3c** (863 nm) and **2c** (852 nm) (Figure 2).[7] New protecting groups for large acenes were successfully introduced, significantly increasing the possible options for large acenes.[7]



Scheme 3. Synthesis of heptacene derivatives **4a**,**b** and **5a**,**b**.[7]

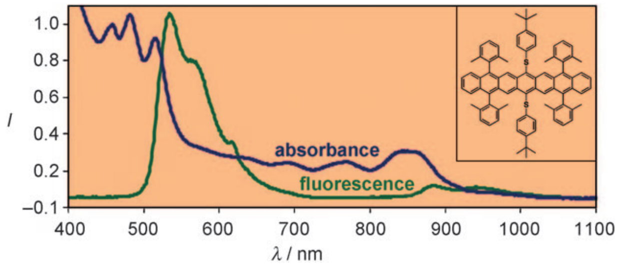
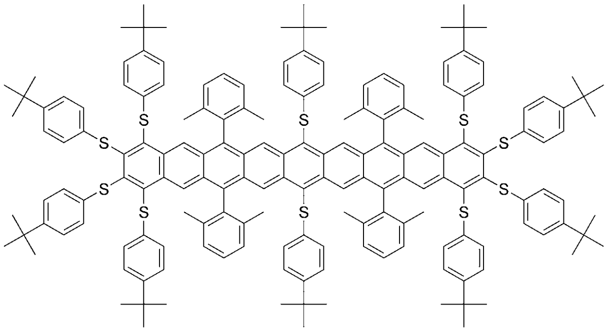


Figure 2. Normalized UV/Vis/NIR (blue line) and fluorescence (green line) spectra of heptacene derivative **5b** in CH_2Cl_2.[7]

In summary, recent experimental studies on heptacene derivatives pave the way for investigations of the electronic properties of larger acenes and provide insight into their structure and reactivity. Protecting groups and their selection are very important for the stabilization of acenes larger than pentacene. These materials have low HOMO–LUMO gaps of about 1.3–1.4 eV. We believe that these advances in the synthesis of substituted heptacenes will stimulate significant new activity in the synthesis of and research on larger acenes. It is expected that future efforts will not only increase the understanding of the electronic structure of larger acenes, but will also lead to their application in organic electronic devices.

Indeed, after this Highlight was accepted, two very important developments in the field of large acenes were reported, which significantly expand the synthetically accessible limit of large acenes. Persistent substituted nonacene with a very small HOMO–LUMO gap has been reported by Miller's group.[17] Nonacene **6** is stable as a solid in the dark for at least six weeks and was characterized by ^1H NMR, ^{13}C NMR, laser-desorption mass spectroscopy, UV/Vis/NIR, and fluorescence techniques, although its degree of purity cannot be assessed. The HOMO–LUMO gap of **6** obtained from the onset of the longest-wavelength absorption is 1.12 eV, which is the smallest experimentally measured HOMO–LUMO gap for any acene. Computationally, **6** was predicted to be a closed-shell species because of the special arrangements of its thio substituents which contribute to its stability. Achievement of a persistent long acene with a very small HOMO–LUMO gap should further accelerate the study of long acenes.



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Another very important study comes from Bettinger's group, who reported the synthesis and spectroscopic detection of unsubstituted octacene (**1**, $n=8$) and nonacene (**1**, $n=9$) under conditions of matrix isolation.[18,19] UV/Vis/NIR detection of unsubstituted octacene and nonacene allowed the bandgap of polyacene to be determined by extrapolation from the HOMO–LUMO gaps of unsubstituted acenes. In this manner, a bandgap of 1.2 eV was extrapolated for polyacene. Given the significant efforts that were devoted to the synthesis of hexacenes and heptacenes, the preparations of unsubstituted nonacene[18,19] and persistent substituted nonacene[17] are real breakthroughs in this field, even if the isolation of these compounds in pure form remains a challenge.

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