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Exploiting Substituent Effects for the Synthesis of a Photooxidatively Resistant Heptacene Derivative

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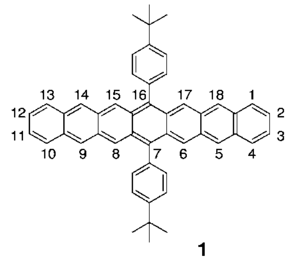
Polycyclic aromatic hydrocarbons composed of linearly annelated benzene rings are called acenes,[1] anthracene representing the smallest member of the series. Tetracene and pentacene, the next two largest, are organic semiconductor compounds that have been utilized extensively in both organic field-effect transistor[2] and organic light-emitting diode[3] applications. Both compounds photooxidize under ambient conditions,[4] a serious problem for acenes that becomes increasingly problematic with increasing length. Likewise, hexacene and heptacene have eluded extensive experimental study because of the ease with which they photooxidize. Recently however, Neckers and co-workers[5] demonstrated a photochemical route for the synthesis of hexacene and heptacene embedded in rigid polymeric media, where the molecules show lifetimes of ~12 and 4 h, respectively. Octacene, nonacene, and larger acenes have never been isolated. They are predicted to have open-shell singlet ground states.[6] Larger acenes are expected to exhibit singlet polyradical character in their ground states.[7]

While acenes larger than pentacene degrade under ambient conditions, their resistance to photooxidation can be altered through chemical functionalization. Anthony and co-workers[8] prepared silylethynyl derivatives of hexacene and heptacene, both of which exhibited enhanced stability relative to their parent hydrocarbons. Recently, Wudl and co-workers[9] prepared a similar silylethynyl derivative of heptacene bearing additional phenyl substituents at positions 5, 9, 14, and 18. Aside from Anthony's and Wudl's silylethynyl derivatives, no other functionalized hexacene or heptacene compounds have been reported, despite the fact that large acenes promise reduced band gaps, greater charge carrier mobilities and lower reorganization energies in molecular electronic applications.[10]

Recently, we completed a substituent-effect study for a large series of pentacene derivatives[11] in which it was revealed that steric effects, electronic effects, and the positional location of substituents are all important factors for determining photooxidative resistances and HOMO−LUMO gaps. For example, phenyl substituents alone do little to enhance photooxidative resistance on pentacene, but those with *o*-alkyl groups provide steric resistance to photooxidation. The phenyl groups reside in time-averaged orthogonal orientations relative to the acene backbone, constraining the *o*-alkyl groups to lie directly over and under the acene π system.The *o*-alkyl groups effectively shield otherwise reactive π electrons leading to longer-lived species. The most impressive substituent effects, however, were observed with thioalkyl and thioaryl substituents, as each dramatically enhanced photooxidative resistance through special electronic effects that render type-II photooxidations[12] less viable. In fact, alkylthio and arylthio substituents are considerably better than silylethynyl substituents at enhancing pentacene photooxidative resistance,[11] and this fact alone suggests new opportunities for preparing large, persistent acenes. We reasoned that by combining arylthio and *o*-dimethylphenyl substituent effects, we could produce a heptacene derivative with enhanced photooxidative resistance. Here we report the successful synthesis of four heptacene derivatives with varying levels of photooxidative resistance (**1** < **2** < **3** < **4**). Heptacene derivatives **1** and **3** bear *p*-(*t*-butyl)phenyl and *p*-(*t*-butyl)thiophenyl substituents, respectively, at positions 7 and 16, while **2** and **4** possess additional *o*-dimethylphenyl substituents at positions 5, 9, 14, and 18. As predicted, derivative **4** is an especially persistent species. It possesses a small optical HOMO−LUMO gap (1.37 eV), rivaled only by Wudl's recent silylethynylated heptacene derivative (1.35 eV).[9]



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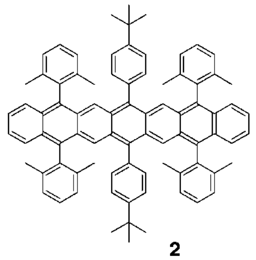

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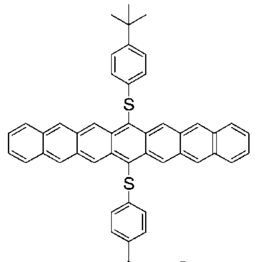

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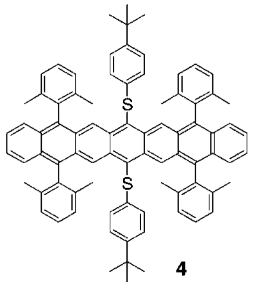

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In view of the ease with which simple aryl-substituted pentacenes photooxidize,[4,11] heptacene derivative **1** was expected to degrade rapidly in solution, and it did not disappoint. Derivative **2**, on the other hand, showed modestly improved photooxidative resistance due to the presence of the sterically demanding *o*-dimethylphenyl substituents at the 5, 9, 14, and 18 positions. With *p*-(*t*-butyl)thiophenyl substituents located at the most reactive carbons, C7 and C16, heptacene derivative **3** is even longer lived, corroborating the impressive substituent effects afforded pentacenes by alkylthio and arylthio substituents.[11] The combination of *p*-(*t*-butyl)thiophenyl substituents at positions 7 and 16 (i.e., arylthio substituents attached to the most reactive ring) and *o*-dimethylphenyl substituents at positions 5, 9, 14, and 18 (i.e., steric resistance on neighboring rings) make heptacene derivative **4** an especially persistent species (Figure 1a) that endures for weeks as a solid, 1−2 days in solution if shielded from light, and several hours in solution when directly exposed to both light and air. Heptacene **4** is soluble in a variety of solvents and has been fully characterized in solution using ^{1}H NMR, ^{13}C NMR, UV−vis, and fluorescence spectroscopies.[13] The solution-phase stability of **4** makes it amenable to thin-film formation using simple, high-rate methods such as blade coating and spin coating.

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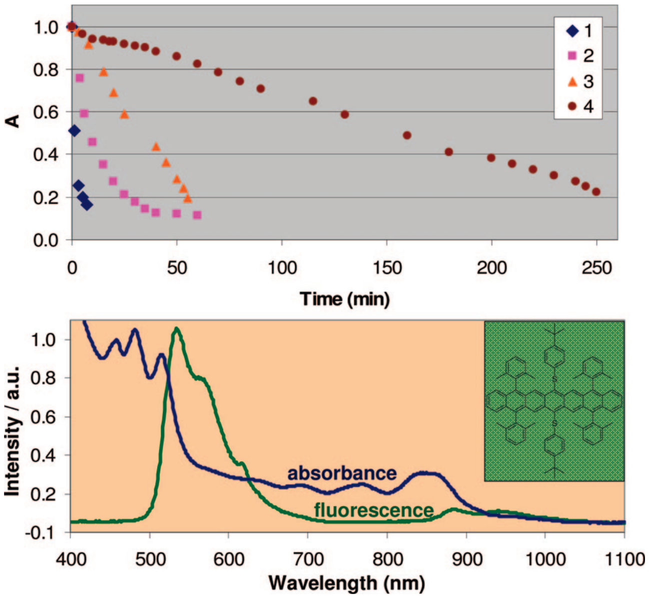
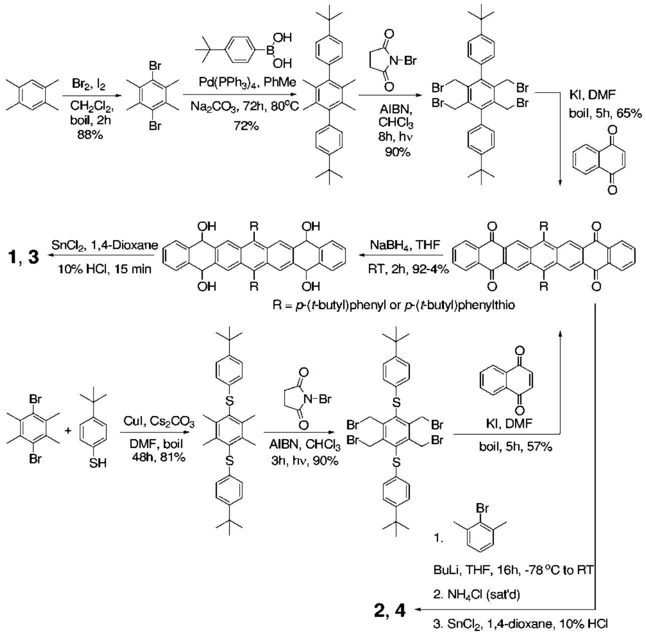


Figure 1. (top) Normalized absorbances of CH_2Cl_2 solutions of heptacene derivatives **1**−**4** as a function of time exposed to light and air (1×10^{-4} M initial concentration) at 25 °C. (bottom) Normalized UV−vis (blue line) and fluorescence (green line) spectra of heptacene derivative **4** that shows unusual photo-oxidative resistance.

Scheme 1. Synthesis of Heptacene Derivatives **1**−**4**



The syntheses of heptacene derivatives **1**−**4** are outlined in Scheme 1. All four compounds pass through 7,16-disubstituted heptacene-5,9,14,18-tetraones prepared via Diels−Alder reactions involving 1,4-naphthaquinone and appropriately substituted 1,2,4,5-tetramethylenebenzene precursors. For **1** and **3**, the tetraones were reduced to tetraols using borohydride and then reductively aromatized using $SnCl_2$. For **2** and **4**, the tetraones were reacted with *o*-dimethylphenyllithium, prepared in situ, to produce a unique set of tetraols that were then reductively aromatized using $SnCl_2$. All four derivatives precipitated as dark-green solids, were isolated by vacuum filtration, washed with water and methanol, and finally dried under vacuum.[13]

Attempts to characterize **1**−**3** by ^{1}H NMR spectroscopy were complicated by their relatively rapid degradation in solution, but useful spectra could nonetheless be obtained by working quickly.[13] As solids stored in the dark, **1**−**3** have significant lifetimes, enabling mass spectral characterization. Laser desorption ionization (LDI) mass spectra of **1** revealed a strong molecular ion at *m/z* 642.6 along with smaller signals at ($M^+ + 32$) and ($M^+ + 16$) corresponding to a $^1O_2$ adduct of **1** and its fragment, respectively.[13] LDI mass spectra of **2** and **3** showed molecular ions at *m/z* 1058.6 (**2**) and 706.3 (**3**) with no sign of $^1O_2$ adducts.[13] High-resolution mass spectra (FAB+) of **1**−**3** indicated molecular ions at *m/z* 642.3257 (**1**, M^+, calcd 642.3287, error = −4.5 ppm), 1058.5770 (**2**, M^+, calcd 1058.5791, error = −1.9 ppm) and 707.2792 (**3**, MH^+, calcd 707.2806, error = −2.0 ppm).

The UV−vis and fluorescence spectra for **4** (Figure 1b) are consistent with a highly conjugated structure possessing a small HOMO−LUMO gap. The longest-wavelength absorption for **4** in CH_2Cl_2 is centered at 865 nm.[14] On the basis of the onset of this absorption, we determined the optical HOMO−LUMO gap for **4** to be 1.37 eV. For comparison purposes, the optical HOMO−LUMO gaps for pentacene and TIPS-pentacene, benchmark organic semiconductor compounds, are 2.08 and 1.81 eV, respectively.[11] LDI mass spectra of **4** showed a strong molecular ion at *m/z* 1122.2 with no sign of $^1O_2$ adduct formation.[13] HR-MS (FAB) indicated an ion at *m/z* 1123.5298 (MH^+, calcd 1123.5310, error = −1.1 ppm).

In summary, we have demonstrated that a combination of arylthio and *o*-dialkylphenyl substituents can be utilized to produce an unusually persistent heptacene derivative. Conventional wisdom suggesting that "the central ring [of heptacene] must be functionalized with alkylsilylethynyl groups in order to provide sufficient stability for isolation and characterization"[9] is now recognized to be overly restrictive. The synthetic-materials chemist interested in preparing large, persistent acenes has additional, attractive options.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra, UV−vis spectra, fluorescence spectra, LDI mass spectra, digital photographs, and synthetic details for **1**−**4** and selected precursors. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) As illustrated in Figure 1, a weaker band of longer wavelength was also observed at 958 nm.

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