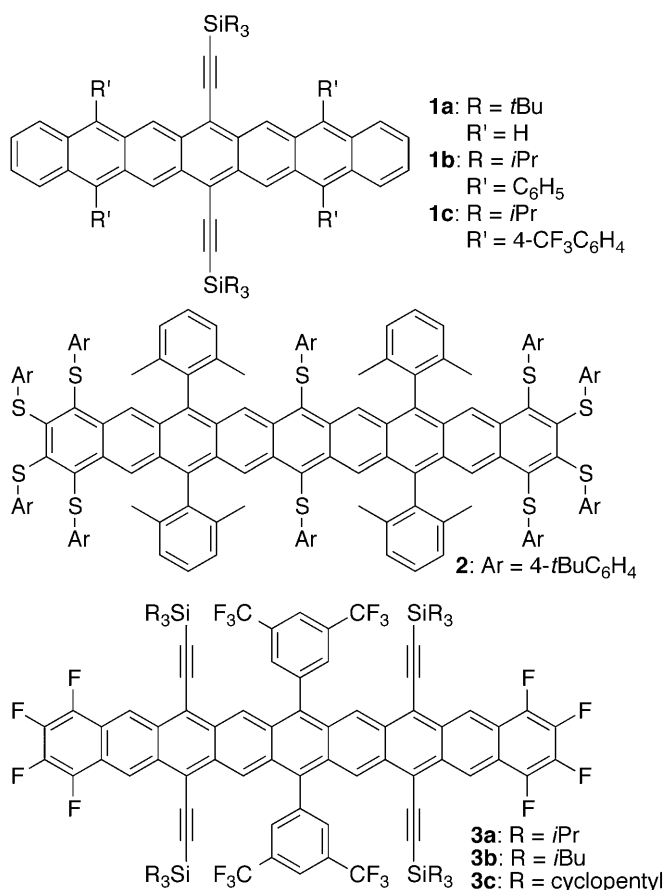


Synthesis and Structural Characterization of Crystalline Nonacenes**

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Acenes and functionalized acenes have played a pivotal role in the development of organic electronic materials.^[1] From the first report of high-mobility organic transistors based on vapor-deposited pentacene,^[2] to high-efficiency organic light-emitting diodes based on anthracene,^[3] and the remarkable transport properties of rubrene,^[4] these linearly fused hydrocarbons have made significant contributions to the understanding of electronic processes in organic semiconductors. Despite the utility of these compounds, the selection of materials suitable for exploration essentially stops at pentacene. Although numerous studies have predicted enticing electronic properties for larger acenes,^[5] the combination of poor solubility and low stability have hindered detailed studies of these materials.

The potential technological importance of higher acenes has created a resurgence of interest in these systems.^[6] Elegant low-temperature matrix-isolation techniques have recently allowed the spectroscopic characterization of hexacene,^[7] heptacene,^[8] octacene, and nonacene,^[9] as well as a few more detailed studies of the electronic structure of heptacene.^[10] Moreover, new functionalization strategies are being developed to allow the isolation and full structural and electronic characterization of larger acenes. The selection of substituents for such strategies is critical to the success of the approach, for example, substitution of hexacene with various aryl groups resulted in no stable materials,^[7] while silylethyne functionalization has provided numerous soluble hexacenes, which have now been extensively characterized.^[11] The silylethyne functionalization approach to engineer solid-state order^[12] has also produced a number of crystalline heptacene derivatives such as **1a**.^[13] Materials prepared using this strategy are often sufficiently crystalline for X-ray diffraction studies, which are critical for the unambiguous structural confirmation of these reactive species. The addition of phenyl substituents to a silylethyne-functionalized heptacene (**1b**) disrupted the π -stacking motif beneficial to charge transport, but in exchange produced a highly stable derivative, which was also fully structurally characterized.^[14] The



enhanced stability likely arises from the perpendicular orientation of the phenyl groups relative to the acene backbone; this orientation hinders the rate of face-to-face dimerization. Later reports demonstrated that the use of electron-deficient arene substituents (**1c**) produced a further incremental improvement to acene stability.^[15]

A more recent functionalization strategy involves the use of extensive thioether substitution around the acene chromophore.^[16] This innovative approach led to the report of a reasonably stable heptacene derivative,^[17] and more recently, a so-called “persistent” nonacene derivative (**2**).^[18] This purported functionalized nonacene is highly unusual because of an almost non-existent absorption corresponding to the S₀–S₁ transition, and fluorescence at remarkably short wavelength. These findings raise interesting questions about the electronic structure and optoelectronic properties of nonacene, and heighten the need for a derivative that is stable enough for full structural and spectroscopic characterization.

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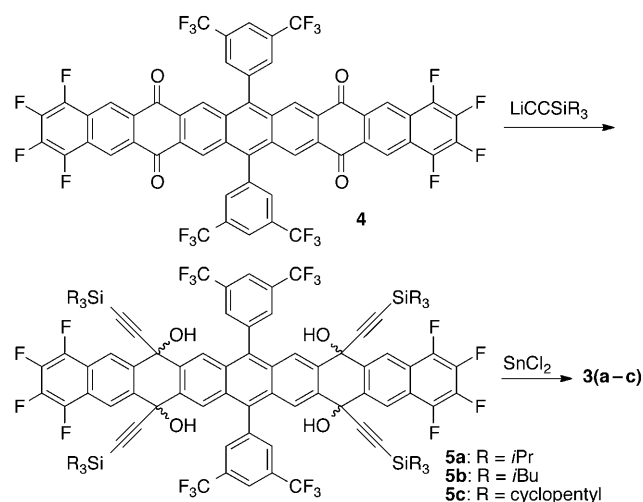
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With these recent reports in mind, we decided to explore the preparation of a structurally characterizable nonacene derivative, in order to better understand the nature of the optoelectronic properties of this chromophore. From our work on hexacene derivatives,^[11] we already knew that the substituents on the alkynes needed to be sufficiently bulky to prevent Diels–Alder reactions between the alkynes and the reactive acene chromophore, and that the solid-state order must be carefully tuned to prevent close contacts between the highly reactive central aromatic rings of the acene backbone. It was also clear from the outset that the incorporation of phenyl substituents, as used by Wudl and co-workers for their highly stable heptacene,^[14] would be critical to the preparation of a stable nonacene. However, our strategy places these substituents on the central ring of the acene in order to leave a reasonable expanse of the acene periphery available for π stacking. Such interactions are critical for the rapid growth of acene crystals, which we reasoned would be necessary for the isolation of a stable, crystalline compound. Finally, our work on partially fluorinated pentacenes^[19] and anthradithiophenes^[20] taught us that fluorine substitution both increases acene stability and enhances π -stacking interactions—perhaps mitigating the impact of the orthogonal phenyl substituents. With these criteria in mind, we envisioned nonacenes **3** as reasonable target molecules.

The synthesis of derivatives **3** was straightforward (Scheme 1), and involved the alkylation of the correspond-



Scheme 1. Synthesis of nonacenes **3**.

ing quinone **4**, which in turn was prepared in four steps from durene (details in the Supporting Information). The addition of a variety of silyl acetylides to **4** produced an isomeric mixture of the corresponding tetraols **5** in good yield, although extensive purification of the crude mixtures was not carried out. Because the functionalized larger acenes are significantly more stable in the crystalline state,^[13] we optimized the reaction conditions to crystallize the nonacenes directly from the deoxygenation reaction mixture (see the Experimental Section). Upon re-dissolving these crystals in toluene, we found that the absorption spectra obtained from

the olive-colored solutions of **3a–c** (Figure 1a) are markedly different from the spectrum reported for **2** (Figure 1c).^[18] Nonacenes **3** show a prominent S_0 – S_1 transition at 1014 nm, and only weak absorptions throughout the visible region

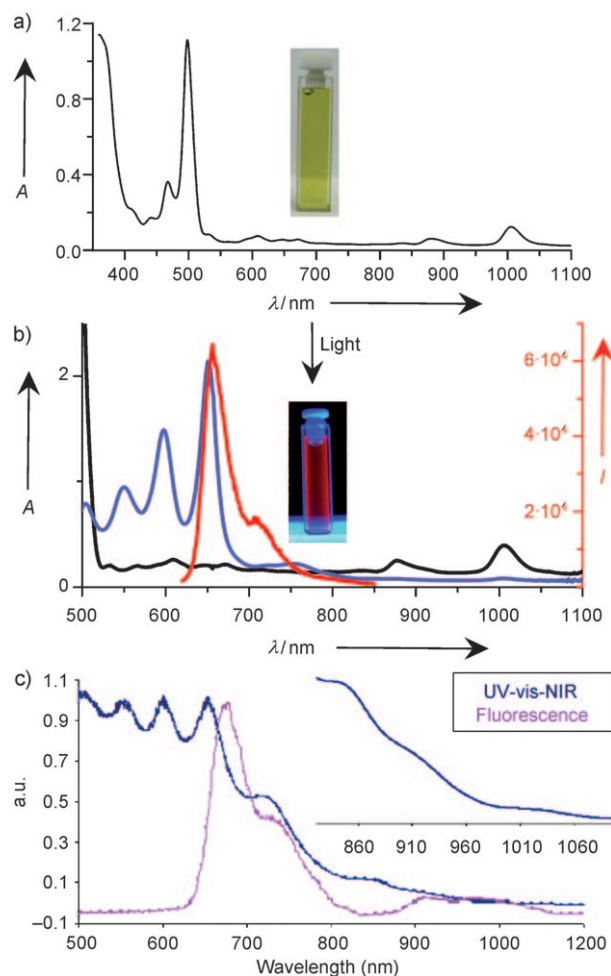


Figure 1. a) Absorption spectrum and image of a sample of **3c** in toluene. b) Absorption (blue trace) and emission (red trace) spectra of the strongly fluorescent decomposition product of **3c**, along with an image of the photodecomposed solution. Absorption spectrum of pure **3c** (black trace) shown for reference. c) Reported UV/Vis/NIR (blue trace) and fluorescence (purple trace) spectra for nonacene **2**. Data for **2**^[23] reprinted from Ref. [18] with permission. Copyright 2010 American Chemical Society.

down to 500 nm, contrasting with the intense absorptions from 500–700 nm and barely observable S_0 – S_1 transition reported for **2**. The absorption onset of **3a** (1033 nm) gives a HOMO–LUMO gap of 1.2 eV (HOMO = highest occupied molecular orbital, LUMO = lowest unoccupied molecular orbital), a value corroborated by electrochemical analysis of **3a** by differential pulse voltammetry (Figure S6 in the Supporting Information), showing oxidation and reduction onsets versus ferrocene/ferrocenium of +0.78 V and –0.41 V ($E_{\text{gap}} = 1.19$ eV). The relatively high oxidation potential is a result of the extensive fluorine substitution, and likely enhances the oxidative stability of nonacenes **3**. While there is little match between the absorption spectrum of **3** and the

spectrum reported for **2**, there is reasonable but red-shifted structural correspondence between the spectra for nonacenes **3** and the spectrum reported for matrix-isolated nonacene,^[9] which also exhibits a strong S_0 – S_1 transition and similar spacing of weak transitions through visible wavelengths.

In the report on **2**,^[18] and in subsequent media releases,^[21] the intense red fluorescence of the isolated compound was noted. It was claimed that this red fluorescence was a diagnostic tool for the presence of the nonacene chromophore. We did not observe red emission from nonacenes **3**, nor did we observe (or expect to observe) any fluorescence in the visible region. Kasha's rule^[22] states that alternant hydrocarbons emit from the first singlet excited state (S_1), thus, with a S_0 – S_1 transition beyond 1000 nm, emission of visible light is most unexpected. Intrigued by this prior report of red fluorescence, we investigated the absorption and emission properties of the decomposition products of **3c**, which were formed by exposing solutions of **3c** to air under bright laboratory lighting. Under these conditions, the nonacene decomposed completely within 6 h to give a dark blue-black solution that did indeed exhibit bright red fluorescence (Figure 1b). The decomposition product was isolated and purified by column chromatography, and crystallographic analysis of this decomposition product (Figure S4) indicates that the nonacene forms an endoperoxide on ring 4 of the structure to produce a pentacene chromophore. The absorption spectrum for this decomposition product (Figure 1b) exhibits strong transitions in the visible region (500–700 nm) and has vibronic structure typical of a pentacene. We also note a striking similarity between both the absorption and emission spectra of this decomposition product and those reported for nonacene **2** (Figures 1b and c).

A key benefit of the silylethyne functionalization approach used here is the ability to engineer easily crystallized materials, and this factor was crucial to the preparation of the first stable hexacene and heptacene derivatives.^[13] We exploited this same rationale to obtain nonacene derivatives as surprisingly stable solids that were formed as crystals directly

from the reaction mixture, and showed essentially no decomposition when stored in the dark at 10°C over more than 2 days. All three nonacene derivatives reported here formed crystals suitable for X-ray analysis (Figure S2), and all structures were amenable to at least some degree of refinement (Figure 2).^[24] Triisopropylsilyl derivative **3a** gave a reasonable data set that showed that the linear acene chromophore is slightly twisted by the backbone substituents and warped by crystal packing effects. This derivative adopted a 2D π -stacked motif similar to that observed for some pentacene derivatives,^[12] although in this case there is minimal π overlap—the spaces above and below the reactive center of the nonacene chromophore are occupied by disordered solvent molecules. Crystals of **3b** were much thicker than those of **3a** or **3c**, and gave significantly better data. This nonacene was almost exactly planar, and exhibited only a small amount of twist due to interactions between the aryl and alkynyl substituents. The nonacene backbones pack as perpendicular 1D “slipped” stacks, with only the terminal rings of the acenes overlapping. As with **3a**, the center of the acene is surrounded by incorporated solvent molecules. Crystals of **3c** were extremely thin, and the data were

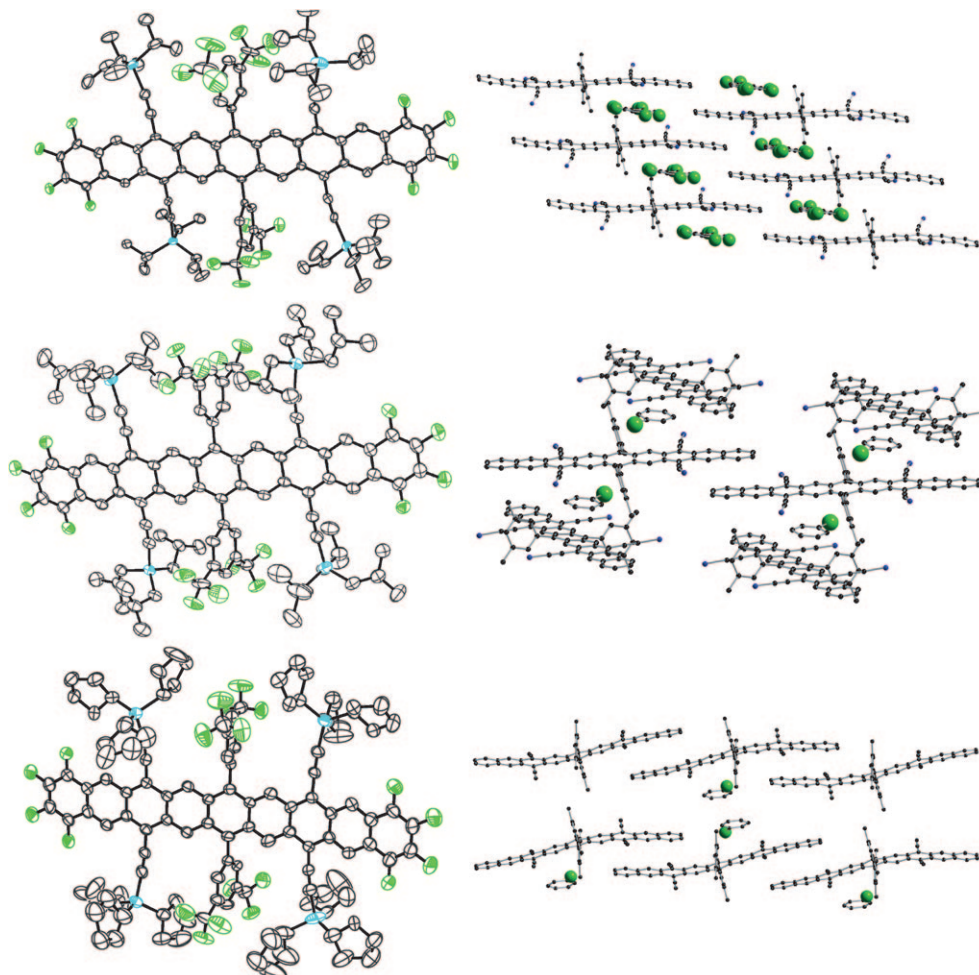


Figure 2. Thermal ellipsoid plots for **3a** (top), **3b** (center), and **3c** (bottom), and packing diagrams (right). F green, Si blue. Alkyl groups and fluorine substituents omitted from packing diagrams for clarity. Thermal ellipsoids set at 50% probability.

correspondingly weak. The nonacene chromophores in this crystal are highly distorted, adopting a 1D “slipped-stack” motif, in this case with significantly more overlap between the nonacene chromophores than observed for **3a** or **3b**. Crystals of **3c** incorporated chlorobenzene, and, as with the other two derivatives, the central part of the chromophore was surrounded by these solvent molecules. The solid-state stability of all of these nonacene crystals is likely enhanced by the presence of low-reactivity solvent molecules that surround the most reactive acene rings in the crystal and thus hinder acene dimerization.

Finally, we note that it proved impossible to collect ^1H NMR spectra for any of these nonacene derivatives. Although the compounds are sufficiently soluble for the experiment, initial scans in the NMR spectrum showed only noise, and over time, broad peaks corresponding to the independently characterized decomposition product began to appear. After leaving a sample exposed to laboratory lighting for a few days, thus leading to complete decomposition of the sample, sharp peaks corresponding to the nonacene decomposition product were the only visible features of the NMR spectrum. Recent theoretical work on larger acenes predicts open-shell structures for species greater than octacene,^[25] thus explaining the lack of signal in the ^1H NMR spectrum. We thus subjected **3b** to EPR analysis, and at both room temperature and at 115 K, a signal was observed in the EPR spectrum with $g = 2.0060$ (Figure 3) that disappeared in a time frame corresponding to the typical lifetime of our nonacene

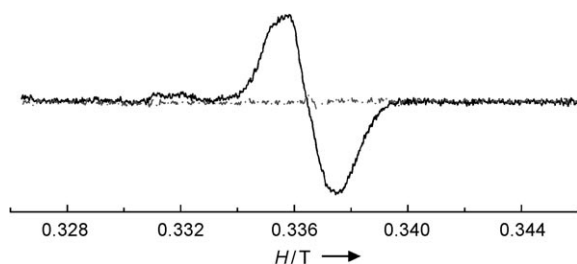


Figure 3. EPR spectrum of **3b** in 2-methyltetrahydrofuran (9.45 GHz, 115 K). Solid line: pristine sample. Dashed line: sample after 48 h exposure to air and light.

derivatives in solution. The signal indicates the presence of a free radical at low concentration, thus explaining the difficulty in obtaining ^1H NMR spectra for **3**, as well as the limited lifetime of the compounds. The radical signal displays evidence of unresolved hyperfine coupling or anisotropy, and is not easily saturated. The oxidation potential of these derivatives, combined with the use of rigorously deoxygenated solvents, make it unlikely that this signal arises from a radical cation oxidation product. The origin of this radical signal, including whether it stems from an intermediate or product of decomposition, or is an intrinsic characteristic of these large acenes, is currently under investigation.

We have demonstrated that the silylethyne functionalization strategy developed to produce stable hexacene and heptacene derivatives can also be used to prepare nonacene derivatives that are stable enough for detailed structural and

spectroscopic characterization. Crystallographic analysis revealed conclusively the presence of the conjugated nonacene chromophores. The spectroscopic properties of these compounds differ significantly from those previously reported for purported nonacene (**2**), and show a strong S_0 – S_1 transition near 1000 nm and no fluorescence in the visible region. Electrochemical analysis supports the observed optical gap, and the absorption maxima and peak structures correlate well with those of the previously reported series of silylethyne-substituted acenes (Figure 4).^[26] While the photo-physical differences between nonacenes **3** and the reported

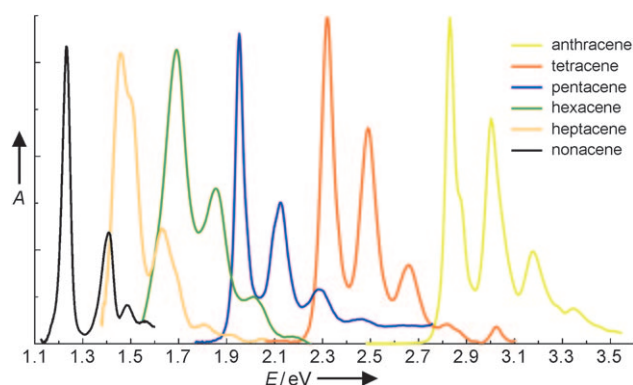


Figure 4. The long-wavelength portion of the absorption spectra for silylethyne-substituted acenes from anthracene to heptacene^[1b] and nonacene **3c**.

derivative **2** may arise from the extensive thiol substitution present in **2**, the strong correspondence between the absorption and emission spectra of decomposed samples of nonacenes **3** and the spectra reported for **2** suggest that the weak S_0 – S_1 transition and unprecedented short-wavelength fluorescence observed for **2** may arise from a decomposition product that makes up the bulk of the sample. The ability to synthesize and characterize larger acenes will provide significant insight into the nature of aromaticity in linearly fused aromatic hydrocarbons, and presents an interesting oligomer study^[27] for the narrowest of zigzag graphene nanoribbons.^[28] However, it must be emphasized that structures must be characterized unambiguously for these studies to be relevant.

Experimental Section

Tetraols **5** were prepared as described in the Supporting Information. For conversion to the nonacenes, solvents were optimized to encourage the nonacenes **3** to crystallize as they were formed. For derivative **3a**, **5a** was deoxygenated by the addition of solid $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to a solution of **5a** in 1,2,4-trichlorobenzene/ethylbenzene/acetonitrile (2:1:1 by volume), followed by brief, vigorous stirring of the solution. When this mixture was left to stand in the dark overnight, crystals of **3a** grew from the solution. Under similar conditions, **3b** and **3c** both crystallized from chlorobenzene/acetonitrile (1:1).

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