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Synthesis and Characterization of Electron-Deficient Pentacenes

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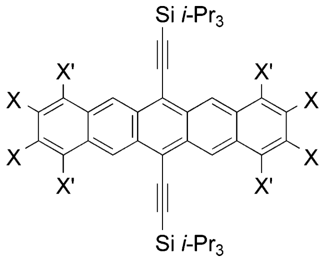
ABSTRACT



Halogen functional groups on pentacene can be used both as synthetic handles for further functionalization as well as to tune the π-stacking in these systems. The halogenated pentacene derivatives described here (X = Br, X′ = H, and X = X′ = F) are all stable and soluble, with reduction potentials significantly lower than that of the parent functionalized pentacene (X = X′ = H). The bromopentacenes could be further elucidated to pentacene nitriles, further decreasing the acene's reduction potential, while the charge-carrier mobility in the fluorinated systems was shown to scale with the degree of fluorine substitution.

One key advantage to the use of organic materials in electronics is the inherent "tunability" of synthetic organic semiconductors. Functionalization of organic molecules used in electronic devices can lead to dramatic changes in solubility, stability, film-forming ability, and oxidation/reduction potentials (and thus HOMO and LUMO energy levels). For example, tetramethyl pentacene has a significantly decreased oxidation potential vs pentacene, which may lead to improved charge injection in electronic devices.[1] Conversely, perfluoropentacene was recently prepared, and the fluorine substitution altered the LUMO energy level sufficiently to make this compound an *n*-type semiconductor.[2]

In our work on silylethynyl-functionalized pentacenes, we found that the addition of cyclic ether groups to the ends of the pentacene fragment lowered the oxidation potential while maintaining the high stability typically associated with these materials.[3] These subtle redox changes led us to consider affecting even more dramatic changes to the silylethynyl-substituted pentacenes by functionalization. We were specifically interested in the preparation of halogen-containing derivatives of silylethynylated pentacenes for two reasons: fluorine-containing pentacenes will provide the ability to alter π-stacking by exploiting aryl−fluoroaryl interactions,[4] while bromopentacenes will allow the further functionalization of the pentacene backbone using palladium-based coupling reactions.

The typical approach to most pentacene derivatives involves the formation of pentacenequinones by an efficient

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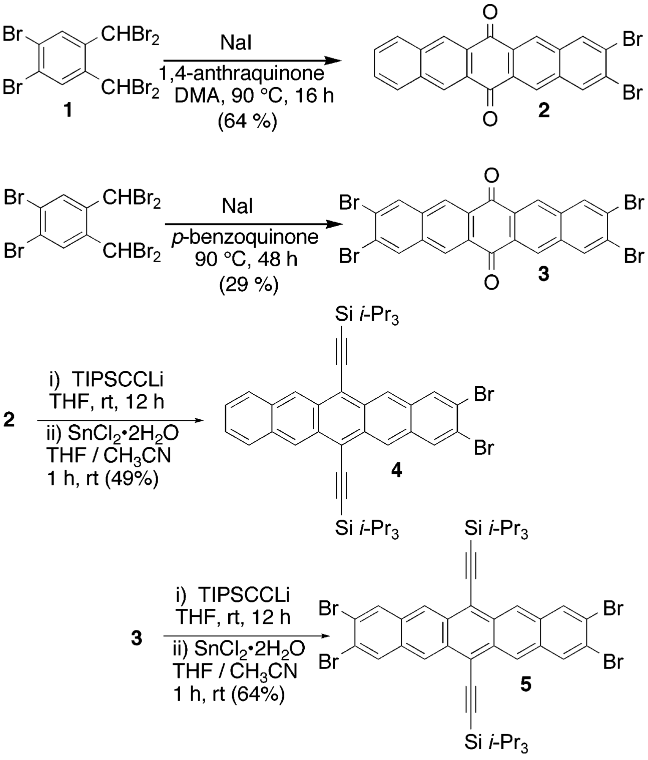
4-fold aldol condensation between a phthalaldehyde and 1,4-cyclohexanedione,[5] followed by further elaboration of the quinone to the desired pentacene. For example, Wudl and co-workers have exploited this approach to form both tetrachloro[6] and tetramethyl[1] pentacene, and we have used this method for the formation of the aforementioned pentacene ethers.[3] Unfortunately, we had no success in applying this route to the formation of either bromo- or fluoropentacenequinones. In the case of the bromine derivative, the requisite phthalaldehyde was easily prepared but formed the corresponding pentacenequinone in very poor yield. In the case of the fluorinated derivative, we were unable to prepare the requisite phthalaldehyde.

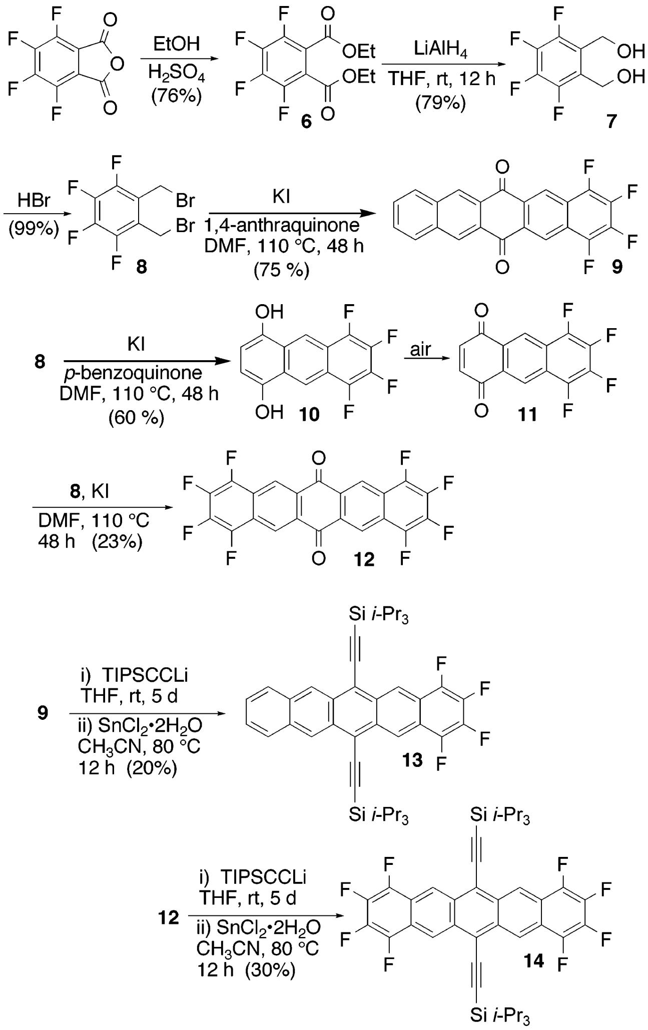
An alternative approach to pentacenequinones utilizes the Cava reaction, which converts α,α,α′,α′-tetrabromo *o*-xylenes to *o*-quinodimethanes in situ by elimination of Br_2 with sodium or potassium iodide as a nucleophile.[7] The quinodimethanes react rapidly with terminal quinones (e.g., benzoquinone, 1,4-anthraquinone) and aromatize to yield internal quinones. While the yield of this reaction is often only moderate, the reaction is simple, and the conditions tolerate a wide array of functionality. Further, application of this reaction to commercially available 1,4-anthraquinone allows the preparation of pentacene derivatives substituted on only one end.

Starting with readily available 3,4-dibromo-α,α,α′,α′-tetrabromo-*o*-xylene **1**,[8] reaction with either 1,4-benzoquinone or 1,4-anthraquinone in a deoxygenated NaI/DMA solution yielded the desired dibromo- and tetrabromopentacenequinones **2** and **3** (Scheme 1). While the yield of the tetrabromo quinone **3** was not high (29%), the low cost of the starting materials and the ease of isolation of this insoluble compound facilitate its preparation in significant quantity. The synthesis of the fluorinated pentacenes begins with 2,3,4,5-tetrafluoro phthalic anhydride, which is converted to dimethanol **7** following literature procedures[9] and then elaborated to the corresponding bromomethyl compound **8** in excellent yield. Treating **8** with KI in the presence of 1,4-anthraquinone at 110 °C yielded tetrafluoropentacenequinone **9** in a remarkable 75% yield. A similar treatment of **8** in the presence of 1,4-benzoquinone did not provide the desired pentacenequinone, yielding only hydroquinone **10** in 60% yield. Fortunately, this material converted rapidly

Scheme 1. Synthesis of Bromopentacenes



Scheme 2. Synthesis of Fluoropentacenes



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to anthraquinone **11** on exposure to air; a second Cava reaction between **11** and **8** yielded the octafluoropentacenequinone **12** in 23% yield. Quinones **2**, **3**, **9**, and **12** were all easily converted to the corresponding triisopropylsilylethynyl-substituted pentacenes using a standard ethynylation/deoxygenation approach.[10] The resulting blue compounds **4**, **5**, **13**, and **14** were all stable both in solution and in the solid state, even when exposed to air and laboratory lighting, and were easily purified by recrystallization. To explore the redox tuning of functionalized pentacene, we wished to substitute strongly electron-withdrawing groups for the bromine functional groups of **4** and **5**. Recent studies of perylene systems showed that the addition of nitrile groups to an aromatic core significantly alters the LUMO levels of the material, leading to facile reduction.[11] A convenient protocol for the conversion of aryl halides to aryl nitriles involves heating the halide in DMF with excess CuCN.[12] Attempts to perform this substitution on bromopentacenes **4** or **5** led only to decomposition of the aromatic compounds. There have been several reports of the conversion of aryl bromides to nitriles mediated by a palladium catalyst, and these reactions typically occur under relatively mild conditions.[13] In the case of the bromopentacenes, palladium-mediated coupling with CuCN yielded the desired pentacene nitriles **15** and **16** in reasonable yield. Electrochemical analysis of pentacenes **4**, **5**, and **13**−**16** showed one reversible oxidation and two reversible reduction waves in the potential window scanned (±1.8 V). In all cases, these substituted pentacenes had significantly higher oxidation potentials than the parent functionalized acene, 6,13-bis(triisopropylsilylethynyl)pentacene **17**. Because there is only a small change in the HOMO−LUMO gap in these substituted materials compared to **17** (as evidenced by a ~7 nm red shift for **13** and **14** compared to **17** and a ~35 nm red shift for **15** and **16** compared to **17**, UV−vis spectra presented in Supporting Information), the significant increase in oxidation potential is accompanied by a similar shift in reduction potential. All of these substituted pentacenes have first reductions well below that of **17**, with the most significant shift occurring for the pentacene nitriles: tetracyano TIPS pentacene **16** undergoes a first reduction at a potential of −0.895 V (vs F_c/F_c^+). Such low reduction potentials in a pentacene derivative may make these pentacenenitriles viable candidates as *n*-type semiconductors.

Scheme 3. Synthesis of Pentacene Nitriles

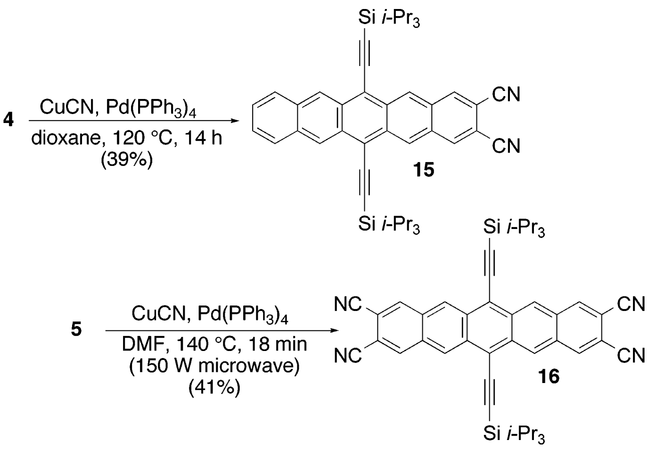

Table 1. Redox Properties of Functionalized Pentacenes (All Values vs (F_c/F_c^+))[a]

compound	E_{red} 1 (mV)	E_{red} 2 (mV)	E_{ox} (mV)
4	−1339	−1838	428
5	−1284	−1786	575
13	−1303	−1803	598
14	−1200	−1715	739
15	−1144	−1633	648
16	−895	−1429	954
17	−1722	−2267	380

[a] Performed in a 0.1 M solution of Bu_4NPF_6 in tetrahydrofuran using a Pt electrode, a scan rate of 150 mV/s, and ferrocene as an internal reference.

Our work with functionalized pentacene has shown that a two-dimensional, π-stacked arrangement in the solid state leads to the highest charge-carrier mobility.[14] We thus subjected derivatives **13**−**16** to single-crystal X-ray crystallographic analysis to determine their solid-state arrangements, which are represented in Figure 1.[15] Derivatives **13** and **15** were disordered by virtue of their sitting on sites of crystallographic inversion and pseudoinversion, respectively. Thus, in Figure 1, the arrangements shown for **13** and especially for **15** likely represent local ordering. Indeed, we suspect that **15** may actually be twinned but with domain sizes too small to be distinguished. In any event, no satisfactory twin model could be found, whereas the disorder model refined well. The crystallographic results do show that while tetracyano **16** adopts a one-dimensional stacking arrangement, the dicyano compound **15** and both fluorinated acenes **13** and **14** adopt two-dimensional, π-stacked arrangements very similar to **17** (Figure 1, bottom). Closer inspection of the packing reveals strong interaction between the π-surfaces of the fluorinated acenes, likely caused by interaction between the fluorinated and nonfluorinated rings, leading to an overall decrease in the spacing between pentacene planes. Compared to the nonfluorinated **17**, with an average interplanar spacing of 3.43 Å, the tetrafluoro compound **13** has an average interplanar spacing of 3.36 Å, while octafluoro **14** has a spacing of 3.28 Å.

It has been shown that charge-carrier mobility is strongly dependent on the spacing between aromatic faces in the

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(15) Crystallography was also performed on bromopentacenes **4** and **5**; the structural data is presented in Supporting Information.

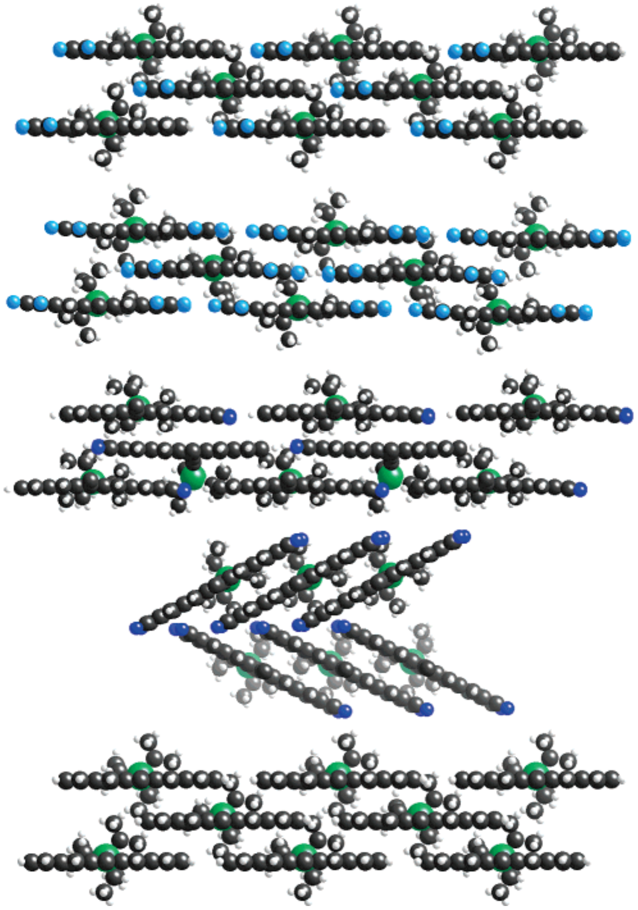

Figure 1. Solid-state arrangement of **13** (top) and **17** (bottom). Frontmost silyl groups have been removed for clarity.

solid,[16] leading to some elegant studies on methods to control this parameter.[17] We were thus led to measure the hole mobility of **13**, **14**, and **17** in a thin-film transistor configuration.

Because optimized deposition conditions would likely be vastly different for the compounds **13**, **14**, and **17**, it was decided to compare the field-effect mobilities of all three derivatives under identical deposition conditions. We evaporated these compounds onto oxidized silicon wafers (the thermally grown SiO_2 served as the gate dielectric) and deposited Au top contacts, defining channels with a width of 1 mm and a legnth of 75 μm. The substrates were held at room temperature. Under these conditions, the parent TIPS pentacene **17** exhibited a hole mobility of 0.001 cm^2/Vs (compared with 0.4 cm^2/Vs under optimized deposition conditions[14]). As expected, the tetrafluoro pentacene **13** showed a significantly higher mobility (0.014 cm^2/Vs) when deposited under these same conditions, while octafluoro pentacene **14**, the molecule in the series with the smallest interplanar spacing, yielded devices with a hole mobility of 0.045 cm^2/Vs. Thus, the field-effect hole mobility scales with the π-face separation in the acenes, which in turn is controlled by the degree of fluorine substitution.

We have shown here that the Cava reaction is a viable alternative to the more common 4-fold aldol condensation for the preparation of halogenated pentacenequinones. The addition of bromine functional "handles" allows further manipulation of the substitution on the pentacene, leading to the ability to tune the electronic properties of the molecule. Finally, by exploiting aryl−perfluoroaryl interactions, it is possible to alter the interplanar spacing between acenes in the solid state and thus improve charge-carrier mobility. Optimization of deposition conditions for the fluorinated pentacenes, as well as device studies of pentacene nitriles, is currently underway.

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Supporting Information Available: Experimental details and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OL050872B

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