Robust, Soluble Pentacene Ethers
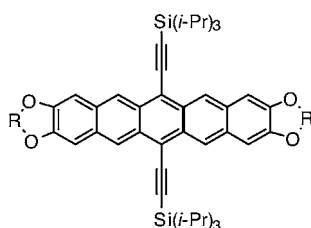
Marcia M. Payne, Jared H. Delcamp, Sean R. Parkin, and John E. Anthony*

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055

anthony@uky.edu

Received March 4, 2004

ABSTRACT

We report the synthesis and characterization of a series of alkoxy-substituted silylethynylated pentacene derivatives (R = CH_2CH_2, CHCH, CH_2). All three compounds are easily prepared, soluble in common organic solvents, and stable both as solids and in solution. Two of the derivatives possess significant π-face interactions in the crystal. Values for λ_{max} for these new pentacene derivatives range from 621 to 674 nm, and oxidation potentials lie between 109 and 301 mV versus ferrocene.

Organic field-effect transistors (OFETs) are at the forefront of the burgeoning field of organic electronics. This field will lead to a new generation of electronic devices for applications requiring large-area coverage for minimal cost. Pentacene has proven to be the most effective active layer in OFETs, with charge-carrier mobilities of >2 cm^2 V^{-1} s^{-1} being the best yet reported.[1] Studies have shown that molecules with increased π-stacking that allow charge carriers to move within stacks could achieve greater charge transport efficiency as a benefit of this type of organized structure.[2] In an attempt to improve molecular ordering in pentacene, we have demonstrated simple synthetic procedures to yield stable and soluble 6,13-disubstituted pentacenes containing various trialkylsilylethynyl functionalities.[3] These planar molecules form well-ordered crystalline states in which the molecular planes are parallel to each other. Recently, OFET devices have been fabricated using 6,13-bis(triisopropylsilylethynyl)-pentacene (TIPS pentacene) with a mobility of 0.38 cm^2 V^{-1} s^{-1} and an on−off current ratio of 10^6 reported for a top-

contact device.[4] Further improvements in these parameters are likely to be limited by the high oxidation potential (E_{ox} = 850 mV) of this pentacene derivative, which hinders charge injection.

By attaching alkyl groups to the four terminal positions (2, 3, 9, and 10) of pentacene, Wudl and Bao et al. have demonstrated the ability to shift the energies of both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) without significantly changing the gap between these two.[5] Alkyl substitution has also been applied to the derivatization of tetrathiafulvalene (TTF) to modify the electronic properties and solubility of this compound. Spurred by the theory that the role of oxygen in superconducting copper oxides is more significant than previously thought, Suzuki et al. added electron-donating alkoxy substituents to TTF to make a bis(ethylenedioxy) derivative (BEDO-TTF).[6] This derivative, when paired with various inorganic anions, has yielded around 25 metallic (and 2 superconducting) cation radical salts.[7] We propose that the same electronic tuning approach can be applied to our TIPS

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pentacene and that alkoxy substitution might also result in a lowering of the oxidation potential.

Our initial approach was to prepare various TIPS pentacene derivatives containing acyclic ethers from methyl to octyl at the four terminal positions. These proved to be so unstable that they decomposed during workup. By analogy with both PEDOT and BEDO-TTF, it seemed reasonable to expect that cyclic ethers might confer further stability.

Silylethynylated pentacenes are typically prepared from the corresponding acene quinones, which in turn are prepared from an aldol condensation of a phthalaldehyde and 1,4-cyclohexanedione.[8] Our initial target, 1,4-benzodioxane-6,7-dicarboxaldehyde, was synthesized from commercially available 1,4-benzodioxane using previously reported methods.[9] This was converted in two steps to the desired pentacene derivative **1** (Scheme 1). Successive recrystallizations of the

Scheme 1. Synthesis of Dioxane TIPS Pentacene **1**[a]
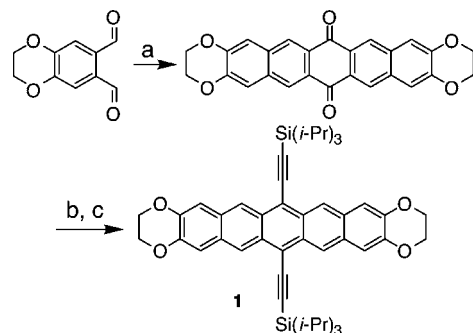
[a] Conditions: (a) 1,4-cyclohexane dione, KOH, EtOH/H$_2$O, 70%; (b) (*i*-Pr)$_3$SiCCLi, hexanes/THF; (c) SnCl$_2$, 10% HCl, 58%.

product from acetone and then toluene yielded blue-green plates that were subjected to single-crystal X-ray analysis to verify the structure and determine the solid-state arrangement (Figure 1). Like BEDO-TTF, this molecule is nonpla-
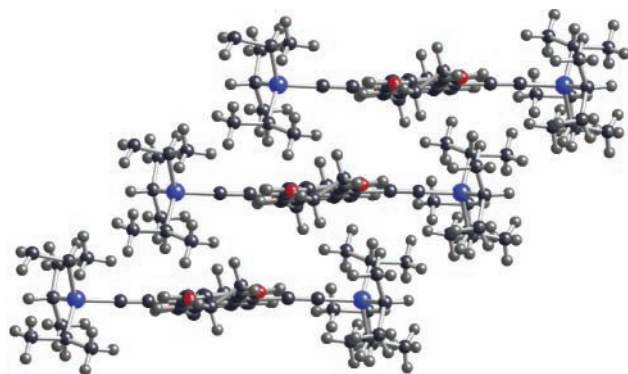

Figure 1. Crystal structure of **1**.

nar, and there is only minimal π-overlap, due to the presence of axial hydrogens on the terminal benzodioxane rings.

Although this material was both stable and more easily oxidized than TIPS pentacene, it was unlikely to possess sufficient carrier mobility to be useful in transistor configurations due to this poor π-overlap.

The most straightforward route to eliminate the axial hydrogens involved the conversion of a benzodioxane to a benzodioxin. Using a bromination/elimination strategy, diethyl 1,4-benzodioxane-6,7-dicarboxylate was converted to derivative **2** in five steps (Scheme 2). The product was

Scheme 2. Synthesis of Dioxin TIPS Pentacene **2**[a]
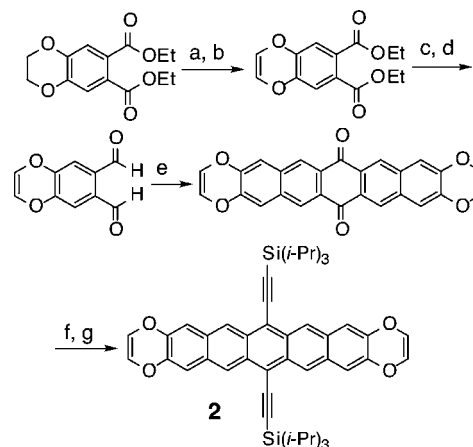
[a] Conditions: (a) NBS, AIBN, CCl$_4$, reflux; (b) NaI, acetone, reflux, 21%; (c) LiAlH$_4$, THF, 93%; (d) Swern oxidation, 85%; (e) 1,4-cyclohexanedione, KOH, EtOH/H$_2$O, quantitative; (f) (*i*-Pr)$_3$SiCCLi, hexanes/THF; (g) SnCl$_2$, 10% HCl, 81%.

recrystallized from acetone and then ethyl acetate to yield green needles that were analyzed by single-crystal X-ray diffraction (Figure 2). As we expected, there is significant
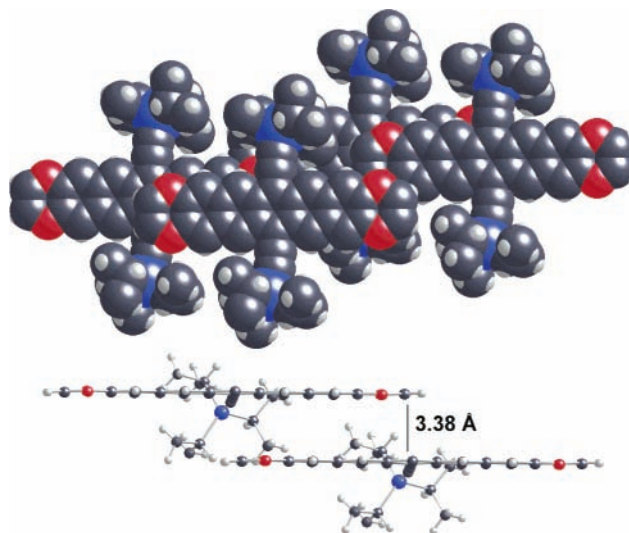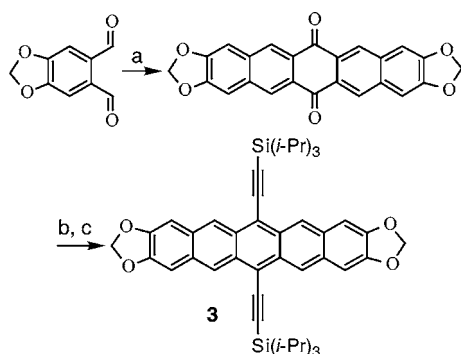

Figure 2. Crystal structure of **2**.

π-overlap with face-to-face interactions of 3.38 Å and extremely close oxygen−oxygen distances of 3.03 Å between stacks.

We conceived an alternative method for removing the axial hydrogens that had disrupted planarity in **1** by shortening the ethyl bridge to a methylene group. Pentacene derivative **3** was easily synthesized from previously reported 1,4-benzodioxolane-6,7-dicarboxaldehyde in good yield (Scheme 3).[10] The product was recrystallized from dichloroethane and

^{a} Conditions: (a) 1,4-cyclohexanedione, KOH, EtOH/H$_2$O, 98%; (b) (*i*-Pr)$_3$SiCCLi, THF; (c) SnCl$_2$, 10% HCl, 75%.

then toluene to give dark blue needles that were analyzed by single-crystal X-ray diffraction (Figure 3). This pentacene
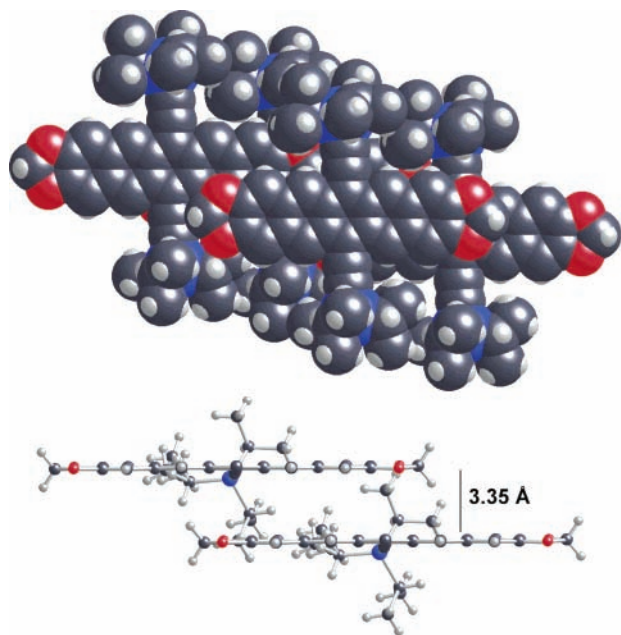

Figure 3. Crystal structure of **3**.

derivative also exhibits significant π-overlap in two dimensions. It is interesting to note that derivative **3** has a smaller

Table 1. Spectroscopic and Electrochemical Data for Compounds **1−3**

compd	π_{max}abs (nm)	π_{max}em^a (nm)	E$_{ox}$ (mV)^b vs Fc/Fc$^+$
pentacene	578	582	100
TIPS pentacene	644	648	390
1	674	683	109, 800
2	639	647	301
3	621	627	217

^{a} Performed in dichloromethane. ^{b} Performed in 0.1 M solution of Bu$_4$NPF$_6$ in dichloromethane, Pt electrode, scan rate of 150 mV/s, ferrocene as the internal standard.

distance between π faces (3.35 Å) than derivative **2**, even though it possesses out of plane hydrogens on its first and seventh rings.

All three of these pentacene derivatives are soluble in common organic solvents, and the crystalline solids are stable for weeks open to air under laboratory conditions. Solutions in dichloromethane fluoresce visibly under laboratory lighting and, if shielded from oxygen, can be kept indefinitely. For each, we recorded absorbance and emission spectra, as well as oxidation potential (Table 1 and Figure 4). Only derivative
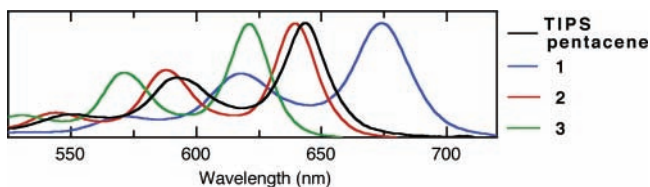

Figure 4. UV absorbance spectra of compounds **1−3**. Recorded in dichloromethane.

1 showed a red-shifted absorbance from TIPS pentacene, indicating that its oxygen lone pairs do contribute to the π-conjugation. Both derivatives **2** and **3** have blue-shifted absorbances from TIPS pentacene, likely associated with their more rigid structures that prevent oxygen lone pairs from interacting with the π-clouds. As expected, compound **1** also exhibits the largest Stokes shift in its emission spectrum, associated with its less rigid structure. However, derivatives **2** and to a lesser extent **3** also exhibit larger Stokes shifts than the parent TIPS pentacene, indicating that the presence of the oxygens contributes some degree of conformational mobility to the excited states of these molecules as well.

All three derivatives exhibit reversible first oxidations that are significantly lower in energy than TIPS pentacene, with derivative **1** also showing a reversible second oxidation. It is surprising that derivative **1**, whose first oxidation potential

(8) See ref 3.
(9) Dallacker, F.; Bloemen, J. *Monatsh. Chem.* **1961**, *92*, 640.
(10) Dallacker, F.; Glombitza, K. W.; Lipp, M. *Justus Liebigs Ann. Chem.* **1961**, *643*, 67.

is very close to that of pentacene, is so much more stable than this parent acene. The presence of the bulky groups on the central rings likely retards the two competing modes of decomposition: dimerization and endoperoxide formation.

Functionalization of TIPS pentacene with electron-rich substituents results in stable and soluble materials that can be engineered to preserve the close π-stacking and increased orbital overlap that may result in high charge carrier mobilities. These substituents can be used to tune the HOMO and LUMO energies, which may be exploitable in the design of future OFETs with improved performance parameters, as well as organic light-emitting diodes with saturated red emission.

Supporting Information Available: Experimental procedures, characterization, and crystallographic data for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL049593Z