ORGANIC
LETTERS

2004
Vol. 6, No. 19
3325−3328

Stable, Crystalline Acenedithiophenes with up to Seven Linearly Fused Rings

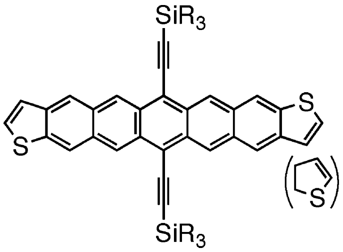
Marcia M. Payne, Susan A. Odom, Sean R. Parkin, and John E. Anthony*

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

anthony@uky.edu

Received July 8, 2004

ABSTRACT



We report the synthesis of a series of crystalline acenedithiophenes with up to seven linearly fused rings and silylethynyl substituents. These functional groups are designed to both improve solubility and enhance cofacial interactions in the solid. We discuss the crystal packing of these materials, as well as their physical properties such as oxidation potential, UV–vis absorption, fluorescence emission, and decomposition pathways.

Polycyclic aromatic hydrocarbons represent a vast library of molecular geometries with properties exploitable for materials chemistry.[1] The linearly fused acenes in particular have applications in field-effect transistors (FETs)[2] and organic light-emitting diodes (OLEDs).[3] Our research has emphasized the functionalization of acenes to improve solid-state ordering and increase solubility and stability. For example, 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS pentacene) packs in a 2-dimensional π-stacked array in the solid state, yielding improved conductivity, reduced band gap,[4] and FET devices with a hole mobility of 0.4 cm^2/Vs.[5] Spurred by these promising results, we wished to apply our functionalization approach to other fused systems, to further our structure−property relationship studies of organic semiconductors.

One of the most promising systems for such study involves a fusion of acenes and oligothiophenes:[6] alkylated anthradithiophene systems were recently reported by Katz and coworkers as part of their search for new materials for use in organic FETs. Their materials,[7] synthesized as an inseparable mixture of *syn*- and *anti*-isomers, exhibited hole mobilities as high as 0.15 cm^2/Vs with good device stability. A recent theoretical treatment of these materials showed them to have great promise if the proper molecular packing could be attained, particularly orderings that enhanced π-face interactions.[8] To us, substitution of thiophene for the "terminal" benzene rings of an acene is attractive because it should not significantly perturb the basic molecular geometry compared to the acene hydrocarbons. Increased stability in these pentacene-like derivatives also indicates that this might be

---

[1] Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New, York, 1964; Vols. I and II.

[2] (a) Butko, V. Y.; Chi, X.; Lang, D. V.; Ramirez, A. P. *Appl. Phys. Lett.* **2003**, *83*, 4773. (b) Zhang, Y.; Petta, J. R.; Ambily, S.; Shen, Y.; Ralph, D. C.; Malliaras, G. C. *Adv. Mater.* **2003**, *15*, 1632. (c) Dimitrakopoulos, C. D.; Kymissis, I.; Purushothaman, S.; Neumayer, D. A.; Duncombe, P. R.; Laibowitz, R. B. *Adv. Mater.* **1999**, *11*, 1372. (d) Lin, Y. Y.; Gundlach, D. J.; Nelson, S.; Jackson, T. N. *IEEE Trans. Electron Devices* **1997**, *44*, 1325.

[3] (a) Wolak, M. A.; Jang, B.-B.; Palilis, L. C.; Kafafi, Z. H. *J. Phys. Chem. B* **2004**, *108*, 5492. (b) Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2003**, *5*, 4245.

[4] (a) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15. (b) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.

[5] Sheraw, C. D.; Jackson, T. N.; Eaton, D. L.; Anthony, J. E. *Adv. Mater.* **2003**, *15*, 2009.

[6] Fichou, D.; Horowitz, G.; Bai, X.; Garnier, F. *Synth. Met.* **1992**, *48*, 167.

[7] Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664.

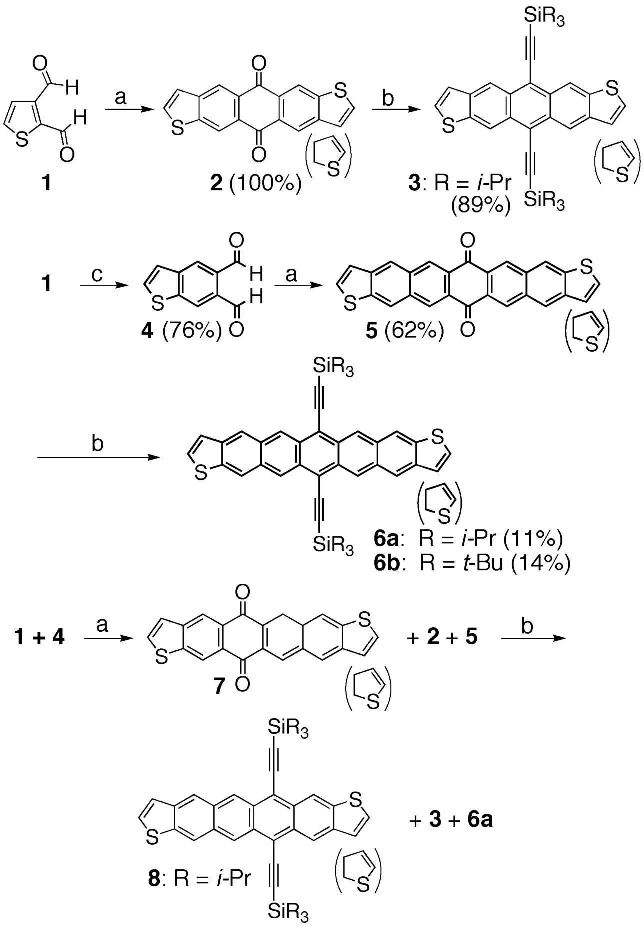
[8] Kwon, O.; Coropceanu, V.; Gruhn, N. E.; Durivage, J. C.; Laquindanum, J. G.; Katz, H. E.; Cornil, J.; Brédas, J. L. *J. Chem. Phys.* **2004**, *120*, 8186.

10.1021/ol048686d CCC: $27.50

a reasonable method for attaining higher acene analogues. We report here the synthesis and characterization of a series of functionalized acenedithiophenes, from anthradithiophene to pentadithiophene.

Silylethynylated acenes are easily prepared from the corresponding acenequinones. Quinone **2** was prepared from dicarboxaldehyde **1**[9] as described previously. Quinone **5** was made from dicarboxaldehyde **4**,[10] synthesized by a four-carbon homologation of **1** (Scheme 1). Addition of trialkylsilylethynyllithium followed by deoxygenation with stannous chloride yielded the desired five- and seven-ring acenedithiophenes. To prepare the six-ringed tetradithiophene **8**, condensation of a 1:2 mixture of dicarboxaldehydes **1** and **4** with 1,4-cyclohexanedione followed by deoxygenative ethynylation yielded an easily separated mixture of **3**, **6a**, and **8**. The acenedithiophenes underwent chromatographic purification on silica gel with minimal decomposition and were further purified by recrystallization. Most importantly, the fact that these materials exist as inseparable mixtures of *syn*- and *anti*-isomers did not significantly interfere with crystallization or X-ray diffraction studies.

Scheme 1[a]



[a] Reagents and conditions: (a) 1,4-cyclohexanedione, ethanol, 1 mL 15% aq NaOH. (b) $R_3SiCCLi$, hexanes, 65 °C, 12 h, then $SnCl_2$/10% HCl, 2 h. (c) 2,5-dimethoxytetrahydrofuran, AcOH 110 °C.

Single-crystal X-ray diffraction studies of **3** and **8** indicated that both compounds were planar and formed crystals of $P2_1/c$ and $P2_1$ space group symmetries, respectively (Figure 1). The structures determined for these compounds exhibited disorder of the thiophene rings expected as a result of the isomeric mixture formed in their synthesis (as shown in the Figure). Both **3** and **8** were modeled as the *anti*-isomer for structure solution purposes only. These materials are stable in the solid state or in (deoxygenated) solution for weeks and can be evaporated or solution-cast to form stable, uniform thin films.

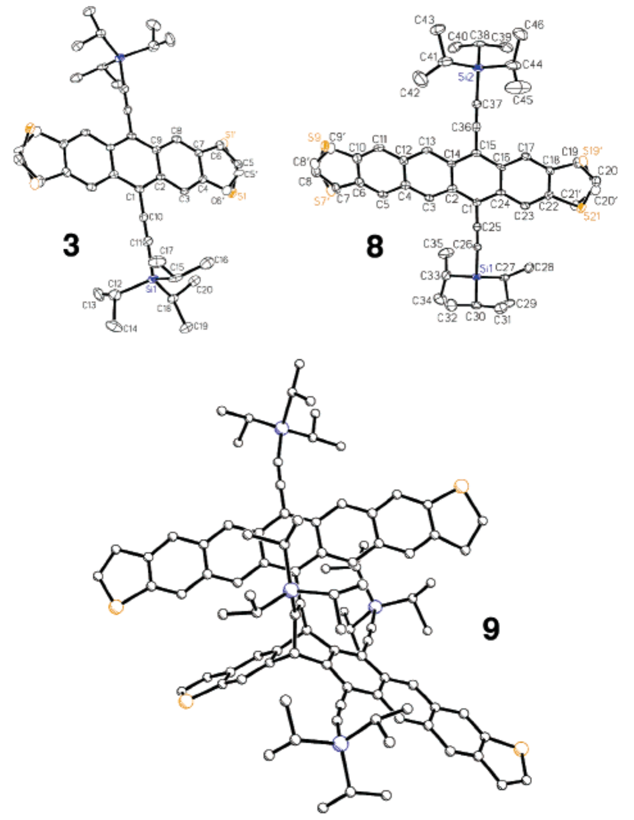


Figure 1. Thermal ellipsoid plots of the **3** and **8** (as a mixture of isomers) and dimerized **6a**.

The seven-ringed compound formed irregular green needles from toluene that were poorly suited for X-ray analysis. Although structure solution was straightforward, refinement was hindered by disorder of both the thiophene rings and isopropyl groups. However, the atom connectivity of the compound could easily be determined, showing the material to be a dimeric species (**9**), formed by a cyclization reaction between the diene within the third ring of one acene and the ethynyl group of a second acene. Further experimentation revealed that the dimerization of **6a** proceeds to completion

---

(9) De la Cruz, P.; Martin, N.; Miguel, F.; Seoane, C.; Albert, A.; Cano, H.; Gonzalez, A.; Pingarron, J. M. *J. Org. Chem.* **1992**, *57*, 6192.

(10) El-Borai, M.; Abdel-Megeed, M. F.; Hassien, M.; Fahmy, M. *Sulfur Lett.* **1987**, *6*, 99.

within a few hours of isolation of this compound, even in relatively dilute solution. Further, formation of the adduct was not reversible at temperatures of up to 180 °C. These results are especially surprising because the triisopropylsilyl group has been used to shield ethynyl substituents from dienes in similar Diels−Alder reactions,[11] which emphasizes the reactive nature of the higher acenes. Because compound **9** still contains an intact seven-ringed chromophore, we postulated that a pentadithiophene could be isolated as a stable material if this intermolecular cyclization were prevented by the use of a more sterically demanding alkyne substituent.

The bulky tri(*tert*-butyl)silyl group has been employed to generate low-coordinate metal complexes and previously unrealizable alkynyl-substituted zirconium and hafnium complexes and therefore seemed a viable alternative.[12] Thus, tri(*tert*-butyl)silylethynyl derivative **6b** was prepared as outlined in Scheme 1. Although this material is significantly less soluble than the corresponding TIPS derivative **6a**, recrystallization from CS_2 yielded dark green needles suitable for single-crystal X-ray diffraction, and we were pleased to discover that this compound did not undergo dimerization. This derivative crystallizes in the $P\bar{1}$ space group and is a remarkable and rare example of a stable, crystalline, linearly fused seven-ringed compound (Figure 2). Acene **6b** is stable both in the solid state and in deoxygenated toluene solution for a period of several weeks.

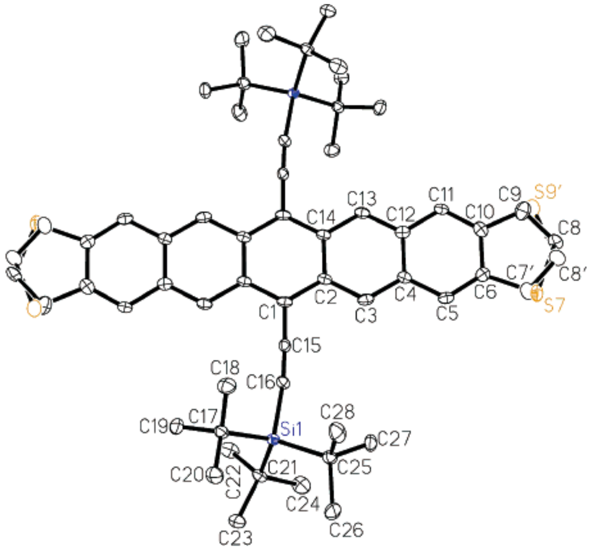


Figure 2. Thermal ellipsoid plot of **6b** (mixture of isomers).

The molecular structures for **3**, **8**, and **6b** all show that the acene backbones of these molecules are planar to within 0.14 Å.[13] The only significant deformation of the acene involves a slight pyramidalization of the aromatic carbon attached to the alkyne, and the degree of pyramidalization increases with increasing acene length. An examination of the crystal packing for these three derivatives reveals that the molecules in the crystal assemble into 1-dimensional π-stacked arrays, as predicted by our model for the packing of ethynylated pentacenes.[4a] This solid-state arrangement not only minimizes the distortion of the aromatic core in the crystal but also leads to close π-face contacts critical for device performance. The average interplanar spacing for compounds **3**, **8**, and **6b** are 3.46, 3.46, and 3.42 Å, respectively (Figure 3). The degree of π-overlap varies with the size of the acene, with the seven-ringed **6b** exhibiting the greatest number of overlapping rings.

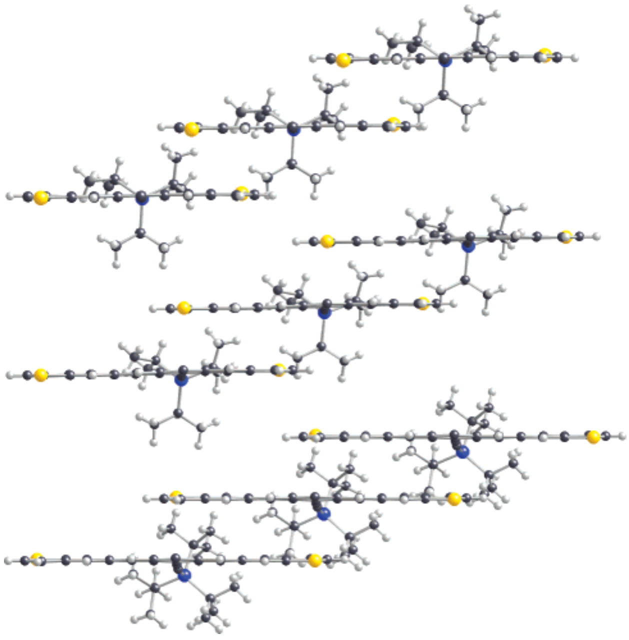


Figure 3. Solid-state ordering of **3**, **8**, and **6b**. View along the acene short axis, with frontmost silylethynyl groups omitted for clarity.

UV−visible absorption spectra for thienyl acenes **3**, **8**, and **6b** were recorded in dichloromethane solution (Figure 4). As expected, the extinction coefficient for the longest-wavelength absorption decreases significantly as the length of the acene increases. The ∼100 nm red shift upon addition of a single aromatic ring in the oligomer series implies that longer oligo(acenedithiophene)s will have impressively small optical gaps. Indeed, a simple plot of long-wavelength cutoff vs 1/(oligomer length) reveals an anticipated HOMO−LUMO gap of 0.9 eV for the infinite-length polymer.[14] This number compares well with energies predicted, both at various levels of theory and by extrapolation of UV−vis

---

[11] Morgenroth, F.; Berresheim, A. J.; Wagner, M.; Müllen, K. *Chem. Commun*. **1998**, 1138.

[12] (a) Vaid, T. P.; Veige, A. S.; Lobvoysky, E. B.; Glassey, W. V.; Wolczanski, P. T.; Liable-Sands, L. M.; Rheingold, A. L.; Cundari, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 10067. (b) Wiberg, N.; Amelunxen, K.; Lerner, H.-W.; Schuster, H.; Noth, H.; Krossing, I.; Schmidt-Amelunxen, M.; Seifert, T. *J. Organomet. Chem.* **1997**, *542*, 1

[13] The planarity of large polycyclic aromatic systems is easily disrupted by crystal packing effects: Holmes, D.; Kumaraswamy, S.; Matzger, A. J.; Vollhardt, K. P. C. *Chem. Eur. J.* **1999**, *5*, 3399.

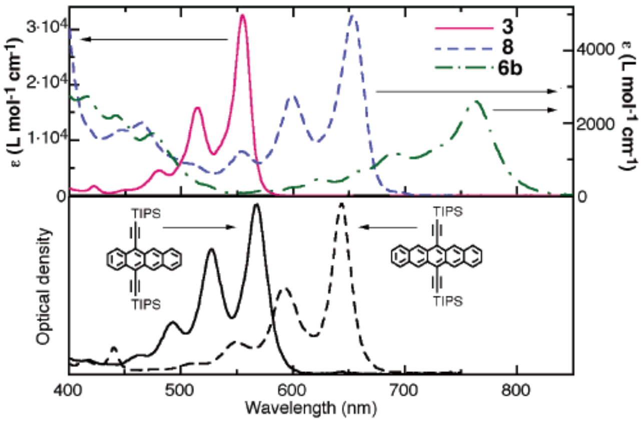


Figure 4. Absorption spectra of the acenedithiophenes (top), compared to the related parent hydrocarbons (bottom).

spectral data, for the parent polyacenes.[15] This correlation is unsurprising, because the absorption spectra of the acenedithiophenes are remarkably similar to those of the related acenes (see the absorption spectra for bis(triisopropylsilylethynyl)tetracene and TIPS pentacene, Figure 4). The acenedithiophenes have absorption behavior that corresponds to the absorptions of acenes that contain one less aromatic ring, likely due to the unique nature of the heteroaromatic thiophene rings. Whereas five-ringed compound **3** exhibits bright pink/orange fluorescence, the longer acenedithiophenes (**8** and **6b**) were only weakly fluorescent in solution.

The oxidation potentials for these compounds span a range of values from ∼600 to 900 mV, corresponding to HOMO energy levels from approximately 5.2 to 4.9 eV for the series. Access to such a wide range of potentials over a structurally homologous series of compounds may prove to be useful in device applications because it allows for a flexible approach to matching the proper material with a particular application and desired electrode metal. These alkyne-substituted acenedithiophenes are soluble and exhibit strong π-stacking interactions in the solid state. By careful selection of the substituent on the alkyne, even the system with a backbone 1.7 nm long consisting of seven linearly fused aromatic rings can be stabilized and solubilized. Studies of the transport properties, including charge carrier mobility and conductivity band gap for each of these materials, are currently underway and will be the subject of a future report.

Table 1. Selected Spectral Data for **3**, **8**, and **6b**

compound	λ_{max} abs (nm)	λ_{max} em[a] (nm)	E_{ox} (mV)[b] vs SCE
3	555	561	900
8	653	665	725
6b	762	802	613

[a] In dichloromethane. [b] In 0.1 M solution of Bu_4NPF_6 in dichloromethane, Pt electrode, scan rate of 150 mV/s, ferrocene as internal standard.

Acknowledgment. The authors are grateful to the Office of Naval Research and the Defense Advanced Research Projects Agency for providing funding for this research.

Supporting Information Available: Full experimental details, molecule characterization, and crystallographic information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OL048686D

---

(14) Schreiber, M.; Anthony, J.; Diederich, F.; Spahr, M. E.; Nesper, R.; Hubrich, M.; Bommeli, F.; Degiorgi, L.; Wachter, P.; Kaatz, P.; Bosshard, C.; Günter, P.; Colussi, M.; Suter, U. W.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Adv. Mater.* **1994**, *6*, 786.

(15) Houk, K. N.; Lee, P. S.; Nendel, M. *J. Org. Chem.* **2001**, *66*, 5517 and references therein.