ORGANIC
LETTERS

2008
Vol. 10, No. 21
4779−4782

Synthesis and Electronic Properties of Conjugated Pentacene Dimers

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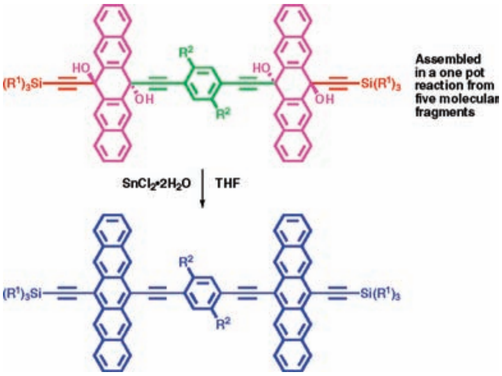
Received August 12, 2008

ABSTRACT



Conjugated pentacene dimers 1−3 were synthesized in two steps from readily available precursors. Noteworthy is the initial step, which assembles five independent fragments to form the carbon-rich molecular framework. Solution-cast films of these materials are air stable. Photocurrent measurements for solution-deposited thin films show that dimer 3 exhibits photoconductive gain >10.

Organic semiconducting materials offer the potential to revolutionize optoelectronics, including applications in photovoltaic cells, chemical sensors, thin film transistors, as well as devices based on nanowires.[1] In an effort to provide materials with improved performance for such goals, polyacenes have been a favorite target, building from the well-established electronic attributes of anthracene and pentacene.[1] One of the biggest breakthroughs in this area has been the development of versatile synthetic protocols to functionalize the pentacene core, and seminal work by Anthony and others have established that such syntheses can provide pentacene derivatives with technologically relevant properties.[1,2]

An obvious challenge to further improving the overall usefulness of pentacene-based materials would be the formation of oligomers and polymers that might show enhanced properties. Oligomers also provide an excellent opportunity for assessing structure−property relationships, via comparisons to the corresponding monomeric analogues. Finally, oligomers and polymers also often facilitate the solution-state deposition of high-quality thin films. Despite these attractive features, pentacene-based oligo- and polymers have, for the most part, remained unrealized until quite recently.[3] On the other hand, the study of anthracene oligomers has demonstrated improved conduction versus the corresponding monomers.[4] This suggests that the formation of conjugated pentacene oligomers should also afford materi-

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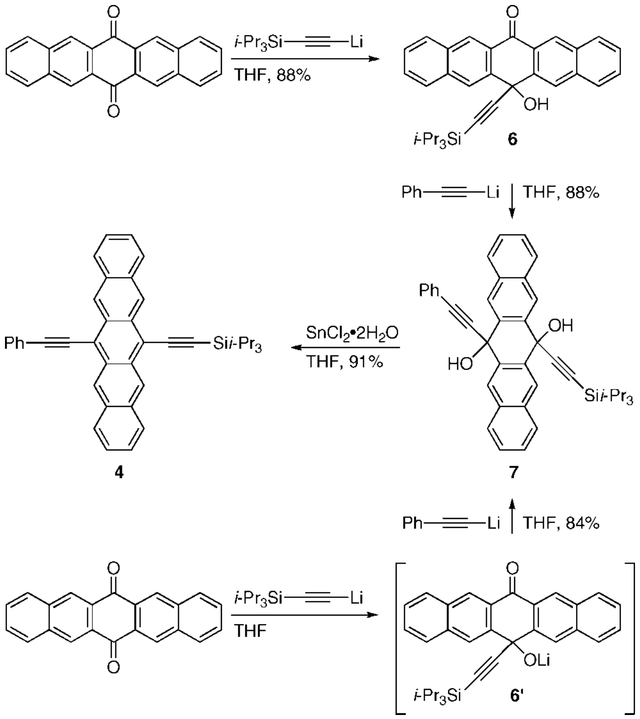
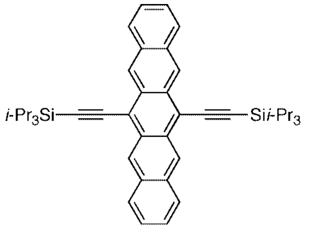
10.1021/ol801886h CCC: $40.75 © 2008 American Chemical Society
Published on Web 09/30/2008

als with unique and enhanced electronic properties. Herein, we report on the development of a stepwise synthetic route that provides stable, conjugated pentacene dimers **1**−**3** (Scheme 2). Furthermore, a preliminary study of semiconducting properties of these compounds has been carried out through the analysis of photoconductive gain in comparison to model compounds **4** (Scheme 1) and **5** (Figure 1).

Scheme 1. Synthesis of Model Compound **4**



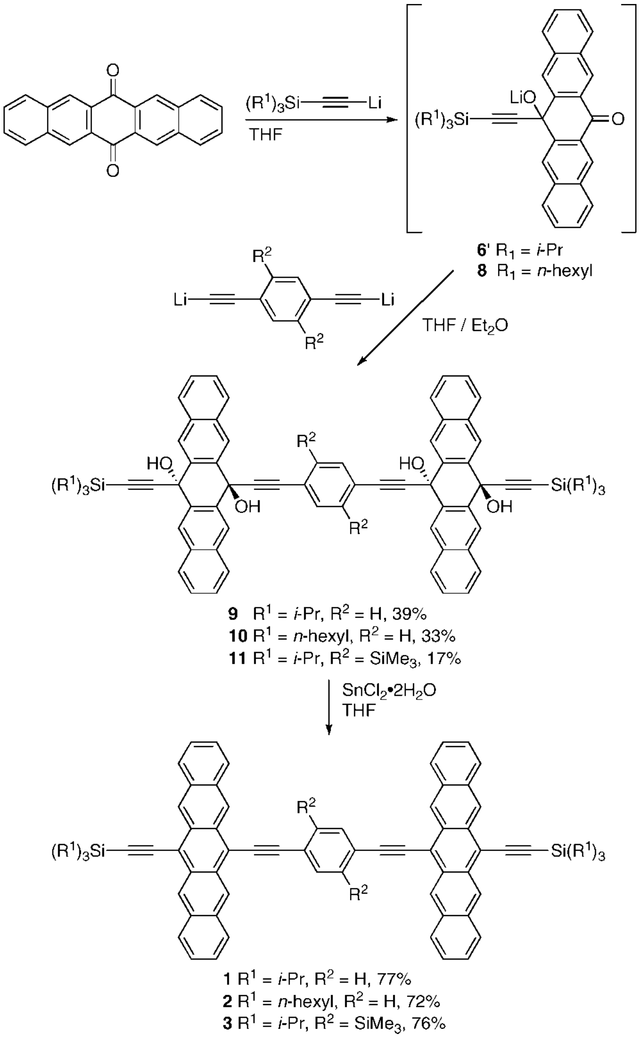


5

Figure 1. Molecular structure of model compound **5**.[5]

The synthesis of conjugated pentacene dimers necessitated a method of desymmetrization of the core of 6,13-pentacenequinone. A general stepwise approach to unsymmetrical pentacene chromophores has recently been reported and is demonstrated in Scheme 1 for the synthesis of model compound **4**.[6] In this protocol, the reaction of 6,13-pentacenequinone with 1 equiv of lithiated triisopropylsilylacetylene (formed via reaction with HexLi) gave monoaddition product **6** in excellent yield.[7,8] The conversion of **6** to diol **7**, however, required the use of excess lithiated phenylacetylene due to the presence of the acidic hydroxy group (which quenched 1 equiv of the acetylide). Unfortunately, this procedure is not amenable to the formation of a conjugated dimer. Clearly, the reaction of monoadduct **6** with a diacetylide is problematic given the presence of a hydroxy group, which would only partially quench an incoming diacetylide via protonation. Furthermore, the use of excess

Scheme 2. Synthesis of Pentacene Dimers **1**−**3**



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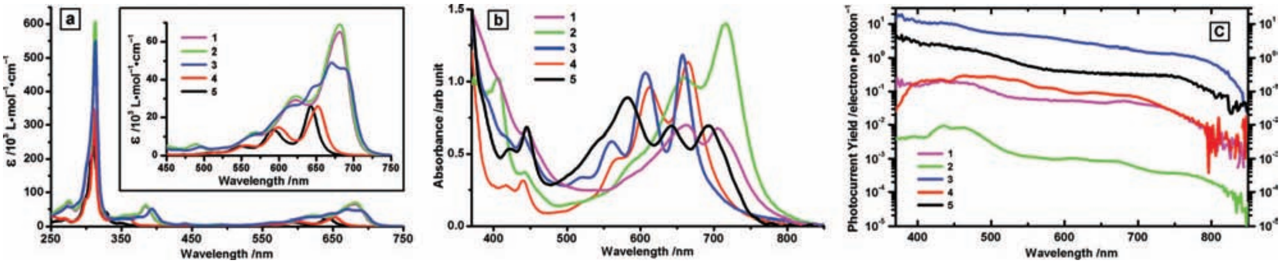

Figure 2. Spectral data for functionalized pentacenes. (a) Solution-state UV−vis absorption spectra of dimers **1**−**3** and **4**−**5** (CH_2Cl_2). Inset: expansion of low energy absorption region (450−750 nm). (b) Solid-state UV−vis absorption spectra. (c) Photocurrent yield.

diacetylide, as in the transformation of **6** to **7**, would not solve this problem. Thus, a one-pot protocol was explored that circumvented the isolation and derivatization of **6**. Lithiated triisopropylsilylacetylene was added to a suspension of 6,13-pentacenequinone in THF to form intermediate **6′**. This reaction mixture was subsequently added to a solution of lithiated phenylacetylene in THF, and following workup and purification by column chromatography, diol **7** was isolated in excellent yield. Aromatization of **7** using $SnCl_2$•$2H_2O$ then gave **4**. Compound **4** is highly soluble in, for example, CH_2Cl_2, $CHCl_3$, and THF, and it can be manipulated under normal laboratory conditions in solution or in the solid state with minimal decomposition.

With a viable one-pot procedure in hand, the synthesis of dimers **1**−**3** followed a similar route. Lithiated trialkylsilylacetylene was added to a suspension of 6,13-pentacenequinone in THF and provided either intermediate **6′** or **8**. A solution of this intermediate was then added to the appropriate dilithiated 1,4-diethynylbenzene to complete the dimerization process and afforded pentacene tetraols **9**−**11** in 17−39% yield. While the isolated yields for **9**−**11** were moderate to low, it is worth noting that, in a single step, four new carbon−carbon bonds have been formed through the reaction of five individual precursors (equivalent to 64−79% yield per bond forming event). Finally, Sn(II)-mediated reduction of **9**−**11** afforded conjugated pentacene dimers **1**−**3** in good yields of 72−77%. All dimers could be stored as solids for months under refrigeration in the presence of both air and water without any observable decomposition. Additionally, solutions of these materials could be handled under normal ambient laboratory conditions for several hours with minimal decomposition.

The thermal stability of pentacene dimers **1**−**3** was evaluated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) in comparison to **4**. Although the TGA showed no significant weight loss (<5%) below 410 °C for all derivatives, the DSC trace of **4** and dimer **2** contained exothermic peaks at much lower temperatures, namely, 180 and 157 °C, respectively. Dimers **1** and **3** showed better thermal stability based on the DSC analyses, with decomposition temperatures of 445 and 389 °C, respectively.

Pentacene dimer **1** shows limited solubility in common organic solvents. Formally replacing the *i*-Pr_3Si groups of **1** with *n*-$hexyl_3Si$ groups to give **2** produced a dimer that is soluble in a number of common solvents (e.g., CH_2Cl_2, $CHCl_3$, and THF). Dimer **3** represents an attempt to maintain solubility through the use of a π-spacer functionalized with two Me_3Si groups while minimizing the potential of disrupting π-stacking interactions that might arise from the terminal *n*-$hexyl_3Si$ groups.[1,9] Surprisingly, **3** does not possess enhanced solubility relative to **1**, although the electronic makeup of the molecule is altered in comparison to that of **1** and **2** (vide infra).[10]

UV−vis spectra of dimers **1**−**3** in CH_2Cl_2 have been examined in comparison to **4** and **5** (Figure 2a). The λ_{max} for **4** (652 nm) is red-shifted versus **5** (643 nm), as expected due to the increased conjugation length as a result of the pendent phenyl ring. The absorptions for pentacene dimers **1**−**3** all show an additional red shift in comparison to **4**, with λ_{max} values centered at ca. 680 nm. While the absorption characteristics of **1** and **2** are similar, that of **3** shows additional fine structure, perhaps as a result of the pendent silicon groups on the central core.[10] To probe the origin of the difference in the solution-state UV−vis absorption profile for **3** relative to **1** and **2**, concentration dependency has been investigated to rule out aggregation. Solutions of **3** in CH_2Cl_2 have been prepared from 1.7×10^{-5} to 5.5×10^{-7} M. No change in λ_{max} values is observed, and molar absorptivity values (ε) confirmed that Beer's Law is obeyed. Since neither the qualitative shape of the absorption nor the ε values change appreciably as a function of concentration, it is concluded that the difference in the spectrum of dimer **3** is not due to aggregation. Thus, subtle electronic effects arising from the Me_3Si groups on the π-spacer of dimer **3** are likely the source of the differences in its UV−vis spectrum.[10]

Solid-state absorption spectra of thin films of **1**, **2**, **4**, and **5** (Figure 2b) are red-shifted compared to their solution-state spectra. The exception to this trend is dimer **3**, which shows a blue-shifted λ_{max} (657 nm), with a value similar to that of

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4 (665 nm). This suggests an interruption of conjugation between the two pentacenes and the aryl π-spacer, perhaps a manifestation of steric demands of the Me_3Si groups in the solid-state packing of this molecule.

The emission properties of pentacene materials **1**−**5** have been investigated as CH_2Cl_2 solutions. As a model compound, **4** shows fluorescence with $\lambda_{max,em} = 661$ nm, representing a small Stokes shift of only 9 nm. This emission is red-shifted in comparison to **5**, which shows $\lambda_{max,em} = 649$ nm and an even smaller Stokes shift of only 6 nm. The fluorescence quantum yield (Φ_F) of **4** is $\Phi_F = 0.12$, comparable to **5** ($\Phi_F = 0.15$), measured in CH_2Cl_2 relative to cresyl violet perchlorate in MeOH ($\Phi_F = 0.67$ at 5.9×10^{-7} M).[11] None of the pentacene dimers **1**−**3** show any significant emission ($\Phi_F < 0.01$) in the range of 560−850 nm when measured under the same conditions.

To explore the semiconducting properties of the newly realized pentacene dimers, measurement of photoconductive yield has been explored using a traditional monochromator and lock-in technique (Figure 2c).[12] Photocurrent yield is defined as the ratio between the photogenerated charge-carrier flow rate and the absorbed photon rate. When the photocurrent yield exceeds unity, the material shows photoconductive gain. It is worth noting that, to date, there have been only a limited number of organic materials that have shown photoconductive gain.[13] Thin films of **1**−**5** (ca. 0.2−0.5 μm) for analysis have been obtained by solution-state spin-casting from $CHCl_3$.[14] As established by AFM analysis, films of **2** and **4** are quite homogeneous, while those of **1** and **3** show a more varied morphology consistent with microcrystalline domains.[8] Photocurrent yield for dimer **1** (Figure 2c) is the same magnitude as pseudomonomer **4**, while dimer **2** has the lowest efficiency, presumably due to the larger size of the pendent *n*-hexyl$_3$Si groups that might disrupt intermolecular interactions between pentacene chromophores. Dimer **3** has the highest efficiency, outperforming **5**, which has become somewhat of a benchmark in the field.[1,2] The photoconductive yield for **3** is greater than 10 electrons per absorbed photon, representing a bulk photoconductive gain >10 (i.e., for every photon absorbed, >10 charge carriers traverse the active region of the device).[15] This efficiency places spin-cast films of dimer **3** within an order of magnitude of thermally-deposited films of pristine pentacene.[16]

A plausible explanation for the efficiency of **3**, supported by the UV−vis spectroscopic analysis, is that the central Me_3Si groups disrupt the planarity of the three aromatic chromophores in the solid state and ultimately reduce the anisotropy of the pentacene chromophores in the film leading to improved efficiency. This is analogous to the improved charge-carrier mobility that is observed in single crystals that have 2-D slipped-stack arrangements vs 1-D stacks.[17,18]

In conclusion, a new synthetic route to stable, processable pentacene dimers has been developed. The subsequent characterization of photoconductive gain has demonstrated the potential for enhancing electronic properties through synthetic design. The methodology presented provides for future optimization of optoelectronic properties through (a) the use of alternate π-spacers, (b) variation of solubilizing end-groups, and (c) formation of longer pentacene-based oligomers. A full account of these efforts will be reported in due course.

Acknowledgment. This work has been generously supported by the University of Alberta and the Natural Sciences and Engineering Research Council of Canada (NSERC) through the Discovery Grant program. We also acknowledge the use of the University of Alberta NanoFab. D.L. thanks NSERC (PGS-D), the Alberta Ingenuity Fund, the University of Alberta, and the Killam Trusts for scholarship support.

Supporting Information Available: Experimental procedures, spectroscopic data for new compounds, and AFM images of thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For a discussion of the mechanisms of photoconductive gain in organic materials, see ref 13f.

(16) Gao, J.; Hegmann, F. A., unpublished results.

(17) For acene solid-state packing terminology and its influence on electronic properties, see ref 1b.

(18) It is also possible that the variations in film morphology between the different samples also plays a role in efficiency, and this premise is currently being explored.