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Pentacene Oligomers and Polymers: Functionalization of Pentacene to Afford Mono-, Di-, Tri-, and Polymeric Materials

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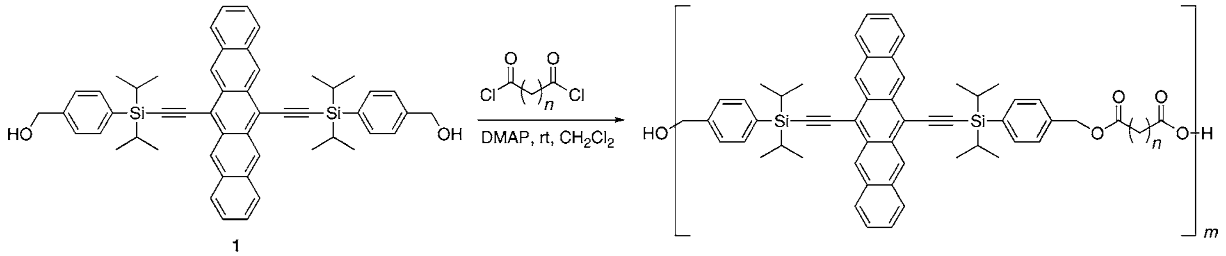
ABSTRACT



8 $n = 3$ 72%; **9** $n = 5$ 85%

The synthesis and characterization of defined-length di- and trimeric pentacenes and the corresponding polymers are described. The synthesis is divergent from two common pentacene building blocks, 1 and 2, allowing for structural diversity. The resulting materials are air stable and exhibit good solubility in common organic solvents.

It was not until a decade ago when organic materials began to have a significant practical impact in optoelectronic applications. Today, the field of organic semiconducting materials is very much active and has the potential to revolutionize applications in photovoltaic cells, chemical sensors, and thin film transistors (TFTs).[1,2] The use of polycyclic aromatic hydrocarbons, such as pentacene, has dominated most studies, but despite the substantial research on pentacene-based devices, relatively few derivatives of pentacene are known.[1−3] To date, much of the work to enhance the performance of pentacene-based materials has been through device fabrication techniques rather than synthetic modification of the pentacene skeleton. Only recently has functionalization been used in an attempt to increase the semiconductive properties (i.e., charge carrier mobilities) and processability of pentacene-based materials.[3] A natural progression in the development of organic advanced materials is the incorporation of functional chromophores into a polymer framework with the goal of increasing the solubility and facile film formation of the material. While oligoanthracenes have been reported,[4] defined-length pentacene-based oligomers remain, to our knowledge, unknown.[5] We report herein the synthesis of oligomers and polymers that contain pentacene in the repeat unit.

It has been shown that substitution of pentacene in the 6,13-positions with ethynylsilanes improves stability versus

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(1) (a) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066−1096. (b) Bendikov, M.; Wudl, F. *Chem. Rev.* **2004**, *104*, 4891−4945.

(2) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028−5048.

(3) For recent examples, see: (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482−9483. (b) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15−18. (c) Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609−1612. (d) Payne, M. M.; Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 3325−3328. (e) Swartz, C. R.; Parkin, S. R.; Bullock, J. E.; Anthony, J. E.; Mayer, A. C.; Malliaras, G. G. *Org. Lett.* **2005**, *7*, 3163−3166. (f) Susumu, K.; Duncan, T. V.; Therien, M. J. *J. Am. Chem. Soc.* **2005**, *127*, 5186−5195. (g) Vets, N.; Smet, M.; Dehaen, W. *Synlett* **2005**, 217−222. (h) Chan, S. H.; Lee, H. K.; Wang, Y. M.; Fu, N. Y.; Chen, X. M.; Cai, Z. W.; Wong, H. N. C. *Chem. Commun.* **2005**, 66−68. (i) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K.-i. *J. Org. Chem.* **2006**, *71*, 7967−7977. (j) Briseno, A. L.; Miao, Q.; Ling, M.-M.; Reese, C.; Meng, H.; Bao, Z.; Wudl, F. *J. Am. Chem. Soc.* **2006**, *128*, 15576−15577. (k) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nuckolls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340−1345. (l) Palayangoda, S. S.; Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2007**, *72*, 6584−6587. (m) For supramolecular assemblies, see: Desvergne, J.-P.; Del Guerzo, A.; Bouas-Laurent, H.; Belin, C.; Reichwagen, J.; Hopf, H. *Pure Appl. Chem.* **2006**, *78*, 707−719.

(4) Ito, K.; Suzuki, T.; Sakamoto, Y.; Kubota, D.; Inoue, Y.; Sato, F.; Tokito, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 1159−1162.

10.1021/ol702094d CCC: $37.00

pristine pentacene,[3b] and this structural motif became the basis of the targeted oligo- and polymers. The Si atoms pendent to the pentacene core also provide an attachment point for two isopropyl groups to enhance solubility and stability,[3b] and a "functional arm" for polymerization (**1** and **2**, Figure 1). For the "functional arm", primary alcohol(s) were chosen to allow for condensation reactions with bis-acid chlorides to form polyesters.

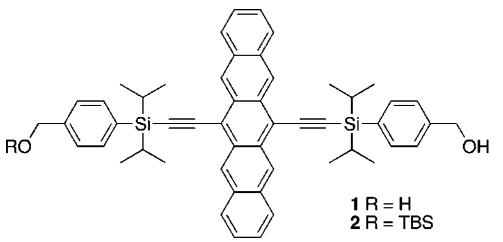
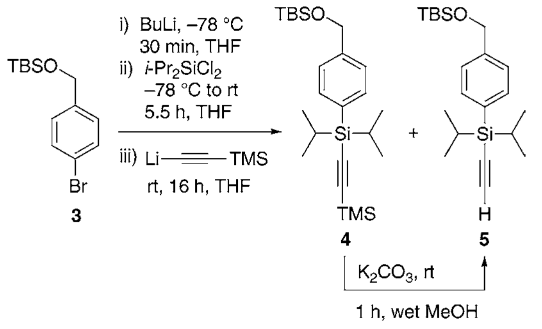


Figure 1. Pentacene building blocks **1** and **2**.

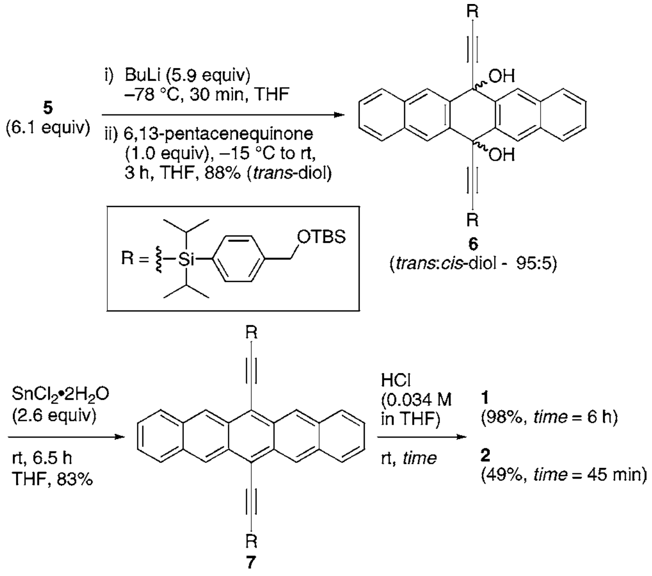
The synthetic scheme begins with **3**,[6] which is available in two steps from 1,4-dibromobenzene.[7] In a one-pot sequence, lithiated **3** (Scheme 1) was added to a solution of i-Pr_2SiCl_2 in THF at −78 °C, followed by the addition of $LiC{\equiv}CSiMe_3$ to afford a ~2:1 mixture of **4** and desilylated **5**. This mixture was subjected to mild desilylation conditions, completing the conversion of **4** to **5** and providing 58% yield (based on **3**). This method is scaleable to tens-of-grams, and it has the added benefit that column chromatography is not required over the four steps from 1,4-dibromobenzene.

Scheme 1. Synthesis of Functionalized Silylacetylene **5**



Compound **5** was then deprotonated at low temperature with BuLi to give the Li-acetylide, which was added to 6,13-pentacenequinone. This provided a mixture of *trans*- and *cis*-diol **6** (~95:5 ratio) from which the *trans*-diol could be isolated in 88% yield by column chromatography (Scheme 2).[8] The best results from this reaction were obtained when an excess of the Li-acetylide derived from **5** was used (2.9 equiv per ketone moiety, 5.9 equiv total). The excess **5** could be recovered almost quantitatively during purification.[7]

Scheme 2. Functionalization of Pentacene



The tin(II)-mediated reduction of purified *trans*-diol **6** in THF provided protected monomer **7** in 83% yield. The success of this step was solvent dependent, both in terms of reaction rate and yield/purity. For example, reactions in acetonitrile or acetone were complete in less than 30 min, but gave numerous byproducts and low yields. Removal of the two TBS groups to unveil the diol functionality of monomer **1** was accomplished by using dilute HCl in THF in 98% yield. If the reaction time was limited to 45 min, monodeprotected **2** was isolated in 49% yield, along with 36% of unreacted **7** and 15% of monomer **1**; all could be easily separated by column chromatography.

Pentacene di- and trimers were synthesized as model compounds to bridge the gap between monomer **1** and polymers **8** and **9** (Scheme 5). Because of the simplicity of this reaction, the synthesis of the dimers with 1−8 methylene groups was done to probe systematically the effects of tether length on solubility, aggregation, and thin-film formation. Slow addition of a solution of the requisite bis-acid chloride to a solution of **2** in the presence of DMAP provided pentacene dimers **10**−**17** in excellent yield (79−97%, Scheme 3). All of the dimers were highly soluble in CH_2Cl_2, $CHCl_3$, and THF. The thermal stability of the dimers was assessed by TGA analysis and showed no significant weight loss (<5%) below 350 °C in all cases.

Dimers with shorter linker chains (**10**, **14**, and especially **11**) had a tendency to aggregate in concentrated solution (~0.06 M) as observed by ^1H NMR spectroscopy. In these

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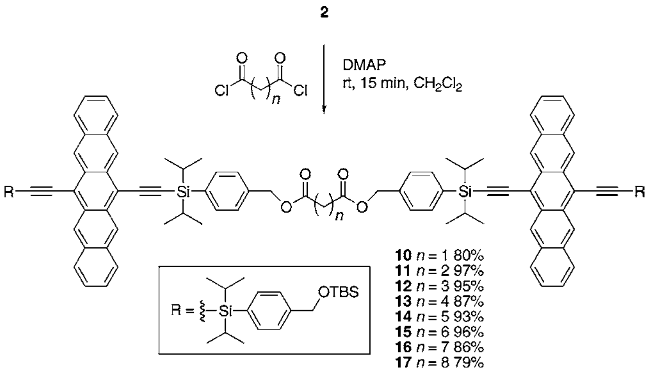
(5) Two reports of pentacene-based polymers have appeared: (a) Tokito, S.; Weinfurtner, K.-H.; Fujikawa, H.; Tsutsui, T.; Taga, Y. *Proc. SPIE - Int. Soc. Opt. Eng.* **2001**, *4105*, 69−74. (b) Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2007**, *129*, 1308−1309.

(6) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704−714.

(7) See Supporting Information for details.

(8) This assignment of the stereochemistry of the addition is based tentatively on the polarity of the two products on silica gel TLC plates. The major isomer is the less polar of the two and thus was assigned as the centrosymmetric *trans*-isomer.

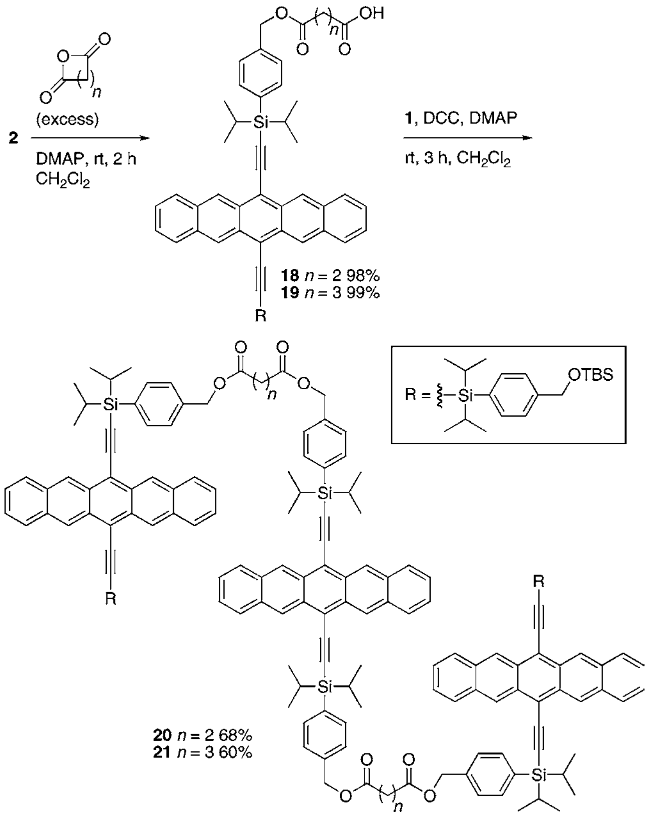
Scheme 3. Synthesis of a Homologous Series of Pentacene Dimers



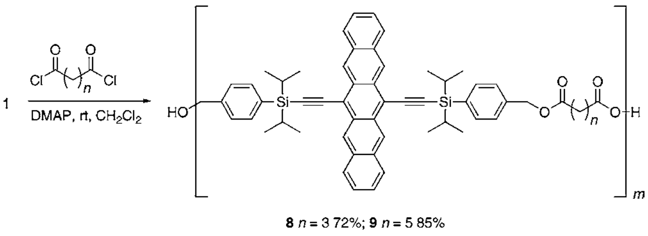
cases, multiple signals were observed where a single resonance was expected. Upon dilution of the NMR sample, these resonances coalesced into a single signal. Furthermore, in more dilute solutions, such as concentration ranges used for UV−vis spectroscopy ($\sim10^{-5}$ to 10^{-6} M), Beer's Law was maintained, confirming that aggregation was not occurring.

Pentacene trimers were synthesized (Scheme 4). Desymmetrized pentacene **2** was reacted with succinic or glutaric anhydride to afford pentacene **18** and **19** with pendent carboxylic acid groups in 98% and 99% yields, respectively. A subsequent DCC-mediated coupling of **18** or **19** with monomer **1** afforded trimers **20** and **21**, respectively. These soluble materials showed thermal stability analogous to that of both monomer **1** and the analogous dimers **11** and **12**.

Scheme 4. Synthesis of Pentacene Trimers



Scheme 5. Synthesis of Pentacene Polymers



Preliminary efforts toward the formation of polymers were then conducted via the reaction of monomer **1** with bis-acid chlorides in the presence of DMAP (Scheme 5). Following aqueous workup, purification of the products was accomplished by recrystallization. MALDI MS analysis showed macromolecules of over m/z 17 000 were achieved (e.g., m = 20 for **8**).[9] DSC analysis showed no glass transition temperature for these polymers, and TGA demonstrated the polymers were as stable as the oligomers, with no significant weight loss (<5%) before 350 °C.

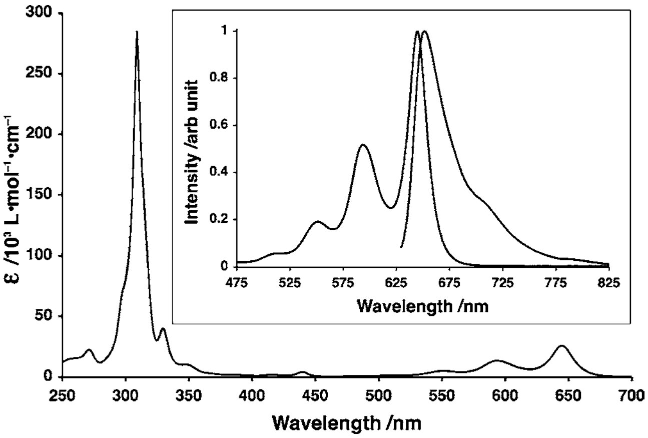


Figure 2. Absorption spectrum of monomer **1** in CH$_2$Cl$_2$. (Inset) Absorption (left trace) and emission (right trace) spectra of monomer **1** in CH$_2$Cl$_2$, illustrating the small Stokes shift.

Figure 2 shows the absorption and emission spectra of monomer **1**, which has a strong absorption at $\lambda_{\max} = 309$ nm and a series of low-energy absorptions with the lowest at 645 nm. The emission is broad and featureless with the $\lambda_{\mathrm{em,max}} = 652$ nm which represents a small Stokes shift of only 7 nm and suggests minimal molecular rearrangement occurs upon photoexcitation of the molecule.

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[9] MALDI MS analyses showed that, in addition to the generalized polymer structure shown in Scheme 5 for **8** and **9** (terminated with an acid and an alcohol), the product mixtures also consisted of structures terminated with two acids, two alcohols, and macrocyclic structures resulting from intramolecular ester formation. See Supporting Information for MS spectra and a more detailed discussion.

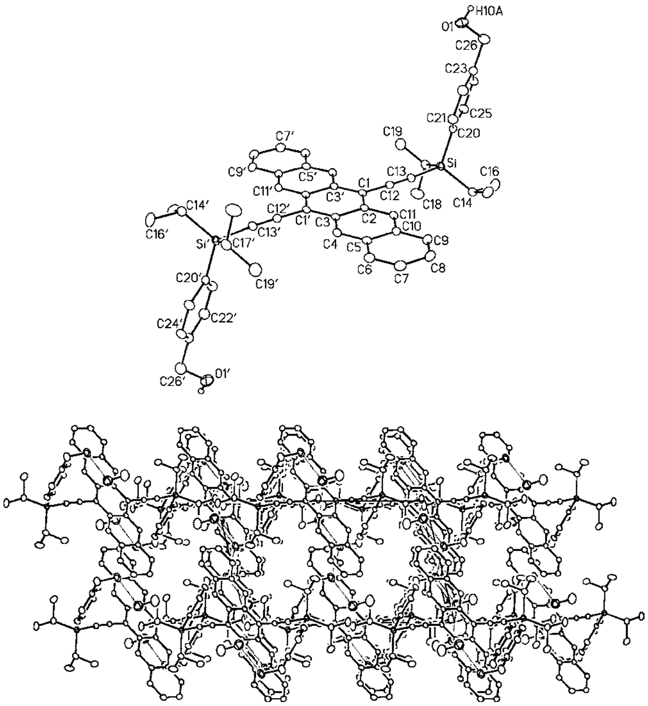

Figure 3. (Above) X-ray structure of **1**. (Below) Solid-state packing of **1** as viewed along the *b*-axis.

The electronic structure of the basic pentacene unit as found in **1** is essentially unaffected by oligomer or polymer formation. Comparing the UV−vis spectra of the homologous series made up of monomer **1**, dimer **12**, trimer **21**, and polymer **8** reveals that all molecules share nearly identical absorption maxima (±1 nm).[7]

Thin films of the polymers **8** and **9** could be cast from a number of solvents, including CH_2Cl_2, $CHCl_3$, and THF. While a complete description of this analysis is beyond the scope of the current discussion, it is worth pointing out that UV−vis characteristics of these films were very similar to those of the monomer and were red-shifted by <10 nm compared to that of the solution-state spectra.[7]

Solid-state packing plays an important role for materials used in molecular electronics because good electronic performance is often observed for compounds that have strong electronic coupling mediated by strong intermolecular interactions between adjacent molecules.[2] The solid-state structure of the common building block of the oligomers, **1**, was determined by X-ray analysis of crystals grown from THF/MeOH.[10] Monomer **1** cocrystallized with two molecules of MeOH, and crystallographic analysis of these crystals revealed that **1** arranged in one-dimensional slipped stacks[11] with an intermolecular distance between the acenes of ca. 3.4 Å (Figure 3). Thus, in terms of π-overlap and orientation in the solid state, compound **1** is well suited for intermolecular communication.

In conclusion, we provide the first reported synthesis of defined-length pentacene oligomers and representative polymeric derivatives, as well as a description of their physical properties. All molecules exhibit good solubility and stability. The synthetic scheme that has been developed is also amenable to inclusion of other terminal groups on the monomer unit toward forming, for example, polyamides. A full account of these efforts will be reported in due course.

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

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[10] X-ray crystallographic data for **1**: $C_{52}H_{54}O_2Si_2 \cdot 2CH_3OH$, $M = 831.22$; monoclinic space group $P2_1/c$ (No. 14); $\rho_c = 1.156$ g cm^{-3}; $a = 8.8223(6)$ Å, $b = 19.0409(13)$ Å, $c = 14.6224(10)$ Å; $\beta = 103.5400(16)°$; $V = 2388.1(3)$ Å^3; $Z = 2$; $\mu = 0.118$ mm^{-1}. Final $R(F) = 0.0433$ (6400 observations $[F_o^2 \geq 2\sigma(F_o^2)]$); $wR_2 = 0.0985$ for 275 variables and 10024 data with $[F_o^2 \geq -3\sigma(F_o^2)]$; CCDC 654502. X-ray data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223−336−033.

[11] See ref 2 for solid-state packing terminology of acenes.