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Sulfur Containing Stable Unsubstituted Heptacene Analogs

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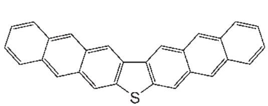
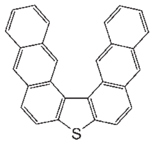
ABSTRACT



1
Dianthra-[2,3-b; 2',3'-d]-thiophene
DAT-2,3



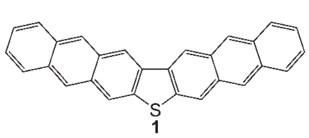
2
Dianthra-[1,2-b; 1',2'-d]-thiophene
DAT-1,2

Heptacene and higher polyacenes have been sought for their high degree of charge carrier mobility in thin film transistors. Such acenes are, however, extremely unstable in ambient conditions. Approaches to obtain stable heptacenes include introduction of suitable substituents, of heteroatoms, or both. Methods to synthesize stable linear and a nonlinear unsubstituted heptacene analogs are discussed. No changes in the UV−visible absorption spectra in solution over time for these materials indicate higher oxidative stability compared to analogous polyacenes.

Acenes with five or more fused aromatic rings have been long known as promising materials for applications in high performance and low-cost organic thin film transistors.[1−8] However, due to their high HOMO energy, such systems are prone to rapid oxidative degradation under ambient conditions.[9−15] Therefore, the search for ideal candidates that will be suitable for solution processing as well as stable under ambient conditions and possess high-charge mobility has been ongoing.[1,3,9,12,16,17]

Pentacene is the largest unsubstituted acene to have been isolated, purified, and characterized. Its thin film transistor mobility is similar to that of amorphous silicon.[18−21] Neckers and co-workers reported successful photogeneration of unsubstituted hexacene and heptacene and registered the photophysical properties of these elusive compounds.[22] Bettinger and co-workers recently reported the photogeneration of unsubstituted octacene and nonacene.[23]

However, because of their lack of stability under ambient conditions, further attempts to introduce suitable substitutions to obtain oxidatively stable hexacene, heptacene,



1
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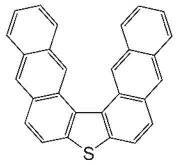
DAT-2,3



2
Dianthra-[1,2-b; 1',2'-d]-thiophene
DAT-1,2

Figure 1. Molecular structures of compounds **1** and **2**.

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and higher acenes are also ongoing.[16,17,23,24] As an alternative, higher *thienoacenes* containing five to seven fused systems have been prepared.[9,25−29] It should be clear however that such thioenoacenes exist in more than one isomer.[19] Recently, thienothiophenes have attracted great attention due to high hole mobility and stability in the air.[30,31] Compared to the *oligothiophenes*, the limited number of sulfur atoms in such compounds results in smaller reorganizational energy and hence higher mobilities.[32] This has inspired much previous work[33,34] substituting different molecular fragments, such as thiophene and acene, in order to develop organic semiconductors with high mobility and stability. Bao, Aspuru-Guzik, and coworkers[35] have shown in their recent work, using computational discovery and experimental characterization, that suitable substitution of thiophene and acenes can lead to new high-performance organic semiconductors for various electronic applications. The compounds discussed in this report[35] have thiophene rings at the center of the acene fragments. It will, therefore, be important to investigate the hole mobility and air stability of *thienoacenes* with the thiophene ring at the center of the acene fragments. Taken together, the present work is motivated by the fact that while there are several reports on *thienoacenes*,[25−29] few attempts have been made to synthesize unsubstituted *thienoacenes* with the thiophene ring at the center of the acene fragments due to the challenges encountered in their synthesis and their existence in several isomeric forms.

We have now prepared two stable unsubstituted heptacene analogs with the thiophene ring at the center of the acene fragments—*thienoacenes*, one containing seven linearly fused aromatic rings (DAT-2,3; **1**), and another with seven nonlinearly fused aromatic rings (DAT-1,2; **2**) (Figure 1). We discuss the synthetic strategy, spectral characterization using mass and ^{1}H NMR spectra, and absorption spectra. Monitoring the absorption spectra in the UV−vis region over time in solution (*o*-dichlorobenzene) indicates higher stability for compounds **1** and **2** compared to analogous polyacenes. Due to a heptacene-like structure, each might have favorable two-dimensional interactions in the thin films in the solid state and is thus expected to have a high degree of charge carrier mobility when assembled in organic transistors.

To avoid solubility issues, we introduced suitable removable substitution (TMS-acetylene in this case) and utilized a zirconia mediated coupling method[36] for the synthesis of **1**, Scheme 1. Commercially available *o*-xylenedibromide was silylated using trimethyl silylacetylene to obtain bissilylated diyne (**3**). Diyne **3** was cyclized through zirconium-mediated cyclization and coupling reactions developed by Takahashi et al.[37] The four silyl groups were then effectively removed by treatment with triflic acid[38] (CF_3COOH) to obtain a tetrahydro heptacene analog (**5**). Subsequent aromatization of **5** afforded the target compound, DAT-2,3 (**1**). Further purification through sublimation produced yellowish orange **1**. DAT-2,3 (**1**) was characterized by mass and ^{1}H NMR spectra (Supporting Information, SI). However, due to its low solubility in common NMR solvents, the ^{13}C NMR spectra could not be recorded.

The synthesis of **2**, a nonlinear isomer of **1**, is outlined in Scheme 2. Commercially available bromomethyl naphthalene was converted to phosphonium ylide **6** using known literature methods via treatment with triphenyl phosphine.[38] Ylide **6** was then treated with 2,5-thiophene dicarboxaldehyde, synthesized following previously reported procedures,[39] in a Wittig type reaction to obtain **7**. Photocyclization of **7** in the presence of iodine in ethylene oxide afforded **2** as the major product. The conversion of **7** to **2** involves a trans to cis conversion of **7**, followed by photocyclization under light ($\lambda \approx 300$ nm). Compound **7** undergoes photoisomerization to cis-conformations around each of the carbon−carbon double bonds to adopt an all-cis conformation (*cis*-**7**). *Cis*-**7** undergoes facile photoinduced electrocyclization to form the tetrahydro heptacene analog **8** which aromatizes under oxidative conditions (I_2). A mercury arc lamp ($\lambda \approx 300$ nm; filter with 325 nm cutoff, intensity $\sim$1.03 mW C m^{-2}) was used as the light source, and compound **7** was irradiated overnight to achieve

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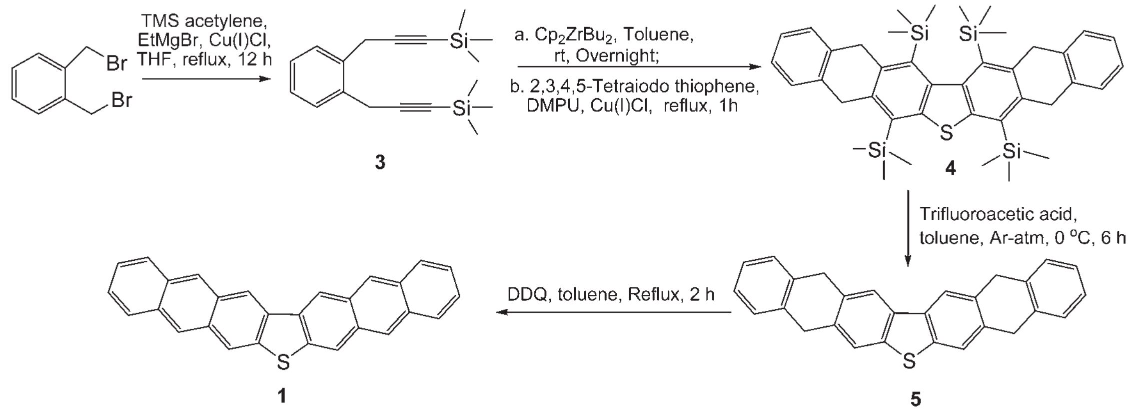
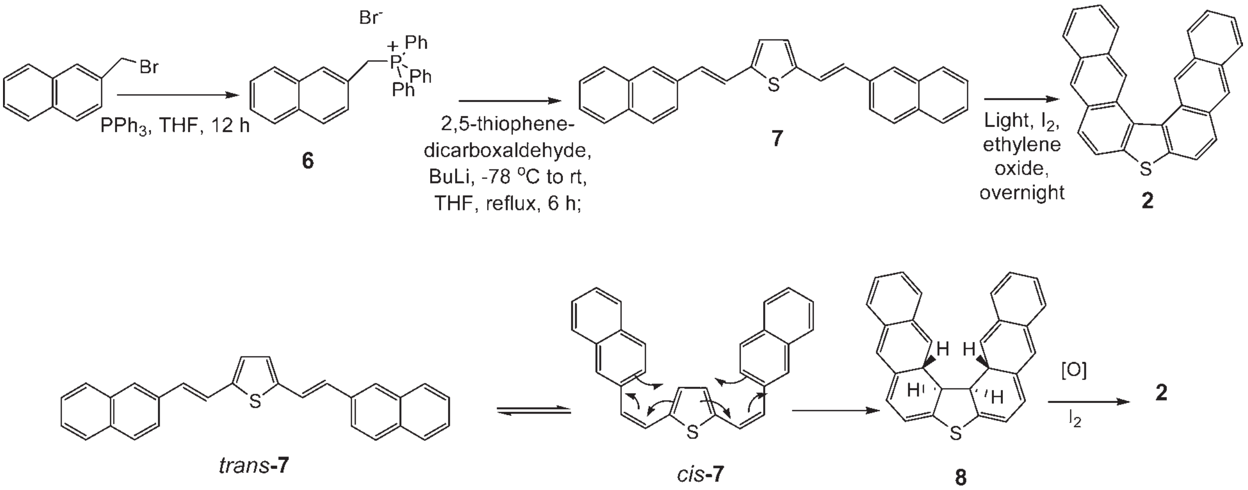
Scheme 1. Synthetic Strategy for DAT-2,3



Scheme 2. Synthetic Strategy for DAT-1,2



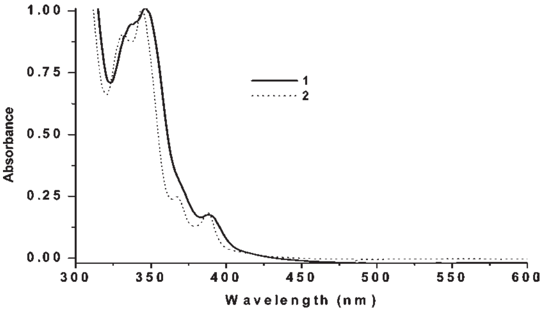


Figure 2. Normalized UV−vis absorption spectra of **1** and **2** in *ortho*-dichlorobenzene.

significant conversion. Long-UV light sources ($\lambda \geq 350$ nm) were avoided as the product **2** also absorbs in that range. The product was isolated as a dark yellow solid and purified through a silica column to obtain compound **2** as a significantly pure yellow solid. DAT-1,2 (**2**) was characterized by mass and ^{1}H NMR spectra (SI). Thus, a nonlinear heptacene analog was synthesized conveniently in three steps.

Spectra of **1** and **2** in *ortho*-dichlorobenzene (*o*-DCB) show λ_{max} to be in the range of ~400−450 nm, Figure 2. The absorption spectra, therefore, correspond with that of anthra-[2,3-*b*]-thiophene[19] suggesting that compounds **1** and **2** exhibit conjugation equivalently to that of anthra-[2,3-*b*]-thiophene.

DATs can, therefore, be considered as two anthra-[2,3-*b*]-thiophene units. However, since their structures are analogous to that of a heptacene, they might have superior two-dimensional interactions in the solid state. Hence, they are expected to exhibit high-charge carrier mobility in thin film transistors. The fact that each is partially soluble in most of the common solvents makes them good candidates for solution processing in transistor devices. Most importantly, these unsubstituted heptacene analogs are stable under ambient conditions. Cyclic voltametry was performed on both to ascertain the highest occupied molecular orbital (HOMO) energy. The HOMO energies (estimated) were found to be 5.18 and 5.12 eV for **1** and **2** respectively, which is comparable to pentacene. Based on the long wavelength absorption edge in the UV–visible spectra in *o*-DCB, the HOMO–LUMO energy gap is found to be 2.38 and 2.26 eV for **1** and **2** respectively, the respective LUMO energies being 2.69 and 2.78 eV.

Therefore, while compounds **1** and **2** each resemble anthra-[2,3-*b*]-thiophene with respect to their optical band gap, their heptacene-like structure is expected to assist in higher degree charge carrier mobility in the thin film transistors. Further studies on experimental charge carrrier mobilities in the organic thin film transistor devices are underway.

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Supporting Information Available. Experimental procedures and spectral data for all compounds. ^{1}H NMR, MALDI-TOF spectra, and cyclic voltametry for compounds **1** and **2**. This materials is available free of charge via the Internet at http://pubs.acs.org.