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A Stable Heptacene Derivative Substituted With Electron-Deficient Trifluoromethylphenyl and Triisopropylsilylethynyl Groups

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ABSTRACT

A heptacene derivative 1 substituted with four electron-deficient trifluoromethylphenyl and two triisopropylsilylethynyl (TIPSE) groups was prepared by a new synthetic strategy. Photo-oxidative resistance studies showed that this newly developed heptacene compound persisted 47 h in solution under ambient light and air conditions, and it represents the most stable heptacene derivative reported to date.

Acenes, linear fused aromatic hydrocarbons, have been the subject of extensive studies owing to their potential applications in organic electronics.[1] While the chemistry of short acenes ($n \leq 5$) is well explored, our knowledge of longer acenes ($n > 5$) is still limited due to the presence of challenges in synthesis. According to Clar's sextet rule, as the length of acene increases, the stability significantly decreases, causing difficulties in synthesis. Furthermore, the intrinsically poor solubility would make those species even more intractable. Thus, in early syntheses of higher acenes, with no exception, all reports aroused controversies.[2] Only recently did Necker and co-workers demonstrate a successful photochemical route for the synthesis of unsubstituted hexacene ($n = 6$) and heptacene ($n = 7$) in a polymer matrix.[3]

Whereas acenes ($n > 5$) without any substituent are unstable under ambient conditions and insoluble in a variety of organic solvents, chemical modifications to introduce substituents have been developed to prepare their stable and soluble derivatives. Anthony and co-workers first reported the synthesis and characterization of silylethynyl derivatives of hexacene and heptacene in 2005.[4] Later, Wudl and co-workers reported a further functionalized silylethynyl hep-

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tacene derivative with additional phenyl rings at the 5, 9, 14, and 18 positions.[5] Miller and co-workers then demonstrated that arylthio substituents can enhance photo-oxidative resistance, and thus, arylthio derivatives of acenes ($n = 7$, 9) were successfully synthesized and fully characterized.[6] It should be noted that a strategy of "center-to-edge" was used both in Wudl's and Miller's work; i.e., the precursors were constructed by a Diels−Alder reaction of a central dienophile (or diene) with two edge diene (or dienophile) components. Aside from reports by these three groups, no other derivatives of higher acene were reported elsewhere, despite theoretical calculations that predicted an array of interesting properties for higher acenes.[7]

In parallel to these works, we have been working on alternative approaches to prepare soluble and stable higher acenes by using different synthetic methods and new solubilizing and stabilizing substituents. Based on previous studies on the higher acenes and also *peri*-fused oligoacenes (e.g., bisanthene),[8] we noticed that steric and electronic effects were important factors in determining the photo-oxidative stability and solubility of largely extended π-conjugated systems. (1) Steric effect: bulky substitution, such as the triisopropylsilylethynyl groups, can prevent the oxidative addition of singlet oxygen to the acene core.[4,9] Meanwhile, the solubility can be also improved as a result of diminished intermolecular interactions. (2) Electronic effect: to form stable acene derivatives, HOMO levels need to be reduced and thus electron-withdrawing groups should be attached.[10,11] Both trifluoromethylphenyl and the triisopropylsilylethynyl (TIPSE) groups are electron-withdrawing groups and expected to enhance the stability of the electron-rich acene core. Herein, we demonstrate that a new heptacene derivative **1** bearing four trifluoromethylphenyl groups at the 5, 9, 14, and 18 positions and two TIPSE groups at the 7 and 16 positions (Scheme 1) was prepared by a new synthetic approach, and it showed significant improvement in its stability against photo-oxidation under different irradiation conditions.

In our synthetic strategy shown in Scheme 1, a heptacene quinone **10** was first prepared by an "edge-to-center" approach, a method generally used in constructing pentacene derivatives.[12] The synthesis began with 2-carboxybenzaldehyde **2**, which was refluxed in dry methanol to give 3-methoxyphthalide **3** quantitatively.[13] Addition of 2 equiv of 4-trifluoromethylphenyl Grignard reagent at 0 °C to a solution of 3-methoxyphthalide **3** in THF, followed by acidic workup, furnished isobenzofuran **4** in 56% yield.[14] Diels−Alder reaction between isobenzofuran **4** and dimethyl maleate gave epoxide **5**, which was subsequently treated with *p*-toluenesulfonic acid (TsOH) in refluxing toluene to remove one molecule of water. The resulting dehydrated compound **6** was reduced by $LiAlH_4$ to give (1,4-bis(4-(trifluoromethyl)-phenyl)naphthalene-2,3-diyl)dimethanol **7**. The Swern oxidation of diol **7** did not give the expected dialdehyde, which was planned to be used for the preparation of the heptacene quinone **10** by base-mediated condensation with 1,4-cyclohexanedione. Alternatively, only one alcohol was oxidized into aldehyde, which then condensed with the neighboring alcohol to give the compound 4,9-bis(4-(trifluoromethyl)phenyl)-1,3-dihydronaphtho[2,3-*c*]furan-1-ol **8** in 55% yield. Fortunately, this type of compound (e.g., **8**) was established as a convenient precursor for isonaphthofurans.[15] Thus, treatment of compound **8** with acetic acid produced the isonaphthofuran intermediate, which then underwent a 2-fold Diels−Alder reaction with benzoquinone to give the dual cycloaddition product **9** in 90% yield. The resulting compound **9** was then treated with TsOH in refluxed toluene with a Dean−Stark apparatus to give the desired heptacene quinone **10** in 50% yield.

Finally, nucleophilic addition of organometallic reagents to the heptacene quinone **10** in toluene followed by reduction of the as-formed diol **11** afforded the desired product. For the formation of diol **11**, use of TIPSE lithium reagent prepared by lithiation of triisopropylsilyl acetylene (TIPSA) with *n*-BuLi was not successful, probably due to side reactions with the trifluoromethyl groups ($-CF_3$). The synthesis of diol **11** required the use of TIPSE Grignard reagent prepared by treatment of TIPSA with *i*-PrMgCl solution to minimize formation of side products, as previously reported by Ong et al.[10b] and Tykwinski et al.[11] Interestingly, we found that low polar solvent was also required, and only one TIPSE group was introduced if THF was used instead of toluene as solvent for the preparation of this diol **11**. Diol **11** was then reduced using excess $SnCl_2{\cdot}2H_2O$ in toluene to obtain our target compound **1** as a yellow green solid.[11] To further improve solubility, we also attempted to replace TIPSE groups with a long alkynyl chain such as $-C{\equiv}CC_{12}H_{25}$. It was found that the reduction of the corresponding diol was not successful because steric hindrance imposed by the alkyl chain ($-C_{12}H_{25}$) was not sufficient to stabilize heptacene.

The heptacene derivative **1** was slightly soluble in chloroform, dichloromethane, and tetrachloroethane. The solubility could be improved in an aromatic solvent such as

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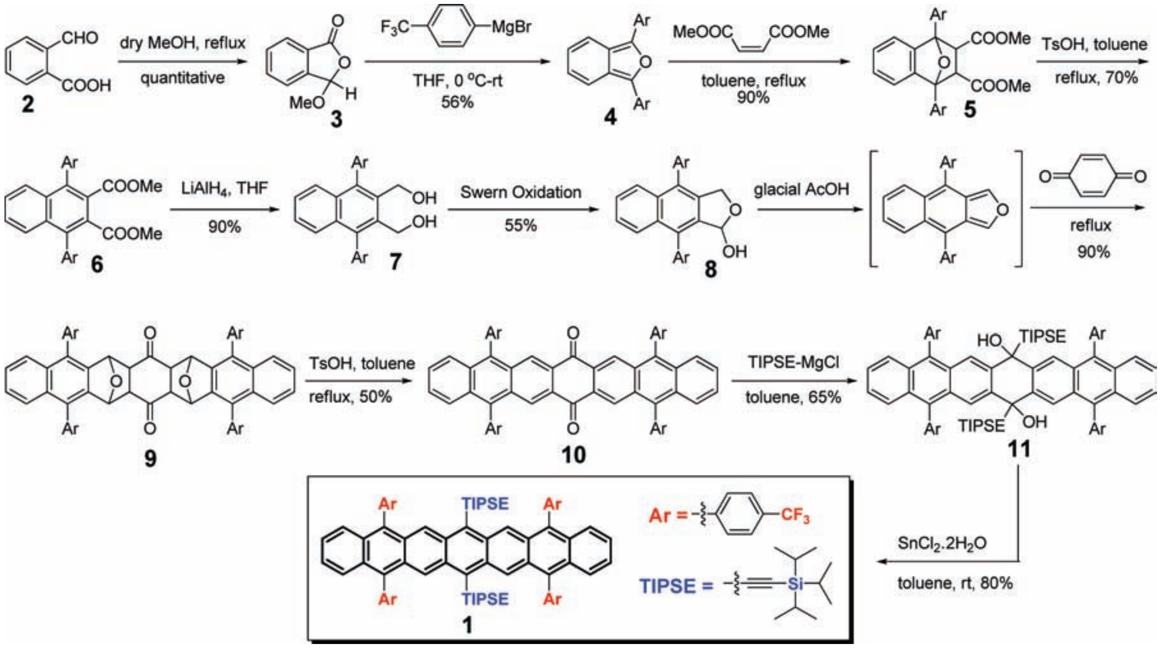
Scheme 1. Synthetic Route of Heptacene Derivative **1**



toluene (ca. 1 mg/10 mL at 30 °C). The solution of compound **1** is stable enough for further characterizations. The ^{1}H NMR signals obtained for compound **1** in $CDCl_2CDCl_2$ (see the Supporting Information) are sharp and can be assigned to the desired structure, indicating that this functionalized heptacene has a closed-shell electronic structure.[4a] The MALDI-TOF mass spectrum of compound **1** shows one molecular ion peak with m/z at 1314.482 with well-resolved isotope distribution (Figure S10b in the Supporting Information), and there are no additional peaks with m/z plus 16 or 32, indicating that this compound is stable and there are no oxygen addition products. The UV−vis−NIR absorption spectrum for **1** (Figure 1a) is consistent with a highly conjugated structure possessing a small HOMO−LUMO gap. Compound **1** shows intense absorption bands at 300−400 nm and weak absorption bands in the longer wavelength. The longest wavelength absorption for **1** in toluene solution is centered at 870 nm. On the basis of the onset of this absorption, the optical HOMO−LUMO gap for **1** was determined to be 1.35 eV. Compound **1** in toluene also shows weak fluorescence with emission maximum at 553 nm when excited at 353 nm (Figure S1, Supporting Information). The electrochemical property of compound **1** was studied by cyclic voltammetry in chlorobenzene. As shown in Figure 1b, two reversible reduction waves with half-wave potentials at −1.33 and −1.64 V (vs Fc^+/Fc) and one reversible oxidation wave with half-wave potential at 0.25 V were observed, indicating that the heptacene unit can be reversibly reduced into radical anions and dianions and oxidized into radical cation. The electron-withdrawing TIPSE and the 4-trifluoromethylphenyl groups are believed to further stabilize the reduced species. A HOMO energy level of −4.93 eV and a LUMO energy level of −3.61 eV were estimated on the basis of the onset potential of the first oxidation and the first reduction wave, respectively.[16] An energy gap of 1.32 eV was then obtained which is in agreement with the optical band gap. It is worth noting that the absence of trifluoromethyl subsitutent could lead to an upshift of about 0.1 eV for both HOMO and LUMO levels as reported in Wudl's heptacene derivative, which has a HOMO at −4.8 eV and LUMO at −3.5 eV.[5]

We then investigated photostability of compound **1** in toluene under different irradiation conditions. The photoinduced degradation was quantified by monitoring the decrease of vibronic absorption in the near-IR region (780−890 nm) as a function of elapsed photolysis time (Figure 2). The photostability was studied with both deoxygenated solution and solution exposed to ambient air atmosphere. Upon irradiation with white light (100 W), UV light (4 W), and ambient light, the deoxygenated solutions gradually decomposed with a decrease of the optical intensity at the NIR band and appearance of new absorption band in the shorter wavelength (ca. 306 and 500 nm) (Figure 2a). In contrast to the unstable parent heptacene, compound **1** is still detectable after 66 h in deoxygenated toluene under ambient light irradiation. The half-lives ($t_{1/2}$) of around 1950, 200, and 100 min were estimated under ambient light, white light (100 W), and UV lamp (4 W), respectively, by plotting the absorption intensity at 870 nm with the irradiation time (Figure 2b). When the solution of **1** in toluene was exposed to air and ambient light irradiation, its presence was detectable after 47 h (Figure S2, Supporting Information). Compared with Wudl's heptacene derivative, which can survive 41 h under the same conditions,[5] our molecule exhibited further improvement in its stability, and this can be explained by the introduction of an electron-withdrawing

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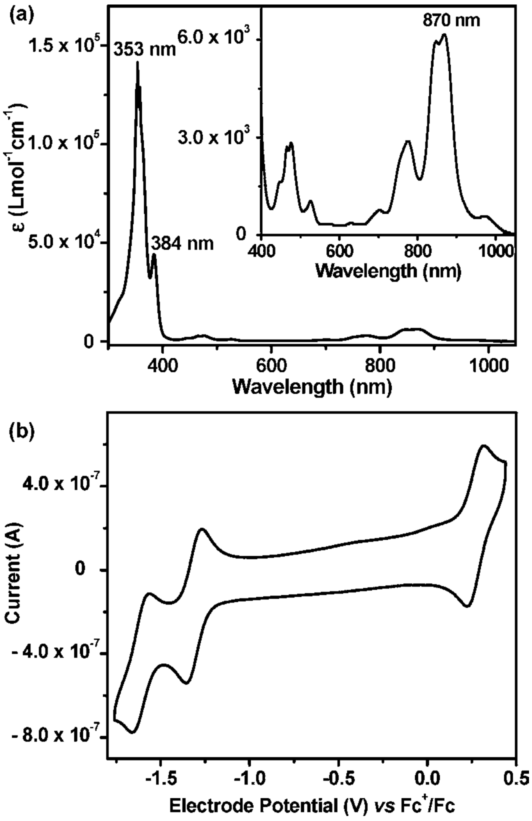

Figure 1. (a) UV−vis−NIR absorption spectrum of **1** in toluene; (b) cyclic voltammogram of **1** in hot chlorobenzene (70 °C) under nitrogen atmosphere with 0.1 M Bu_4NPF_6 as supporting electrolyte, AgCl/Ag as reference electrode, Au disk as working electrode, Pt wire as counter electrode, and scan rate at 50 mV/s. Fc^+/Fc was used as internal reference.

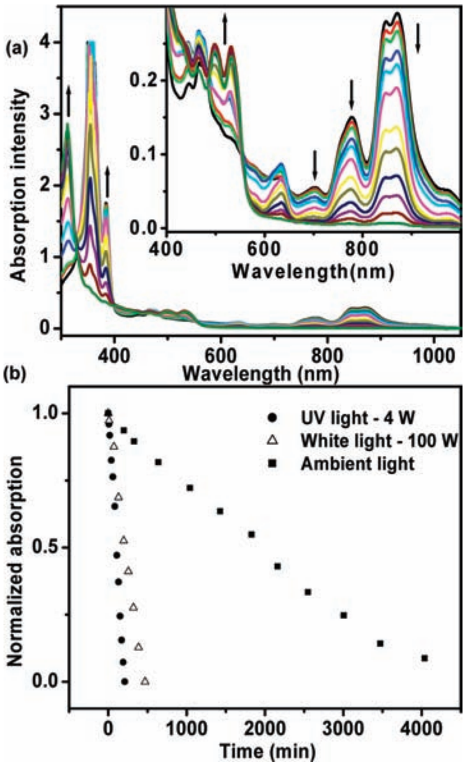

Figure 2. (a) Change of UV−vis−NIR absorption spectra of a deoxygenated solution of **1** when exposed to UV light (4 W) irradiation. (b) Change of the optical density at 870 nm of deoxygenated toluene solution of **1** (3.7×10^{-5} M) as a function of irradiation time in ambient light, white light (100 W), and UV light (4 W).

trifluoromethyl group onto the phenyl rings. During irradiation, in all cases, the color of compound **1** in solution changed from yellow green to light red and the FAB mass spectrum of the solution after irradiation revealed a small peak with *m*/*z* at 1314.5 [M^+] along with two intense peaks at ($M^+ + 32$) and ($M^+ + 16$) corresponding to a $^1O_2$ adduct of **1** and its fragment, respectively. This kind of color change and the appearance of UV absorption around 500 nm, in combination with the mass spectrum, indicated that tetracene-containing species were presumably formed during the photo-oxidative process.[5]

In conclusion, we have prepared the stable and soluble heptacene derivative **1** utilizing an "edge-to-center" approach. Attachment of electron-withdrawing groups such as 4-trifluoromethylphenyl groups further improved the photostability of the higher acenes. Compound **1** represents the most stable heptacene derivative reported to date. Our synthetic methodology may also lead to opportunities to prepare stable higher acenes with electron-deficient substituents in the future.

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Supporting Information Available: Experimental procedures, characterization data of all new compounds, fluorescence spectrum, and photo-oxidative resistance studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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