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Single-Molecule Nanosized Polycyclic Aromatics with Alternant Five- and Six-Membered Rings: Synthesis and Optical Properties

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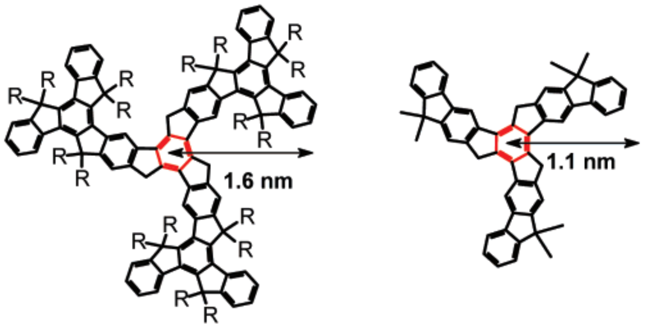
ABSTRACT



A synthetic protocol for a novel family of symmetric polycyclic aromatics with a benzene or cyclooctatetraene (COT) ring as the core and alternant fused benzene and cyclopentadiene rings as branches has been developed. The $TiCl_4$-promoted cyclizations construct both planar trimers and tubelike tetramers via the "in situ" generation of the benzene or COT skeleton. The structures of 6b, 7a, 7b, and 10 have been characterized by ^1H and ^{13}C NMR spectra and MALDI-TOF mass spectroscopy. These polycyclic aromatics also exhibit interesting optical properties.

Recently, a renaissance of polycyclic aromatic hydrocarbons (PAHs) has been triggered by the construction of theoretically interesting molecules as well as fullerenes, carbon nanotubes, and self-assembled supramolecular architectures and also by their prospective utilization in molecular electronics and optoelectronics, including solar cells, liquid crystal displays, organic light-emitting diodes (OLEDs), and organic field effect transistors (OFETs).[1] The unique properties stemming from the extended π-conjugation within planar or curved backbones are affected by the geometries (sizes, symmetries, boundaries, and cores) of the corresponding molecules.[2]

The modern synthetic approaches to PAHs have been essential for the emergence of diverse, previously inaccessible PAH families, which have dramatically advanced the fundamental knowledge of these molecules.[3] Two structurally well characterized categories, fully benzenoid hexabenzocoronene-type (HBC)[4] and benzene-cyclobutadiene alternant [*N*]-phenylene-type,[5] have attracted undiminished interest of practical and theoretical chemists. It would be revealing to

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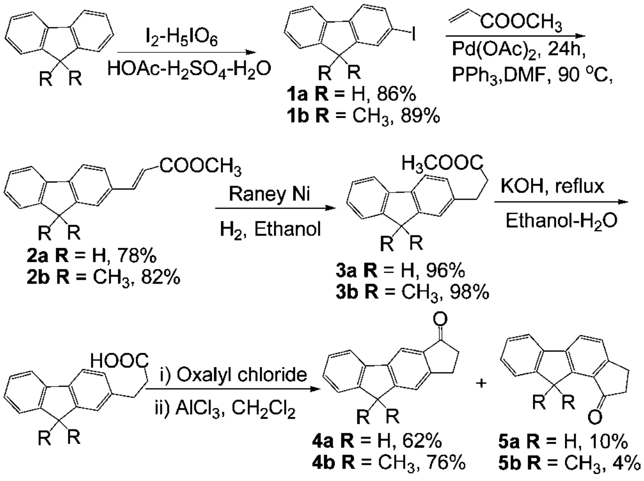
Scheme 1

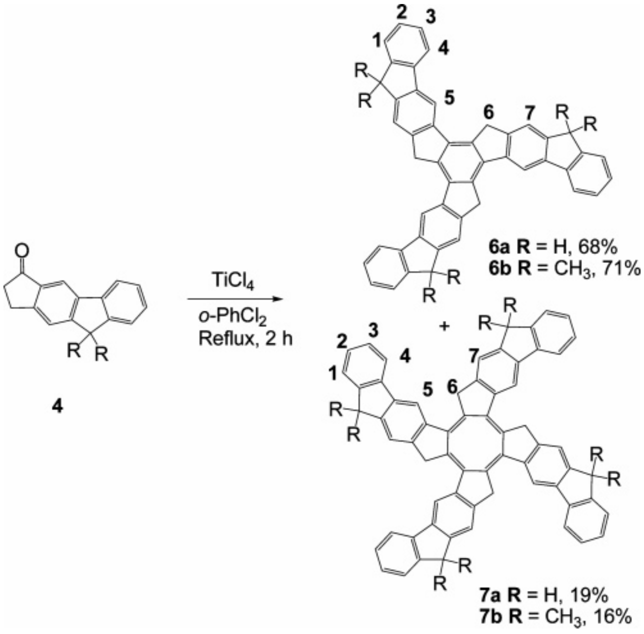


develop a series of novel PAHs based on alternant fused benzene and cyclopentadiene rings to bridge the gap between both families.

As demonstrated by the linear fluorene-type analogues, oligo- and polyfluorenes exhibited distinct yet promising properties.[6] Truxene has been explored as a C_3 tripod starting material for the construction of larger polyarenes and bowl-shaped fragments of fullerenes, liquid crystals, and asymmetric catalysts.[7] Our group previously reported powerful routes to C_3-symmetric, fused polycyclic aromatics and dendrimers.[7d,8] Construction of novel, nanosized, soluble, flat polycyclic aromatics is of great interest. In this contribution, we have developed an efficient approach to a novel family of polycyclic aromatics with a benzene or cyclooctatetraene (COT) ring as the core and fused benzene and cyclopentadiene rings as branches. The diameter of these trimer molecules is about 2−3 nm. They also show interesting physical properties.

As shown in Scheme 1, compound **1** with either methyl or no substitution at the C-9 bridge[9] underwent Heck reaction and subsequent Raney Ni-catalyzed hydrogenation to afford **3**. Hydrolysis with potassium hydroxide/ethanol and then acidification of **3** afforded the acids followed by transformation into ketones **4a**,**b** with side-products **5a**,**b** by the Friedel−Crafts cyclization in good yields. It is noteworthy that the content of the side-products decreased with the introduction of alkyl chains at the C-9 bridge, probably caused by the increasing steric hindrance. We did not obtain compound **5** when the R group was a hexyl substituent, and the yield was nearly zero.

Scheme 2



The dropwise addition of **4** (as *o*-dichlorolobenzene solutions) to a refluxing *o*-dichlorolobenzene solution of TiCl$_4$ (6 equiv) immediately produced a deep purple mixture. After 2 h, quenching the reaction with hydrochloric acid followed by column chromatography provided the desired polycyclic aromatic derivatives **6a**,**b** (trimers) and another series **7a**,**b** (tetramers). The TiCl$_4$ protocol was powerful in this system, providing light yellow or pale products in both high purity and excellent yields. Scheme 2 shows that the final TiCl$_4$-promoted cyclizations of **4** at high temperature[7a,b,10]

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efficiently generated "in situ" the corresponding products with a central benzene core and another series with a COT skeleton.

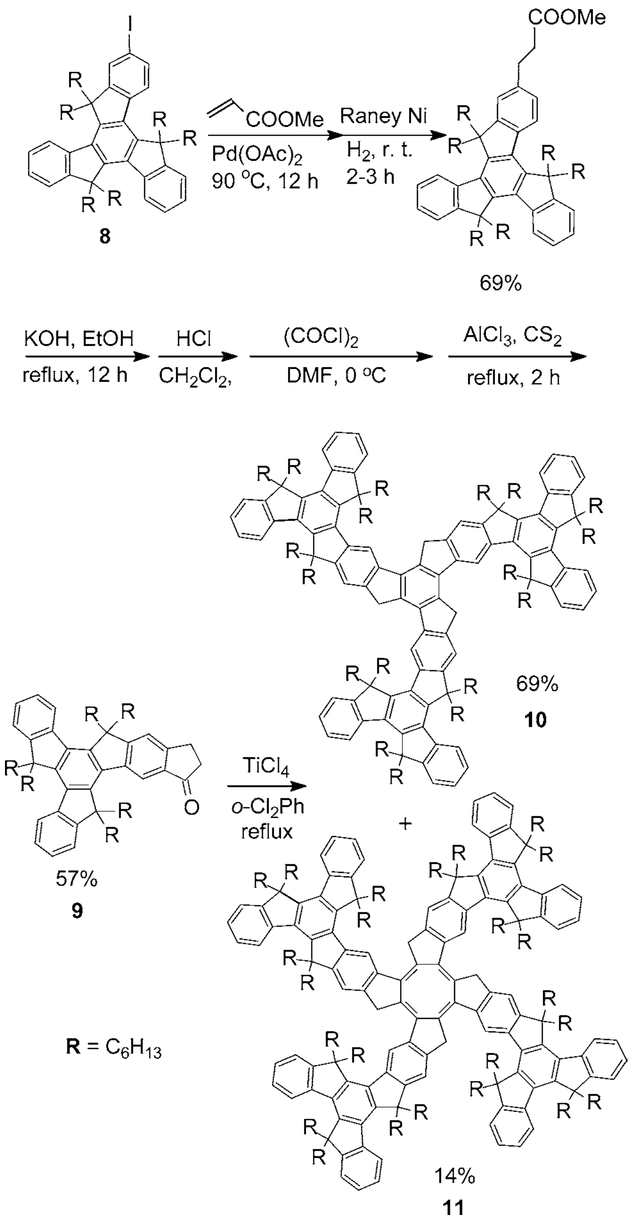
Scott also found the formation of COT derivatives in $TiCl_4$-catalyzed cyclizations;[7a] however, they did not isolate the pure product due to the poor solubility. As the smallest stable nonaromatic annulene, COT and its derivatives have been attractive synthetic targets and played a notable role in diverse aspects of organic, organometallic, and theoretical chemistry.[11] Most of the existing syntheses assembled a COT ring from simple alkyne precursors by either Ni-catalyzed cyclotetramerizations or [4 + 4] couplings. Herein, we also developed the initial synthesis and characterization of a series of novel COT derivatives containing four fully π-conjugated aromatic planes. Tetramers **7a** and **7b** were isolated from the trimers by column chromatography. To the best of our knowledge, we have synthesized and isolated the largest fully π-conjugated COT derivatives up to now.

We guess that a mixture of diastereoisomers **7** might exist in our experiments according to the structure of **7**. However, we obtained fine ^1H and ^{13}C NMR spectra, which suggested that only one of the isomers **7** was separated after column chromatography. Unfortunately, we did not obtain other isomers. These tetramers have exhibited interesting structures, and we are still investigating them through crystallography and molecular modeling to confirm the accurate configuration of **7**.

We also employed this cyclization on the larger precursor containing truxene skeleton (**10**) prepared through the same procedures from **1** to **4** by employing monoiodotruxene derivative **8** as the starting material. As we mentioned, the Friedel−Crafts cyclization catalyzed by $AlCl_3$ only afforded **9** in high yield due to the presence of hexyl groups at the truxene moiety. We obtained the MALDI-TOF spectrum of **11**. Unfortunately, its NMR spectra were not recorded due to the small amount of compound available. Scheme 3 illustrates the synthetic route from **8** to **10** and **11**. We successfully obtained PAHs with diverse boundaries and enlarged sizes, **10** containing 13 benzene rings, and **11** containing 16 benzene rings, which represented the largest monodispersed member of this family.

Molecular modeling indicated that molecules **10** and **6b** span 3.0 and 2.2 nm in the planar conformation, respectively. The strategy for constructing our polycyclic aromatic with alternant five- and six-membered rings was very efficient. These compounds exhibited large molecular weights, high flexibility, and thus potential new properties. Some new compounds have been characterized by a variety of spectroscopic techniques. The structures and purities of intermediates and some target molecules have been confirmed by ^1H and ^{13}C NMR spectra, as well as MALDI-TOF mass spectrum. The NMR spectrum data of **6a** was not obtained due to its poor solubility (see Supporting Information).

Scheme 3



We investigated the remarkable NMR behaviors of trimers and tetramers. For example, Figure 1 shows the comparison of ^1H NMR spectra of trimer **6b** and tetramer **7b**. We observed that **6b** revealed a singlet at about δ 4.10 ppm for the H-6 (belonging to protons at newly generated methylene bridges) and two singlets at about δ 8.12 (H-5) and 7.68 (H-7) ppm, while **7b** exhibited a pair of doublets ($J = 23.4$ Hz) with chemical shifts at about δ 4.35 and 3.55 ppm for the H-6 as well as two singlets at about δ 7.77 (H-5) and 7.62 (H-7) ppm. The ring currents within the planar trimers provided more deshielding on H-5 than its corresponding tetramers.

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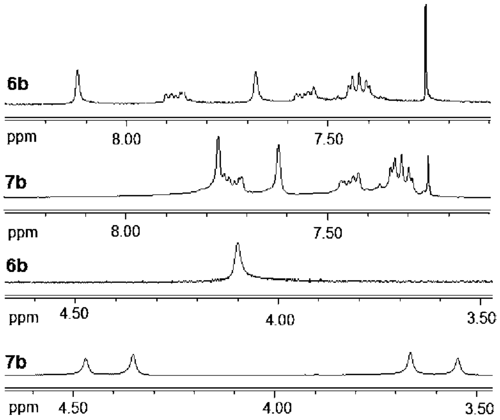

Figure 1. Comparison of ^{1}H NMR spectra of **6b** and **7b**.

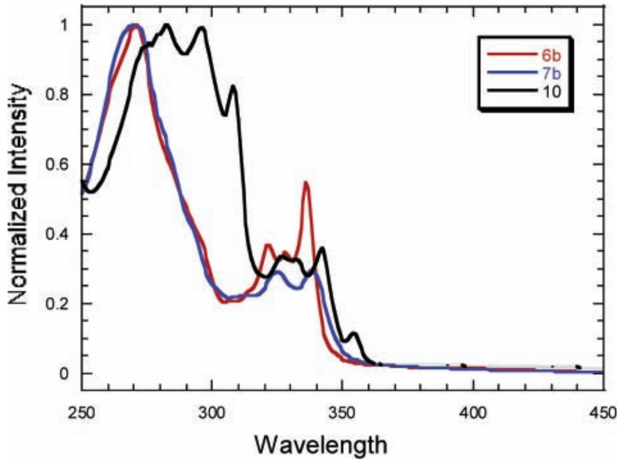

Figure 2. Normalized absorbance of **6b**, **7b**, and **10** in THF solutions at room temperature.

The UV−vis absorption spectra of trimers **6b**, **7b**, and **10** were measured in dilute THF solutions. Normally, polycyclic aromatics show a very strong $\pi-\pi^*$ electron absorption band in the UV−visible region, which progressively red-shifts with an increase in the effective conjugation length. The solution concentration of three compounds was about 1.0×10^{-6} M. Figure 2 presents the combined absorption spectra of **6b**, **7b**, and **10**. From absorption spectra in Figure 2, in the region of above 320 nm, we observed that the absorption $\lambda_{\max}$ (336 nm for **6b**, 338 nm for **7b**, and 342 nm for **10**, respectively) exhibited a red shift after the cyclization in comparison with those of fluorene (298 nm) and truxene moieties (307 nm), which were contributed by the increase in the effective conjugation length. The results indicated that such large, flat polycyclic aromatic molecules are useful for the π-delocalization of whole molecules. Moreover, the absorption spectrum of **10** showed very strong peaks at 308 nm belonging to the truxene moiety. We also observed a small peak at 354 nm in the absorption spectrum of **10**. It is noteworthy that the absorption behaviors of **6b** were quite similar to those of **7b**. We are still investigating such interesting phenomena through the synthesis of more such polycyclic aromatics.

In conclusion, an effective synthetic protocol producing novel PAH families with dramatically distinct topologies has been developed. The $TiCl_4$-promoted cyclizations construct both planar trimers and nonplanar tube tetramers via the in situ generation of benzene or COT rings as the core. The largest monodispersed truxene analogue (**10**) and fully π-conjugated COT derivative (**11**) containing up to 13 and 16 benzene rings have been prepared, respectively. These molecules span about 2−3 nm. Trimer **6b** exhibits similar absorption behaviors as tetramer **7b**. We are still investigating the optical properties of these polycyclic aromatics. Our COT derivatives should also be of potential application in coordination and organometallic chemistry. The door to novel PAH families with unique topologies is now opened.

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Supporting Information Available: Experimental procedures, additional data, and details. This material is available free of charge via the Internet at http://pubs.acs.org.

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