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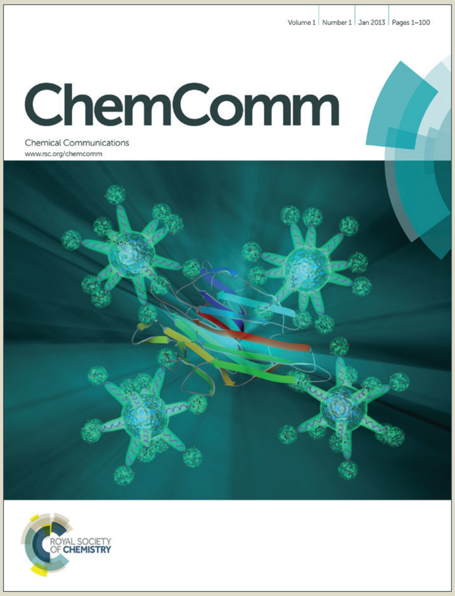

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Tetrabenzanthanthrenes by mitigation of rearrangements in the planarization of *ortho*-phenylene hexamers

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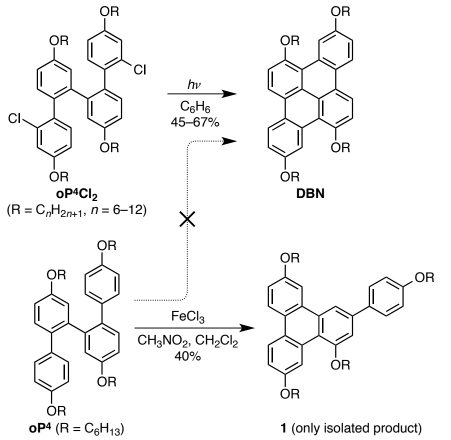
In general, *ortho*-phenylene hexamers are not good substrates for oxidative planarization because of competing backbone rearrangements. However, by first planarizing the ends, a target tetrabenzanthanthrene has been obtained by oxidation in good yield. DFT calculations suggest that the larger polycyclic aromatic subunits of the preplanarized substrate increase the rate of planarization relative to that of rearrangement. By implication, it may be possible to prepare graphene structures that cannot be made directly from simple polyphenylenes by instead designing precursors with larger polycyclic aromatic moieties. The photophysical properties of the tetrabenzanthanthrene core indicate that it may have promise as a functional chromophore.

The oxidative planarization of polyphenylenes represents an important strategy for the bottom-up synthesis of graphene nanostructures, affording a structural precision that is unavailable from top-down methods.[1] Pioneered by Müllen and co-workers, recent work has extended this methodology to important classes of graphenes, including quantum dots[2] and nanoribbons.[3] However, while broadly used, the effectiveness of this reaction is highly substrate-dependent.[4] The *ortho*-phenylenes,[5,6] for example, are prototypical examples of poor substrates, having been shown by King to undergo backbone rearrangements under typical conditions for planarization.[7]

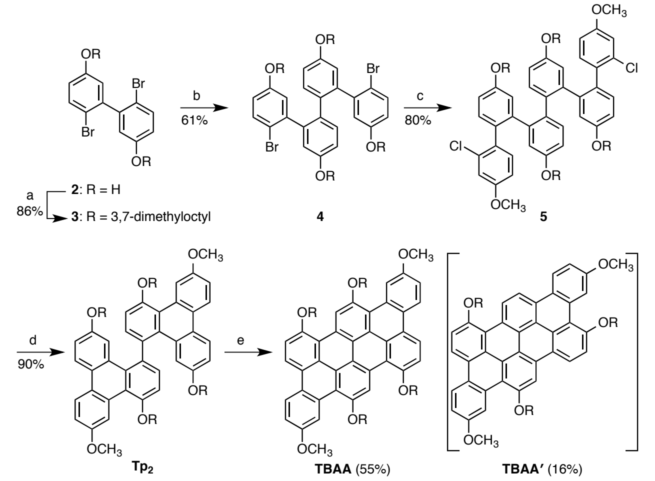
While challenging, planarization of *o*-phenylenes (and related polyphenylenes) is an important goal: the products would be armchair graphene nanoribbons approaching the structural limit of narrowness. Even short planarized oligomers are of interest as board-like polycyclic aromatics that complement much more common discotics (e.g., hexabenzocoronenes). For example, in recent work[8] we showed that formal planarization of *o*-phenylene tetramers yields liquid crystalline dibenzonaphthacenes **DBN** (Scheme 1). Despite their large aromatic surfaces, these compounds exhibit phases analogous to those of calamitics (rod-like compounds), but with properties that can be attributed to their board-like shapes (e.g., increased intercore correlations).



Scheme 1. Planarization of *o*-phenylene tetramer **oP^{4}Cl$_2$** through photochemical dehydrohalogenation. Direct oxidative planarization of **oP^4** fails because of backbone rearrangement.

The obvious extension of this work is to further elongate the aromatic core to increase its aspect ratio. This requires formal planarization of *o*-phenylene hexamers to tetrabenzanthanthrenes, a class of compounds which have received little attention (see below). Unfortunately, the strategy used for the synthesis of the **DBN** series is not easily applied to longer *o*-phenylenes. Rearrangements had been suppressed by using chlorine atoms on precursor tetramers **oP^{4}Cl$_2$** to direct photochemical dehydrohalogenation, as shown in Scheme 1 (top), but it is impractical to halogenate every point of cyclization in longer oligomers. We therefore revisited direct oxidation of *o*-phenylenes. Consistent with the work of King,[7] all attempts to directly oxidize short *o*-phenylenes yielded either intractable mixtures or partially planarized products resulting from skeletal rearrangements. For example, treatment of **oP^4** with $FeCl_3$ gives compound **1** as the only isolable product, as shown in Scheme 1 (bottom).

We then became interested in exploring whether the overall planarization of a polyphenylene could be divided into separate steps, providing access to graphenes that would be impossible to obtain directly. Here, we show that tetrabenzanthanthrenes can indeed be synthesized by formal planarization of *o*-phenylene hexamers through this approach. The mechanism has been probed using DFT calculations to assess the prospects for generalization of the strategy. The properties of the resulting tetrabenzanthanthrenes are also discussed.



Scheme 2. Synthesis of tetrabenzanthanthrene **TBAA**. Reagents and conditions: (a) 1-bromo-3,7-dimethyloctane, K_2CO_3, KI, DMF 80 °C; (b) (i) *n*-BuLi, THF, −78 °C, (ii) CuCN, −78 °C to rt, (iii) duroquinone, rt; (c) 2-chloro-4-methoxyphenylboronic acid, $Pd(PPh_3)_4$, Na_2CO_3(aq), toluene, ethanol, 100 °C; (d) $Pd(PCy_3)_2Cl_2$, DBU, Cs_2CO_3, NMP, 150 °C; (e) $FeCl_3$, CH_3NO_2, CH_2Cl_2.

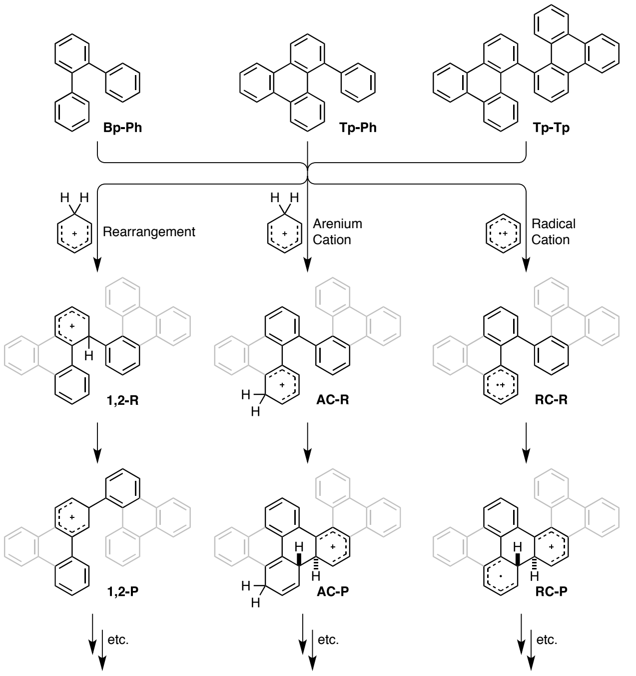
Our plan for the synthesis was to use dehydrohalogenation to first planarize the ends of an *o*-phenylene hexamer and then to explore the oxidation of the resulting triphenylene dimer **Tp$_2$**. As shown in Scheme 2, compound **Tp$_2$** was synthesized using standard methods.[6] Photochemical dehydrohalogenation of *o*-phenylene hexamer **5** (as for **oP^{4}Cl$_2$**) gave only partially planarized products; however, under palladium-catalyzed conditions[9] **Tp$_2$** was obtained in excellent yield. Gratifyingly, when compound **Tp$_2$** was subjected to standard conditions for oxidative planarization ($FeCl_3$ in dichloromethane), a good yield (55%) of the target tetrabenzanthanthrene **TBAA** was obtained along with byproduct **TBAA′** (16%). Formation of **TBAA′** can be rationalized by a 1,2-shift of one of the triphenylenes followed by planarization with loss of 1 eq of ROH (and 1 eq of H_2).[‡] Both compounds were thoroughly characterized to ensure that the correct connectivity was assigned, given that rearrangements can, in some cases, give products with subtle changes to substitution patterns.[7] In both cases the ^1H and ^{13}C NMR spectra are in complete agreement with the expected symmetries and coupling constants. For the lower-symmetry **TBAA′**, the structural assignment was further supported by comparison of the ^{13}C chemical shift assignments with DFT calculations.[‡]

The planarizations of **Tp$_2$** and **oP^4** are analogous (i.e., 2 bonds formed in both cases), and so we wanted to explore the suppression of rearrangements in **Tp$_2$**. One key difference between these substrates is, of course, that the triphenylene moieties in **Tp$_2$** prevent one of the possible rearrangement pathways by tying up the ends of the oligomer. However, it is also possible that the larger aromatic moieties in **Tp$_2$** affect the relative rates of planarization and rearrangement. Fortunately, recent reports have shown that DFT calculations provide a valuable tool for the analysis of both reactions of polyphenylenes.[10–14] We compared the reactions at the B3LYP/6-31+G(d,p) level, the same functional and a similar basis set to those used in this previous work. Because we were interested in these effect of planarization in a general sense, only the unsubstituted parent compounds were considered.

Three different starting substrates, **Bp-Ph**, **Tp-Ph**, and **Tp-Tp**, were considered, as shown in Scheme 3. 1,2-Rearrangements were assumed to occur following ipso protonation, as is well-precedented in polyphenylene chemistry.[14,15] As the oxidative planarization of polyphenylenes is thought to occur via either arenium cation ("Scholl reaction") or radical cation ("oxidative aromatic coupling") mechanisms, depending on the substrate and reagents used,[4] both were considered explicitly.[§] For the arenium cation planarization, protonation para to the site of attack was found to be favored over ortho, in agreement with previous work.[12] For convenience, protonated benzene ($C_6H_7^+$) and benzene radical cation ($C_6H_6^{\cdot+}$) were chosen as the reference acid and oxidant, respectively.

For 1,2-rearrangement, we assumed that the migration itself is rate-determining, consistent with recent work by Johnson.[14] Identification of the rate-determining step for the arenium cation planarization is challenging because the transition states for the deprotonation and oxidation steps are difficult to model without explicit knowledge of the actual acids and oxidants involved. However, King has provided a useful framework for estimating the activation energies: (de)protonation was assigned a barrier of 4 kcal/mol based on high-level ab initio calculations and dehydrogenation a barrier of 7 kcal/mol based on experimental data.[12] The loss of H_2 is predicted to be rate-determining only if the actual proton source is as acidic as $C_6H_7^+$; however, $C_6H_7^+$ is much stronger than the likely acids in solution ($pK_a \approx -24$).[16] Referencing the calculations to "weaker" acids (e.g., triflic acid) suggests that cyclization has a higher transition state energy by >10 kcal/mol. We therefore conclude that cyclization is rate determining. Similarly, we assume that cyclization is also rate determining for the radical cation mechanism. While the analysis is complicated by the identification of the specific oxidant, this assumption is consistent with previous work by Di Stefano and Negri on the oxidative cyclization of *o*-terphenyl.[11] Similarly, Tonner and

Hilt have previously shown that calculated barriers for cyclization of polyphenylene radical cations can be used to explain the regioselectivity of oxidative aromatic coupling.[13]



Scheme 3. Reaction pathways considered using DFT.

As shown in Figure 1, the triphenylene moieties in **Tp-Ph** and **Tp-Tp** are predicted to accelerate all three reactions relative to **Bp-Ph**. This result is fully consistent with experimental (and computational) work on the oxidative planarization of hexaphenylbenzene, which indicates a "slippery slope" mechanism (acceleration as the reaction progresses to more-planarized intermediates).[10,12] Notably, however, for structure **Tp-Tp** the barriers to both planarization mechanisms are predicted to decrease more than that to rearrangement ($\Delta\Delta G^{\ddagger} < -9$ kcal/mol for the planarizations vs −5.9 kcal/mol for rearrangement). The opposite effect is predicted for **Tp-Ph**: its rearrangement is expected to be accelerated more than either planarization process.

Thus, the experimental and computational results are consistent with a greater tendency to oxidative planarization only if *both* reacting moieties of the substrate are polycyclic aromatics. This result has consequences for the design of precursors to graphene targets. For example, it may not be possible to preplanarize only isolated subunits of a larger polyphenylene and then propagate planarization through the structure (e.g., cyclize just the ends of a longer *o*-phenylene and then planarize throughout). Instead, efforts would be better focused on constructing polyphenylenes entirely out of larger polycyclic repeat units (e.g., triphenylenes). While this is a greater synthetic challenge, the key conclusion is that it may be possible to make graphene architectures that would be otherwise unattainable from simple polyphenylenes.¶

Isolated tetrabenzanthanthrenes analogous to **TBAA** (and **TBAA′**) are rare, with a single report of the parent compound 50 years ago from Clar[17] and a small amount of a veratrole-derived compound reported by King.[7] Graphene structures of this size have significant technological potential, however, as they are small enough to maintain solubility, but large enough for interesting optoelectronic properties derived from the expanded aromatic cores.[18] For example, the tetrabenzanthanthrene core is only slightly smaller than those of hexabenzocoronenes (HBCs), which have found significant interest as discotic liquid crystals[19,20] and in supramolecular self-assembly,[21] including applications in organic electronics.[22,23] Like hexa-*peri*-hexabenzocoronenes, TBAAs comprise only Clar sextets and thus should have high chemical stability. However, their board-like shape should make them prone to lamellar self-assembly, complementing the discotic HBCs.

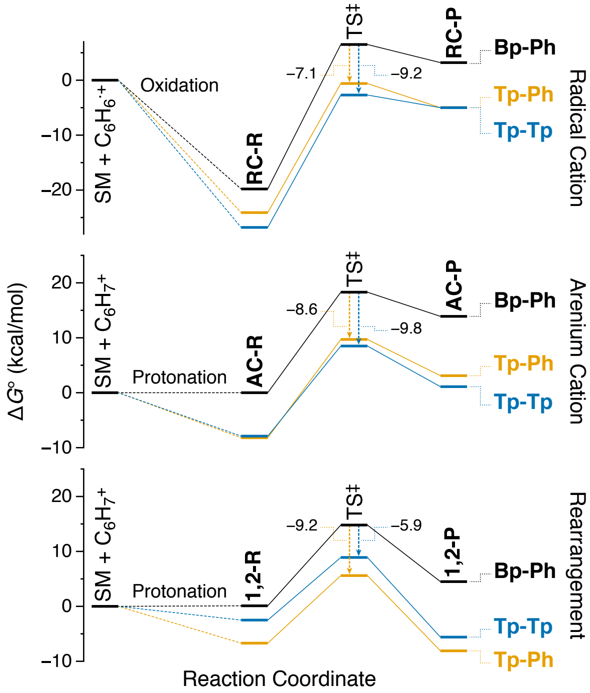


Figure 1. Energetics of the rearrangement and planarization reactions.

The core of **TBAA** is expected to be contorted from planarity by steric interactions between the alkoxy groups and opposing hydrogen atoms within the bay regions. DFT optimization indicates that the core should adopt a twisted, C_2-symmetric conformation.‡ Despite this twisting, upfield shifts of the ^{1}H NMR signals of **TBAA** with increasing concentration indicate dimerization in chloroform-*d* ($K_d = 42 \pm 6$ M^{-1}).‡

With this new chromophore in hand, we carried out preliminary characterization of its photophysical properties. Absorbance and emission spectra of **TBAA** in dichloromethane are shown in Figure 2, with additional photophysical measurements in the Supporting Information (including spectra of $\mathbf{Tp_2}$). The energies of absorption and fluorescence of **TBAA** are quite similar to those of hexaalkoxy-substituted hexa-*peri*-hexabenzocoronenes,[24] although the fine structure of the bands is (of course) quite different. Likewise, the photophysical properties are comparable to those of partially planarized HBCs from Dichtel (blue-shifted by ~30–40 nm)[25] and hexa(4-alkoxyphenyl)hexa-*peri*-hexabenzocoronenes from Moore.[26] Given the importance of HBCs as functional materials, these similarities are encouraging for the future utility of the tetrabenzanthanthrene chromophore.

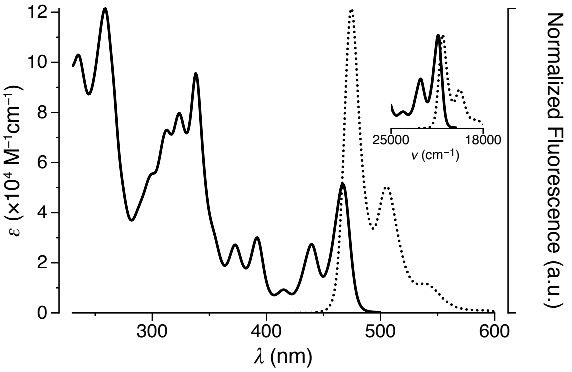


Figure 2. UV–vis (solid) and fluorescence (dashed) spectra of **TBAA** in CH_2Cl_2 (Φ = 0.51).

In summary, we have developed a strategy for the synthesis of tetrabenzanthanthrenes through sequential planarization of *o*-phenylene hexamers. This work demonstrates that, in cases where direct oxidative planarization of simple polyphenylenes yields only rearranged byproducts, the targets may be accessible by beginning with a substrate comprised of larger polycyclic aromatic subunits. DFT analysis of the competing reaction mechanisms suggests that it is not sufficient to preplanarize a small part of a starting polyphenylene; planarization is promoted only between two expanded aromatic moieties. While rearrangements are not completely suppressed, these results suggest that precursors based on polycyclic repeat units (e.g., triphenylenes) may allow access to graphene structures that cannot be made directly from simple polyphenylenes. Photophysical characterization of the new tetrabenzanthanthrene prepared here indicates that it is a promising chromophore for applications in functional materials.

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Notes and References

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† Electronic Supplementary Information (ESI) available: Experimental details referred to in the text, synthetic procedures, NMR spectra, computational data and geometries. See DOI: 10.1039/c000000x/

‡ See the Supporting Information for details.

§ Given our use of $FeCl_3$ and that **Tp_2** is electron-rich, it seems likely that planarization to **TBAA** proceeds via a radical cation mechanism.

¶ A referee pointed out the possible relationship between this work and surface-assisted planarization of polyphenylenes. While we agree that it is an interesting connection, to the best of our knowledge these reactions are thought to proceed through a radical-based mechanism distinct from those considered here. See: M. Treier, C. A. Pignedoli, T. Laino, R. Rieger, K. Müllen, D. Passerone, and R. Fasel, *Nature Chem.*, 2010, **3**, 61–67.

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