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Polycyclic Aromatic Triptycenes: Oxygen Substitution Cyclization Strategies

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Abstract

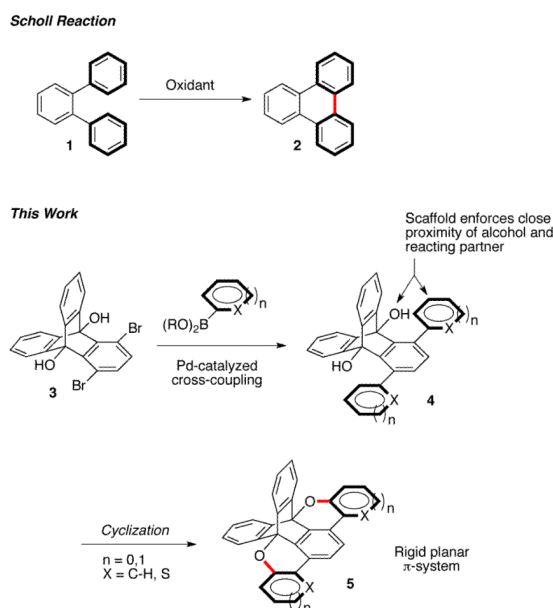
The cyclization and planarization of polycyclic aromatic hydrocarbons with concomitant oxygen substitution was achieved through acid catalyzed transesterification and oxygen-radical reactions. The triptycene scaffold enforces proximity of the alcohol and arene reacting partners and confers significant rigidity to the resulting π system, expanding the tool set of iptycenes for materials applications.

Polycyclic aromatic hydrocarbons (PAH) have attracted considerable attention because of the promise these materials hold for molecular electronics.¹⁻⁵ Inherent to the structure of many PAHs is an overall planar topology, which is generally desired to create the highest π -orbital overlap and electron delocalization.⁵⁻⁷ A common method to access PAHs is by the intramolecular oxidative cyclodehydrogenation of adjacent phenylene vertices through the Scholl reaction⁸ (**1**→**2**). This chemistry has seen broad application because of its ability to form multiple bonds between unfunctionalized C-H bonds under mild conditions with relatively high efficiency. Indeed, two dimensional graphene nanoribbons up to 12 nm in length have been synthesized from preassembled frameworks.⁹ However, tolerance of heteroatoms—which can dramatically modify the electronic properties of PAHs¹⁰—has proven a synthetic challenge.¹¹⁻¹⁶

The rigid three-dimensional structure of iptycene-derived scaffolds has proven to be an exceptionally versatile motif for creating high performance and new material properties.^{17,18} Recently, our group reported an efficient synthesis of 1,4-dibromotriptycene diols (TD, **3**) through a rhodium-catalyzed [2+2+2] cycloaddition.^{19,20} To expand the diversity of iptycene scaffolds for PAH applications, we envisioned **3** might be elaborated through palladium cross-coupling methods (**3**→**4**). The resulting extended π -system (**4**) bears close proximity to the TD hydroxyl group—enforced by the triptycene scaffold—affording the opportunity for cyclization reactions to create oxygen substituted PAHs (**5**). We recently demonstrated this principle for cyclization of alkyne π -systems to transition between two classes of conjugated polymer back-bones.¹⁹ Herein, we report the extension of this principle for the cyclization and planarization of a variety of arene π -systems—through both oxidative and non-oxidative methods—to give triptycene incorporated PAHs with oxygen heteroatom substituents (**4**→**5**). Further, the [2,2,2]-ring system on which the triptycene is based appears to confer considerable rigidity, resulting in extremely sharp photophysical features, introducing a new aspect of iptycene structure for electronic material design.

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Supporting Information. Experimental protocols and analytical data. This material is available free of charge via the Internet at <http://pubs.acs.org>.



Compound **3** provided a convenient branch point to explore the proposed cyclization through diversification using palladium catalyzed Suzuki-Miyaura cross-coupling; to this end, **6** was synthesized in excellent yield (Scheme 1). The Scholl reaction is generally thought to proceed through an aromatic cation,²¹⁻²³ and we envisioned the proximal electron rich oxygen of the hydroxyl group might be coaxed into reaction with the oxidized arene. Unfortunately, under several Scholl-type oxidants (FeCl_3 ,^{24,25} DDQ,^{22b,26} CuCl_2 ,^{27,28}), only starting material was isolated. Concurrently, we also tested conditions likely to generate an oxygen-centered radical²⁸ (Ce^{IV} ,²⁹⁻³² $\text{Pb}(\text{OAc})_4$,³³ $\text{Cu}^{\text{II}}/\text{S}_2\text{O}_8^{2-}$,^{34,35}). Encouragingly, cerium ammonium nitrate produced small amounts of the half-cyclized intermediate, but the $\text{Cu}^{\text{II}}/\text{S}_2\text{O}_8^{2-}$ protocol gave the fully cyclized **7** in good yield with spot-to-spot conversion by TLC. The structure of **7** was unambiguously confirmed by X-ray crystallography (Figure 1). Reports of the $\text{Cu}^{\text{II}}/\text{S}_2\text{O}_8^{2-}$ conditions have invoked both aromatic radical cations³⁶ and oxygen-centered radical mechanisms,^{34,35} but we believe the oxygen-radical hypothesis to be the dominant pathway for this system (*vide infra*).

We next applied these conditions to higher order π -systems (**11**). Compound **8**—an intermediate in the synthesis of TDs²⁰—was further elaborated to **9** by a [2+2+2] cycloaddition with diphenylacetylene and Wilkinson's catalyst. Application of the $\text{Cu}^{\text{II}}/\text{S}_2\text{O}_8^{2-}$ conditions led to successful cyclization of the TD hydroxyl groups (**10**) as anticipated, but failed to convert **9** to a fully cyclized compound. This observation lends support to our oxygen-radical hypothesis for cyclization, as an arene centered cation might have led to a fully cyclized product by a Scholl-type mechanism. Attempts to cyclize the remaining arenes with FeCl_3 led to complex oligomeric mixtures (**11**) most likely coupled *para* to the installed oxygen following established Scholl reactivity for such compounds.²³ The proposed structure **11** is based on UV/vis (see Figure 3b and associated text for explanation) and MALDI-TOF mass spectrometry.

We also investigated the $\text{Cu}^{\text{II}}/\text{S}_2\text{O}_8^{2-}$ conditions with thiophene derivatives (Scheme 2, **12** and **13**). Initial progress was hampered due to rapid deboronation of 2-thiophene boronic acid derivatives under cross-coupling conditions. However, application of a recently developed palladium precatalyst in the Buchwald laboratory³⁷ allowed for milder conditions and returned the desired product in excellent yield. Unfortunately, application of the $\text{Cu}^{\text{II}}/$

S₂O₈ 2-conditions produced complex mixtures and insoluble material. These results indicated the conditions to be too harsh for more electron rich aromatics. Further, we also desired a milder alternative as these oxidative conditions have been shown to oxidize the benzylic position of appended alkanes³⁵—substituents relevant for PAH solubility.

We were inspired by the acid catalyzed transesterification of 3-methoxythiophenes³⁸ and synthesized **13** in a similar manner as for **12**. In the context of **13**, the rigid TD scaffold holds the alcohol in close proximity to the 3-position of the thiophene (Scheme 2). Thus, protonation of the thiophene ring with *p*-toluenesulfonic acid in refluxing toluene allowed for 6-membered transition state attack—via a C=OMe⁺ oxonium resonance structure—and substitution of the TD alcohol at the thiophene 3-position to give the cyclized product **13** in high yield (spot to spot conversion by TLC). The cyclization was confirmed by X-ray crystallography (Figure 1).

The acid catalyzed transesterification of 3-methoxythiophenes has largely been applied for the attachment of alkyl side chains. Its application for annulation and planarization of π -systems is rare.¹⁶ We envisioned this reaction might hold promise more generally as a strategy for electron rich, oxygen-substituted, phenyl systems. Such systems have been problematic for PAHs because they are prone to quinone formation under the Scholl conditions. Further, the largely hydrocarbon family of PAHs are generally tolerant of protic acid conditions. To this end, we synthesized **15** from **3** and, in the presence of acid in boiling mesitylene, **16** was synthesized in excellent yield.³⁹ Finally, the structure was confirmed by X-ray crystallography (Figure 1).

The successful cyclization of both transesterification substrates (**14** and **16**) was marked by the removal of rotational disorder in their ¹H NMR spectra (Figure 2). For both **13** and **15**, steric clash between the methyl ether and TD hydroxyl groups led to broadening of these signals as well as the aryl-H signals on the “wings” of the TD, possibly due to rotomers and intramolecular hydrogen bonding. Upon cyclization and planarization, the rotational isomerism—in addition to the signals for the hydroxyl proton and methyl ether—was removed.

The effects of the cyclization reaction on all of the π systems under study were most distinctly visualized in their UV/vis and fluorescence signatures relative to their respective starting materials (Figure 3a-d). The absorbance maxima for each compound red-shift by almost 100 nm after cyclization (reducing the Stokes shift, Table 1). This closing of the HOMO-LUMO gap is ascribed to both the increased planarity and the presence of electronrich oxygen donor atoms that raise the HOMO level. Additionally, distinctly sharper absorbance and emission features (vibrational fine structure) for each compound were also observed. Finally, as expected, there is an associated increase in fluorescence quantum yield for the cyclized products relative to their precursors (Table 1). These effects result from the removal of vibrational relaxation through planarization and the enforced rigidity of the [2,2,2] ring system of the triptycene scaffold. An exception to this being **16**, which shows slightly broadened vibrational transitions likely due to rotational relaxation from the methoxy substituents. As mentioned above, the proposed structure of **11** is partially based on its absorbance spectrum (Figure 3b), which is indicative of a tribenzo[*fg,ij,rst*]pentaphene chromophore⁴⁰ and supports the notion that portions of the oligomer are at least partially cyclized as **11** did show signs of electrochemical cyclization⁴¹ (see Supporting Information for further details).

Cyclic voltammetry was used to investigate the redox behavior of the cyclized compounds (Figure 3e-h). Planarization and introduction of electron-donating oxygen atoms to the π systems was anticipated to encourage oxidation by raising the HOMO level. This was

indeed the case, as both **7** and **10** showed reversible oxidation peaks upon cyclization where **6** and **9** showed no redox behavior over the voltage scanned. Additionally, the more electron rich arenes in **14** and **16** showed two resolved single-electron oxidation peaks at lower potentials relative to **13** and **15** upon cyclization (Table 1).

To summarize, we have developed a strategy that takes advantage of the surrounding molecular architecture for the enforced proximity of reacting partners. The cyclization reactions succeed in the formation of low strain six-membered rings for extended planar PAHs with installed oxygen substituents and incorporated triptycene scaffolds. The triptycenes—in addition to fixing the hydroxyl group and arene into a favorable position—contribute significant rigidity to the resulting PAH. This effect on π -systems appears to be a design aspect not yet reported for three-dimensional ip-tycene materials. While this strategy was demonstrated to work under oxidative conditions commonly employed for PAH syntheses, the pre-organized framework also encouraged transesterification reactions with suitably functionalized arenes under Brønsted acid conditions. This acid-catalyzed mode of reactivity has not seen broad use in the field of PAH synthesis, and might provide an avenue towards more heteroatom-substituted platforms. We hope to extend this strategy to other aromatic moieties and side chain functional groups.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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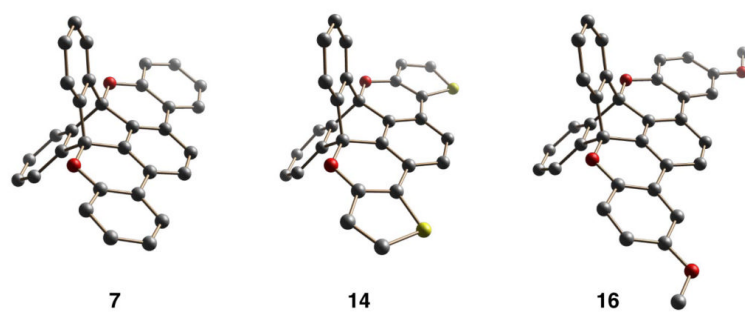


Figure 1.
X-ray crystal structures of cyclized compounds.

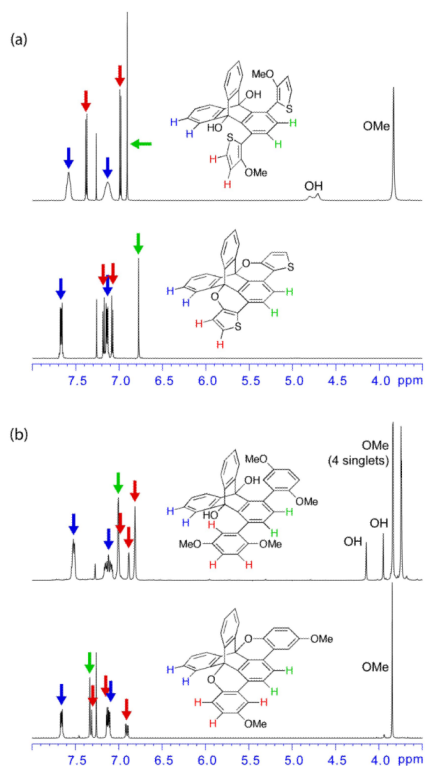


Figure 2. ^1H NMR comparison of (a) **13**→**14** and (b) **15**→**16**. Signal assignments based on 1D coupling constants and 2D NMR experiments (see Supporting Information for further details).

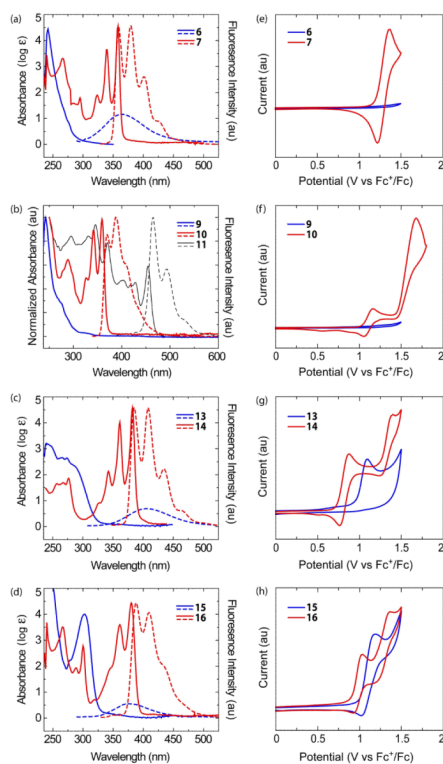
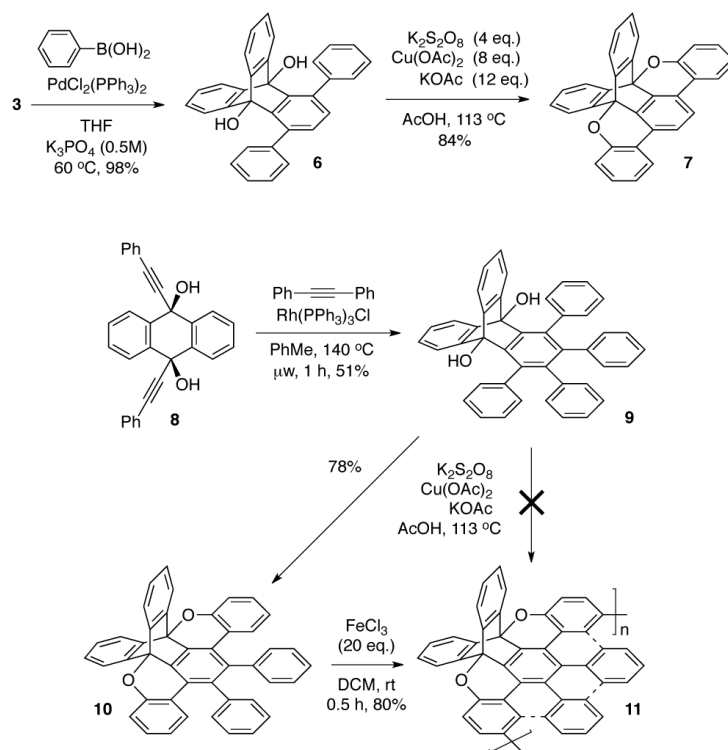
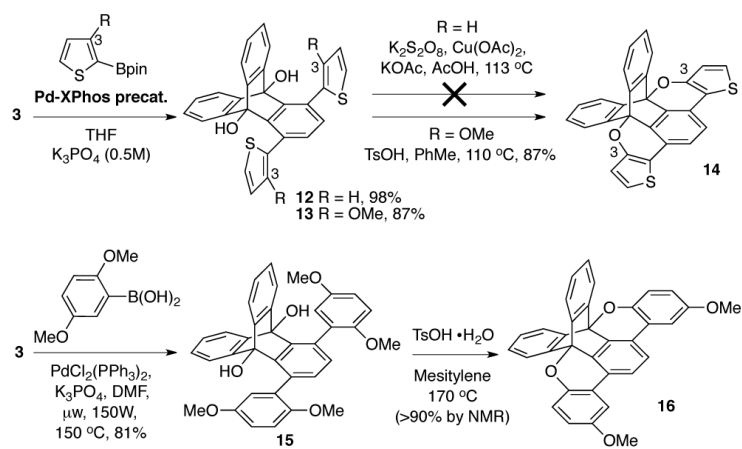


Figure 3. (a-d) UV/Vis absorbance (solid) and fluorescence (dashed) spectra in CHCl₃; (e-h) Cyclic voltammograms in CH₂Cl₂ with nBu₄NPF₆ as electrolyte (see Supporting Information for further details).



Scheme 1.
Oxidative cyclization of phenylene substrates.



Scheme 2.
Acid catalyzed transesterification cyclization.^a

Table 1

Summary of photophysical data.

	abs λ_{max}^a [nm]	em λ_{max}^a [nm]	$\log \epsilon^b$	ϕ_F	τ_F [ns]	E_{ox}^c [V]
6	242	363	4.44	0.20	1.41	
7	358	359	4.56	0.81	1.43	1.28
9	242		4.55			
10	360	387	4.58	0.83	1.5	1.11
11	455 ^b	465		0.70	3.1	
13	275	407	3.20	0.09	1.87	0.53
14	384	386	4.58	0.30	0.97	0.83/1.33
15	302	375	4.00	0.03	1.39	1.08
16	380	388	4.44	0.71	2.22	0.95/1.24

^aAll values measured in CHCl₃.^bBased on red-most abs λ_{max} .^cAll values measured in CH₂Cl₂ with *n*Bu₄NPF₆ as electrolyte.