Alternating oligo(o,p-phenylenes) via ruthenium catalyzed diol–diene benzannulation: orthogonality to cross-coupling enables de novo nanographene and PAH construction†

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Ruthenium(0) catalyzed diol–diene benzannulation is applied to the conversion of oligo(p-phenylene vinylenes) 2a–c, 5 and 6 to alternating oligo(o,p-phenylenes) 10a–c, 11–13. Orthogonality with respect to conventional palladium catalyzed biaryl cross-coupling permits construction of p-bromo-terminated alternating oligo(o,p-phenylenes) 10b, 11–13, which can be engaged in Suzuki cross-coupling and Scholl oxidation. In this way, structurally homogeneous nanographenes 16a–f are prepared. Nanographene 16a, which incorporates 14 fused benzene rings, was characterized by single crystal X-ray diffraction. In a similar fashion, p-bromo-terminated oligo(p-phenylene ethane diol) 9, which contains a 1,3,5-trisubstituted benzene core, is converted to the soluble, structurally homogeneous hexa-peri-hexabenzocoronene 18. A benzothiophene-terminated pentamer 10c was prepared and subjected to Scholl oxidation to furnish the helical bis(benzothiophene)-fused picene derivative 14. The steady-state absorption and emission properties of nanographenes 14, 16a,b,d,e,h and 18 were characterized. These studies illustrate how orthogonality of ruthenium(0) catalyzed diol–diene benzannulation with respect to classical biaryl cross-coupling streamlines oligophenylene and nanographene construction.

Introduction

Oligophenylenes comprise a wide-ranging and varied class of PAH compounds, which due to their tunable physical properties are promising candidates for organic photovoltaic materials. Additionally, Scholl oxidation of oligophenylenes and related structures enables access to structurally homogeneous nanographene materials. Despite the long-standing importance of oligophenylenes and nanographenes to the field of molecular electronics, their construction de novo remains challenging and relatively few methods for their synthesis are broadly applied. Strategies involving biaryl cross-coupling followed by Scholl oxidation or palladium catalyzed cyclo-dehydrohalogenation are among the most powerful. While many other benzannulation protocols have been reported, scalable, non-cryogenic catalytic methods that are orthogonal to biaryl cross-coupling would be especially valuable in terms of streamlining access to PAH chemical space.

Utilizing the concept of alcohol-mediated carbonyl addition, a ruthenium(0) catalyzed diene–dil [4 + 2] cycloaddition was recently developed in our laboratory (Scheme 1). Aromaticization of the cycloadducts occurs readily, enabling access to products of benzannulation from abundant diol and alcohol precursors.

Benzannulation via ruthenium(0) catalyzed [2+2] cycloaddition (ref. 12a,13c)

Scheme 1 Alternating o,p-oligophenylenes and nanographenes via ruthenium catalyzed diol–diene benzannulation.
diene reactants. In an initial application of this method, a homologous series of rod-like triple-stranded phenylene cages was prepared. This exercise suggested the feasibility of modular nanographene syntheses wherein diol-diene benzannulation is used to generate bromide-containing oligophenylenes amenable to late-stage diversification through metal catalyzed biaryl cross-coupling followed by Scholl oxidation. In fulfillment of this objective, we report syntheses of alternating oligo(o,p-phenylene) via ruthenium(0) catalyzed diol-diene benzannulation and, therefrom, structurally homogeneous nanographene materials containing as many as 22 aromatic rings.

Research design and methods

Synthesis of oligo(o,p-phenylenes) and related PAH compounds

The synthesis of the requisite oligo(p-phenylene vinylene) diols 3a–3c is readily accomplished through Wittig olefination (Scheme 2). Thus, in close analogy to the literature procedure, terephthalaldehyde 1a was exposed to the indicated phosphonium salts in the presence of BuOK to furnish the respective oligo(p-phenylene vinylenes) 2a–c in good yields. Alternate bases such as KOH, NaOH, NaOBut, BuLi and lithium diisopropylamide (LDA) led to incomplete conversion and the use of Horner–Wadsworth–Emmons (HWE) reagents was accompanied by substantial quantities of homo-coupling byproducts. Dihydroxylation of the oligo(p-phenylene vinylenes) 2a–c proved challenging due to competing oxidative cleavage to form aldehyde byproducts. Upjohn dihydroxylation conditions using N-methylmorpholine N-oxide (NMO) as the terminal oxidant attenuated this side reaction, delivering the oligo(p-phenylene vinylene) diols 3a–c in good to excellent yields. In a similar manner, a three-directional synthesis of tris-diol 9 was accomplished from benzene-1,3,5-tricarbaldehyde 1b (eqn (1)).

The synthesis of higher oligo(p-phenylene vinylene) diols 7 and 8 was accomplished in an iterative fashion through homologation of dibromo-styrene 4 and the 4-bromoterminated oligo(p-phenylene vinylene) 2b (Scheme 2). Thus, lithiation of 4 and 2b followed by treatment with DMF provided the respective formyl derivatives, which upon Wittig olefination furnished the homologous 4-bromoterminated oligo(p-phenylene vinylenes) 5 and 6. Exposure of the oligo(p-phenylene vinylenes) 5 and 6 to Upjohn dihydroxylation provided the oligo(p-phenylene vinylene) diols 7 and 8. To minimize competitive oxidative cleavage to form aldehydes observed in the formation of 8, a higher loading of OsO4 was required to shorten the reaction time. Additionally, for the synthesis of 7 and 8, use of the predominantly (Z)-selective Wittig olefination was important, as the less soluble products of (E)-selective HWE olefination were difficult to engage in dihydroxylation.

As the ruthenium(0) catalyzed [4 + 2] cycloaddition can be conducted from the ketol oxidation level, routes involving benzoin condensation were explored. The crossed-benzoin condensation of terephthaldehyde 1a with benzaldehyde occurred efficiently using an N-heterocyclic carbene (NHC) catalyst, providing ketol dehydro-3a in good yield (eqn (2)). However, these conditions were quite substrate dependent and attempted benzoin condensation of 4-bromo benzaldehyde and 2-benzo thiophene carboxaldehyde was inefficient due to competing self-condensation.

Benzannulation of oligo(p-phenylene vinylene) diols 3a–3c, 7–9 to form alternating oligo(o,p-phenylenes) 10a–c, 11–13 was next explored (Table 1). To our delight, the ruthenium(0) catalyzed cycloaddition of 1,3-butadiene with oligo(p-phenylene vinylene diol 1c and the respective formyl derivatives, provided the respective formyl derivatives, which upon Wittig olefination furnished the homologous 4-bromoterminated oligo(p-phenylene vinylenes) 5 and 6. Exposure of the oligo(p-phenylene vinylenes) 5 and 6 to Upjohn dihydroxylation provided the oligo(p-phenylene vinylene) diols 7 and 8. To minimize competitive oxidative cleavage to form aldehydes observed in the formation of 8, a higher loading of OsO4 was required to shorten the reaction time. Additionally, for the synthesis of 7 and 8, use of the predominantly (Z)-selective Wittig olefination was important, as the less soluble products of (E)-selective HWE olefination were difficult to engage in dihydroxylation.

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vinylene) diols 3a−3c, 7−9 proceeded smoothly in the presence of a carboxylic acid cocatalyst to furnish the corresponding cyclohexene diols in good to excellent yield.\(^{12,13}\) Subsequent exposure of the cycloadducts to substoichiometric quantities of \(p\)-toluenesulfonic acid (\(p\)-TsOH) resulted in dehydration to form the alternating oligo(\(p\)-phenylene) 10a−c, 11−13 in moderate to high yields.\(^{11a}\) The dehydration reaction is highly temperature dependent and minor deviations from the optimal temperatures identified for each substrate caused a significant decrease in yield. Perhaps related to this observation, one-pot cycloaddition−dehydration, which was effective for the synthesis of fluoranthenes and acenes,\(^{13a}\) was less efficient in the context of the present oligo(\(p\)-phenylene) syntheses.

The alternating oligo(\(p\)-phenylene) 10a−c, 11−13 prepared by our methods raise numerous possibilities for the synthesis of diverse PAH compounds, including helicenes, graphene nanodots and nanoribbons. To illustrate, the benzothiophene derived oligomer 10c was subjected to Scholl oxidation conditions employing anhydrous FeCl\(_3\) (ref. 3b) to form the derived oligomer 14−8. To illustrate, the benzothiophene derivative 10c was subjected to Scholl oxidation conditions employing anhydrous FeCl\(_3\) (ref. 3b) to form the derived oligomer 14−8. To illustrate, the benzothiophene derivative 10c was subjected to Scholl oxidation conditions employing anhydrous FeCl\(_3\) (ref. 3b) to form the derived oligomer 14−8. To illustrate, the benzothiophene derivative 10c was subjected to Scholl oxidation conditions employing anhydrous FeCl\(_3\) (ref. 3b) to form the derived oligomer 14−8. To illustrate, the benzothiophene derivative 10c was subjected to Scholl oxidation conditions employing anhydrous FeCl\(_3\) (ref. 3b) to form the derived oligomer 14−8. To illustrate, the benzothiophene derivative 10c was subjected to Scholl oxidation conditions employing anhydrous FeCl\(_3\) (ref. 3b) to form the derived oligomer 14−8.

Access to bromo-terminated oligomers, such as 11, led us to explore modular nanographene syntheses wherein late-stage diversification through metal catalyzed biaryl cross-coupling is followed by Scholl oxidation (Schemes 3 and 4). Toward this end, heptaphenylene 11 was subjected to Suzuki cross-coupling conditions\(^{25}\) with aryl boronate or aryl boronic acid partners that were selected to facilitate Scholl oxidation and confer solubility to the resultant nanographenes (Scheme 3).\(^{26}\) Thus, heptaphenylene 11 was converted to the bis[2,4,6-trimethylphenyl] nonaphenylene 15a, which was exposed to DDQ and triflic acid.\(^{27}\) However, as confirmed by single crystal X-ray crystallography (Fig. 1), Scholl oxidation was accompanied by aryl and methyl migration to form 16a, which was highly soluble in chloroform. Skeletal rearrangement is often observed during Scholl oxidation and can be difficult to predict.\(^{26,28}\) Alternate Scholl oxidation conditions resulted in diminished yields of 16a or produced complex mixtures of numerous products. The structure of nanographene 16a, which contains 14 fused aromatic rings, is nevertheless quite remarkable, as crystal structures of large planar PAH compounds remain quite uncommon.\(^{29,30}\) The supramolecular structure of nanographene 16a in the solid state is dominated by \(\pi−\pi\) stacking interactions, consistent with King's observation that large flanking groups on nanographenes disrupt the herringbone packing typically seen in crystal structures of PAH materials.\(^{26,31,32}\)

![Scheme 3 Palladium catalyzed cross-coupling of 11 to form oligo(phenylene) 15a−g.](image)

*Yields are of material isolated by silica gel chromatography. *<sup>b</sup> Pinacol boronate. *<sup>c</sup> Boronic acid.
An effort was made to design oligophenylenes that are less prone to skeletal rearrangement under Scholl oxidation conditions. It was recognized that Scholl oxidation to form triangular tribenzo[a,g,m]coronene motifs occurs in a highly efficient manner. Hence, Suzuki coupling was conducted with ortho-biarylboron reagents to form oligomers 15b–f (Scheme 3). Additionally, oligomer 15g, which incorporates pentamethylphenyl termini, was targeted, as methyl migration is not possible on the fully substituted aromatic ring. Indeed, Scholl oxidation using either DDQ and triflic acid or FeCl₃ gave the nanographene 16h in 65% yield (eqn (4)). This derivative was soluble enough to be characterized by ¹H and ¹³C NMR, in addition to MALDI-TOF mass spectrometry.

Hexa-peri-hexabenzocoronenes (HBCs) represent yet another class of fully benzenoid PAHs that have garnered interest as potential materials for opto-electronic devices. However, current methods available for HBC synthesis are limited. This is especially true for HBCs with low symmetry, electron deficient HBCs or those substituted at the bay region. The synthesis of the electron deficient D₃h symmetric HBC 17, which incorporates bromo-substituents in the bay region, was achieved through Scholl oxidation of the branched heptaphenylene 13 under DDQ and triflic acid conditions (eqn (5)). Although the resulting HBC 17 is quite insoluble, Sonogashira coupling occurred in good yield to furnish the chloroform-soluble 18, which was characterized by ¹H and ¹³C NMR and MALDI-TOF mass spectrometry.

Spectroscopic analysis
The photophysical properties of a subset of the molecules presented herein that were sufficiently soluble in dichloromethane (14, 16a,b,d,e,h, 18) were characterized by steady-state absorption and fluorescence spectroscopies. Experimental details and spectra measured for 16a and 18 are included in the ESI.† Fig. 2a displays absorption and emission spectra of the helicene 14. This compound features a broad absorption profile that
rises from ~2.9 eV and contains a series of sharp resonances best explained by comparison with similar picene and helicene examples previously explored.\textsuperscript{46,47} In particular, the absorption spectrum can be qualitatively explained as a combination of low-lying higher helicene transitions\textsuperscript{48} and high-energy transitions associated with the fused thiophene rings contained in the picene backbone, as studied by Morin and coworkers.\textsuperscript{10b} Likewise, the emission spectrum of 14 is consistent with other higher helicenes, particularly [7]-helicene, the first in the series for which ring overlap begins with an increasing number of rings.\textsuperscript{46,48} It is worth noting that helicenes, particularly higher helicenes containing thiophenes, have attracted interest as chiral nonlinear optical materials.\textsuperscript{42} To our knowledge, compound 14 is the first reported example of a picene-helicene hybrid and we believe its chiroptical properties will be of future interest.

Fig. 2b displays absorption and emission spectra of the nanographenes 16b,d,e, and h. Although these compounds feature the largest extended \( \pi \)-conjugated systems among the compounds we have characterized spectroscopically, their absorption and emission spectra peak at higher energies than compounds 14, 16a, and 18. This is best explained by the sole presence of arm-chair edges along the periphery of these materials, which are thought to bestow nanographenes with larger bandgaps.\textsuperscript{41} Interestingly, reducing the number of rings along the nanographene short axis, as is done for 16h, acts to reduce its optical bandgap relative to 16b, 16d, and 16e even though this also reduces the size of its \( \pi \)-system.

Conclusions

In summary, we report the synthesis of oligophenylenes and various PAH materials constructed through the use of Ru(0)-catalyzed diol–diene cycloaddition coupling.\textsuperscript{2} Oligo-1,2-diols were constructed \textit{via} iterative Wittig coupling and dihydroxylation. Furthermore, orthogonality to Pd-catalyzed cross coupling allows for bromo-terminated polyphenylenes that could be functionalized to provide various nanographenes 16a–h after Scholl oxidation. Additionally, Scholl oxidation of 10c and 13 provided benzothiophene helical picene 14 and hexaperi-hexabenzocoronene 18, respectively. Thus, we have demonstrated the use of Ru(0) catalyzed diol–diene benzannulation in the fabrication of three distinct types of PAH materials. Photophysical analysis of 14, 16a,b,d,e,h and 18 demonstrated that nanographenes prepared by these synthetic routes can display highly variable optical properties, which make these methods useful for the preparation of organic electronic materials. Future studies will focus on the development of related methods for alcohol-mediated benzannulation and their application to PAH construction, including the use of symmetric 2,3-diaryl-substituted butadiene building blocks.

Conflicts of interest

There are no conflicts to declare.

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