The Synthesis, Characterization, and Study of Discrete Boronic Acid-Based Materials and Designer Liquid Crystals

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry

by

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ABSTRACT OF DISSERTATION

The Synthesis, Characterization, and Study of Discrete Boronic Acid-Based Materials and Designer Liquid Crystals

by

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Framework materials such as covalent organic frameworks (COFs) are the focus of increasing interest for their remarkable materials properties. The demand for their rational engineering is tempered by their insolubility, which leads to an incomplete understanding of COF formation and their incorporation into devices. Presented herein is research undertaken to i) develop discrete, soluble model systems that are expected to provide valuable insight into optimizing the synthesis of related, “infinite” COFs (Chapter 1), ii) provide straightforward characterization for boronic acid-based COPs and COFs using IR spectroscopy and computational modeling (Chapter 2), iii) develop routes to synthetically challenging secondary building units (Chapter 3), and iv) to introduce a new generation of students to the synthesis, study, and application of advanced framework materials similar to COFs (metal organic frameworks, Chapter 4). With the overarching goal of straightforward, de novo design, synthesis, and characterization of framework materials and related assemblies, we discovered a new class of soluble, covalent organic polygons (Chapter 1), bands in the IR region that can be used spectroscopically to diagnostically distinguish between boronic acid, boroxine anhydride, and boronate ester species (Chapter 2), and a straightforward, reliable, and scalable synthesis of designer liquid crystals based on mixed-substituent triphenylene derivatives (Chapter 3), while also promoting the study of framework materials through the development of experimental protocols designed to engage students in areas of fundamental chemistry, advanced materials (MOFs), and broader environmental impacts of chemistry (Chapter 4).
Chapter 1 – Discrete, Soluble Covalent Organic Boronate Ester Polygons
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1.0. Abstract

The facile self-assembly of nanoscale boronate ester rectangles from linear bis-catechols and 1,4-benzene diboronic acid is described. Spectroscopic and computational analyses reveal the influence of extended π-conjugation on the rectangles’ absorption and fluorescence properties. The rectangles represent a new class of discrete, organic soluble covalent organic polygons. These results are expanded upon to explore the challenge of synthesizing such assemblies, which lies primarily in the balance between the solubility of assembled structures and that of their organic precursors. To gain insight into these underlying influences, a library of six variably soluble, nanoscale, oval-shaped boronate ester assemblies were synthesized. Through structural variation of solubilizing moieties, we probe the limits of boronate ester assembly solubility, restrictions on their characterization through traditional methods, and investigate their structural, thermal, and optical properties, which will contribute to our understanding of and help pave the way toward a greater variety of discrete, soluble boronate ester assemblies. The results are expected to provide additional insight into in optimizing the synthesis of related, “infinite” covalent organic frameworks (COFs).

1.1. Introduction

Boronic acids have long played several central roles in synthetic, bioorganic, and analytical chemistry.\(^1\) Traditionally used as mild Lewis acids, they also serve as key building blocks for Suzuki-Miyaura cross-coupling reactions,\(^1,2\) form the basis of myriad saccharide receptors,\(^1,3\) function as selective anion sensors,\(^1,4\) and can enhance electrophoretic separations.\(^1,5\) The neutral, sp\(^2\)-hybridized trivalent boron center possess an empty p orbital, aligning the CBO\(_2\) plane coplanar with aromatic moieties, and leading to enormous structural diversity of aryl boronic acid-based compounds.\(^1,1\) The structural variety of aryl poly-boronic acids, along with well-defined rigid geometry of reactive sites have led to significant and increasing interest in the dynamic covalent assembly\(^1,6\) of boronic-acid-derived materials.\(^1,7\) The dynamically reversible self-condensation of boronic acids to form boroxine anhydrides and the similarly reversible assembly of boronic acids with organic diols to generate boronate esters (Scheme 1.1) have enabled the facile, thermodynamically driven synthesis of multiple complex molecular and
supramolecular compounds, e.g., macrocycles,\textsuperscript{1,8} capsules,\textsuperscript{1,9} dendrimers,\textsuperscript{1,10} polymers,\textsuperscript{1,11} and mechanically interlocked molecules.\textsuperscript{1,12}

**Scheme 1.1:** Boronic acids are able to dynamically self-assemble into boroxine anhydrides (top) and boronate esters (bottom), which serve as fundamental secondary building units (SBUs) for the design and synthesis of complex boronic-acid-derived materials.

As the demand for rational engineering of nanoscale materials increases, dynamic covalent chemistry has moved to the forefront of self-assembly techniques,\textsuperscript{1,6} as a thermodynamically controlled method of producing covalently linked structures. A system under thermodynamic control will initially move toward a dynamic equilibrium favoring kinetic intermediates, which will continuously decompose and recombine until the lowest energy conformation is achieved, and further inter-conversion is disfavored. Boronic acids are especially well-suited to this type of chemistry, thanks in part to their two reaction pathways, and to the aforementioned structural diversity of both reactive subunits and products.

Particularly exciting is the recent growth in the area of boronic-acid-based covalent organic frameworks\textsuperscript{1,13} (COFs). First reported by Yaghi and co-workers\textsuperscript{1,14} in 2005, COFs represent a class of rigid, highly ordered, nanoporous crystalline polymers. Careful selection of secondary-building units (SBUs) according to the principles of reticular chemistry allows for the rational design of COFs, imparting long range structural order. Two-dimensional, planar COFs tend to stack into multilayered structures, whereas three-dimensional COFs adopt different net topologies. Since their discovery, interest in boronic-acid-derived COFs has grown exponentially with several research groups, e.g., Yaghi,\textsuperscript{1,15} Jiang,\textsuperscript{1,16} Dichtel,\textsuperscript{1,17} Lavigne,\textsuperscript{1,18} and others.\textsuperscript{1,19}
making significant contributions to the field. Much of the interest in boronic-acid-derived COFs is due, in large part, to their outstanding physical properties: strong covalent linkages, low mass densities, high thermal stabilities, and permanent porosity.\textsuperscript{1.13} One particular COF (COF-108) holds the distinction of being the least dense known solid, with a density of 0.17 g/cm\textsuperscript{3}.\textsuperscript{1.15a} Furthermore, the high porosity and internal surface areas typical of many boronic-acid based COFs make them ideal candidates for applications in gas absorption. In fact, certain porous boronic acid-based COFs with high internal surface areas approach DOE targets for hydrogen absorption. COF-105 is a notable example; absorbing 10\% H\textsubscript{2} by weight at 77K.\textsuperscript{1.15c} These two remarkable frameworks, COF-108 and 105, share more than potential for industrial applications; both COFs are prepared from the same boronic acid subunit (Figure 1.1). In the case of boroxine anhydride COF-105, the tetrahedral tetra-boronic acid precursor is self-condensed, while in boronate ester COF-108, the same poly-boronic acid is reacted with an organic poly-catechol. Not only do these examples demonstrate the versatility of boronic acid reactivity in preparing novel materials, but they also reflect the significant differences in net topology of products upon subtle SBU variation. In light of these desirable physical and structural characteristics, COFs have found applications in and beyond gas uptake and storage;\textsuperscript{1.13a, 1.14, 1.15a-c} spanning catalysis,\textsuperscript{1.20} charge carrier materials,\textsuperscript{1.15d, 1.16e-i} and optoelectronics.\textsuperscript{1.16a-c}

![Figure 1.1: a) COF-105 synthesis from tetra-boronic acid precursor, showing the high internal surface area of boroxine anhydride COF-105. b) COF-108 synthesis employing the same tetra-boronic acid precursor to react with hexa-hydroxy-triphenylene. The boronate ester COF-108 product adopts a notably different 3D structure than COF-105. Adapted from reference 1.15a.](image-url)
Despite their remarkable applications, the synthesis and characterization of boronic acid-based COFs and related complex molecular and macromolecular structures remains challenging, as COFs are by their very nature, insoluble powders. Complementary methods of powder X-ray diffraction (PXRD) and infrared (IR) spectroscopy are generally among the techniques used to characterize COF powders. These solid-state methods, while providing valuable insight in the connectivities and chemical functionalities of COFs, lack the detail of solution phase analysis. In spite of the explosion of interest in boronic-acid derived-COFs, we still have an incomplete understanding of their formation and how they may be incorporated into devices. The nature of COF materials may prevent solution processing, but the development of analogous, soluble model materials can provide the desired traditional solution phase analyses, including nuclear magnetic resonance (NMR) and X-Ray crystallography.

While multiple examples of infinitely periodic 2- and 3-dimensional boronate ester COFs have been reported since their discovery\textsuperscript{1,14} there have been few examples\textsuperscript{1,9a,d,f} of discrete analogues: \textit{i.e.} porous, highly unsaturated covalent organic polygons or polyhedra (COPs) built from boronic acids and oligo-catechols.\textsuperscript{1,12,1,20} The seminal example of boronate-ester COFs, COF-5, is formed through the condensation of 1,4-benzene diboronic acid (BDBA) with 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) in mesitylene/dioxane (Scheme 1.2a).\textsuperscript{1,14} The preparation of a soluble COP with a chemical structure directly analogous to COF-5, for example, can provide valuable solution-phase characterization information applicable to analysis of the COF-5 crystallite (Scheme 1.2b).

Whether discrete (COPs) or infinite (COFs), synthesis is significantly influenced by the choice of solvent, solubility and availability of starting materials, adequate reversibility of initial oligomers and kinetic intermediates to allow for error correction, and available methods of characterization. In this chapter, we will explore the challenges and advances in the dynamic assembly of discrete, soluble boronic acid-based polygons, as well as investigating their materials properties. Proof of concept synthesis of discrete nanoscale covalent organic rectangles was undertaken (Section 1.2), followed by a detailed study in the factors affecting the solubility and stability of discrete boronic acid-derived assemblies, using a family of substituted nanoscale oval COPs based on polycyclic aromatic subunits as sample systems (Section 1.3).
1.2. Discrete, Soluble Covalent Organic Boronate Ester Rectangles

1.2.1. Introduction

In line with our efforts to prepare and characterize soluble, discrete COF analogues, we initially undertook a proof-of-concept synthesis of small, rectangular boronate-ester assemblies. Herein we report the synthesis and dynamic self-assembly of two shape-persistent, alkyl-functionalized covalent organic boronate ester rectangles. Spectroscopic investigations reveal the dynamic nature of their self-assembly as well as their structure-dependent absorption and fluorescence properties.
1.2.2. Synthesis of Precursors

Linear bis-catechols 1.1 and 1.2 containing at their core 2,3-bis(hexyloxy)phenylene or diethynyl-2,3-bis(hexyloxy)phenylene, respectively, were designed to function as 0° secondary building units in accordance with the directional-bonding\textsuperscript{1,22} approach to molecular self-assembly. Hexyloxy solubilizing groups were found to be essential for the current study as neither unsubstituted nor methoxy substituted linear bis-catechols were sufficiently soluble to allow adequate solution phase assembly and characterization of assemblies 1.3 and 1.4.

The synthesis of substituted bis-catechols 1.1 and 1.2 is shown in Scheme 1.3. Compound 1.4\textsuperscript{1,23} was modified to provide protected catechols 1.6 and 1.7, which when coupled with central aromatic units would ultimately afford bis-catechols 1.2 and 1.1, respectively. Compound 1.8\textsuperscript{1,24} was coupled with 1.7 using conditions developed by Buchwald and coworkers\textsuperscript{1,25} to provide protected bis-catechol 1.9, which was deprotected via hydrogenation, affording bis-catechol 1.1.

The ethynyl spacers in bis-catechol 1.2 were introduced through Sonogashira coupling of compound 1.8 with TMS-acetylene. Cleavage of the TMS group and subsequent Sonogashira of 1.10 to 1.6 provided orthoformate protected, ethynyl-spaced, bis-catechol 1.12. Mildly acidic conditions were employed to cleave the protecting groups and afford bis-catechol 1.2.

\textbf{Scheme 1.3:} Synthesis of bis-catechols 1.1 and 1.2.
1.2.3. Self-Assembly of Boronate Ester Rectangles

There is literature precedent\textsuperscript{1.9b,1.9f,1.11d} for the dynamic assembly of discrete and oligomeric boronate esters in hydrophobic solvents such as CHCl\textsubscript{3} and CH\textsubscript{2}Cl\textsubscript{2}. 1,4-Benzene diboronic acid (BDBA), however, is insoluble in CDCl\textsubscript{3} where it self-condenses into boroxine anhydride species, thus preventing assembly with either 1.1 or 1.2 in CDCl\textsubscript{3}. We found that the addition of CD\textsubscript{3}OD catalyzes the dissociation of boroxine anhydride species and, likewise, the dynamic self-assembly of BDBA with 1.1 and 1.2. Indeed, within 10 min of mixing 1.1 or 1.2 with BDBA (10 : 1 CDCl\textsubscript{3}–CD\textsubscript{3}OD, 50 °C) the \textsuperscript{1}H NMR spectrum of both assemblies become substantially disordered as dynamic covalent exchange between BDBA and 1.1 or 1.2 initially results in the formation of various kinetic intermediate assemblies. Within 3 h these dynamic libraries of oligomers have largely collapsed to their most thermodynamically favored structures, as indicated by considerable sharpening of their \textsuperscript{1}H NMR spectra. Full conversion to rectangles 1.3 and 1.4, however, is not complete until H\textsubscript{2}O and CD\textsubscript{3}OD are removed by stirring over 4 Å molecular sieves,\textsuperscript{1.26} providing rectangles 1.3 and 1.4 in near quantitative yield (Scheme 1.4).

Scheme 1.4: Solution-phase synthesis of boronate ester rectangles 1.3 and 1.4 from the dynamic self-assembly of linear bis-catechols 1.1 and 1.2 with benzene diboronic acid (BDBA).
In addition to increasing the rectangles' solubility, the alkyl chains of 1.3 and 1.4 likely aid in rendering both assemblies highly resistant to hydrolysis\(^{1,27}\) as hydrolytic disassembly could only be achieved by refluxing in a 1 : 1 mixture of D\(_2\)O–CD\(_3\)OD.

### 1.2.4. Spectroscopic Analyses of Soluble Rectangles

The formation of rectangles 1.3 and 1.4 is supported by key shifts of diagnostic signals in their \(^1\)H NMR spectra. Catechol Ar–OH signals at 7.61 and 6.01 ppm for tetraol 1.1, for example, are no longer present in the \(^1\)H NMR spectrum of rectangle 1.3 (Figure 1.2). Catechol protons H\(_a\)–H\(_c\) shift collectively downfield by 0.3 ppm while the proton signal H\(_d\) of the central aromatic unit of 1.1 shifts from 7.33 ppm in the free tetraol to 7.41 ppm in assembly 1.3. A new singlet corresponding to the aromatic protons of the central boronate unit is observed at 8.25 ppm.

![Figure 1.2: Partial \(^1\)H NMR spectra (CDCl\(_3\), 300 MHz, 298 K) of bis-catechol 1.1 (a) and boronate ester rectangle 1.3 (b) indicating diagnostic shifts of proton signals H\(_a\)–H\(_d\) upon self-assembly.](image)

Analogous changes occur in the \(^1\)H NMR spectrum of rectangle 1.4 (Appendix A.I.1.1). The sharp signals observed in the CDCl\(_3\) spectra of 1.3 and 1.4 suggest assemblies of high symmetry rather than collections of oligomers.

Further characterization of covalent organic rectangles 1.3 and 1.4 is provided by infrared (IR) spectroscopy. The IR spectra of linear catechols 1.1 and 1.2 (Appendix A.I.4.) reveal broad catechol CO–H stretching bands at 3272 and 3311 cm\(^{-1}\), respectively, while the IR spectrum of BDBA shows a BO–H band centered at 3286 cm\(^{-1}\) (Appendix A.I.4.). IR spectra of
rectangles 1.3 and 1.4, however, contain no stretching bands above 3000 cm\(^{-1}\), indicating full dehydration of each species. New B–O stretching bands at and 1326 cm\(^{-1}\) (rectangle 1.3) and 1333 cm\(^{-1}\) (rectangle 1.4) support the formation of boronate esters, but cannot rule out the formation of anhydrides. Boronate anhydrides display a characteristic\(^{1,28}\) absorption band between 570–580 cm\(^{-1}\), however neither the IR spectra of 1.3 nor 1.4 contains a peak in this region providing more definitive evidence that boronate esters rather than anhydrides are formed. Furthermore, rectangles 1.3 and 1.4 display bands at 660 and 656 cm\(^{-1}\), respectively, corresponding to boronate ester out of plane bending modes. Assignments of vibrational modes were supported by frequency analysis obtained from density functional theoretical calculations. Vibrational analyses were carried out at the B3LYP/6-31g(d) level and the resulting frequencies were used to aid in assigning relevant vibrational modes. Calculated frequencies were scaled by a factor of 0.960.\(^{1,36}\) Key boronate ester vibrational modes obtained from theoretical calculations, and their corresponding experimental modes, are given in Table 1.1 and Figure 1.3.

**Table 1.1.** Comparison of computed and experimental B-O stretching frequencies and out of plane boronate ester vibrational frequencies that are characteristic of boronate esters. All values are reported in wavenumbers (cm\(^{-1}\)). Computed frequencies are scaled by 0.0960.

<table>
<thead>
<tr>
<th>Assembly</th>
<th>B–O stretch (cm(^{-1}))</th>
<th>C–B–(O)(_2) out of plane bend (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>1326</td>
<td>660</td>
</tr>
<tr>
<td>1.4</td>
<td>1333</td>
<td>656</td>
</tr>
</tbody>
</table>

![Figure 1.3.](image.png)

Figure 1.3. Snapshots at maximal and minimal displacements of diagnostic B-O stretching (a) and boronate ester out of plane bending (b) vibrational modes obtained from DFT calculations. Rectangle 1.4 is shown as a representative example; analogous modes were also found for rectangle 1.3.

NMR and IR spectroscopic analyses, while supportive of the formation of boronate ester assemblies, cannot rule out the possibility that alternative, highly symmetric boronate ester oligomers have formed or are present. Accurate mass MALDI mass spectrometry was
therefore used to investigate the molecularity of assemblies 1.3 and 1.4. The MALDI mass spectrum of rectangle 1.3 reveals a peak of \( m/z = 1199.565 \) \([\text{M} + \text{Na}]^+\), which is in agreement with the calculated value of 1199.560. The MALDI mass spectrum of rectangle 1.4 shows a peak of \( m/z = 1272.572 \) \([\text{M}]^+\) compared to a calculated value of 1272.571. MALDI mass spectrometry results quantitatively establish the molecularity of covalent organic rectangles 1.3 and 1.4 as being discrete species rather than oligomers.

The most prominent structural difference between linear bis-catechols 1.1 and 1.2, and likewise rectangles 1.3 and 1.4, is the presence of ethynyl moieties in 1.2 and 1.4. These ethynyl groups have two noteworthy effects: (i) catechol moieties of 1.2 are able to adopt syn-periplanar and anti-periplanar conformations while those of 1.1 cannot due to steric interactions at its biaryl C–C bonds, and (ii) \( \pi \)-conjugation is increased in 1.2 relative to 1.1. UV/Vis and fluorescence spectroscopy were used to investigate the effects of increased conjugation on the absorption and emission properties of rectangles 1.3 and 1.4. Plotted in Figure 1.4 are the UV/Vis and fluorescence spectra of rectangles 1.3 and 1.4 (1.0 × 10^{-5} \text{ M, CHCl}_3).

![Figure 1.1: Absorption (solid lines) and normalized fluorescence (dashed lines) spectra of boronate ester rectangles 1.3 and 1.4. All spectra were recorded in CHCl_3 (1.0 × 10^{-5} \text{ M}). Excitation wavelengths: \( \lambda_{\text{ex}} = 270 \text{ nm (1.3), } \lambda_{\text{ex}} = 320 \text{ nm (1.4). See Appendix (A.1.3.)} \]

The absorption of rectangle 1.3 (\( \lambda_{\text{abs}} = 264 \text{ nm, } \varepsilon = 3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \)) is almost identical to that of the boronate ester obtained by condensation of BDBA with catechol (\( \lambda_{\text{abs}} = 282 \text{ nm, } \varepsilon = 2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \)),\(^{1,11c}\) underscoring the fact that conjugation is broken at the twisted biaryl bonds of 1.3. Absorption of rectangle 1.4, by contrast, is red-shifted by 93 nm relative to 1.3 (\( \lambda_{\text{abs}} = 357 \))
nm, $\varepsilon = 2.5 \times 10^4 \text{M}^{-1} \text{cm}^{-1}$) reflecting the increased conjugation provided by the ethynyl spacers. The effect of extended $\pi$-conjugation is again observed, though to a lesser extent, in the fluorescence spectra of 1.3 ($\lambda_{em} = 383$ nm) and 1.4 ($\lambda_{em} = 400$ nm). Stokes shifts of 119 nm and 43 nm are observed for rectangles 1.3 and 1.4, respectively, indicating the more conformationally flexible rectangle 1.3 undergoes greater relaxation upon excitation than the planar, more conjugated rectangle 1.4. Both boronate ester rectangles show significant emission in the blue region of the spectrum, making them possible candidates for soluble, stable blue emitters for organic light emitting diode (OLED) applications.\(^{1.29}\)

### 1.2.5. Computational Studies of Boronate-Ester Rectangles

Additional insight into increased $\pi$-conjugation in rectangle 1.4 relative to 1.3 was obtained through density functional theory. Models of both rectangles with hexyloxy functionalities replaced with methoxy groups were constructed within the input mode of the program Maestro v9.9.109.\(^{1.30}\) Each rectangle was subjected to a 1000 step Monte Carlo Multiple Minimization (MCMM) conformational search using the OPLS force field\(^{1.31}\) in a solvent model for chloroform with a total number of 2000 iterations per minimization step in order to determine the lowest energy conformation of 1.3 and 1.4.

**Figure 1.2:** Exterior and interior dimensions of porous, shape persistent rectangles 1.3 and 1.4 as obtained from DFT calculations. All values are reported in nm.
The global energy minimum structures obtained for 1.3 and 1.4 were imported into the program Gaussian09.1,32 The lowest energy structure of each rectangle (Figure 1.5) was optimized to full convergence at the B3LYP/6-31+g(d,p) level¹.³³ in a PCM¹.³⁴ solvent model for CHCl₃ using the program Gaussian 09. Shown Figure 1.5, the lowest energy conformation of 1.3 is non-planar, with dihedral angles of 129° between its conjugated boronate ester aromatic units and central alkoxy-substituted aromatic rings. Rectangle 1.4, however, does adopt a planar conformation.

Natural bond orbital (NBO)¹.³⁵ analysis was invoked using pop=(full,nbo) keyword. HOMO-LUMO gaps were computed as the difference in energy between the highest energy occupied and lowest energy virtual orbitals obtained for each molecule from theoretical calculations.

![Figure 1.3](image)

**Figure 1.3:** (a) Top views of the highest-occupied and lowest-unoccupied molecular orbitals of boronate ester rectangles 1.3 and 1.4 computed at the B3LYP/6-31+g(d,p) level (CHCl₃ solvent) along with computed HOMO–LUMO gaps (eV). (b) Edge views of both rectangles highlighting the non-planar structure of 1.3 and planar structure of 1.4. Molecular orbitals were visualized using GaussView5. Coordinates can be found in the Appendix (A.I.5.).
As can be seen in Figure 1.6, NBO analysis reveals that the HOMO orbitals of rectangles 1.3 and 1.4 are quite similar: both predominantly localized on their more electron-rich catechol-based units. Their LUMO orbitals, however, differ considerably. The LUMO of 1.3 is entirely localized on its central, electron-poor boronate moieties. The LUMO of 1.4 is fully delocalized across the entire \( \pi \)-conjugated rectangle. Increased conjugation is also reflected in calculated HOMO–LUMO gaps of 4.29 and 3.52 eV for rectangles 1.3 and 1.4, respectively.

1.2.6. Conclusion

Soluble, shape-persistent covalent organic polygons bearing alkyl functionalities are likely to allow for the design and fabrication of new boronate ester materials –e.g. porous boronate ester mesogens, the organized assembly of covalent organic polygons into self-assembled monolayers, and the use of soluble covalent organic polygons as sensors for halide anions. The violet-blue emission of rectangles 1.3 and 1.4 opens possibilities for these and related assemblies to be used as soluble, thermally robust\(^{1.37} \) components of OLEDs. Furthermore, we anticipate soluble COPs will play an important role in understanding and optimizing structure–function relationships of related COFs by providing valuable solution phase analysis that cannot otherwise be easily obtained given the insoluble nature of rigid, infinitely periodic frameworks. We are actively investigating the solution phase assembly and sensing applications of rectangles 1.3 and 1.4 as well as the synthesis and self-assembly of additional soluble, discrete covalent organic polygons.

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1.3. Boronate Ester Ovals

1.3.1. Introduction

Dynamic assembly of extended framework materials has been the focus of increasing interest\(^{1.13,1.38} \) in the materials science community since the discoveries of metal organic frameworks (MOFs) in 1999\(^ {1.39} \) and covalent organic frameworks (COFs) in 2005\(^ {1.14} \) by Yaghi and coworkers. Formed through the reversible covalent linkage of organic subunits, COFs are particularly attractive synthetic targets, thanks to their outstanding physical properties. These lightweight, highly ordered, porous polymers exhibit high thermal stabilities, low densities, and high internal surface areas\(^ {1.13,1.17d,e} \) leading to potential applications in optoelectronics\(^ {1.15d,1.16c,g} \), energy storage\(^ {1.16f} \), heterogeneous catalysis\(^ {1.40} \), and gas sequestration and storage\(^ {1.41,1.13a} \).
According to the principles of reticular chemistry\textsuperscript{1,22} and the selection of appropriately reversible dynamic covalent reactions, specific combinations of shape-persistent organic subunits can allow for the rational design of COFs with predictable framework geometries, pore sizes, and chemical properties. Boronic acids have proven especially useful in this regard as they are able to reversibly self-condense into boroxine anhydrides and can also undergo dynamic assembly with diols, such as catechol derivatives, to produce boronate esters.\textsuperscript{1.14,1.3d,1.4c,1.7b,1.8a,1.11d,1.42} Both systems are well suited for the modular assembly of periodic 2- and 3-dimentional COFs; indeed, several structurally diverse polyfunctional boronic acids and oligo-catechols have been used to produce the majority of COFs to date.\textsuperscript{1.13,1.15a,b,1.16j,1.18a,1.19a-c,1.43}

Despite the emerging interest in the synthesis and characterization of boronic acid-based COFs, discrete assemblies formed from boronic acids are less common. Examples of porous, highly unsaturated covalent organic polygons or polyhedra (COPs) prepared from shape-persistent boronic acid and oligo-catechol monomers include porous boronate-ester cages, capsules, and cavitands,\textsuperscript{1.8d,1.9,1.44} and boroxine cyclophanes.\textsuperscript{1.45} Related examples of discrete boronic acid based assemblies have also been reported as complexes with sp\textsuperscript{2} hybridized nitrogen compounds.\textsuperscript{1.46} Generally absent from this array of macromolecules are discrete assemblies that are structurally analogous to COFs and prepared from monomers that are similar or identical to those used to prepare extended frameworks. If soluble, these ‘COF analogue’ COPs can aid in elucidating the dynamic and kinetic details of COF formation, and provide insight into the influence of functionality and directionality on monomer assembly. As COF analogues, discrete COPs are porous, shape-persistent structures that have potential applications in catalysis and gas uptake. Their materials properties and applications may even extend beyond those of COFs, as they are likely to form aggregates and higher-order assemblies in solution\textsuperscript{1.15a,b,1.16j,1.18a,1.19a-c,1.46} and on solid substrates.\textsuperscript{1.47} With the potential to form higher-order assemblies in solution COPs may find applications in liquid crystals, self-assembled monolayers, solution-processable organic photovoltaics, and as tuneable solid-state structures.

In spite of their potential, there remain very few examples of discrete, shape-persistent boronic acid-based assemblies, likely because their synthesis and study is complicated by the same difficulties that have made the characterization and study of COF materials quite challenging. In particular, the inherent insolubility of boronic-acid based COFs, most COPs, and their boronic
acid-based subunits has presented several challenges to their preparation and characterization. It is notable that, since their discoveries, thousands of examples of MOFs have been reported,$^{1,38,1,39}$ while there have been less than fifty unique COFs$^{1,13,1,43}$ and even fewer discrete boronic acid-based assemblies.$^{1,8d,1,9,1,44,1,45}$ Similarly, in contrast to the many examples of single crystalline MOFs, no single crystals of a boronic acid-based COF have been grown. To date, only one example of a single crystalline COF – an imine-based framework – has been reported.$^{1,48}$ The insolubility of COFs has also been a barrier to detailed analysis of their formation. Mechanistic and kinetic analysis of COF formation has been significantly hampered by their poor solubility, however Dichtel and co-workers have recently used turbidity analysis to quantify the kinetics of early stage COF formation from within homogenous reaction solutions,$^{1,49}$ a considerable advance in the study of COFs and related materials. Still, the insolubility of such frameworks remains a persistent challenge to their characterization and study.

Even those groups that have reported soluble, discrete boronic acid-based assemblies (Figure 1.7) have been forced to confront issues of solubility. Mastalerz and coworkers synthesized an impressive mesoporous cuboctahedral boronate ester cage compound by refluxing a tetrahydroxy tryptacene derivative and 1,3,5-benzene triboronic acid in chloroform. The introduction of solubilizing ethyl-groups on the tryptacene monomer was found to be essential for cage assembly and analysis. The solubility of the boronate ester cuboctahedron was found to be so precarious that, upon desolvation, the resulting solid could not be redissolved to any extent.$^{1,44}$ Kobayashi and coworkers reported soluble boronate ester cavitands based on tetra-boronic acid calixarenes and 1,2-bis(3,4-dihydroxyphenyl)ethane. Despite the inherent flexibility of both the calixarene and the bis-catechol starting materials, tetra-functionalization of the calixarene with heptyl moieties was found to be crucial to promote assembly formation and to ensure the solubility of the resulting cages.$^{1,9a}$ In the related realm of boroxine anhydrides, the triply ferrocene-bridged boroxine cyclophane reported by Miljanic and coworkers crystallized out of solution, but was otherwise poorly soluble.$^{1,45}$ In the previous section, we reported the synthesis and characterization of soluble covalent organic boronate ester rectangles composed of rigid triphenyl bis-catechol derivatives and benzene diboronic acid. Hexyloxy functionalization was found to be necessary for solution phase self-assembly and characterization.$^{1,50}$ Collectively,
these results highlight the sensitivity of dynamic covalent assembly to the solubility of both the secondary building unit (SBU) precursors and the desired assemblies themselves.

**Figure 1.7.** Soluble covalent boronic acid-based assemblies a) a boronate ester-based cubeoctahedron with solubilizing ethyl chains (shown in purple), b) soluble boronate ester rectangles with solubilizing hexyloxy chains (purple), c) ferrocene-bridged boroxine cyclophane assemblies, d) soluble calixarene-based cavitands solubilized with peripheral heptyl groups (purple).

The preparation of boronic acid-derived assemblies is further complicated by their often-observed sensitivity to the choice of reaction solvent(s). The choice of appropriate solvent
systems that promote high-yields of desired assemblies from within dynamically exchanging complex mixtures of oligomers and secondary building units often requires combinatorial screening of multiple different solvent mixtures in varying ratios. There is considerable literature precedent for the dynamic assembly of boronate ester materials in hydrophobic solvents such as dichloromethane, chloroform, toluene, and benzene, although boronate ester COFs are typically synthesized under solvothermal conditions in mixtures of mesitylene and dioxane. Some examples of discrete boronic acid-based assemblies have also been prepared in mesitylene:dioxane (1:1), such as the ferrocene-based boroxine cyclophane prepared by Miljanic and coworkers (Figure 1.7b). In regards to the other examples presented in Figure 1.7, the mesoporous cubeoctahedron prepared by Mastalerz and coworkers (Figure 1.7a) was assembled in chloroform. Chloroform was also used by Kobayashi and coworkers (Figure 1.7d) to prepare boronate ester cavitands. Protic solvents such as methanol, ethanol, and water have played varying roles in the synthesis of boronate ester and boroxine anhydride assemblies. The formation of boronate ester rectangles (Figure 1.7b), for example, could not be achieved in pure chloroform though a mixture of chloroform and methanol (10:1) gave the desired rectangles in high yields. Dichtel and Lavigne have demonstrated that the addition of small amounts of methanol can increase the rate of boronate ester assembly and COF formation, likely by catalyzing dynamic exchange of boronic acid and catechol derivatives. Large equivalents of methanol or water, however, have been shown by Kobayashi, Lavigne, and Northrop to promote the disassembly of boronate ester-based assemblies and frameworks. In an interesting counter example to this observation, ferrocene-based boroxine anhydride assemblies (Figure 1.7b) can be soaked in pure ethanol without any disruption of the assembly, however the assemblies hydrolyze within minutes in the presence of water. From these examples alone it is clear that the successful formation of boronic acid-based assemblies, whether discrete (COPs) or infinite (COFs), is significantly influenced by the choice of solvent. A careful balance must be struck between providing sufficient solubility of the starting material SBUs to initiate assembly, adequate reversibility of initial oligomers and kinetic intermediates to allow for error correction, and a robust tolerance of thermodynamically stable product assemblies within the solvent mixture such that they do not revert back to starting materials. Ultimately, the structures and solubilities of both starting materials and products in a
given solvent mixture will determine both what species are present at equilibrium and what analytical methods can be used to investigate them.

Herein we expand upon earlier work in the area of soluble boronate ester rectangles and explore, in greater depth, the roles that starting material and product solubilities play in the synthesis and analysis of discrete boronate ester assemblies. In the current study, we report the synthesis of six variably functionalized, phenanthrene-based bis-catechol derivatives and evidence for their dynamic self-assembly with benzene-1,4-diboronic acid (BDBA) to form shape-persistent boronate ester ovals (Figure 1.8). Insight gained from examining the influence of different solubilizing groups attached to the phenanthrene bis-catechols will contribute more generally to our overall understanding of assembly formation and help pave the way toward a greater variety of discrete, soluble boronate ester assemblies.

**Figure 1.8:** a) Synthesis of soluble covalent organic rectangles from the assembly of benzene diboronic acid (blue) with tricyclic bis-catechols (green) functionalized with hexyloxy chains (purple) for solubility, b) proposed polycyclic aromatic oval analogue (red/blue) to reported rectangle (green/blue), both with solubilizing groups (purple).
1.3.2. Influence of Functionality and Solubility on Stability of Assemblies

In previous investigations of discrete boronate ester rectangles (Figure 1.7b), the solubility of linear bis-catechols was imparted by functionalization of their central phenyl rings with hexyloxy chains. Upon the successful use of these linear bis-catechol SBUs in the self-assembly of discrete boronate ester rectangles it became of interest to explore the scope of the synthetic approach. Phenanthrene-based subunits were chosen for the current study in part because of the increased \( \pi \)-conjugation of their polycyclic aromatic core. The earlier boronate ester rectangle assemblies were found to fluoresce in the violet-blue region of the spectrum (350-460 nm), and the increased conjugation of phenanthrene may enable fluorescence to be shifted further toward longer wavelengths. Furthermore, multiple routes are available for the addition of solubilizing groups at positions 9 and 10 of phenanthrene as well as subsequent functionalization of positions 3 and 6 with catechol derivatives (Scheme 1.5). Three different functionalities were added at positions 9 and 10 in an effort to increase the solubility of both the starting bis-catechol phenanthrene derivatives and their resulting assemblies: hexyloxy substituents (compounds 1.13 and 1.14), which are hydrophobic; diethylene glycol monomethyl ether substituents (DEG-CH\(_3\), compounds 1.15 and 1.16), which are more hydrophilic; and 3,4,5-tri(hexyloxy) benzyl substituents (THB, compounds 1.17 and 1.18), which is a significantly larger solubilizing group with potential for promoting aggregation in solution.\(^1\) The catechol moieties were introduced such that they can be oriented in the same direction and thus the bis-catechols can function as 180° secondary building units analogous to the linear bis-catechols used to prepare boronate ester rectangles. Additionally, the catechol units at positions 3 and 6 of phenanthrene were either directly linked as biaryls (compounds 1.13, 1.15, and 1.17) or linked via an acetylene spacer (compounds 1.14, 1.16, and 1.18). The different linkages result in boronate ester assemblies with larger or smaller shape-persistent cores, thus allowing the relationship between increased or decreased \( \pi \)-surface area and the solubility of resulting assemblies to be investigated. Overall the design is expected to promote a 2x2 condensation of bis-catechols 1.13-1.18 with BDBA (Scheme 1.5).
Scheme 1.5: Synthesis of bis-catechols 1.13-1.18. i) Solubilizing group (3 eq.), K₂CO₃ (10 eq.), 18C6 (cat.), DMF, 80°C, 24h. ii) Compound 1.38 (2.5 eq.), K₃PO₄ (4 eq.), Pd(OAc)₂ (2 mol %), Sphos Buchwald ligand (4 mol %), toluene:water (10:1), 100°C, 24h. iii) Compound 1.41 (3 eq), Pd(PPh₃)₂Cl₂ (0.1 eq), CuI (0.2 eq), triethylamine:THF (1:1), 100°C, 18h. iv) Compound 1.41 (3 eq), Pd(PPh₃)₂Cl₂ (0.1 eq), CuI (0.2 eq), triethylamine:THF (1:1), 100°C, 18h. v) BrC₆H₁₃ (6 eq.), K₂CO₃ (10 eq.), 18C6 (cat.), CH₃CN, 80°C, 24h (61%). vi) LiAlH₄, THF (91%). vii) PPh₃, CBr₄, CH₂Cl₂ (83%).

1.3.2a. Minimally Soluble Assemblies

As shown in Scheme 1.5, hexyloxy chains were introduced first as solubilizing groups, as they had been shown to solubilize related rectangular assemblies. Phenanthrene-based bis-catechol derivatives 1.13-1.16 were found to be poorly soluble in chloroform, as is the bis-boronic acid linker BDBA. The addition of 10% methanol, resulting in a 10:1 mixture of CDCl₃/CD₃OD, aided in the dissolution of both starting materials and promoted their assembly (Scheme 1.6). The formation of boronate ester ovals 1.19 and 1.20 was monitored by ¹H NMR spectroscopy. Preliminary evidence supportive of the formation of hexyloxy-substituted boronate ester oval 1.19 was observed by general symmetry of low intensity spectroscopic signals and the appearance of a new singlet corresponding to the incorporation of BDBA in its ¹H NMR spectrum (in CD₃COCD₃, see Appendix A.I.1.2), however low solubility of assembly 1.19
prevented conclusive analysis based on \(^1\)H NMR spectra alone. Acetylene-conjugated boronate ester oval 1.20, however, displayed no evidence of solubility by \(^1\)H NMR spectroscopy. The formation of DEG-CH\(_3\)-substituted boronate ester oval 1.21 showed more promise as a soluble assembly as compared to its hexyloxy analogue 1.19, however acetylene-conjugated oval 1.22 again showed no spectral resolution due to its lack of solubility. Attempts to obtain NMR spectra in alternative solvents (C\(_6\)D\(_6\), CD\(_3\)CN, CD\(_2\)Cl\(_2\), CD\(_3\)SOCD\(_3\), and C\(_2\)D\(_2\)Cl\(_4\)) gave similar results.

NMR spectroscopic analysis of minimally soluble assemblies 1.19 and 1.21 cannot rule out the alternative formation of symmetric boronate-ester oligomers. Furthermore, NMR analysis of assemblies 1.20 and 1.22 provided essentially no insight into their structure as they were insoluble in every NMR solvent tried. Accurate mass MALDI mass spectrometry was therefore employed to more conclusively establish the molecularity of assemblies 1.19-1.22. The MALDI mass spectra of ovals 1.19 and 1.20 reveals peaks of \(m/z = 1376.6329 \ [M]^+\) (compared to calculated value 1376.6330) and \(m/z = 1448.5331 \ [M]^+\) (compared to calculated value 1448.5297) respectively. Both these values are in agreement with the calculated values, quantitatively supporting the formation of discrete assemblies 1.19 and 1.21. Quantitative mass spectra of acetylene-conjugated boronate ester assemblies 1.20 and 1.22, on the other hand, could not be obtained, likely due to their insolubility.

Infrared (IR) spectroscopy provided more definitive analysis of the chemical structures of boronate ester assemblies 1.19-1.22. IR spectra of all four assemblies and their precursors were obtained and locations of diagnostic peaks are summarized in the Appendix (A.I.3). All four phenanthrene-based bis-catechols displayed broad peaks centered around 3300 cm\(^{-1}\) corresponding catechol O–H stretching modes. These peaks disappear upon assembly with BDBA, indicating the absence of OH functionalities in the resulting assemblies and, by
extension, the complete consumption of both bis-catechol and BDBA starting materials. Evidence specific to boronate ester formation is observed primarily in the fingerprint region of the IR spectra of assemblies 1.19-1.22. Strong bands centered between 658-660 cm\(^{-1}\) were observed for assemblies 1.19-1.22, corresponding to out-of-plane displacements of boron and oxygen atoms specific to boronate ester functionalities. Boroxine anhydrides, by contrast, reveal out-of-plane boron displacements above 700 cm\(^{-1}\). Furthermore, assemblies 1.19-1.22 each displayed sharp B–O and C–O stretching modes between 1050-1070 cm\(^{-1}\) and between 1230-1250 cm\(^{-1}\), respectively. Stretches in these ranges are again diagnostic of boronate ester functionalities.\(^1\)Overall, IR spectroscopic analysis of assemblies 1.19-1.22 is supportive of the conclusion that all starting materials have been consumed (absence of O–H stretching modes) and boronate esters have been formed. No evidence of the formation of boroxine anhydride species could be found, indicating consumption of BDBA occurred through its reaction with starting bis-catechols 1.13-1.16 rather than through self-condensation.

Taken together the collective spectroscopic evidence discussed above is supportive of the formation of boronate ester ovals 1.19-1.22. In particular, MALDI mass spectrometric analysis of assemblies 1.19 and 1.21 indicates that they are discrete boronate ester species. Overall, however, the proposed boronate ester ovals are minimally soluble at best. Neither hexyloxy nor diethylene glycol monomethyl ether substituents are capable of providing sufficient solubility to balance the high \(\pi\)-surface area of the polycyclic aromatic core of each assembly. The assemblies are, however, thermally robust as all four compounds display melting points above 200 °C. Furthermore, boronate ester assemblies 1.19-1.22 display characteristically high extinction coefficients, and therefore UV/Vis and fluorescence spectra of dilute solutions (10\(^{-5}\) M in acetone) of each assembly could be obtained even though the same solutions had proven too dilute for the acquisition of quality \(^1\)H and \(^{13}\)C NMR spectra: assembly 1.19 (\(\lambda_{\text{abs}} = 328\)nm, \(\varepsilon = 2.1\times10^4\) M\(^{-1}\) cm\(^{-1}\)), 1.20 (\(\lambda_{\text{abs}} = 348\)nm, \(\varepsilon = 6.8\times10^4\) M\(^{-1}\) cm\(^{-1}\)), 1.21 (\(\lambda_{\text{abs}} = 327\)nm, \(\varepsilon = 3.5\times10^4\) M\(^{-1}\) cm\(^{-1}\)), and 1.22 (\(\lambda_{\text{abs}} = 348\)nm, \(\varepsilon = 4.3\times10^4\) M\(^{-1}\) cm\(^{-1}\)). All four assemblies showed significant fluorescence, with 1.19 (\(\lambda_{\text{em}} = 413\)nm) and 1.21 (\(\lambda_{\text{em}} = 413\)nm) emitting in the violet region of the spectra, and 1.20 (\(\lambda_{\text{em}} = 474\)nm) and 1.21 (\(\lambda_{\text{em}} = 475\)nm) emitting in the blue range.

Given the significant structural similarity between target boronate ester assemblies 1.19-1.22 and previously reported boronate ester rectangles (Figure 1.7b) it is surprising and interesting to
observe such a dramatic difference in the solubility of this new series of compounds relative to those previously studied. Within this series it appears that the increase in π-surface is the dominant influence limiting the solubility of boronate ester assemblies 1.19-1.22. Each of the target assemblies 1.19-1.22 possess greater π-surface area at their core than the notably more soluble boronate ester rectangles shown in Figure 1.7b. Only assemblies 1.19 and 1.21, i.e. those possessing less overall π-surface area within a smaller shape-persistent core, could be definitively characterized by mass spectrometric analysis as being discrete boronate ester ovals. The larger acetylene-linked assemblies (1.20 and 1.22) with greater π-surface area proved to be too insoluble for definitive characterization by NMR or mass spectrometry. It is of interest to investigate whether functionalization of the phenanthrene moieties of biaryl and acetylene-linked bis-catechols with larger solubilizing groups would be sufficient to overcome the observed insolubility imposed by their relatively large π-surface areas. Therefore, phenanthrene-based bis-catechols 1.17 and 1.18 were synthesized and their assembly with BDBA was investigated.

1.3.2b. Soluble Assemblies

The synthetic route used to prepare phenanthrene bis-catechols 1.13-1.16 (Scheme 1.5) is easily adaptable to allow a wide variety of solubilizing moieties to be incorporated at positions 9 and 10 of their phenanthrene moiety. In an attempt to prepare notably more soluble analogues of boronate ester assemblies 1.19-1.22 a tris(hexyloxy) derivative of gallic acid was introduced. Reaction of 3,6-dibromophenanthrene-9,10-diol (1.26) with 3,4,5-tris(hexyloxy) benzyl bromide (1.48) provided highly functionalized bis-catechols 1.17 and 1.18 following the route used to prepare bis-catechols 1.13-1.16.

Initial attempts to assemble boronate ester ovals 1.23 and 1.24 relied upon the same reaction conditions as were used to prepare assemblies 1.19-1.22, namely stirring an equimolar amount of BDBA and bis-catechol derivative 1.17 or 1.18 at 50 °C in a mixture of CDCl₃ and CD₃OD (10:1). ¹H NMR spectra recorded shortly after mixing (~15 minutes) revealed significantly increased solubility of the species in solution. After 3 hours of mixing the ¹H NMR spectrum remained highly complex, and it was clear that multiple species were present in solution. It is common for initial spectra to reveal multiple species as different oligomers and kinetic intermediates equilibrate toward a final thermodynamically stable product. In the case of target boronate esters 1.23 and 1.24, however, signals in each assemblies’ ¹H NMR spectrum did not
sharpen as a function of time. These results were somewhat surprising given the overall structural similarities boronate ester ovals 1.23 and 1.24 share with assemblies 1.19 and 1.21, which did collapse into a preferred minimum as indicated by MALDI mass spectral analysis.

The primary difference between assemblies 1.19 and 1.21 versus 1.23 and 1.24 is the introduction of hexyloxy-substituted gallic acid derivatives. It was hypothesized that these larger solubilizing groups may have increased the solubility of bis-catechol starting materials 1.17 and 1.18 so significantly that, in a 10:1 mixture of CDCl₃/CD₃OD, the dynamic equilibrium was shifted toward starting materials and small oligomers bearing terminal -OH functionalities (Scheme 1.7a). To investigate this hypothesis further the self-assembly of boronate ester ovals 1.23 and 1.24 was attempted in pure CDCl₃. Returning to purely hydrophobic conditions and forgoing the catalytic methanol proved successful, and provided assemblies 1.23 and 1.24 in good to excellent yields (Scheme 1.7b). The formation of boronate ester ovals 1.23 and 1.24 is supported by key shifts in their ¹H NMR spectra (Figure 1.9). Most notably, catechol –OHₐ and –OHₐ signals, which appear at 6.1 and 5.8 ppm for bis-catechol 1.18,¹ ¹ ³ disappear upon assembly. The disappearance of catechol –OH signals is coincident with the emergence of singlet Hγ at 8.0 ppm, which corresponds to the proton of BDBA in assembly 1.24. Free BDBA and its corresponding anhydride are insoluble in chloroform, therefore appearance of an aromatic boronate ester signal around 8.0 ppm is strongly indicative of the assembly of BDBA with bis-catechol 1.18. Assembly is further supported by 0.6-0.3 ppm downfield shifts of aromatic...
catechol unit peaks. Analogous changes were observed for the formation of boronate ester oval assembly 1.23 (see Appendix A.I.1.2).

The sensitivity of boronate ester ovals 1.23 and 1.24 to protic solvents was further investigated by adding increasing equivalents of CD$_3$OD to a CDCl$_3$ solution of each assembly. The resulting $^1$H NMR spectra became disordered upon the addition of 10 equivalents of CD$_3$OD, and continued to increase in disorder until it had fully reverted to starting materials by 50 equivalents of CD$_3$OD (see Appendix A.I.1.2). This observation is in direct contrast to less soluble boronate ester assemblies 1.19-1.22, which showed no indication of product formation in pure CDCl$_3$ and were stable in 10% CD$_3$OD. For additional comparison, the closely related boronate ester rectangle assemblies (Figure 1.7b) could only be reverted to starting materials by refluxing in a mixture of 1:1 D$_2$O:CD$_3$OD. These observations provided additional evidence that the 3,4,5-tris(hexyloxy)benzyl substituents of bis-catechol derivatives 1.17 and 1.18 both increase the

![Figure 1.9. Partial $^1$H NMR spectra (CDCl$_3$, 300 mHz, 298 K, 0.05M) of phenanthrene bis-catechol 1.18 (a) and oval boronate ester assembly 1.24 (b) indicting diagnostic shifts of protons H$_a$-H$_g$, disappearance of Ar-OH$_{\alpha,\beta}$, and appearance of aryl boronate protons H$_\gamma$.](image-url)
solubility of boronate ester assemblies 1.23 and 1.24 while also decreasing their stability in the presence of protic solvents.

Further support for the formation of boronate ester ovals was obtained by IR spectroscopy. Strong intensity bands were observed at 1225, 1063, 638 cm\(^{-1}\) (oval 1.23) and at 1222, 1050, and 659 cm\(^{-1}\) (oval 1.24). These three IR bands are characteristic to boronate esters and correspond to symmetric C-O stretching, B-O stretching, and out-of-plane displacement of boron and oxygen atoms within the boronate ester C\(_2\)O\(_2\)B ring. These IR results were consistent with the observed results for minimally soluble ovals 1.19-1.22. The UV/VIS and fluorescence results (10\(^{-5}\) M in CHCl\(_3\)) were also found to be comparable with the results obtained for assemblies 1.19-1.22, with high extinction coefficients for assemblies 1.23 (\(\lambda_{\text{abs}} = 332\)nm, \(\varepsilon = 4.2\times10^4\) M\(^{-1}\) cm\(^{-1}\)) and 1.24 (\(\lambda_{\text{abs}} = 353\)nm, \(\varepsilon = 3.7\times10^4\) M\(^{-1}\) cm\(^{-1}\)), and significant blue-range emission for both (1.23, \(\lambda_{\text{em}} = 394\)nm and 1.24, \(\lambda_{\text{em}} = 409\)nm).

As discussed previously, \(^1\)H NMR and IR spectroscopy alone cannot rule out the formation of highly symmetric boronate ester oligomers as opposed to discrete assemblies. Mass spectrometry was used to quantitatively establish the molecularity of boronate ester ovals 1.23 and 1.24. Unfortunately, despite considerable effort, mass spectral analysis of both assemblies by MALDI and electrospray ionization, both considered generally “soft” ionization techniques, revealed only starting materials and fragments. In general, all investigations of assemblies 1.23 and 1.24 have shown that they are significantly more labile than related boronate ester assemblies 1.19-1.22, as well as previously studied boronate ester rectangles. Differential scanning calorimetry (DSC) and melting point analyses of all six boronate ester assemblies reported herein further corroborates this difference between the stability of THB-substituted assemblies 1.23 and 1.24 and the stability of hexyloxy and DEG-CH\(_3\) functionalized assemblies 1.19-1.22. DSC traces of 1.23 revealed sudden decomposition, without a coherent melt, at 195°C. By comparison, the less soluble assemblies 1.19-1.22 were stable well above 200 °C. It is believed that the general lability of highly-functionalized assemblies 1.23 and 1.24 is the primary underlying factor in the difficulty of obtaining mass spectra of the discrete assemblies. It is of course possible that the proposed boronate ester assemblies 1.23 and 1.24 are not in fact discrete and are instead mixtures of various oligomers. Such oligomers would have near identical IR spectra as boronate ester ovals 1.23 and 1.24. However, it is believed that the proposed discrete assemblies 1.23 and 1.24
are the dominant, thermodynamic species in solution given that initial complex mixtures observed by $^1$H NMR spectroscopy collapse to a generally well-defined final structure.

Analysis of THB-functionalized boronate ester assemblies 1.23 and 1.24 indicates that sufficiently large solubilizing groups are able to overcome the general insolubility observed for assemblies 1.19-1.22. Within this series of compounds, however, increased solubility comes at the cost of increased lability in the presence of protic solvents. If the free energy of solvation of starting materials (SBUs) and/or oligomers is comparable to the free energy of forming discrete boronate ester assemblies then such assemblies can be expected to be highly labile or may not form at all. On the other hand, if initial starting materials and oligomers are poorly soluble then there is a thermodynamic benefit to forming discrete, closed boronate ester assemblies. Such discrete assemblies, however, can be expected to be poorly soluble or even insoluble.

The results presented herein suggest that this balance between solubility, assembly formation, and assembly stability can be highly sensitive. This research builds upon recent related work (highlighted in Figure 1.7) where seemingly subtle differences in functionality can dramatically influence the success or failure of obtaining discrete, shape-persistent boronate ester (or boroxine anhydride) assemblies. In order to fully develop the chemistry and applications of discrete boronate ester assemblies it is necessary to obtain a better understanding the many factors that determine (i) whether discrete assemblies will form, (ii) to what extent such assemblies will form, and (iii) under what conditions such assemblies will remain stable. Understanding the roles that functionality, solubility, and stability play in the assembly of discrete boronate ester COPs can be expected to contribute to the optimization of reaction conditions used to synthesize COFs. Without a thorough understanding of the experimental and structural influences that underlie the assembly of discrete boronate ester polygons/polyhedra, and infinite boronate ester COFs, it can be expected that the discovery of new frameworks and the optimization their synthesis will largely be an effort of trial and error. The results presented herein hope to chart some small, yet important, steps toward a better understanding of boronate ester self-assembly with the ultimate goal of more judicious, de novo design and synthesis of new COPs and COFs.
1.4. Conclusions

Soluble, shape-persistent covalent organic polygons functionalized with solubilizing moieties are likely to allow for the design and fabrication of new boronate ester assembled materials such as porous boronate ester mesogens or self-assembled monolayers. Soluble covalent organic polygons may find applications as sensors for halide anions, and the violet-blue emission of boronate ester rectangles and ovals opens possibilities for these and related assemblies to be used as soluble, thermally robust components of OLEDs. The future of this work holds significant promise. The understanding of the roles that functionality, solubility, and stability play in the assembly of discrete boronate ester COPs will be applied to the construction of soluble COF-5 analogues based on triphenylene-derived subunits. Furthermore, we anticipate soluble COPs will play an important role in understanding and optimizing structure–function relationships of related COFs by providing valuable solution phase analysis that cannot otherwise be easily obtained given the insoluble nature of rigid, infinitely periodic frameworks. These advancements will contribute to our understanding of and help pave the way toward a greater variety of discrete, soluble boronate ester assemblies.

1.5. Experimental and Computational Methods

Materials

Chemicals were obtained from commercial sources and used as purchased. Reagent-grade solvents were used as obtained from commercial sources. Anhydrous solvents were dried using an Innovative Technologies SPS-400–5 solvent purification system.

Instrumentation

$^1$H and $^{13}$C NMR spectra were recorded with a Varian Mercury (300 and 75 MHz, respectively) spectrometer using residual solvent as the internal standard. All chemical shifts are quoted using the $\delta$ scale and all coupling constants are expressed in Hertz (Hz). Infrared spectroscopic analysis was performed on a PerkinElmer Spectrum BX FT-IR system. UV/Vis spectroscopy was recorded on a Varian Cary 100 Bio UV-Visible spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q20. The DSC is equipped with an RCS90 cooling system. DSC traces were acquired at rates of 10 °C min$^{-1}$ (heating) and 5 °C
min$^{-1}$ (cooling) in the temperature range of (−50)–100 °C. ESI/APCI and MALDI MS analysis was carried out at the University of California, Riverside, Mass Spectrometry Facility (See Appendix I for all spectral data.)

**Computational Details**

All calculations were performed with the Gaussian09 suite of programs.$^{1,32}$ Prior to geometry optimization, dihedral scans were performed at a low level of theory (HF/3-21G) to approximate the global energy minimum conformation of molecular species containing easily rotating torsion angles. Ground-state geometries were then optimized to full convergence at the B3LYP/6-31G(d) level of theory.$^{1,33}$ Vibrational analyses were carried out at the same level and the resulting frequencies were used to aid in assigning IR absorption bands observed experimentally. Calculated frequencies were scaled by a factor of 0.960.$^{1,36}$

**Compounds from Section 1.2**

**Compound 1.4** was prepared according to literature procedures.$^{1,55}$

**Compound 1.5:** To a solution of 1.4 (977 mg, 3.70 mmol) dissolved in dry dichloromethane (37 mL), boron tribromide (1.1 mL, 11.1 mmol) was added slowly under an inert atmosphere at 0 °C. The reaction mixture was allowed to return slowly to room temperature and stir for 3 hours, at which point the reaction was chilled to 0 °C and quenched with a minimum volume of water. The mixture was concentrated under reduced pressure, and the residue extracted with ethyl acetate (3x50 mL). The combined organic extracts were dried over MgSO$_4$ and concentrated in vacuo to yield solid 3-iodocatechol intermediate (870 mg). This solid was used directly in the following step without further purification. To a solution of 3-iodocatechol intermediate (870 mg, 3.69 mmol), potassium carbonate (2.04 g, 14.8 mmol), potassium iodide (123 mg, 0.738 mmol), in dry acetone (46 mL) was added benzyl bromide (1.1 mL, 9.22 mmol) under an inert atmosphere. The reaction solution was stirred under reflux for 12 hours. The solvent was evaporated under reduced pressure, water (50 mL) added, and the aqueous layer extracted with ethyl acetate (3x50 mL). The combined organic extracts were washed with brine, dried over MgSO$_4$, and concentrated under reduced pressure. The resulting residue was purified via column chromatography using a gradient starting with 9:1 hexanes:dichloromethane and increasing to 4:1 hexanes:dichloromethane, yielding white solid 1.5 (1.01 g, 67%). Mp 62-64 °C; APCI-MS
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(m/z) [M+NH₄]⁺ calculated for C₂₀H₂₁NO₂I, 434.0612; found 434.0615 (ppm error = 0.8); ¹H NMR (CDCl₃, 300 MHz): δ 7.52-7.32 (m, 11H), 6.97 (dd, J = 8.1, 1.5 Hz, 1H), 6.79 (t, J = 8.7 Hz, 1H), 5.12 (s, 2H), 5.04 (s, 2H); ¹³C NMR (CDCl₃, 300 MHz): 152.34, 148.56, 137.23, 136.75, 131.45, 129.01, 128.83, 128.53, 128.34, 128.32, 127.74, 126.24, 115.04, 93.49, 74.82, 71.37 ppm.

**Compound 1.7.** Modified from a literature procedure.¹⁵⁶ To a pressure flask charged with nitrogen was added 1.5 (600 mg, 1.44 mmol), 2-dicyclohexylphosphino-2'-6'-dimethoxybiphenyl (Buchwald S-Phos ligand) (24 mg, 0.058 mmol), and bis(acetonitrile)palladium(II)chloride (3.7 mg, 0.014 mmol). The pressure flask was capped with a septum, evacuated and nitrogen filled three times before dry 1,4-dioxane (1 mL) and dry triethylamine (0.6 mL) were added. Pinacolborane (0.31 mL) was added quickly, and the flask immediately capped. The reaction was allowed to stir at 110 °C until the residue darkened and became thick (3 hours). The reaction mixture was filtered through Celite, eluting with ethyl acetate, and the filtrate concentrated under reduced pressure. The pure product was recrystallized from the reaction residue from dichloromethane/ethanol yielding colorless solid 1.7 (546 mg, 81%). Mp = 83-84 °C; APCI-MS (m/z) [M+Na]⁺ calculated for C₂₆H₂₉BO₄Na, 439.2051; found 439.2054 (ppm error = 0.7); ¹H NMR (CDCl₃, 300 MHz): δ 7.47-7.28 (m, 11H), 7.04-6.96 (m, 2H), 5.05 (s, 2H), 4.98 (s, 2H), 1.26 (s, 12H); ¹³C NMR (CDCl₃, 300 MHz): 154.04, 152.14, 138.39, 137.49, 129.00, 128.70, 128.32, 128.06, 127.90, 127.73, 124.43, 118.52, 83.83, 76.06, 71.49 ppm.

**Compound 1.6.** To a solution of 1.4 (1.0 g, 3.8 mmol) dissolved in dry dichloromethane (30 mL), was added boron tribromide (0.91 mL, 9.5 mmol) slowly under an inert atmosphere at 0 °C. The reaction mixture was allowed to return slowly to room temperature and stir for 3 hours, at which point the reaction was chilled to 0 °C and quenched with a minimum volume of water. The mixture was concentrated under reduced pressure, and the residue extracted with ethyl acetate (3x50 mL). The combined organic extracts were dried over MgSO₄ and concentrated in vacuo to yield solid 3-iodocatechol intermediate (0.9 g). This solid was taken up directly in dry toluene (38 mL). To this reaction solution was added ethyl orthoformate (1.9 mL, 11.4 mmol) and Amberlyst (19 mg, 5mg/mol intermediate), and the reaction mixture stirred at reflux for 12 hours. After cooling to room temperature, the reaction mixture was filtered through Celite.
eluting with ethyl acetate). The filtrate was concentrated in vacuo onto silica, and the residue carried directly to column chromatography, eluting with 4:1 hexanes to dichloromethane to yield clear oil 1.6 (744 mg, 68%). APCI-MS (m/z) [M+H]+ calculated for C_{9}H_{10}O_{3}I, 292.9669; found 292.968 (ppm error = 3.7); ^{1}H NMR (CDCl_{3}, 300 MHz): δ 7.17 (dd, J = 8.4, 1.2 Hz, 1H), 6.91 (s, 1H), 6.82 (dd, J = 7.5, 0.9 Hz, 1H), 6.64 (t, J = 7.8 Hz, 1H), 3.74 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (CDCl_{3}, 300 MHz): 148.00, 145.25, 130.49, 123.58, 118.39, 108.37, 70.73, 59.88, 15.08 ppm.

**Compound 8** was prepared according to a literature procedure.\textsuperscript{1.25}

**Compound 1.9.** To a mixture of 1.8 (170 mg, 0.32 mmol), 1.7 (400 mg, 0.96 mmol), and potassium carbonate (530 mg, 3.84 mmol) was added Buchwald SPhos palladacycle (24 mg, 0.038 mmol) under an inert atmosphere. Degassed solvents toluene (3.2 mL) and water (0.32 mL) were added and the solution stirred at 90°C for 48 hours. The reaction solution was allowed to cool; water (25 mL) was added, and extracted with ethyl acetate (3x25 mL). The combined organic extracts were dried over MgSO_{4} and concentrated under reduced pressure. The crude material was purified through column chromatography using a gradient of 4:1 hexanes:dichloromethane moving to 2:1 hexanes:dichloromethane yielding 244 mg (0.29 mmol, 89%) colorless oil 1.9. APCI-MS (m/z) [M+H]+ calculated for C_{58}H_{63}O_{6}, 855.4619; found 855.4615 (ppm error = -0.5); ^{1}H NMR (CDCl_{3}, 300 MHz): δ 7.50-7.47 (m, 4H), 7.42-7.33 (m, 6H), 7.15-7.00 (m, 18H), 5.18 (s, 4H), 4.93 (s, 4H), 3.73 (t, J = 6.5 Hz, 4H), 1.39 (t, J = 6.9 Hz, 4H), 1.14-1.03 (m, 12H), 0.80 (t, J = 7.1 Hz, 6H); ^{13}C NMR (CDCl_{3}, 300 MHz): 152.40, 150.81, 138.19, 137.48, 134.23, 133.33, 128.75, 128.34, 128.20, 128.10, 127.72, 127.64, 125.63, 124.21, 123.70, 113.96, 74.84, 73.55, 71.28, 31.82, 30.40, 25.75, 22.86, 14.31 ppm.

**Compound 1.10.** To a foil-wrapped 50mL Schlenk flask was added 1.8 (300 mg, 0.566 mmol), trans-dichlorobis(triphenylphosphine)palladium (II) (79 mg, 0.113 mmol), and copper iodide (17 mg, 0.091 mmol) in that order. These solids were dissolved in a 1:1 solution of dry, degassed triethylamine (11 mL) and THF (11 mL), under nitrogen. To the reaction flask was added 0.32 mL (2.26 mmol) of tri-methyl-silylacetylene, and the solution was allowed to stir under nitrogen for 36 hours. The reaction mixture was concentrated under reduced pressure, and water (50 mL) was added. This aqueous layer was extracted with dichloromethane (3x50 mL), and the combined organic extracts washed with brine, dried over MgSO_{4}, and concentrated under
reduced pressure to provide a black oil. The residue was purified by column chromatography with hexanes/dichloromethane (elutes 9:1) to afford 250 mg (0.531 mmol, 94%) of yellow oil 1.10. R_f = 0.27 (9:1 hexanes/CH_2Cl_2); APCI-MS (m/z) [M+Na]^+ calculated for C_{28}H_{46}O_2NaSi_2, 493.2929; found 493.2936 (ppm error = 1.5); ^1^H NMR (CDCl_3, 300 MHz): δ 7.06 (s, 2H), 4.07 (t, J = 6.7 Hz, 4H), 1.78-1.75 (m, 4H), 1.54-1.51 (m, 4H), 1.35-1.32 (m, 8H), 0.90 (t, J = 7.0 Hz, 6H); ^13^C NMR (CDCl_3, 300 MHz): 154.20, 128.13, 119.57, 100.97, 100.27, 74.37, 31.92, 30.51, 25.93, 22.79, 14.26, 0.13 ppm.

**Compound 1.11.** To a solution of 1.10 (208 mg, 0.442 mmol) and potassium fluoride (154 mg, 2.65 mmol) in methanol (4.4 mL) was added ethyl acetate dropwise until the solution became homogenous. The reaction was stirred overnight at room temperature, then acidified with 1N HCl (12 mL). The methanol and ethyl acetate were evaporated in vacuo, and the aqueous mixture extracted with ethyl acetate (3x25 mL). The combined organic extracts were washed with brine, dried over MgSO_4, and concentrated under reduced pressure to yield orange oil 1.11 (416 mg, 95%). APCI-MS (m/z) [M+H]^+ calculated for C_{22}H_{31}O_2, 327.2319; found 327.2333 (ppm error = 4.4); ^1^H NMR (CDCl_3, 300 MHz): δ 7.11 (s, 2H), 4.09 (t, J = 6.6 Hz, 4H), 3.31 (s, 2H), 1.78-1.75 (m, 4H), 1.54-1.51 (m, 4H), 1.35-1.32 (m, 8H), 0.90 (t, J = 6.9 Hz, 6H); ^13^C NMR (CDCl_3, 300 MHz): 154.52, 128.42, 119.00, 82.80, 79.75, 74.52, 31.87, 30.42, 25.89, 22.87, 14.29 ppm.

**Compound 1.12.** To a foil-wrapped 50mL Schlenk flask was added 1.11 (150 mg, 0.459 mmol), 1.6 (470 mg, 1.61 mmol), trans-dichlorobis(triphenylphosphine)palladium (II) (64 mg, 0.092 mmol), and copper iodide (14 mg, 0.073 mmol) in that order. These solids were dissolved in a 1:1 solution of dry, degassed triethylamine (9.2 mL) and THF (9.2 mL), under nitrogen, and the reaction allowed to stir for 48 hours. The reaction mixture was concentrated under reduced pressure, and water (25 mL) was added. The aqueous layer was extracted with dichloromethane (3x25 mL), and the combined organic extracts washed with brine, dried over MgSO_4, and concentrated under reduced pressure onto silica. The residue was immediately subjected to column chromatography, eluting with 24:1 hexanes:ethyl acetate to yield bright yellow solid 1.12 (280 mg, 93%). Mp = 89-90°C; LIFDI-MS (m/z) [M]^+ calculated for C_{40}H_{46}O_8, 654.3187; found 654.3214 (ppm error = 4.1); ^1^H NMR (CDCl_3, 300 MHz): δ 7.21 (s, 2H), 7.02-7.00 (m, 2H), 6.94 (s, 2H), 6.87-6.83 (m, 4H), 4.17 (t, J = 6.9 Hz, 4H), 3.76 (q, J = 6.9 Hz, 4H), 1.87-1.80 (m, 4H),...
1.54-1.51 (m, 4H), 1.35-1.32 (m, 8H), 0.90 (t, \( J = 7.0 \) Hz, 6H); \(^{13}\)C NMR (CDCl\(_3\), 300 MHz):
153.94, 147.12, 146.24, 127.98, 125.05, 121.73, 119.51, 108.71, 104.99, 90.12, 88.88, 74.64, 59.51, 31.99, 30.57, 26.05, 22.88, 15.02, 14.29 ppm.

**Compound 1.1.** To a Parr flask was added 1.9 (240 mg, 0.28 mmol), tetrahydrofuran (5 mL), and 10% palladium on carbon (50 mg). The flask was placed on a Parr reactor and shaken for 4 hours under 45 psi hydrogen gas. The reaction residue was filtered through a pad of Celite, eluting with ethyl acetate, and the filtrate concentrated under reduced pressure. The reaction residue was subjected to column chromatography, eluting with dichloromethane to yield yellow oil 1.1 (111 mg, 80%). APCI-MS (m/z) [M+H]\(^+\) calculated for C\(_{30}\)H\(_{39}\)O\(_6\), 495.2741; found 495.2732 (ppm error = -0.9); IR (powder, ATR) 3272.00, 2928.20, 1592.15, 1462.31, 1374.87, 1203.52, 1129.69, 1005.21, 770.03, 729.53 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta \) 7.61 (s, 2H), 7.33 (s, 2H), 7.01-6.89 (m, 6H), 6.01 (s, 2H), 3.93 (t, \( J = 6.0 \) Hz, 4H), 1.66-1.58 (m, 4H), 1.34-1.15 (m, 12H), 0.87 (t, \( J = 6.0, \) 6H); \(^{13}\)C NMR (CDCl\(_3\), 300 MHz): 148.30, 147.17, 140.57, 132.98, 128.48, 126.34, 122.40, 121.84, 114.75, 76.39, 31.60, 30.05, 25.62, 22.72, 14.12 ppm.

**Compound 1.2.** To a solution of 1.12 (130 mg, 0.199 mmol) in tetrahydrofuran (9.5 mL) was added concentrated HCl (0.5 mL) and allowed to stir overnight. Water (10 mL) was added, and the tetrahydrofuran evaporated under reduced pressure. The aqueous mixture was extracted with ethyl acetate (3x25 mL), and the combined organic extracts washed with brine, dried over MgSO\(_4\), and concentrated under reduced pressure. The resulting residue was subjected with column chromatography using a gradient starting with dichloromethane and increasing to 5% methanol in dichloromethane, yielding bright yellow solid 1.2 (55 mg, 51%). Mp = 89-90 \(^\circ\)C; APCI-MS (m/z) [M+H]\(^+\) calculated for C\(_{34}\)H\(_{39}\)O\(_6\), 543.2741; found 543.276 (ppm error = 3.5); IR (powder, ATR) 3310.81, 2926.60, 1617.17, 1581.61, 1465.64, 1438.01, 1374.96, 1332.25, 1226.08, 1065.31, 1008.93, 816.15, 776.00 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 300 MHz): \( \delta \) 7.22 (s, 2H), 6.92-6.88 (m, 4H), 6.76 (t, \( J = 9.0, \) 2H), 6.23 (s, 2H), 5.32 (s, 2H), 4.12 (t, \( J = 6.0 \) Hz, 4H), 1.80-1.69 (m, 4H), 1.42-1.33 (m, 4H), 1.27-1.16 (m, 8H), 0.79 (t, \( J = 9.0 \) Hz, 6H); \(^{13}\)C NMR; Solubility precluded collection of a \(^{13}\)C spectrum in CDCl\(_3\); (CDCl\(_3\):MeOD (10:1), 300 MHz):
152.88, 144.74, 127.98, 123.52, 120.36, 119.46, 116.36, 110.59, 90.83, 90.26, 74.94, 31.79, 30.30, 25.94, 22.72, 14.07 ppm.
**Compound 1.3.** To a solution of 1.1 (40.9 mg, 0.083 mmol) and 1,4-benzenediboronic acid (13.7 mg, 0.083 mmol) in deuterated chloroform (8.3 mL) was added deuterated methanol (0.83 mL), and the solution allowed to stir at 50 °C for 3 hours. The reaction solution was allowed to cool slowly to room temperature and 4Å molecular sieves added. The solution was allowed to stir over sieves overnight, and the resulting cloudy solution decanted and concentrated under reduced pressure, yielding 90 mg (0.076mmol, 93%) grey solid 1.3. Mp = ( >200°C); MALDI (m/z) [M+Na]⁺ calculated for C₇₂H₇₆B₄O₁₂Na, 1199.5601; found 1199.565 (ppm error = 4.1); IR (powder, ATR) 2927.80, 1521.06, 1364.98, 1325.50, 1246.59, 1198.83, 1145.13, 1083.55, 1018.85, 779.57, 738.10, 659.75 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.25 (s, 8H), 7.41-7.16 (m, 16H), 3.97 (t, J = 6.0 Hz, 8H), 1.53-1.44 (m, 8H), 1.35-1.27 (m, 8H), 1.17-1.04 (m, 16H), 0.76 (t, J = 6.0 Hz, 12H); ¹³C NMR; Solubility precluded collection of a ¹³C spectrum in CDCl₃; (CDCl₃:MeOD (10:1), 300 MHz): 150.32, 148.68, 146.66, 140.83, 132.89, 128.04, 126.39, 121.93, 114.80, 75.89, 31.57, 30.01, 25.55, 22.65, 14.09 ppm.

**Compound 1.4.** To a solution of 1.2 (11.8 mg, 0.022 mmol) and 1,4-benzenediboronic acid (3.6 mg, 0.022 mmol) in deuterated chloroform (2.2 mL) was added deuterated methanol (0.22 mL), and the solution allowed to stir at 50 °C overnight. The reaction solution was allowed to cool slowly to room temperature and 4Å molecular sieves added. The solution was allowed to stir over sieves overnight, and the resulting solution decanted and concentrated under reduced pressure, yielding 13.2 mg (0.011mmol, 98%) grey solid 1.4. Mp = ( >200°C); IR (powder, ATR) 2926.32, 1627.59, 1521.72, 1437.45, 1368.13, 1333.21, 1249.99, 1141.49, 1019.44, 849.52, 732.30, 656.2 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.31 (s, 8H), 7.39-7.31 (m, 12H), 7.16 (t, J = 9.0 Hz, 4H), 4.33 (t, J = 6.0 Hz, 8H), 2.02-1.92 (m, 8H), 1.64-1.25 (m, 24H), 0.85 (t, J = 6.0 Hz, 12H); Solubility precluded collection of a ¹³C spectrum in CDCl₃; ¹³C NMR (CDCl₃:MeOD (10:1), 300 MHz): 152.87, 144.74, 132.62, 127.98, 123.51, 120.51, 119.47, 116.35, 110.14, 90.82, 90.28, 74.95, 31.79, 30.30, 25.83, 22.72, 14.07 ppm.

**Compounds from Section 1.3**

**Compound 1.43.** To a mixture of 1.26 (313 mg, 0.85 mmol), 2-(2-methoxy-ethoxy)-ethyl-toluenesulphonate (700 mg, 2.55 mmol), potassium carbonate (705 mg, 5.10 mmol), 18-crown-6 (catalytic), and lithium bromide (catalytic) under an inert atmosphere was added a minimum amount of dry dimethylformamide (~3 mL). The reaction solution was stirred at 80°C overnight.
and allowed to cool and poured over water (15 mL). The organic material was extracted (3x) with ethyl acetate, and the combined organic layers washed twice with water, dried over MgSO₄, and concentrated under reduced pressure. The crude oily product was purified by flash chromatography, eluting with 3:1 hexanes:ethyl acetate, affording a pale yellow oil that gradually solidified as pure product **1.43** (410 mg, 88% yield). Mp = 55.7-56.6°C. APCI-MS (m/z) [M+H]⁺ calculated for C₂₄H₂₉O₆Br₂, 571.0325; found 571.0334 (ppm error = 1.5). ¹H NMR (CDCl₃, 300 MHz): δ 8.65 (s, 2H), 8.26 (d, J = 9.4 Hz, 2H), 7.71 (d, J = 11.4 Hz, 2H), 4.43-4.39 (m, 4H), 3.88-3.84 (m, 4H), 3.72-3.69 (m, 4H), 3.61-3.58 (m, 4H), 3.42 (s, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 142.9, 130.5, 128.9, 128.5, 125.2, 124.7, 120.5, 72.4, 72.0, 70.5, 70.4, 59.1 ppm.

**Compound 1.44.** To a mixture of **1.26** (135 mg, 0.368 mmol), potassium carbonate (510 mg, 3.86 mmol), and catalytic 18-crown-6 was added dimethylformamide (2.6 mL) under nitrogen. The mixture was allowed to stir for 5 minutes. To the stirring mixture was added **1.48** (517 mg, 1.10 mmol) dissolved in dimethylformamide (1 mL). The reaction was allowed to stir at 80°C under nitrogen for 24 hours. The suspension was allowed to cool, and water was added (20 mL). The crude product was extracted with hexanes (3x20 mL) and washed with water (20 mL) and brine (50 mL). The combined organic layers were dried over MgSO₄ and the solvent removed under reduced pressure. The crude material was purified via column chromatography, eluting with 1:1 hexanes:dichloromethane, affording the pure product as yellow solid (261 mg, 62%). Mp = 73-75°C. ESI/APCI (m/z) [MNH₄⁺] calculated for C₆₄H₉₆NO₈Br₂, 1164.5497; found 1164.5459. ¹H NMR (CDCl₃, 300 MHz): δ 8.65 (s, 2H), 8.06 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 9.7 Hz, 2H), 6.6.4 (s, 4H), 5.20 (s, 4H), 3.94 (t, J = 6.0 Hz, 4H), 3.88 (t, J = 6.7 Hz, 8H), 1.79-1.70 (m, 12H), 1.51-1.40 (m, 12H), 1.38-1.29 (m, 24H), 0.92 (t, J = 6.3 Hz, 18H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 153.2, 143.1, 138.2, 131.9, 130.4, 128.8, 128.5, 125.3, 120.6, 106.8, 75.8, 73.4, 69.1, 31.7, 31.5, 30.2, 25.7, 22.6, 14.0 ppm.

**Compound 1.27.** To a mixture of **1.42** (404 mg, 0.712 mmol), **1.38** (1.00 g, 2.15 mmol), Buchwald SPhos Palladacycle (19.0 mg, 0.028 mmol), and potassium carbonate (393 mg, 2.85 mmol) was added a degassed 10:1 toluene:water mixture (2.8 mL:0.28 mL) under an inert atmosphere. The reaction was stirred at 90°C for 48 hours, at which point it was allowed to cool and water (10 mL) was added. The product was extracted with ethyl acetate (3x) and the
combined organic layers washed with brine, dried over MgSO₄, and the solvents removed under reduced pressure. The crude product was purified by column chromatography, eluting with 10:1 hexanes:dichloromethane, and the pure product isolated as an white solid (753 mg, 99% yield). (Note: 1.27 has also been isolated using the same reaction conditions as 1.29, with a lower yield [~50%].) Mp = 104.9-105.7°C. ¹H NMR (CDCl₃, 300 MHz): δ 8.81 (s, 2H), 8.27 (d, J = 8.5 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.31-7.23 (m, 4H), 6.97 (d, J = 7.6 Hz, 2H), 4.24 (t, J = 12 Hz, 4H), 1.99-1.89 (m, 4H), 1.64-1.57 (m, 4H), 1.44-1.39 (8H), 1.05 (s, 18H), 1.04 (s, 18H), 0.95 (t, J = 6.0 Hz, 6H), 0.29 (s, 12H), 0.27 (s, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 147.1, 146.6, 143.1, 138.1, 134.8, 128.8, 128.6, 125.8, 122.8, 121.4, 120.4, 120.3, 73.7, 31.7, 30.5, 25.9, 22.7, 18.6, 14.1, -4.0 ppm.

**Compound 1.29.** This procedure was modified from an existing a literature procedure. To a small pressure flask charged with nitrogen was added 1.43 (365 mg, 0.638 mmol), 1.38 (889 mg, 1.91 mmol), potassium phosphate (542 mg, 2.55 mmol), SPhos Buchwald biaryl phosphine ligand (10.5 mg, 0.026 mmol), and palladium acetate (8.6 mg, 0.013 mmol) in that order. The flask was evacuated and backfilled with nitrogen immediately. The reagents were then dissolved in a degassed 10:1 toluene:water mixture (1.3 mL:0.13 mL), and the flask quickly sealed. The reaction was stirred at 100°C overnight, allowed to cool, and diluted with ether. The black reaction mixture was filtered through a pad of Celite, and the filtrate concentrated under reduced pressure. The crude product was purified by column chromatography, eluting with 12:1 dichloromethane:ethyl acetate, to afford pure 1.27 as a pale yellow solid (623 mg, 90% yield). Mp = 89.4-92.3°C. (APCI-MS (m/z) [M+Na]⁺ calculated for C₆₀H₉₄O₁₀NaSi₄, 1109.5816; found 1109.5851 (ppm error = 3.1). ¹H NMR (CDCl₃, 300 MHz): δ 8.80 (s, 2H), 8.32 (d, J = 8.5 Hz, 2H), 7.73 (dd, J = 8.5, 1.5 Hz, 2H), 7.43-7.09 (m, 8H), 6.83 (d, J = 8.2 Hz, 2H), 4.46-4.43 (m, 4H), 3.90-3.87 (m, 4H), 3.74-3.71 (m, 4H), 3.63-3.60 (m, 4H), 3.43 (s, 6H), 1.03 (s, 18H), 1.01 (s, 18H), 0.27 (s, 12H), 0.24 (s, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 147.1, 146.7, 142.8, 138.3, 134.8, 132.1, 129.5, 128.9, 128.4, 125.8, 123.5, 123.2, 121.4, 120.4, 120.3, 72.4, 72.1, 70.6, 59.1, 26.1, 18.6, -4.0 ppm.

**Compound 1.31.** To a heavy walled pressure vessel was added 1.44 (230 mg, 0.200 mmol), 1.38 (232 mg, 0.500 mmol), and potassium phosphate (170 mg, 0.800 mmol). The flask was flushed with nitrogen, and palladium (II) acetate (3.0 mg, 0.004 mmol) and SPhos Buchwald ligand (3.3
mg, 0.008 mmol) were added. The flask was purged and backfilled with nitrogen (3x), and degassed toluene (0.40 mL) and water (0.04 mL) were added. The flask was sealed and stirred at 100°C overnight. The reaction suspension was allowed to cool and filtered over Celite, eluting with dichloromethane. The filtrate was concentrated under reduced pressure and purified via column chromatography, eluting with pure dichloromethane, affording **1.31** as a yellow solid (157 mg, 47%). Mp = 55-57°C. ESI/APCI (m/z) [MNa]+ calculated for C₁₀₀H₁₅₈O₁₂NaSi₄, 1686.0723; found 1686.0682. **¹H NMR** (CDCl₃, 300 MHz): δ 8.83 (s, 2H), 8.28 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.27-7.22 (m, 4H), 6.97 (d, J = 7.9 Hz, 2H), 7.75 (s, 4H), 5.5 (s, 4H), 3.99-3.91 (m, 12H), 1.82-1.71 (m, 12), 1.54-1.41 (m, 12H), 1.39-1.27 (m, 24H), 1.06 (s, 18H), 1.05 (s, 18H), 0.95-0.86 (m, 18H), 0.29 (s, 12H), 0.28 (s, 12H) ppm. **¹³C NMR** (CDCl₃, 75 MHz): 153.2, 147.2, 146.7, 143.1, 138.4, 138.0, 134.7, 132.5, 129.0, 128.3, 125.8, 123.0, 121.4, 120.4, 120.3, 106.6, 75.8, 73.4, 69.1, 31.8, 31.6, 30.3, 29.4, 26.0, 25.8, 22.6, 18.5, 14.0, -4.0 ppm.

**General Procedure for preparing TBDMS-protected, ethynyl-spaced, substituted phenanthrenes:** To a nitrogen-charged Schlenck flask was added 3,6-dibromo-9,10-bis(substituted)phenanthrene (1 equivalent), **12** (3 equivalents), and triphenylphosphine (0.2 equivalents). To the mixture was added trans-dichlorobis(triphenylphosphine)palladium (0.1 equivalent), and copper iodide (0.2 equivalents) in that order. The flask was evacuated and purged with nitrogen immediately, and darkened. To the reaction flask was added dry, degassed piperidine and tetrahydrofuran (0.27M and 0.125M with respect to phenanthrene), and the reaction stirred over ~65 hours, at which point water was added, and the product extracted with an organic solvent. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography.

**Compound 1.28.** The crude product was extracted with dichloromethane, and eluted from the column in 10% dichloromethane in hexanes. Reaction scale: **1.42** (177mg, 0.331 mmol), yield 160 mg (0.145 mmol, 44%). The product was isolated as a yellow oil. **¹H NMR** (CDCl₃, 300 MHz): δ 8.80 (s, 2H), 8.19 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.13-7.08 (m, 4H), 6.83 (d, J = 8.2 Hz, 2H), 4.22 (t, J = 7.3 Hz, 4H), 1.96-1.87 (m, 4H), 1.63-1.58 (m, 4H), 1.43-1.36 (m, 8H), 1.03 (s, 18H), 1.01 (s, 18H), 0.94 (t, J = 7.3 Hz, 6H), 0.27 (s, 12H), 0.24 (s, 12H) ppm. **¹³C
NMR (CDCl₃, 75 MHz): 148.0, 146.8, 143.7, 129.8, 129.2, 127.9, 126.0, 125.6, 124.2, 122.4, 121.1, 120.9, 116.1, 90.2, 88.4, 73.8, 31.7, 30.4, 25.9, 22.7, 18.5, 14.1, -4.0 ppm.

**Compound 1.30.** The crude product was extracted with ethyl acetate, and eluted from the column in 5% ethyl acetate in dichloromethane. Reaction Scale: 1.43 (1.4 g, 2.45 mmol), yield 695 mg (0.612 mmol, 25%). The product was isolated as a dark oil. ¹H NMR (CDCl₃, 300 MHz): δ 8.80 (s, 2H), 8.82 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.13-7.08 (m, 4H), 6.84 (d, J = 8.2 Hz, 2H), 4.46-4.43 (m, 4H), 3.90-3.86 (m, 4H), 3.74-3.71 (m, 4H), 3.63-3.60 (m, 4H), 3.43 (s, 6H), 1.03 (s, 18H), 1.01 (s, 18H), 0.27 (s, 12H), 0.24 (s, 12H) ppm. Solubility precluded collection of a well-resolved ¹³C NMR spectrum.

**Compound 1.32.** To a heavy-walled pressure vessel was added 1.44 (120 mg, 0.104 mmol) and 1.41 (114 mg, 0.313 mmol). The vessel was flushed with nitrogen and bis(triphenylphosphine)palladium (II) dichloride (7.3 mg, 0.010 mmol) and copper iodide (4.0 mg, 0.021 mmol) were added. The flask was purged and backfilled with nitrogen (3x). Dry, degassed tetrahydrofuran (0.9 mL) and triethylamine (0.9 mL) were added and the flask sealed and darkened. The reaction was allowed to stir at 60°C for 48 hours. After cooling to room temperature, the residue was filtered over Celite, eluting with dichloromethane. The filtrate was concentrated under reduced pressure, and the crude material purified by column chromatography, eluting with 1:1 hexanes:dichloromethane, affording pure 1.32 as a yellow semisolid (93 mg, 52%). ESI/APCI (m/z) [M+Na]⁺ calculated for C₁₀₄H₁₅₈O₁₂NaSi₄, 1734.0723; found 1734.0746. ¹H NMR (CDCl₃, 300 MHz): δ 8.81 (s, 2H), 8.17 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.16-7.08 (m, 4H), 6.84 (d, J = 8.2 Hz, 2H), 6.69 (s, 4H), 5.23 (s, 4H), 3.99-3.87 (m, 12H), 1.80-1.74 (m, 12H), 1.54-1.42 (m, 12H), 1.36-1.30 (m, 24H), 1.04 (s, 18H), 1.01 (s, 18H), 0.93-0.89 (m, 18H), 0.27 (s, 12H), 0.25 (s, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 153.2, 148.0, 146.8, 138.2, 132.2, 129.8, 129.0, 128.1, 126.0, 125.6, 124.2, 122.6, 121.3, 121.1, 116.0, 106.9, 90.4, 88.3, 75.8, 73.4, 69.1, 31.8, 31.6, 30.3, 29.3, 26.0, 25.8, 22.6, 14.0, -4.1 ppm.

**General Procedure for the Deprotection of TBDMS groups to afford Phenanthrene Tetraols:** To a solution of protected phenanthrene monomer dissolved in dry dimethylformamide (0.1 M with respect to phenanthrene) was added potassium fluoride (8 equivalents), followed by concentrated hydrobromic acid (0.6 equivalents). The reaction was monitored by TLC and stirred overnight, at which point 2M HCl was added (excess), and the product extracted with an
organic solvent. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography. Note: yield not optimized for expanded phenanthrene deprotections.

**Compound 1.13.** To quench the reaction, 20 mL 2M HCl was added, and the crude product was extracted with diethyl ether. The pure product eluted from the column with 100% ethyl acetate. Reaction Scale: **1.27** (570 mg, 0.542 mmol), yield 274 mg (0.461 mmol, 85%). The product was isolated as a lavender solid. Mp = 154.6-147.5°C. APCI-MS (m/z) [M]+ calculated for C₃₈H₄₂O₆, 594.2976; found 594.2995 (ppm error = 3.2). ¹H NMR (DMSO-d₆, 300 MHz): δ 9.01 (s, 2H), 8.28 (d, J = 8.8 Hz, 2H), 8.08 (s, 2H), 8.04 (s, 2H), 7.88 (dd, J = 8.8, 1.8 Hz, 2H), 7.40 (d, J = 2.4 Hz, 2H), 7.37 (dd, J = 8.2, 2.4 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 4.26 (t, J = 6.4 Hz, 4H), 2.00-1.91 (m, 4H), 1.69-1.59 (m, 4H), 1.47-1.36 (m, 8H), 0.94 (t, J = 7.3 Hz, 6H) ppm. Solubility precluded collection of a well-resolved ¹³C NMR spectrum.

**Compound 1.14.** Instead of pure dimethylformamide, the solvent used for this reaction was a 2:1 solution of tetrahydrofuran:dimethylformamide. To quench the reaction, 10 mL 2M HCl was added, and the crude product was extracted with diethyl ether. The pure product eluted from the column with 1:1 hexanes:ethyl acetate. Reaction Scale: **1.28** (158 mg, 0.144 mmol), yield 50 mg (0.078 mmol, 54%). The product was isolated as a purple solid. Mp = 131.7-132.3°C (note, the dark, oily nature of this material makes observing the melting point difficult). ¹H NMR (DMSO-d₆, 300 MHz): δ 8.94 (s, 2H), 8.31 (s, 4H), 8.24 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 1.8 Hz, 2H), 7.04 (dd, J = 8.2 Hz, 1.8 Hz, 2H), 6.88 (d, J = 7.9 Hz, 2H), 4.23 (t, J = 6.6 Hz, 4H), 1.97-1.88 (m, 4H), 1.65-1.55 (m, 4H), 1.43-1.38 (m, 8H), 0.92 (t, J = 6.9 Hz, 6H) ppm. Solubility precluded collection of a well-resolved ¹³C NMR spectrum.

**Compound 1.15.** To quench the reaction, 20mL 2M HCl was added, and the crude product was extracted with ethyl acetate. The pure product eluted from the column with 100% ethyl acetate. Reaction Scale: **1.29** (620 mg, 0.570 mmol), yield 161 mg (0.255 mmol, 45%). Product was isolated as dark red oil. APCI-MS (m/z) [M+Na]+ calculated for C₃₆H₃₈O₁₀Na, 653.2357; found 653.2346 (ppm error = -1.7). ¹H NMR (DMSO-d₆, 300 MHz): δ 9.01 (s, 2H), 8.45 (d, J = 8.8 Hz, 2H), 8.10 (s, 2H), 8.05 (s, 2H), 7.88 (dd, J = 8.5, 1.5, 2H), 7.40 (d, J = 2.1 Hz, 2H), 7.29 (dd, J = 8.2, 2.1 Hz, 2H), 6.99 (d, J = 8.2 Hz, 2H), 4.46-4.43 (m, 4H), 3.92-3.89 (m, 4H), 3.72-3.69
(m, 4H), 3.59-3.56 (m, 4H), 3.35 (s, 6H) ppm. Solubility precluded collection of a well-resolved $^{13}$C NMR spectrum.

**Compound 1.16.** To quench the reaction, 30 mL 2M HCl was added, and the crude product was extracted with dichloromethane. The pure product eluted from the column with 1:1 acetone:hexanes. Reaction Scale: **1.30** (690 mg, 0.608 mmol), isolated yield 33 mg (0.049 mmol, 12%). The product was isolated as a dark solid. Mp = 93.7-94.0°C (note, the dark, oily nature of this material makes observing the melting point difficult). $^1$H NMR (CO(CD$_3$)$_2$, 300 MHz): δ 8.92 (s, 2H), 8.40 (d, $J$ = 8.5 Hz, 2H), 8.31 (s, 4H), 7.72 (d, $J$ = 8.5 Hz, 2H), 7.10 (d, $J$ = 1.8 Hz, 2H), 7.02 (dd, $J$ = 8.2 Hz, 1.9 Hz, 2H), 6.86 (d, $J$ = 7.9 Hz, 2H), 4.43-4.40 (m, 4H), 3.86-3.84 (m, 4H), 3.67-3.64 (m, 4H), 3.54-3.51 (m, 4H), 3.31 (s, 6H) ppm. Solubility precluded collection of a well-resolved $^{13}$C NMR spectrum.

*For tetra-ols and assemblies 1.17, 1.18, 1.23, and 1.24, in spite of the increased solubility, carbon spectra were omitted due to poor spectral resolution.*

**Compound 1.17.** To **1.31** (153 mg, 0.092 mmol) was added an excess of tetraethylene-glycol (1.4 g, 7.36 mmol). Tetrahydrofuran was slowly added, with stirring, until reaction became homogenous (~2mL). Potassium fluoride (43 mg, 0.735 mmol) was added, provoking an immediate color change from yellow to dark green. The reaction was monitored by thin layer chromatography, and was complete within 30 minutes. Water was added (30 mL), and the product extracted with diethylether (3x20 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL). The combined aqueous layers were back extracted with diethylether (1x20 mL), and the combined organic layers dried over MgSO$_4$ and concentrated under reduced pressure. The residue was purified by column chromatography, eluting with 25% diethylether in dichloromethane, affording pure product **1.16** as a dark yellow solid (89 mg, 80%). Decomposition: 125-135°C. ESI/APCI (m/z) [MNa]$^+$ calculated for C$_{78}$H$_{102}$O$_{12}$Na, 1229.7264; found 1229.7233. $^1$H NMR (CDCl$_3$, 300 MHz, 0.05M, variable based on concentration): δ 8.40 (s, 2H), 8.20 (d, $J$ = 8.5 Hz, 2H), 7.60 (d, $J$ = 8.1 Hz, 2H), 7.12-6.86 (m, 6H), 6.71 (2H), 6.51 (s, 4H), 5.50 (2H), 4.47 (s, 4H), 4.04 (t, $J$ = 6.6 Hz, 4H), 3.79 (t, $J$ = 6.4 Hz, 8H), 1.86-1.78 (m, 12H), 1.74-1.66 (m, 12H), 1.41-1.26 (m, 24H), 0.91 (t, $J$ = 6.7 Hz, 18H) ppm. (CO(CD$_3$)$_2$, 300 MHz): δ 9.01 (s, 2H), 8.29 (d, $J$ = 8.5 Hz, 2H), 8.06 (s, 4H), 7.85 (d, $J$ = 8.5 Hz, 2H), 7.39 (s, 2H), 7.26 (dd, $J$ = 7.9, 2.2 Hz, 2H), 7.0 (d, $J$ = 7.9 Hz, 2H), 6.83 (s, 4H), 5.27 (s,
4H), 3.94-3.88 (m, 12H), 1.77-1.66 (m, 12H), 1.56-1.40 (m, 12H), 1.39-1.27 (m, 24H), 0.89 (t, \( J = 6.5 \) Hz, 18H) ppm.

**Compound 1.18.** To 1.32 (130 mg, 0.076 mmol) was added an excess of tetraethylene-glycol (1.2 g, 6.07 mmol). Tetrahydrofuran was slowly added, with stirring, until reaction became homogenous (~1mL). Potassium fluoride (35 mg, 0.607 mmol) was added, provoking an immediate color change from yellow to red. The reaction was monitored by thin layer chromatography, and was complete within 3 hours. Water was added (30 mL), and the product extracted with ethyl acetate (6x10 mL). The combined organic layers were washed with water (30 mL) and brine (30 mL). The combined aqueous layers were back extracted with ethyl acetate (1x20 mL), and the combined organic layers dried over MgSO\(_4\) and concentrated under reduced pressure. The residue was purified by column chromatography, eluting with 10% diethylether in dichloromethane, affording pure product 1.17 as a dark yellow solid (41 mg, 43%).

Decomposition: XX°C. ESI/APCI (m/z) \([\text{MNa}]^+\) calculated for \(C_{78}H_{102}O_{12}\Na\), 1229.7264; found 1229.7233. ¹H NMR (CDCl\(_3\), 300 MHz, 0.05M): \( \delta \) 8.59 (s, 2H), 8.05 (d, \( J = 8.5 \) Hz, 2H), 7.56 (d, \( J = 7.9 \) Hz, 2H), 7.08-6.84 (m, 6H), 6.73 (s, 4H), 6.11 (s, 2H), 5.78 (s, 2H), 5.15 (s, 4H), 3.99 (t, \( J = 5.6 \) Hz, 4H), 3.90 (t, \( J = 6.4 \) Hz, 8H), 1.80-1.70 (m, 12H), 1.53-1.49 (m, 12H), 1.37-1.26 (m, 24H), 0.90 (t, \( J = 5.9 \) Hz, 18H) ppm.

General procedure for the self-assembly of ovals 1.19-1.22: To a mixture of organic tetra-ol (1 equivalent) and 1,4-benzenediboronic acid (1 equivalent) was added 10:1 chloroform:methanol (chloroform 0.01 M with respect to reagents). The reaction solution was stirred at 50°C for 3 hours at which point 4Å molecular sieves were added, and the reaction stirred overnight at room temperature. The reaction mixture was dried over MgSO\(_4\), filtered (rinsing with acetone), and the solvents removed via rotary evaporation. The solid residue was subjected to high vacuum at 90°C for 1 hour to afford solvent free assemblies.

**Assembly 1.19.** Reaction Scale: 1.27 (17.0 mg, 0.029 mmol), yield 18.8 mg (95%). The product was isolated as a grey solid. Mp = >200°C. MALDI (m/z) \([\text{M}]^+\) calculated for \(C_{88}H_{84}\text{B}_4\text{O}_{12}\), 1376.6330; found 1376.6329 (ppm error = 0.0). Solubility precluded collection of NMR spectra.
**Assembly 1.20.** Reaction Scale: **1.28** (21.0 mg, 0.033 mmol), yield 23.4 mg (97%). The product was isolated as a black solid. Mp = >200⁰C. Solubility precluded collection of NMR or mass spectral data.

**Assembly 1.21.** Reaction Scale: **1.29** (32.1 mg, 0.052 mmol), yield 26.5 mg (72%). The product was isolated as a lavender solid. Mp = >200⁰C. MALDI (m/z) [M]^+ calculated for C₈₄H₇₆B₄O₂₀, 1448.5297; found 1448.5331 (ppm error = 2.4). Solubility precluded collection of NMR spectra.

**Assembly 1.22.** Reaction Scale: **1.30** (17.9 mg, 0.026 mmol), yield 17.9 mg (82%). The product was isolated as an olive solid. Mp = >200⁰C. Solubility precluded collection of NMR or mass spectral data.

**Assembly 1.23.** A suspension was prepared of compound **1.17** (12.9 mg, 0.0107 mmol) and benzene diboronic acid (2.0 mg, 0.0121 mmol) in chloroform-d (4.3 mL) and refluxed at 90⁰C overnight. The resulting solution was allowed to cool, passed through a Teflon syringe filter, and concentrated under reduced pressure to afford pure **1.23** as an orange solid (13.9 mg, <99%). Decomposes at 199⁰C. ¹H NMR (CDCl₃, 300 MHz): δ 8.65 (s, 4H), 8.28-8.12 (m, 4H), 8.23 (s, 8H), 7.83-7.70 (m, 8H), 7.36-7.30 (m, 8H), 6.72 (s, 8H), 5.22 (s, 8H), 3.98-3.88 (m, 24H), 1.81-1.72 (m, 24H), 1.55-1.43 (m, 24H), 1.40-1.23 (m, 48H), 0.91 (t, J = 5.0 Hz, 36H) ppm.

**Assembly 1.24.** A suspension was prepared of compound **1.18** (15.7 mg, 0.0125 mmol) and benzene diboronic acid (2.3 mg, 0.0138 mmol) in chloroform-d (5.0 mL) and refluxed at 90⁰C overnight. The resulting solution was allowed to cool, passed through a Teflon syringe filter, and concentrated under reduced pressure to afford pure **1.24** as an orange solid (13.9 mg, 82%). Decomposes at XX⁰C. ¹H NMR (CDCl₃, 300 MHz): δ 8.52 (s, 4H), 8.04 (d, J = 20 Hz, 4H), 7.97 (s, 8H), 7.63-7.59 (m, 8H), 7.20-7.15 (m, 8H), 6.56 (s, 8H), 4.81 (s, 8H), 3.94 (t, J = 6.6 Hz, 8H), 3.87 (t, J = 6.2 Hz, 16H), 1.81-1.72 (m, 24H), 1.52-1.42 (m, 24H), 1.40-1.29 (m, 48H), 0.93 (t, J = 6.6 Hz, 36H) ppm.

**Compound 1.48.** To a solution of triphenylphosphine (6.3 g, 24.10 mmol) in dichloromethane (80 mL) was added carbon tetrabromide (4.0 g, 12.05 mmol). A solution was prepared of 3,4,5-tris(hexyloxy)benzyl alcohol (4.9 g, 12.05 mmol) in dichloromethane (24 mL), which was added to the stirring triphenylene phosphine and carbon tetrabromide solution at 0⁰C. The reaction was...
stirred at 0°C for 1.5 hours, at which point water was added (150 mL), and the crude product extracted with chloroform (3×100 mL). The combined organic layers were washed with brine (150 mL), dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified using a pad of silica, eluting with 1:1 hexanes:dichloromethane, affording pure 5 as an orange oil (4.7 g, 83%). ESI/APCI (m/z) [MH]+ calculated for C₂₃H₄₄O₃Br, 471.2468; found 471.2464. ¹H NMR (CDCl₃, 300 MHz): δ 6.58 (s, 2H), 4.45 (s, 2H), 4.00-3.92 (m, 6H), 1.85-1.74 (m, 6H), 1.50-1.46 (m, 6H), 1.35-1.33 (m, 12H), 0.96-0.89 (m, 9H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 153.2, 132.3, 107.0, 73.4, 69.1, 47.0, 31.7, 31.5, 30.2, 29.3, 25.7, 22.6, 14.0 ppm.
1.6. References and Notes


### 1.9.

### 1.10.

### 1.11.

### 1.12.

### 1.13.

### 1.14.


2005, 127, 4685-4696.


1.26. This drying step was found to be essential as the dynamic equilibrium formation of rectangles 1.3 or 1.4 stalls around 90-95% conversion (by NMR) in the presence of residual H2O or methanol.

1.27. Alkylation of the pores of COFs has been shown to increase their hydrolytic stability, see Lanni, J. M.; Tilford, R. W.; Bharathy, M.; Lavigne, J. J. J. Am. Chem. Soc., 2011, 133, 13975, however ortho substitution of the catechol moieties may also be a contributing factor. We are currently investigating this further.


1.32. Frisch, M. J.; et al., Gaussian 09, Revision A.1, (see Appendix A.1.6 for the full reference).


1.37. Melting points of boronate rectangles 1.3 and 1.4 are both $>200^\circ$C.


1.53. It is worth mentioning that in both cases, the $^1$H NMR spectra for bis-catechols 1.17 and 1.18 were complicated somewhat by concentration-dependent peaks shifts in chloroform. Peak shifts were not observed in deuterated acetone for 1.17 and 1.18, suggesting a lack of aggregation in highly polar solvents. Deuterated acetone was not used as the characterization solvent, as assemblies 1.23 and 1.24 were insoluble in acetone. Dilution series NMR studies provided some evidence of higher order, non-specified aggregation (See Appendix A.I.1.2). Alkylated gallic acid derivatives are known to act as mesogens in certain cases, and their directional opposition from the highly polar tetra-hydroxy moieties may be causing amphiphilic, pseudo-liquid crystalline aggregation (although differential scanning calorimetry did not indicate a mesophase). This effect is significantly diminished upon assembly.

1.54. Note that the UV-Vis and fluorescence spectra for assemblies 1.19-1.22 were obtained in acetone while 1.23 and 1.24 were collected in chloroform, for reasons of solubility. This change accounts for the small discrepancies between the six compounds.


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2.0. Abstract

The vibrational characteristics of 28 different boronic acid, boroxine anhydride, and boronate ester species have been systematically investigated using a combination of experimental infrared (IR) spectroscopy and computational modeling. IR bands characteristic to each boron-containing functionality have been categorized and assigned in conjunction with density functional theory (B3LYP/6-31G(d)), with the aim of better understanding and distinguishing the vibrational characteristics of covalent organic frameworks (COFs) built from boronic acids. In several cases, vibrational assignments differ from those previously reported in the literature on boronic acid-based COFs. Vibrations commonly regarded as diagnostic for one functionality are found in regions of the IR spectrum where other functionalities also show characteristic peaks. The collective experimental and computational results reveal that several alternative bands in the IR region can be used to more diagnostically distinguish between boronic acid, boroxine anhydride, and boronate ester species. The results presented herein provide the tools for straightforward characterization of boroxine anhydride and boronate ester species using IR spectroscopy. The results can be applied to additional theoretical studies of larger COF-like assemblies as well as the analysis of other boronic-acid-based materials.

2.1. Introduction

2.1.1. Traditional Characterization for Boronic-Acid Based Materials

As discussed in Chapter 1, unlike most discrete boronate ester and boroxine anhydride materials, boronic-acid-based COFs are, by their very nature, insoluble powders. Two-dimensional, planar COFs tend to stack into multilayered structures, whereas three-dimensional COFs adopt different net topologies.\(^2\) As the range of methods and compounds (secondary building units, SBUs) used to synthesize new COFs has expanded, two techniques—powder X-ray diffraction (PXRD) and infrared (IR) spectroscopy—have emerged as the most prominent means of analyzing these new materials, though solid-state NMR, elemental analysis, and X-ray photoelectron spectroscopy (XPS) have also been used. PXRD is able to provide insight into the long-range 2D and 3D ordering of COFs by comparing experimentally obtained diffraction data to predictions obtained from molecular simulations. PXRD, however, does not provide information regarding chemical
composition or connectivity. IR spectroscopy, on the other hand, provides this complementary analysis of chemical functionalities and connectivities while being unable to provide long-range structural information. In reviewing the literature of COFs,\textsuperscript{2,1-2.7} and in conjunction with our own efforts\textsuperscript{2,8} to synthesize and characterize discrete, soluble COF analogues, we have found that IR spectroscopic analysis and characterization of boronate ester and boroxine anhydride materials can be misleading, as many spectral bands reported as diagnostic for one functionality (i.e., boronic acid, boroxine anhydride, or boronate ester) are also present in others. Many, if not most, of the absorption bands typically reported as characteristic of a particular structure are supportive of, but not diagnostic for, the structures they aim to describe. Few absorption bands have been assigned to specific vibrational modes characteristic of boronic acid, boroxine anhydride, or boronate ester species. Given the many structural similarities among secondary building units used in COF synthesis, it is likely that vibrational bands seemingly correlated with boroxine anhydride and/or boronate ester assemblies are actually attributable to other commonly shared vibrational modes not associated with boron-containing species. As the complexity of boronic-acid-derived COF materials expands it becomes increasingly important to be able to distinguish and assign those vibrational modes that are characteristic of and unique to boronic acid, boroxine anhydride, and boronate ester linkages.

The vibrational mode most commonly cited as being characteristic of both boroxine anhydride and boronate ester formation is a strong absorption band(s) in the region between 1300 and 1400 cm\(^{-1}\).\textsuperscript{2.1} Given that strong absorptions exist in this region for boronic acids, boroxine anhydrides, and boronate esters, it is generally not possible to characterize the chemical linkages present in boronic-acid-based COFs using only the vibrational absorption bands present between 1300 and 1400 cm\(^{-1}\). Other bands attributed to boroxine anhydride or boronate ester linkages have been also noted in the literature, though less frequently. In particular the regions between 1220 and 1250 cm\(^{-1}\), 1000–1090 cm\(^{-1}\), and 500–750 cm\(^{-1}\) have been assigned to C–O stretches,\textsuperscript{2,2, 2.3a, 2.4a-c, 2.4e-f, 2.7a-b, 2.7d} B–C stretches,\textsuperscript{2,2, 2.3a, 2.4a-e, 2.4g-i, 2.4k, 2.5a, 2.7a-b, 2.7d} and out-of-plane vibrations,\textsuperscript{2,2, 2.6a-b} respectively. In some cases, however, assignments of C–O and B–C stretches appear switched, with bands in the region between 1100 and 1200 cm\(^{-1}\) being assigned\textsuperscript{2.4d, 2.4g, 2.4j, 2.7e} to C–O stretches and those in the region between 1200 and 1270 cm\(^{-1}\) assigned\textsuperscript{2.2, 2.3a, 2.4d, 2.7e} to B–C stretches. In their study of oligo(dioxaborole)s, Rambo and Lavigne\textsuperscript{2,9} critically compared the IR spectra of two discrete bis-boronate esters, one oligo-boronate ester, and one boroxine anhydride
and convincingly point out that the fingerprint region provides a more direct means of distinguishing boroxine anhydrides from boronate esters.

In response to these discrepancies, we have undertaken a systematic investigation, combining experimental IR spectroscopy and density functional modeling, of the vibrational characteristics of 28 different boronic acid, boroxine anhydride, and boronate ester species (Figure 2.1). The combination of synthesis, IR spectroscopy, and computational frequency analysis allows us to directly visualize and assign experimental absorption bands to particular vibrational modes. The selection of 28 different individual components and assemblies has allowed us to determine those vibrational modes that are shared between different functionalities and those that are distinct and diagnostic. Theoretical vibrational analysis is then expanded to representative larger COF-like assemblies to further investigate the relationships between IR spectra of such large assemblies and their smaller SBU components. The results presented herein will enable more definitive characterization of boronate ester and boroxine anhydride species by IR spectroscopy, and can be applied to the analysis of other boronate ester and anhydride materials in general.

2.1.2. Representative Model Systems

Symmetry plays a central role in the synthetic design of infinitely repeating 2D and 3D COFs. Symmetry also plays a fundamental role in determining which vibrational modes of COFs, and their component secondary building units, are IR active versus Raman active. As such, the compounds selected for this study were chosen to maintain, in general, a high degree of symmetry across both secondary building units (boronic acid and catechol derivatives) and the discrete COF-like assemblies built from them. With a few exceptions, the starting materials and assemblies investigated herein (Figure 2.1) are members of the point groups $C_{2v}$, $C_{2h}$, $D_{2h}$, or $D_{3h}$. This intentional utilization of symmetry serves as a starting point from which a more thorough understanding of the IR active spectroscopic modes characteristic of boronic acids, boroxine anhydrides, and boronate esters can be developed.
Figure 2.1: Chemical structures and ideal point group symmetries of (a) boronic acid, (b) boroxine anhydride, and (c) boronate ester species used in the current study.
The series of compounds chosen also provides a means of investigating the effects of aromatic substitution on the vibrational characteristics of each species. Specifically, boronic acids 2.2–2.6 bear electron-donating (alkyl, fluoro, methoxy) and electron-withdrawing groups (ester, cyano) at their para position, allowing a means of investigating the influence of electronic effects on vibrational spectra. Similarly, ortho-dimethyl phenylboronic acid (2.8) provides a means of investigating the influence of sterics on vibrational modes.

The relationships between individual vibrational modes of simple discrete assemblies and those of fully assembled COFs may be better determined by combining experimental and computational analyses while systematically progressing from simple to more complex systems. For example, as discrete COF-like analogues progress from simple monoesters (e.g., 2.17) to more complex diesters (e.g., 2.26) and triesters (e.g., 2.28) the number of related yet symmetrically distinct vibrational modes increases. Experimentally, such closely related yet distinct vibrational modes can lead to broadening of IR absorption bands. Furthermore, the specific symmetry of each individual vibrational mode will determine the magnitude of its dipole vector and, thus, intensity. With computational frequency analysis, all symmetrically similar yet vibrationally distinct vibrational modes can be more directly “resolved” and analyzed individually.

2.2. Characteristic Vibrational Modes

The following three sections are divided according to the different boron-containing functionalities involved in boronic-acid-based COF formation: boronic acids, boroxine anhydrides, and boronate esters. Vibrational modes characteristic of each boron-containing functionality have been assigned according to their symmetry and intensity as well as the maximum, minimum, and average frequency observed across the range of compounds investigated within each group. Once all modes characteristic of each boron-containing functionality are explored it becomes possible to distinguish which modes are diagnostic, rather than simply supportive, of the different functionalities. When appropriate, absorption bands within each region that are conserved across several boronate esters and/or boroxine anhydrides but do not arise from boron-specific chemical linkages are also discussed as potential “red
herrings.” The results are then applied to the theoretical study of larger COF-like assemblies to investigate how knowledge of small molecule analogues relates to larger systems, which is key to diagnostic IR analysis of “infinite” 2D and 3D COFs. Overall, the results provide a straightforward means of evaluating the IR spectra of myriad new boronic-acid-based COF materials and allow significantly more definitive vibrational assignments to be made.

2.2.1. Boronic Acids 2.1–2.10

Shown in Figure 2.2 are the six vibrational modes that directly involve the boronic acid \( \text{B(OH)}_2 \) moiety and are conserved across the ten boronic acids studied. Arrows or \((+)/(−)\) symbols are provided to highlight the atomic displacements that characterize each different mode. Also provided in Figure 2 are the symmetry and relative intensity of each mode as well as the maximum, minimum, and average frequency found computationally for boronic acids 2.1–2.10. Phenyl boronic acid (2.1), the simplest aryl boronic acid in the series, is used as a representative example for all compounds in the series. For complete results detailing the symmetry, frequencies, and intensities specific to each individual boronic acid see Table 2.1. It should be noted that only computational results are provided for acids 2.1–2.10 as it is not possible to obtain experimental IR spectra of purely discrete boronic acids given their propensity to undergo spontaneous self-assembly into boroxine anhydrides, the presence of which convolute experimental results.

Theoretical calculations predict that the hydroxyl stretching frequencies of boronic acids 2.1–2.10 (not shown in Figure 2.2) all fall within the narrow range of 3629–3634 cm\(^{-1}\). Symmetric O–H stretching modes were predicted to occur at higher frequencies and higher intensities than asymmetric modes for all compounds investigated. The attenuation of hydroxyl stretching modes in experimental IR spectra of COFs is often cited\(^{2.1\text{-}2.7}\) as evidence for the formation of boroxine anhydride or boronate ester functionalities. Hydroxyl peaks do not disappear entirely for even well-formed COFs because their leading edges will inevitably be composed of hydroxyl units from either unassembled boronic acids or organic catechol derivatives. Although it can be instructive to note where O–H stretches of boronic acids 2.1–2.10 occur, in practice it is unlikely that the specific range of O–H frequencies will aid in the characterization of COF materials. This conclusion is drawn from the fact that O–H frequencies are well-known to be broad and their
Intensities are often variable. Few definitive conclusions can be drawn from subtle changes in peak location and intensity. It should be noted, however, that all boroxine anhydride and boronate ester assemblies in the current study are discrete species with no terminal hydroxyl functions.

**Figure 2.2:** Depictions of the six vibrational modes involving the B(OH)$_2$ functionality that were found to be conserved across boronic acids 2.1–2.10. Symmetries are assigned based on the $C_{2v}$ symmetry of phenylboronic acid (2.1). Relative intensities (weak, medium, or strong) and maximum, minimum, and average frequencies (in wavenumbers, cm$^{-1}$) were obtained from theoretical frequency analysis of optimized structures. At the bottom is a visual representation of the relative location, average (black dashed line), and span of each B(OH)$_2$ vibrational mode within the IR region from 450 to 1450 cm$^{-1}$. 
Table 2.1: Vibrational frequencies calculated for boronic acids 2.1-2.10. Vibrations are given in units of cm$^{-1}$ and are assigned in accordance with displacements shown in Figure 2.2a-e. Intensities are classified as strong (S), medium (M), or weak (W). The symmetry of each vibrational mode is given and based on the overall symmetry of each acid (see Figure 2.1). The average frequency of each mode is listed at the bottom of the table.

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Two distinct vibrational modes are calculated in the region extending from 1306 to 1353 cm$^{-1}$ for boronic acids 2.1–2.10. These two vibrations correspond to an asymmetric B–O stretching mode (Figure 2.2a) and a symmetric B–C stretching mode (Figure 2.2b). The intensities of both vibrational modes in the 1300 cm$^{-1}$ region are strong. For most boronic acids the B–O stretching mode was observed to occur at a higher frequency than the B–C stretching mode. The separation between the B–O and B–C modes for any given boronic acid 2.1–2.10, however, was found to average 12 cm$^{-1}$. Although the two vibrational modes are easily distinguished by computational frequency analysis, it is less likely that experimental IR spectroscopic analysis of “bulk” samples would resolve the two bands.

The region from 900 to 1000 cm$^{-1}$ also contains two well-defined and distinct IR active modes that are conserved across boronic acids 2.1–2.10. Figure 2.2c shows a representative example of the higher-frequency vibrational mode consisting of a coupled B–O stretch and O–H in-plane bend. For the ten boronic acids investigated this coupled mode spans a region of ca. 24 cm$^{-1}$. In general the intensity of this coupled B–O stretch and O–H in-plane bending mode is predicted to be strong with the exception of triboronic acid 2.10, which is predicted to display a medium intensity peak in this region due to the smaller dipole change associated with asymmetric stretching in such 1,3,5-substituted systems. The lower frequency mode in this region (Figure 2.2d) is more tightly focused between 907 and 920 cm$^{-1}$ and consists solely of symmetric, in-plane O–H bending. The intensity of this mode centered at 910 cm$^{-1}$ was also found to be high for all boronic acids. Both modes in the 900–1000 cm$^{-1}$ region are characteristic of boronic acids.
and distinct from the O–H in-plane bending modes typical of catechol derivatives (e.g., catechol, 1,2,4,5-tetrahydroxybenzene, and 2,3,6,7,10,11-hexahydroxytriphenylene), which are typically observed between 1120 and 1180 cm\(^{-1}\). For the series of compounds studied the coupled B–O stretch/O–H in-plane bending mode does not have an analogue outside boronic acids. Given that both boronic acid vibrational modes in the 900–1000 cm\(^{-1}\) region are sharper and more distinct than hydroxyl stretches around 3600 cm\(^{-1}\), we propose that their attenuation will provide a better means of evaluating the self-assembly of COF materials than the attenuation of hydroxyl O–H stretching bands. Indeed, a survey of several IR spectra of boroxine anhydride and boronate ester COFs reported in the literature\(^{2.2, 2.3a-b, 2.3d, 2.4a, 2.4c, 2.4i-k, 2.5a, 2.5c-h, 2.6, 2.7}\) reveal a general lack\(^{10}\) of medium- or high-intensity peaks centered around 974 or 909 cm\(^{-1}\).

Boronic acids \(2.1–2.10\) also display two characteristic out-of-plane bending modes in the fingerprint region of their IR spectra. These last two vibrational modes are shown in Figure 2.2e,f. The first, centered around 622 ± 17 cm\(^{-1}\) corresponds to the out-of-plane bending of boron atoms syn with out-of-plane bending of aryl hydrogen atoms (Ar–H). This mode was found to be of medium to high intensity for the ten acids investigated. A significantly less intense mode was also observed for out-of-plane displacements of boron and aryl hydrogen atoms anti to each other. The anti relationship of out-of-plane displacements results in a very minor dipole change and, consequently, a very weak IR absorption. The anti out-of-plane mode was, therefore, not included in the discussion of characteristic boronic acid vibrational modes. Shown in Figure 2.2f is the second prominent vibrational mode in the fingerprint region, which corresponds to out-of-plane displacements of hydroxyl hydrogen atoms. The out-of-plane bending of hydroxyl hydrogens was found to average 520 cm\(^{-1}\) for the ten boronic acids studied computationally and its intensity is predicted to be strong. Several other out-of-plane and in-plane bending modes are present in the fingerprint region of boronic acids \(2.1–2.10\). The intensities of these modes were predicted to be less than half, and typically less than a quarter, of the intensities of the boronic acid specific modes shown in Figure 2.2e,f. Furthermore, the out-of-plane modes specific to boronic acids were separated by a minimum of 8 cm\(^{-1}\) and an average of 45 cm\(^{-1}\) from all other out-of-plane and in-plane bending modes in the region. Given the medium–strong intensities, narrow range of frequencies, and general separation from other modes in the region it is expected that the boronic acid specific modes around 622 and 520 cm\(^{-1}\) can be distinguished from other vibrations in the fingerprint region.
It should be reiterated that this discussion of boronic acid vibrational modes is based solely on computational frequency analysis, not experimental IR spectra. However, we\textsuperscript{2,8} and others\textsuperscript{2,11–2,13} have found good agreement (±8 cm\textsuperscript{-1}) between scaled B3LYP/6-31G(d) frequencies and experimental IR frequencies as well as reasonable agreement between the intensities of theoretically predicted and experimentally determined IR modes. Conclusions regarding the vibrational characteristics of boronic acids that have been drawn from computational analysis of compounds 2.1–2.10 are therefore expected to be applicable across a range of aryl boronic acids.

2.2.2. Boroxine Anhydrides 2.11–2.16

Figure 2.3 outlines the six vibrational modes characteristic to the central B\textsubscript{3}O\textsubscript{3} ring of boroxine anhydrides 2.11–2.16. The symmetry, relative intensity, range, and average frequency of each boroxine anhydride mode are also given in Figure 2.3. Experimental frequency results are given in black text while computational results are in blue text. Assignments of vibrational modes in Figure 2.3 were based on comparisons of experimental IR spectra and computational frequency analysis. The boroxine anhydride formed upon self-condensation of phenyl boronic acid, 2.11, is shown in Figure 2.3 as a representative example for purposes of visualizing each vibrational mode. As before, complete details regarding the symmetry, frequencies, and intensities specific to boroxine anhydrides 2.11–2.16 are shown in Table 2.2.

Three distinct vibrational modes of boroxine anhydrides 2.11–2.16 were found to involve stretching of the B–C(aryl) bond (Figure 2.3a–c). Figure 2.3a shows a representative example of the highest frequency B–C stretching mode, which was observed to range from 1332 to 1344 cm\textsuperscript{-1} and to involve a combination of B–C stretching coincident with stretching of the two B–O bonds oriented parallel to the B–C stretch. The intensity of this vibrational mode was strong for all boroxine anhydrides 2.11–2.16.
Figure 2.3: Representative examples of the 6 vibrational modes involving the $\text{B}_3\text{O}_3$ functionality found to be conserved across boroxine anhydrides 2.11–2.16. Symmetries are assigned based on the $D_{3h}$ symmetry of anhydride 2.11. Relative intensities (weak, medium, or strong) are based on experimental FTIR data. Maximum, minimum, and average frequencies obtained experimentally (black text) and computationally (blue text) are given in wavenumbers (cm$^{-1}$). Modes shown in d and e involve symmetric displacements of all aryl C–H, though only five are shown for simplicity. At the bottom is a visual representation of the relative location, average (black dashed line), and span of each B$_3$O$_3$ vibrational mode within the IR region from 450 to 1450 cm$^{-1}$. 
Table 2.2. Vibrational frequencies (cm\(^{-1}\)) calculated and observed for boroxine anhydrides 2.11-2.16. The top frequency listed for each anhydride is computational while the bottom value listed was obtained experimentally. Vibrations are assigned in accordance with displacements shown in Figure 2.3a-f. Intensities are classified as strong (S), medium (M), or weak (W). The symmetry of each vibrational mode is given based on the overall symmetry of the anhydride (see Figure 2.1). The average frequency of each distinct mode is listed at the bottom of the table (the top value is computational and the bottom value is experimental). The difference between average computed and observed frequency is also given in cm\(^{-1}\).

Vibrational modes depicted in Figures 2.3b,c both involve displacements of boron atoms not involved in the dominant B–C stretch. Where they differ is in their relative displacements with respect to the aryl carbon atoms they are covalently attached to: the higher frequency mode (1298–1310 cm\(^{-1}\), Figure 2.3b) involves displacement of aryl carbon atoms in the opposite direction of boron displacements, while in the lower frequency mode (1242–1259 cm\(^{-1}\), Figure 2.3c) displacements of aryl carbon atoms and their covalently linked boron atoms are oriented in the same direction. Intensities of these two modes were found to be variable. The high-frequency B–C stretching mode shown in Figure 2.3b was found to be strong for all but methoxy-substituted anhydride 2.14. The B–C stretch shown in Figure 2.3c was found, both experimentally and theoretically, to be either weak or strong but in no cases was it medium in intensity. Interestingly, anhydrides of \(D_{3h}\) symmetry (2.11, 2.13, 2.16) displayed weak intensity for this mode while \(C_{3h}\) anhydrides (2.12, 2.14, 2.15) were observed to have strong intensity. A greater range of anhydrides would be necessary to determine whether this trend applies more broadly, but within the current set of structures this observation again highlights the importance of symmetry in influencing the IR spectra of boroxine anhydrides. No correlation was found between vibrational frequencies and the electron withdrawing or electron donating nature of substituents at the para position of aryl rings of boroxine anhydrides 2.11–2.16.
There have been reports\textsuperscript{2,2, 2.4b, 2.9} of boroxine anhydride IR peaks in the regions between 1000 and 1100 cm\textsuperscript{-1} that have been assigned as B–C stretching modes. Indeed boroxine anhydrides \textsuperscript{2.11–2.16} all show absorption bands of medium to high intensity within these two regions. Computational simulations of the vibrational frequencies of anhydrides \textsuperscript{2.11–2.16} indicate that none of the vibrational modes between 1000 and 1100 cm\textsuperscript{-1} involve the displacement of boron or oxygen atoms of their central B\textsubscript{3}O\textsubscript{3} rings. IR bands in this region instead arise from aryl C–H in-plane bending modes of varying symmetry.

The next two modes found to involve displacements of atoms in the central B\textsubscript{3}O\textsubscript{3} ring of anhydrides \textsuperscript{2.11–2.16} are shown in Figure 2.3d,e. Both modes involve out-of-plane displacements of boron atoms. Interestingly, the three oxygen atoms of the central B\textsubscript{3}O\textsubscript{3} moiety were observed to be relatively stationary, which is in contrast to the out-of-plane vibrations of boronic acids \textsuperscript{2.1–2.10} (Figure 2.2e) where oxygen atoms of B(OH)\textsubscript{2} moieties are prominently displaced in the opposite direction of the boron atom. The two modes shown in Figure 2.3d and 2.3e differ in the displacements of central boron atoms relative to aryl hydrogen atoms. The higher frequency mode, ranging from 736 to 762 cm\textsuperscript{-1}, involves boron displacements that are anti to the displacements of aryl hydrogen atoms. The lower frequency out-of-plane vibrational mode (677–696 cm\textsuperscript{-1}) involves displacements of boron atoms syn to the displacements of aryl hydrogen atoms. The intensity of this lower band was observed to be strong for all anhydrides \textsuperscript{2.11–2.16}, likely because of the greater dipole change that occurs when boron and aryl hydrogen atoms are all displaced in the same out-of-plane direction. Both out-of-plane vibrational modes of boroxine anhydrides \textsuperscript{2.11–2.16} are observed at higher frequencies than the out-of-plane vibrations of their component boronic acids (604–649 cm\textsuperscript{-1}, Figure 2.2e), likely providing a convenient means of distinguishing between boronic acid and boroxine anhydride species.

The last distinct vibrational mode characteristic of boroxine anhydrides \textsuperscript{2.11–2.16} is a sharp peak of medium-strong intensity observed between 500 and 628 cm\textsuperscript{-1} (Figure 2.3f). This vibrational mode involves the “squeezing” of the central B\textsubscript{3}O\textsubscript{3} ring in a manner analogous to the \textit{v}\textsubscript{6b} mode\textsuperscript{2.14} of unsubstituted benzene. The range of this vibrational mode overlaps significantly with the out-of-plane vibration of hydroxyl hydrogen atoms of boronic acids \textsuperscript{1–10} (492–548 cm\textsuperscript{-1}, Figure 2.2f). The two out-of-plane boroxine anhydride vibrational modes shown in
Figures 2.3d,e, which do not overlap with modes characteristic to boronic acids, are therefore expected to be more useful for distinguishing between condensed boroxine anhydride species and their boronic acid components.

2.2.3. Boronate Esters 2.17–2.28

Twelve boronate esters (2.17–2.28) were investigated experimentally and computationally. Figure 2.4 outlines the five vibrational modes that were found to be conserved across the 12 esters studied. Boronate ester 2.17 is used in Figure 2.4 as a representative example for the purposes of graphically displaying the displacements involved in each vibrational mode. The symmetry, relative intensity, range, and average frequency of each vibrational mode as obtained experimentally (black text) and assigned by computational frequency analysis (blue text) are also given in Figure 2.4. Complete analysis of the symmetry, frequencies, and intensities specific to boronate esters 2.17–2.28 can be found in Table 2.3.

IR characterization of essentially all reported COFs that contain boronate esters note one or two strong IR absorption bands in the 1300 cm\(^{-1}\) region\(^{2,1}\). Most reported boronate ester-based COFs assign\(^{2.2, 2.3a-b, 2.4a, 2.4c-k, 2.5a, 2.5d, 2.5f, 2.7, 2.9}\) these IR bands to B–O stretches within the C\(_2\)O\(_2\)B ring. Indeed, both experimental and computational analyses of boronate esters 2.17-2.28 revealed two distinct vibrational modes in the 1300 cm\(^{-1}\) region (Figure 2.4a,b); however, analysis of these modes reveals that they involve stretching of the B–C bond rather than the B–O bonds. The two modes differ in the relationship between the B–C and C═C stretches within the 5-member boronate ester ring. In the higher frequency mode, which spans from 1355 to 1422 cm\(^{-1}\) (Figure 2.4a), the boronate ester B–C bond lengthens as the C═C bond shortens and vice versa. This results in a net shrinking and subsequent expansion of the boronate ester 5-member ring that can be likened to a “breathing” motion within the C\(_2\)O\(_2\)B ring. The second vibrational mode in this region (Figure 2.4b) ranges between 1272 and 1342 cm\(^{-1}\) for the 12 boronate esters investigated. In this mode the B–C and C═C bonds shorten and lengthen in unison. For all 12 boronate esters investigated the B–C stretching mode shown in Figure 2.4a was observed at a higher frequency than the B–C stretching mode shown in Figure 2.4b, with the intensity of both modes being strong. It should be noted that the peaks associated with B–C stretching modes in
the IR spectra of nonlinear boronate esters 2.26–2.28 are broad relative to those of linear boronate esters 2.17–2.25. It is believed, based on computational frequency analysis, that this broadening results from symmetric and asymmetric B–C stretching modes that are of similar frequency but slightly different intensity.

Figure 2.4: Representations of the five vibrational modes that involve displacements of atoms within the C₂O₂B ring systems of compounds 2.17–2.28. Symmetries are assigned based on the C₂ᵥ symmetry of ester 2.17. Relative intensities (weak, medium, or strong) are based on experimental FTIR data. Maximum, minimum, and average frequencies obtained experimentally (black text) and computationally (blue text) are given in wavenumbers (cm⁻¹). At the bottom is a visual representation of the relative location, average (black dashed line), and span of each C₂O₂B vibrational mode within the IR region from 450 to 1450 cm⁻¹. The outlying C–O vibration of ester 2.24 is indicated by a dashed blue line.
Table 2.3: Vibrational frequencies (cm\(^{-1}\)) calculated and observed for boronate esters \textbf{2.17-2.28}. The top frequency listed for each ester is computational while the bottom value listed was obtained experimentally. Vibrations are assigned in accordance with displacements shown in Figure 2.4a-f. Intensities are classified as strong (S), medium (M), or weak (W). The symmetry of each vibrational mode is given based on the overall symmetry of each boronate ester (see Figure 2.1). The average frequency of each distinct mode is listed at the bottom of the table (the top value is computational and the bottom value is experimental). The difference between average computed and observed frequency is also given in cm\(^{-1}\).

Two additional stretching modes (Figure 2.4c, d) were found to be characteristic of boronate ester \(\text{C}_2\text{O}_2\text{B}\) rings. The higher frequency mode, found between 1138 and 1241 cm\(^{-1}\) (Figure 2.4c) for boronate esters \textbf{2.17–2.28}, corresponds to symmetric stretching of both C–O bonds in the 5-member boronate ester ring. For nine of the 12 boronate esters investigated, this symmetric C–O stretching mode was observed to be more intense than either B–C stretching mode in the 1300 cm\(^{-1}\) region and, in fact, the most intense IR band above 800 cm\(^{-1}\). The three exceptions to this observation were diesters \textbf{2.24} and \textbf{2.26}, which both had medium intensity absorptions in this region, and triester \textbf{2.27}, for which the intensity of this C–O stretch was nearly equal to stretches in the 1300 cm\(^{-1}\) region. Compound \textbf{2.24}, at 1138 cm\(^{-1}\), is particularly interesting as it is the only ester studied for which this mode falls outside the narrow range of 1219–1241 cm\(^{-1}\). This notably

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<td></td>
<td>1306</td>
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</tr>
<tr>
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<tr>
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<td>1321</td>
<td>S</td>
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<tr>
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<td>S</td>
<td>(A_1)</td>
<td>1292</td>
<td>S</td>
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<td></td>
<td></td>
<td>1284</td>
<td>S</td>
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<td></td>
<td></td>
<td>1299</td>
<td>S</td>
</tr>
<tr>
<td>1364</td>
<td>S</td>
<td>(E')</td>
<td>1309</td>
<td>S</td>
</tr>
<tr>
<td>1352</td>
<td></td>
<td></td>
<td>1321</td>
<td>S</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
<td>1309</td>
<td>S</td>
</tr>
<tr>
<td>Avg.</td>
<td></td>
<td></td>
<td>1318</td>
<td>S</td>
</tr>
<tr>
<td>Diff.</td>
<td></td>
<td></td>
<td>7.3</td>
<td></td>
</tr>
</tbody>
</table>

\(\text{Sym.} = \text{Symmetry}\)
low frequency is observed for 2.24 because the C–O vibrations are coordinated through the adjoining aromatic ring. Given the typically high intensity of the C–O stretching mode of boronate esters, and the general lack of other intense peaks in this region, it is believed that C–O stretch can be considered more diagnostic of boronate ester compounds than the often cited B–C stretches in the 1300 cm$^{-1}$ region.

Shown in Figure 2.4d is the fourth stretching mode characteristic of boronate esters, which involves symmetric stretching of both B–O bonds of the 5-member boronate ester ring. As stated previously, much of the literature of boronate ester COFs assigns bands in this region to B–C stretching rather than what we have found to be B–O stretching. The intensity of the B–O stretching mode, which was more variable than the intensities of higher frequency modes shown in Figure 2.4a–c, ranged between medium to strong. While the range of B–O stretching frequencies is listed as spanning from 1033 to 1080 cm$^{-1}$, it should be noted that all but one of the 12 boronate esters displayed B–O stretching frequencies between a much tighter range of 1064–1080 cm$^{-1}$. The one ester that lies outside this range is ortho-dimethyl boronate ester 2.23 for which experimental IR spectra shows (and computational frequency analysis supports) a B–O stretching frequency of 1032 cm$^{-1}$. The B–O stretching mode for esters 2.17–2.22 and 2.24–2.28 is coupled with in-plane bending of aryl hydrogen atoms at the ortho and meta positions of the boron-linked aryl ring. In the case of ortho-dimethyl ester 2.23, however, ortho positions are occupied by methyl groups rather than hydrogen atoms. These methyl groups do not undergo any displacement in conjunction with the B–O stretch, resulting in a lower vibrational frequency. Apart from this outlier, the B–O stretching frequency is especially diagnostic for boronate esters, with most compounds falling between a narrow range centered at 1072 cm$^{-1}$ and spanning only 16 cm$^{-1}$.

The last vibrational mode found to be conserved across the 12 boronate esters investigated involves the out-of-plane displacement of the boron and oxygen atoms of the boronate ester ring (Figure 2.4e). As shown, out-of-plane displacements of the boron atom are coupled with out-of-plane displacements of aryl hydrogen atoms (Ar–H), most prominently those at the 3 and 5 positions of monoesters 2.17-2.23. Boronate ester oxygen atoms are displaced in the opposite direction of boron and Ar–H motions. The out-of-plane vibrations of boronate esters were observed to fall between 633 and 658 cm$^{-1}$ and were all strong intensity. The B$_3$O$_3$ out-of-plane
modes of boroxine anhydrides 2.11–2.16 were observed in the ranges 736–762 and 677–714 cm\(^{-1}\) (Figure 2.3d,e), showing no overlap with the out-of-plane vibrations of boronate esters. There is, however, overlap between the out-of-plane vibrations of boronate esters (633–636 cm\(^{-1}\)) and boronic acids (604–649 cm\(^{-1}\), Figure 2.2e). Consideration of a combination of vibrational modes, however, does allow a more definitive distinction between acids and boronate esters.

### 2.3. Extending Vibrational Analyses to Larger COF-Analogues

As stated above, it is instructive to investigate whether trends observed for simple model systems (e.g., acid 2.1, anhydride 2.11, and ester 2.17) carry over to larger, more complex assemblies. To help answer this question we computationally investigated the vibrational modes of three larger COF-like assemblies: boroxine anhydride assembly 2.29 and boronate ester assemblies 2.30 and 2.31 (Figure 2.5). Investigations of 2.29–2.31 were limited to computational frequency analysis, as it is not currently possible to prepare perfectly monodisperse, discrete COFs experimentally.

![Figure 2.5](image)

**Figure 2.5:** Space filling representations of COF-like boroxine anhydride (2.29) and boronate ester (2.30, 2.31) assemblies investigated computationally (gray = C, red = O, green = B, white = H). Anhydride 2.29 can be envisioned as a “second generation” analogue of anhydride 2.11, whereas esters 2.30 and 2.31 can be envisioned as “second generation” analogues of esters 2.27 and 2.28, respectively.
Listed in Tables 2.4 and 2.5 are the relevant vibrational frequencies of second generation COF-like assemblies 2.29–2.31. Also provided in Tables 2.4 and 2.5 are vibrational frequencies computed for boroxine anhydride and boronate ester assemblies that can be considered small subunits of second generation assemblies 2.29–2.31 as well as the average frequencies of all boroxine anhydrides and boronate esters studied. Finally, Tables 2.4 and 2.5 include FTIR data from as-synthesized COFs that are the most closely related “infinite” analogues of computationally investigated COF-like assemblies; COF-1, COF-6, and COF-5 can be considered larger, periodically repeating analogues of 2.29, 2.30, and 2.31, respectively.

Table 2.4: Calculated vibrational frequencies for 2nd generation COF-like boroxine anhydride assembly 2.29.

<table>
<thead>
<tr>
<th>mode</th>
<th>2.29</th>
<th>2.11</th>
<th>COF-1</th>
<th>avg</th>
</tr>
</thead>
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<tr>
<td>3a</td>
<td>1345</td>
<td>1331</td>
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<tr>
<td>3b</td>
<td>1281</td>
<td>1292</td>
<td>1301</td>
<td>1296</td>
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<tr>
<td>3c</td>
<td>1252</td>
<td>1250</td>
<td>1260</td>
<td>1252</td>
</tr>
<tr>
<td>3d</td>
<td>766b</td>
<td>762</td>
<td>762c</td>
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<td>691</td>
<td>711</td>
<td>683</td>
</tr>
<tr>
<td>3f</td>
<td>632</td>
<td>566</td>
<td>665</td>
<td>542</td>
</tr>
</tbody>
</table>

*a*Key vibrational modes involving atoms within the B<sub>3</sub>O<sub>3</sub> ring are categorized according to their designations in Figure 2.3a–f. The vibrational frequencies calculated for anhydride 2.11 (a smaller analogue of 2.29), experimentally reported vibrational frequencies of COF-1 (an “infinite” analogue of 2.29), and average calculated frequencies for anhydrides 2.11–2.16 are also provided for comparison. Data are given in cm<sup>-1</sup>. bThe intensity of this mode, on account of its symmetry, is very weak and likely would not be distinguishable from the baseline. cThis peak at 762 cm<sup>-1</sup> is reported<sup>2.2</sup> for COF-1; however, its intensity is nearly at the baseline, in agreement with computational modeling of COF-like assembly 766 cm<sup>-1</sup>.

Each second generation assembly is predicted to have a multiple IR-active vibrations in the 1300–1400 cm<sup>-1</sup> region. This greater number of distinct vibrational modes results from the increased number of symmetric and asymmetric modes that exist for each fundamental vibration shown in Figures 2.3 and 2.4. Differences in the symmetries of each vibrational mode result in significant differences in their IR intensities such that only one, or a limited few, of each type of...
vibration is expected to rise significantly above the baseline. Unless otherwise noted, Tables 2.4 and 2.5 list those vibrations that are predicted to be of medium-strong intensity and that relate directly to fundamental vibrations already discussed.

Table 2.5: Calculated vibrational frequencies for 2\textsuperscript{nd} generation COF-like boronate ester assemblies 2.30 and 2.31\textsuperscript{a}.

<table>
<thead>
<tr>
<th>mode</th>
<th>2.30</th>
<th>2.17</th>
<th>2.24</th>
<th>2.26</th>
<th>2.27</th>
<th>COF-6</th>
<th>2.31</th>
<th>2.25</th>
<th>2.28</th>
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<td>1221</td>
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<tr>
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<td>1068\textsuperscript{b}</td>
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<td>1049</td>
<td>1065</td>
<td>1069</td>
<td>\textsuperscript{c}</td>
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<td>648</td>
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<td>665</td>
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</tbody>
</table>

\textsuperscript{a}Key vibrational modes involving atoms within the C\textsubscript{2}O\textsubscript{2}B ring are categorized according to their designations in Figure 2.4a-e. The vibrational frequencies calculated for smaller analogues of each ester (compounds 2.17 and 2.24–2.28), experimentally reported vibrational frequencies of COF-6 and COF-5 ("infinite" analogues of 2.30 and 2.31, respectively), and average calculated frequencies for boronate esters 2.17–2.28 are also provided for comparison. Data are given in cm\textsuperscript{-1}. \textsuperscript{b}The intensity of this mode, on account of its symmetry, is very weak and likely would not be distinguishable from the baseline. \textsuperscript{c}No peaks were observed\textsuperscript{2,3b, 2,6a} in this region for COF-6, which is in agreement with computational modeling that indicates weak intensity of the 4d mode of COF-like assembly 2.30.

Computational studies of second generation assemblies 2.20–2.31 lend further support to the conclusion that B–O and B–C IR bands in the 1300–1400 cm\textsuperscript{-1} region are less diagnostic for boroxine anhydrides and boronate esters than bands in other regions of the spectrum. Considerably more variation is observed for IR bands between 1300 and 1400 cm\textsuperscript{-1} for both boroxine anhydrides and boronate esters, and bands of boroxine anhydrides and boronate esters in this region overlap. This result is observed in both theoretically modeled and experimentally measured systems. Both this increased variability and general overlap of frequencies that can be assigned to anhydrides and esters precludes the diagnostic characterization of such assemblies based solely on bands in this region. Other regions of the IR spectrum, particularly the fingerprint region, are notably more diagnostic as will be discussed in the following section.
Despite the general difficulty of assigning IR bands in the 1300–1400 cm\(^{-1}\) region, the results in Tables 2.4 and 2.5 suggest that simple, discrete boroxine anhydride and boronate ester assemblies can, when appropriately chosen, serve as valuable model systems for understanding the vibrational properties of related COFs. Care must be taken, however, in determining what small analogue(s) will serve as appropriate models for infinitely repeating structures. The boronate ester C–O vibrations (Figure 2.4c) of second-generation assembly 2.30 provides a good example. Assembly 2.30 contains boronate esters built from 1,2,4,5-tetrahydroxybenzene, which are analogous to bis-ester 2.24. As mentioned earlier, assembly 2.24 was shown experimentally and computationally to have C–O vibrations well outside the range of 1219–1241 cm\(^{-1}\) found for all other boronate esters investigated. Assembly 2.24, however, is the simplest discrete analogue that accurately represents (Table 2.4) the C–O frequency of second generation COF 2.30 and its “infinite” analogue, COF-6. Other closely related assemblies 2.17, 2.26, and 2.27 do not possess bis-ester functions joined by 1,2,4,5-tetrahydroxybenzene and therefore do not accurately\(^{2,15}\) model assembly 2.30. Discrete systems used as models for related COFs should therefore be chosen carefully to accurately capture all relevant functionalities present in the larger COF. As the complexity, functionality, and size of SBUs used to prepare COFs continue to increase, such systems can be broken into several discrete species that are each more straightforward to investigate. Alternatively, modeling of a second generation assembly such as 2.29–2.31 can provide a wealth of highly useful and diagnostic vibrational information, provided such structures are computationally feasible.

2.4. **Distinguishing Boron-Containing Functionalities by IR Spectroscopy**

Taken together, the above experimental and computational results provide the background necessary to more definitively distinguish between boronic acid, boroxine anhydride, and boronate ester species based on their IR spectra. Figure 2.6 plots the collective spectral ranges of IR active modes characteristic to the boron-containing functionalities of compounds 2.1–2.28. Highlighted in gray in Figure 2.6 are vibrations that (i) are conserved across boroxine anhydride or boronate ester species, (ii) do not involve boron-containing functionalities, and (iii) appear in regions of the spectrum that are characteristic of other boron-containing functionalities. These gray areas play a prominent role in the diagnostic characterization of boroxine anhydride and
boronate ester materials as they highlight regions of the IR spectrum where other common vibrational modes may be misinterpreted or provide false positives of boroxine anhydride or boronate ester formation. The data provides a convenient means of distinguishing which vibrational modes are diagnostic for, rather than simply supportive of, each functionality. Although the results presented in Figure 2.6 are based on a set of only 28 different compounds, we expect that they can be applied to a broad range of boronic acid, boroxine anhydride, and boronate ester species used in COF synthesis.

Figure 2.6.: Summary of IR active vibrational modes that involve displacements of the boron-containing functionalities of boronic acids 2.1–2.10 (a, highlighted in orange), boroxine anhydrides 2.11–2.16 (b, highlighted in purple), and boronate esters 2.17–2.28 (c, highlighted in blue). Dotted black lines represent the average observed vibrational frequency within each range. Areas shaded in gray highlight regions of the IR spectrum where vibrational modes that do not involve the boron-containing moiety of compounds 2.1–2.28 are commonly found that may be mistaken as characteristic of alternative structures.

Rambo and Lavigne\textsuperscript{2,9} have previously cautioned against considering bands in the 1300 cm\textsuperscript{-1} region of IR spectra to be diagnostic for boroxine anhydrides or boronate esters, given that boronic acids, boroxine anhydrides, and boronate esters all display prominent peaks in this region. Bands in this region are most often attributed to B–O stretches. The data presented in Figure 2.6 partially corroborates this conclusion, clearly showing the spectral overlap of boronic
acid, boroxine anhydride, and boronate ester peaks in the 1300 cm$^{-1}$ region. Where the current results and previous reports differ is in the assignment of these vibrational modes. Some boronic acid and boroxine anhydride peaks in the 1300 cm$^{-1}$ region do correspond to B–O stretches (e.g., those shown in Figures 2.2a and 2.3a), however most are predominantly B–C stretches (e.g., Figures 2.2b, 2.3b,c, and 2.4a,b) as assigned computationally. Regardless, the current study also recommends that peaks in the 1300 cm$^{-1}$ region not be considered diagnostic for a particular boron-containing functionality given the overlap of strong vibrational modes between 1300 and 1400 cm$^{-1}$.

Several studies$^{2.2, 2.3a-b, 2.4a, 2.4c-k, 2.6a, 2.7}$ have indicated the presence of one or more sharp, intense bands between 1000 and 1050 cm$^{-1}$ that can be attributed to boronate ester formation. The results of this current study suggest that, indeed, boronate esters $^{2.17–2.28}$ display a sharp, medium-to-strong intensity B–O stretching mode (Figure 2.3c) in this region. Despite how characteristic this mode is for B–O stretching of boronate esters, it is believed that care should be taken when attempting to distinguish between boroxine anhydride and boronate ester assemblies based upon IR bands in the 1000 cm$^{-1}$ region. The reason for caution extends from the fact that B–O stretching modes in this region are generally of the same intensity as neighboring peaks, most of which are different variations of symmetric and asymmetric C–H in-plane bending modes that are observed for all species (acids, anhydrides, and esters). Often, these in-plane Ar–H bending modes are difficult to distinguish from each other and can be mistaken for boronate ester B–O stretches. IR bands in this region have also been previously attributed to the formation of B$_3$O$_3$ rings, however no IR active B$_3$O$_3$ vibrational modes between 1000 and 1180 cm$^{-1}$ were found for compounds $^{2.11–2.16}$. In-plane C–H bending modes, rather, dominate this region.

In addition to the above discussion, several overall conclusions can be drawn from the vibrational summary presented in Figure 2.6:

1. The consumption of boronic acid functionalities can be best evaluated by the attenuation of IR bands between 900 and 1000 cm$^{-1}$. As stated above, B–O stretching and O–H wagging frequencies observed in this region (Figure 2.2) are sharper, more distinct, and more diagnostic than O–H stretches in the 3000 cm$^{-1}$ region. It should be noted that most of boroxine anhydrides $^{2.11–2.16}$ display C–H out of plane bending vibrations between 940 and 960 cm$^{-1}$, however their intensities are weak to very weak. All boroxine anhydrides in the current study
show medium intensity in-plane bending of Ar–H bonds between 1010 and 1040 cm$^{-1}$. Given the relatively weaker intensities of these boroxine anhydride vibrational modes and their general separation from the strong intensity modes specific to boronic acids, it is not expected that these boroxine anhydride bands will be confused for boronic acids.

2. The fingerprint region is especially valuable for distinguishing between boroxine anhydride and boronate ester species, as has been noted previously by Lavigne and co-workers.$^{2,9}$ Two areas of the fingerprint region are particularly notable: the region from 677 to 714 cm$^{-1}$ is diagnostic for boroxine anhydrides while the region between 633 and 658 cm$^{-1}$ is diagnostic for boronate esters. Both vibrational modes involve out-of-plane displacements of boron atoms that are $syn$ to out-of-plane displacements of aryl hydrogen atoms. These out-of-plane vibrations are especially diagnostic in 2D COF and COF-like assemblies because their intensity is not dependent on the overall in-plane symmetry of the assembly. Furthermore, the fundamental differences in connectivity between six-member boroxine anhydride and five-member boronate ester moieties underlie differences in their out-of-plane vibrations. Specifically, the strong intensity out-of-plane vibrations of boroxine anhydrides (Figure 2.3e) involve symmetric displacement of three boron atoms within each $B_3O_3$ ring while the boroxine anhydride oxygen atoms remain relatively stationary. The out-of-plane vibrations characteristic of boronate esters (Figure 2.4e) involve the displacement of only one boron atom per $C_2O_2B$ ring rather than three, and the two oxygen atoms of the boronate ester moiety are more prominently displaced in the opposite direction of the boron atom. These fundamental differences between out-of-plane vibrational modes of boroxine anhydride and boronate ester assemblies ensure the two modes appear in two distinct ranges of the IR fingerprint region. It is also important to note that as COF-like assemblies grow in size (e.g., ester series 2.17 → 2.24 → 2.28 → 2.31) asymmetric out-of-plane vibrations of multiple boroxine anhydride or boronate ester moieties decrease in relative intensity as their net dipole change becomes negligible. By contrast, the single, fully symmetric out-of-plane vibration of large assemblies increases in intensity such that it becomes increasingly distinct and diagnostic. For these reasons, it is believed that the symmetric out-of-plane vibrations of boroxine anhydride and boronate esters are especially valuable for distinguishing between the two assemblies.

Two additional conclusions about vibrations in the fingerprint region can be drawn from the summary presented in Figure 2.6. First, the higher frequency, lower intensity out-of-plane
vibrational mode of boroxine anhydrides (Figure 2.3d), while conserved across anhydrides 2.11–2.16, is not a reliably diagnostic mode. Out-of-plane Ar–H displacements of hydrogen atoms in catechol and oligocatechol derivatives also appear in this region for both boroxine anhydrides and boronate esters, and they are of medium to strong intensity. It is also important to note that this higher frequency mode involves out-of-plane boron displacements that are *anti* to out of plane Ar–H displacements. In larger assemblies, such as structure 2.29, the intensity of such *anti* out-of-plane vibrations drops essentially to the baseline. Second, the lowest-frequency vibration of boroxine anhydrides (Figure 2.4f) is also not reliably diagnostic for boroxine anhydrides. This low-frequency mode is observed to have variable intensity, span wide range of frequencies (500–628 cm$^{-1}$), and overlap with strong intensity low-frequency modes characteristic of boronic acids.

3. A strong C–O stretching mode between $\sim$1220–1240 cm$^{-1}$ (Figure 2.4c) is highly characteristic of boronate ester formation. This vibrational mode was observed to have the strongest intensity of all vibrations outside the fingerprint region for all but one of the 12 boronate esters investigated. Related C–O stretches of unassembled catechol and oligocatechol derivatives, while strong, occur at frequencies above 1250 cm$^{-1}$. No analogue of this mode exists for boroxine anhydrides as they simply do not contain the same C–O functionality. Boroxine anhydrides do share a common vibrational mode (Figure 2.3c) at frequencies just above the boronate ester C–O vibration. This boroxine anhydride mode, however, is often overshadowed by other stronger intensity boroxine anhydride modes above 1300 cm$^{-1}$ and is quite easily distinguished from the boronate ester C–O vibration. The only boronate ester observed to have a C–O stretch outside of 1220–1240 cm$^{-1}$ was compound 2.24, which is assembled from 1,2,4,5-tetrahydroxybenzene. The C–O stretches of boronate esters based on this tetraol, including theoretically investigated second generation assembly 2.30 and synthetically prepared COF-6, are observed at much lower frequencies around 1130–1160 cm$^{-1}$ (dashed blue line in Figure 2.6) for reasons discussed earlier. Overall, the sharpness and very high intensity of boronate ester C–O stretches in the 1220–1240 cm$^{-1}$ region of the IR spectrum render these bands to be some of the most diagnostic of boronate ester formation, especially when further supported by out-of-plane vibrations in the fingerprint region.
Conclusion

Boronic-acid-derived COFs exhibit a variety of useful, unique, and structure-dependent materials properties. Proper characterization of the structures and chemical connectivity of such COFs is therefore of significant importance. IR spectroscopy has arisen as one of the most prominent means of analyzing and characterizing COFs, however a survey of the literature has revealed that the vibrational characteristics of boronic acid derived COFs are often inconsistently assigned and generally not well categorized. The results presented herein provide a systematic investigation of the vibrational properties of a series of 28 different boronic acid, boroxine anhydride, and boronate ester species. IR bands observed experimentally have been assigned computationally. The collective data has allowed IR active vibrations conserved across the $\text{B(OH)}_2$, $\text{B}_3\text{O}_3$, and $\text{C}_2\text{O}_2\text{B}$ functionalities of boronic acids, boroxine anhydrides, and boronate esters, respectively, to be clarified and classified. IR bands present in one boron-containing functionality that may be mistaken as diagnostic for another have also been assigned through the combination of experimental and computational analysis. The results caution against using the commonly cited 1300–1400 cm$^{-1}$ as confirmation of boroxine anhydride or boronate ester species as strong bands are present in this region for all three boron-containing functionalities. Other regions of the IR spectrum are shown to be significantly more diagnostic for specific boron-containing functionalities. The collective results provide a straightforward means of determining which boron-containing functionalities are present in dynamically assembled 2D and 3D COFs and other boronic acid-derived materials. Although the series of 28 structures investigated cannot encompass the increasingly wide variety of secondary building units used in COF synthesis, the fact that vibrational modes characteristic of boronic acids, boroxine anhydrides, and boronate esters each fall within generally well-defined regions of the IR spectrum suggests that the conclusions presented herein can be applied broadly. Simple guidelines are also provided for the design of appropriate model systems to computationally investigate the vibrational properties of alternative COF structures. We anticipate the results and guidelines presented in this study will help provide greater clarity and consistency in the characterization of COFs and other boronic-acid-derived materials.
2.6 Experimental and Computational Methods

Materials
Chemicals were obtained from commercial sources and used as purchased. Reagent-grade solvents were used as obtained from commercial sources. Anhydrous solvents were dried using an Innovative Technologies SPS-400–5 solvent purification system.

Instrumentation
$^1$H and $^{13}$C NMR spectra were recorded with a Varian Mercury (300 and 75 MHz, respectively) spectrometer using residual solvent as the internal standard. All chemical shifts are quoted using the $\delta$ scale and all coupling constants are expressed in Hertz (Hz). Infrared spectroscopic analysis was performed on a PerkinElmer Spectrum BX FT-IR system. See Appendix II.1 for infrared spectra. CI and LIFDI TOF-MS analysis was carried out at the University of California, Riverside, Mass Spectrometry Facility (See Appendix II.2 for mass spectrometric data.

Computational Details
All calculations were performed with the Gaussian09 suite of programs. Prior to geometry optimization, dihedral scans were performed at a low level of theory (HF/3-21G) to approximate the global energy minimum conformation of molecular species containing easily rotating torsion angles. Ground-state geometries were then optimized to full convergence at the B3LYP/6-31G(d) level of theory. Vibrational analyses were carried out at the same level and the resulting frequencies were used to aid in assigning IR absorption bands observed experimentally. Calculated frequencies were scaled by a factor of 0.960. Several studies have demonstrated that geometry optimization and frequency analysis of polycyclic aromatic molecules performed at the B3LYP/6-31(d) level provides results that are in good agreement with experimental vibrational frequencies and intensities. Indeed, in the current study, frequencies obtained theoretically at the B3LYP/6-31G(d) level were observed to have a mean absolute deviation (MAD) of $\pm 8$ cm$^{-1}$ relative to experimental frequencies. For Cartesian coordinates, see Appendix II.3.
General Procedure for Boroxine Anhydrides 2.10–2.15

Boronic acids 2.1-2.6 were suspended in chloroform (0.5 M) in a round-bottom flask and ethyl acetate was added dropwise until a homogeneous solution was obtained. Each solution was then allowed to stir open to atmosphere and at room temperature for 30 min. A small amount of anhydrous MgSO$_4$ was then added to each flask and the resulting suspensions were allowed to continue stirring for 3 h. After this time the suspensions were filtered and the solvents were removed under reduced pressure to afford boroxine anhydrides 2.11–2.16. No attempts were made to optimize the synthetic yields of anhydrides 2.11–2.16. Emphasis was instead placed on isolating each assembly in its purest form to limit the possibility of obtaining IR spectra convoluted by incompletely assembled anhydride species and/or residual boronic acid.

2.11: Reaction scale. Boronic acid 2.1 (100 mg, 0.820 mmol). Yield: 75 mg, 0.241 mmol (88%). Boroxine anhydride 2.11 was isolated as a white solid. Mp > 200 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.27 (dd, $J = 7.9$, 1.2 Hz, 6H), 7.60–7.65 (m, 3H), 7.53 (t, $J = 7.0$ Hz, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 135.6, 132.7, 128.0 ppm. Characterization matched reported analysis.$^{2,19}$

2.12: Reaction scale. Boronic acid 2.2 (222 mg, 1.25 mmol). Yield: 182 mg, 0.387 mmol (91%). Boroxine anhydride 2.12 was isolated as a white solid. Mp = 174–179 °C. TOF MS FD$^+$ (m/z) [M]$^+$ calcd for C$_{30}$H$_{39}$B$_3$O$_3$, 480.3173; found 480.3195. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.21 (d, $J = 8.1$ Hz, 6H), 7.58 (d, $J = 8.4$ Hz, 6H), 1.42 (s, 27H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 172.1, 150.3, 102.1, 54.5, 54.0 ppm.

2.13: Reaction scale. Boronic acid 2.3 (250 mg, 1.79 mmol). Yield: 215 mg, 1.79 mmol (99%). Boroxine anhydride 2.13 was isolated as a white solid. Mp > 200 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.20–8.25 (m, 6H), 7.17–7.23 (m, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 130.1, 130.1, 138.0, 115.4, 115.2 ppm. Characterization matched reported analysis.$^{2,19}$

2.14: Reaction scale. Boronic acid 2.4 (250 mg, 1.64 mmol). Yield: 119 mg, 0.297 mmol (54%). Boroxine anhydride 2.14 was isolated as a white solid. Mp > 200 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.17 (d, $J = 8.8$ Hz, 6H), 7.02 (d, $J = 8.8$ Hz, 6H), 3.89 (s, 9H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 163.1, 137.5, 113.5, 55.1 ppm. Characterization matched reported analysis.$^{2,20}$
2.15: Reaction scale. Boronic acid 2.5 (250 mg, 1.39 mmol). Yield: 216 mg, 0.445 mmol (96%). Boroxine anhydride 2.15 was isolated as a white solid. Mp = >200 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.33 (d, $J = 8.2$ Hz, 6H), 8.19 (d, $J = 8.2$ Hz, 6H), 3.99 (s, 9H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 193.42, 135.61, 133.49, 128.92, 53.73 ppm. Characterization matched reported analysis.$^{221}$

2.16: Reaction scale. Boronic acid 2.6 (100 mg, 0.681 mmol). Yield: 66 mg, 0.504 mmol (74%). Boroxine anhydride 2.16 was isolated as a white solid. Mp > 200 °C. TOF MS FD$^+$ (m/z) [M]$^+$ calculated for C$_{21}$H$_{12}$B$_3$N$_3$O$_3$, 387.1152; found 387.1168. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.32 (d, $J = 8.1$ Hz, 6H), 7.82 (d, $J = 8.4$ Hz, 6H) ppm. Solubility precluded collection of a $^{13}$C NMR spectrum.

**General Procedure for Boronate Esters 2.17–2.28**

Three general methods were used to assemble discrete boronate ester species. No attempts were made to optimize the synthetic yields of esters 2.17–2.28. **Method A:** To a suspension of boronic acid in dichloromethane (0.3 M) was added the appropriate organic catechol. Ethyl acetate was added dropwise until a homogeneous solution was obtained and the resulting mixture was stirred at room temperature overnight. The reaction solution was dried over anhydrous MgSO$_4$, filtered, concentrated under reduced pressure, and purified via column chromatography eluting with a solution of hexanes:dichloromethane. **Method B:** To a suspension of boronic acid in chloroform (0.1 M) was added catechol (1.0 equiv. per boronic acid) and DOWEX (1 equiv by mass with respect to the boronic acid). The resulting suspension was stirred at 50 °C for 3 h, allowed to cool down to room temperature, dried over anhydrous MgSO$_4$, filtered, and concentrated under reduced pressure to afford pure boronate ester product. **Method C:** To a suspension of boronic acid in dichloromethane (0.3 M) was added the appropriate organic catechol. Ethyl acetate was added dropwise until a homogeneous solution was obtained and the resulting mixture was stirred at room temperature overnight. The reaction solution was dried over anhydrous MgSO$_4$, filtered, and allowed to slowly evaporate leaving clear crystals on the sides of the flask. When the solution had been reduced to approximately one-third of its original volume the remaining solvent was removed by pipet and the resulting crystals washed thoroughly with hexanes to afford pure boronate ester product.
2.17: Synthesized by Method A. Reaction scale. Boronic acid 2.1 (1.0 g, 8.20 mmol) and catechol (1.4 g, 12.3 mmol). Crude boronate ester 2.17 was subjected to column chromatography, eluting with 1:1 hexanes:dichloromethane, to afford 1.3 g (6.63 mmol, 81%) of a white solid product. This resulting solid was further purified by slow evaporation from a dilute solution of dichloromethane, yielding clear crystals that were isolated and washed thoroughly with hexanes. Mp = 104–105 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.12 (d, $J = 8.2$ Hz, 2H), 7.58–7.63 (m, 1H), 7.51 (t, $J = 7.2$ Hz, 2H), 7.31–7.36 (m, 2H), 7.12–7.18 (m, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 148.5, 135.0, 132.4, 122.8, 122.5 ppm. Spectroscopic analysis of pure 2.17 matched that reported in the literature.$^{2,22}$

2.18: Synthesized by Method B. Reaction scale. Boronic acid 2.2 (100 mg, 0.562 mmol) and catechol (62 mg, 0.562 mmol). Yield: 122 mg, 0.484 mmol (87%). The product was isolated as a white solid. Mp = 74–75 °C. TOF MS Cl$^+$ (m/z) [MH]$^+$ calcd for C$_{16}$H$_{18}$BO$_2$, 253.1394; found 253.1389. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.04 (d, $J = 7.8$ Hz, 2H), 7.53 (d, $J = 7.8$ Hz, 2H), 7.34–7.31 (m, 2H), 7.14,7.11 (m, 2H), 1.38 (s, 9H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 156.0, 148.8, 135.2, 125.5, 122.9, 112.8, 35.3, 31.4 ppm.

2.19: Synthesized by Method C. Reaction scale. Boronic acid 2.3 (250 mg, 1.79 mmol) and catechol (217 mg, 1.97 mmol). Yield: 133 mg, 0.622 mmol (35%). The product was isolated as a white solid. Mp = 90–91 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.07–8.12 (m, 2H), 7.30–7.35 (m, 2H), 7.11–7.23 (m, 4H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 167.4, 164.0, 148.5, 137.2, 122.8, 115.7, 112.5 ppm. Spectroscopic analysis matched literature values.$^{2,23}$

2.20: Synthesized by Method B. Reaction Scale: Boronic acid 2.4 (100 mg, 0.658 mmol) and catechol (72 mg, 0.658 mmol). Yield: 132 mg, 0.584 mmol (89%). The product was isolated as a white solid. Mp = 104–105 °C. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 8.04 (d, $J = 7.9$ Hz, 2H), 7.29–7.32 (m, 2H), 7.10–7.13 (m, 2H), 7.03 (d, $J = 8.8$ Hz, 2H), 3.89 (s, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 148.6, 136.8, 122.6, 113.9, 112.4, 55.2 ppm. Spectroscopic analysis matched literature values.$^{2,24}$

2.21: Synthesized by Method B. Reaction scale. Boronic acid 2.5 (100 mg, 0.556 mmol) and catechol (61 mg, 0.556 mmol). Yield: 92 mg, 0.362 mmol (65%). The product was isolated as a white solid. Mp = 176–177 °C. TOF MS Cl$^+$ (m/z) [MH]$^+$ calcd for C$_{14}$H$_{12}$BO$_4$, 255.0823;
found 255.0824. $^1$H NMR (CDCl$_3$, 300 MHz): δ 8.15–8.14 (m, 4H), 7.35–7.31 (m, 2H), 7.16–7.13 (m, 2H), 3.95 (s, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 167.1, 148.6, 135.1, 133.5, 129.3, 123.3, 113.0, 52.6 ppm.

2.22: Synthesized by Method B. Reaction scale. Boronic acid 2.6 (100 mg, 0.681 mmol) and catechol (75 mg, 0.681 mmol). Yield: 108 mg, 0.489 mmol (72%). The product was isolated as a white solid. Mp = 164–165 °C. TOF MS Cl$^+$ (m/z) [MH$^+$] calculated for C$_{13}$H$_9^{11}$BNO$_2$, 222.0721; found 222.073. $^1$H NMR (CDCl$_3$, 300 MHz): δ 8.19 (d, J = 7.5 Hz, 2H), 7.77 (d, J = 8.7 Hz, 2H), 7.36–7.32 (m, 2H), 7.18–7.15 (m, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 148.5, 135.5, 131.9, 123.5, 115.9, 113.1 ppm.

2.23: Synthesized by a modified Method C wherein pentane was used as the primary solvent with ethyl acetate added dropwise until all starting materials dissolved, and MgSO$_4$ was added to the reactants prior to stirring overnight. Reaction scale. Boronic acid 2.7 (200 mg, 1.33 mmol) and catechol (147 mg, 1.33 mmol). Yield 189 mg, 0.844 mmol (63%). The product was isolated as a waxy off-white solid. Mp = 67–68 °C. TOF MS Cl$^+$ (m/z) [MH$^+$] calculated for C$_{14}$H$_{14}^{11}$BO$_2$, 225.1081; found 225.1085. $^1$H NMR (CDCl$_3$, 300 MHz): δ 7.34–7.31 (m, 2H), 7.17–7.01 (m, 5H), 2.47 (s, 6H) ppm. $^{13}$C NMR (CD$_3$COCD$_3$, 75 MHz): 148.3, 144.1, 131.0, 127.4, 123.2, 120.8, 112.7, 22.4 ppm.

2.24: Synthesized by Method C. Reaction scale. Boronic acid 2.1 (258 mg, 2.11 mmol) and 1,2,4,5-tetrahydroxybenzene (143 mg, 1.01 mmol). Yield: 30 mg, 0.096 mmol (9%). The product was isolated as a white solid. Mp = >200 °C. $^1$H NMR (CDCl$_3$, 300 MHz): δ 8.09 (dd, J = 6.9, 1.5 Hz, 4H), 7.57–7.62 (m, 2H), 7.48–7.53 (m, 4H), 7.33–7.35 (m, 2H) ppm. Solubility precluded collection of a satisfactory $^{13}$C NMR spectrum. Spectroscopic analysis matched literature values.$^2$9

2.25: Synthesized by modified Method C. Reaction scale: Boronic acid 2.8 (100 mg, 0.603 mmol) and catechol (133 mg, 1.21 mmol). Yield: 68 mg, 0.217 mmol (36%). The product was isolated as a pinkish-white solid. Mp > 200 °C. $^1$H NMR (CDCl$_3$, 300 MHz): δ 8.21 (s, 4H), 7.34–7.36 (m, 4H), 7.16–7.18 (m, 4H) ppm. Solubility precluded collection of a $^{13}$C NMR spectrum. Spectroscopic analysis matched literature values.$^{2,25}$
2.26: Synthesized by Method C. Reaction scale: Boronic acid 2.9 (106 mg, 0.640 mmol) and catechol (148 mg, 1.34 mmol). Yield: 136 mg, 0.433 mmol (68%). The product was isolated as a white solid. Mp = >200 °C. TOF MS FD+ (m/z) [M]+ calculated for C_{18}H_{12}^{11}B_{2}O_{4}, 314.0916; found 314.0931. 1H NMR (CDCl$_3$, 300 MHz): δ 8.84 (s, 1H), 8.28 (dd, $J$ = 7.8, 1.5 Hz, 2H), 7.62 (t, $J$ = 7.8 Hz, 1H), 7.36–7.32 (m, 4H), 7.18–7.13 (m, 4H) ppm. Solubility precluded collection of a 13C NMR spectrum.

2.27: To a freshly prepared suspension of 1,3,5-benzenetriboronic acid 2.10 (585 mg, 2.79 mmol) in hexanes (20 mL) and water (5 mL) was added catechol (952 mg, 8.65 mmol). Catalytic methanol (0.5 mL) and ethyl acetate (3 mL) were added to increase solubility of the inhomogeneous mixture, which was then stirred for 30 min at room temperature. Following removal of the solvent under reduced pressure the resulting residue was taken up ethyl acetate, dried over anhydrous MgSO$_4$, filtered, and concentrated to afford a gray powder, which was washed with ethyl acetate and dichloromethane to give pure ester 2.27. Yield: 376 mg, 0.871 mmol (31%). Mp = >200 °C. TOF MS FD+ (m/z) [M]+ calculated for C$_{24}$H$_{15}$^{11}B$_{3}$O$_{6}$, 432.1142; found 432.1137. 1H NMR (CDCl$_3$, 300 MHz): δ 9.02 (s, 3H), 7.38–7.36 (m, 6H), 7.19–7.15 (m, 6H) ppm. Solubility precluded collection of a 13C NMR spectrum.

2.28: A mixture of 2,3,6,7,10,11-hexahydroxytriphenylene (140 mg, 0.431 mmol) and phenylboronic acid 2.1 (158 mg, 1.29 mmol) was suspended in 1:1 solution of mesitylene:dioxane (8.6 mL) in a 3 dram screw cap vial. The suspension was sonicated for 30 min and then heated in a convection oven at 100 °C overnight. The resulting suspension was filtered and the solids were washed with acetone. The crude material was then re-suspended in anhydrous acetonitrile for 90 min, filtered, and the solid was washed with acetone to afford 124 mg (0.213 mmol, 52% yield) of 2.28 as a lavender solid. Mp > 200 °C. TOF MS FD+ (m/z) [M]+calcd for C$_{36}$H$_{21}^{11}$B$_{3}$O$_{6}$, 582.1612; found 582.1639. 1H NMR (CDCl$_3$, 300 MHz): δ 8.46 (s, 6H), 8.20 (d, $J$ = 8.4 Hz, 6H), 7.73–7.56 (m, 9H) ppm. Solubility precluded collection of a 13C NMR spectrum.
2.7. References and Notes.


2.10. It should be noted that medium to strong intensity bands in the region between 900-1000 cm\(^{-1}\) have been observed for some COFs. The reported bands, however, are attributed to vibrational modes of more complex functionalities (e.g. borosilicates\(^{2.3c}\), benzothiadiazoles\(^{2.4e}\), or porphyrins\(^{2.4d}\)) present in the reported COFs.


2.15. Calculations predict assembly \(2.30\) to have two distinct frequencies for C–O vibrations: the one at 1127 cm\(^{-1}\) mentioned in the text and another at 1229 cm\(^{-1}\). The lower frequency
mode corresponds to C–O vibrations within the hexagonal ring of 2.30 while the higher frequency mode corresponds to C–O vibrations of the six phenyl boronate esters that line the periphery of the assembly. The significant difference between the endo and exo boronate ester C–O vibrational frequencies again highlights the influence of 1,2,4,5-tetrahydroxybenzene moiety.

2.16. Gaussian 09, Revision A.1, Frisch, M. J. et al., see Appendix A.II.4.

2.17. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. We note that additional density functionals and basis sets were benchmarked against the experimental FTIR spectra of a subset of boroxine anhydride and boronate ester and the combination of B3LYP/6-31G* provided the best balance of computational cost and consistency with experimental results.


Chapter 3 – Novel Triphenylene-Based Liquid Crystals
This Chapter is based on the following work:


and

Work in progress titled: ‘Symmetric and Mixed-Substituent Benzo[h]pentaphene Derivatives: Synthesis and Regio-Dependent Phase Behavior.’ (Smith, M.K.; Goldberg, A. R.; Northrop, B. H.). Originally submitted as a communication, at the recommendation of reviewers we are gathering more data and re-submitting as a full article.

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3.0. Abstract

A straightforward, reliable, and scalable synthesis of rationally designed, mixed-substituent triphenylene derivatives from *ortho*-terphenyl precursors is described. Three isomers of bis(hexyloxy)-tetrahydroxy triphenylenes were synthesized and functionalized with monomethyl di(ethylene glycol) chains to provide new amphiphilic, mixed substituent triphenylenes. Oxidative triphenylene annulation, tetra-ol formation, and subsequent functionalization were supported by significant changes in phase and melting point, and confirmed by mass spectrometry, differential scanning calorimetry, and UV/Vis, $^1$H, and $^{13}$C NMR spectroscopies. The thermal phase properties of amphiphilic mixed-substituent triphenylene derivatives were found to vary between the different isomers, demonstrating how small changes in substitution pattern can result in significant differences in mesogenic behavior. The controlled synthetic route to *de novo* designed triphenylene derivatives is dependable, wide in scope, and can be applied to the synthesis of a vast array of other mixed-substituent triphenylene derivatives, thus enabling the preparation of libraries of novel triphenylene and triphenylene-containing materials. To that end, the first synthesis of four hexa-substituted benzo[h]pentaphene derivatives is described. The high-yielding synthetic protocols provide regioselectively substituted expanded triphenylene derivatives with useful optical and physical properties, including significant emission in the violet region of the spectrum. Positioning of varying length alkoxy chains on the phenyl or naphthyl moieties reveals regio-dependent liquid crystallinity, providing insight into the influence of chain length versus $\pi$-surface area in macrodiscotic mesogens.

3.1. Tetra-Hydroxy and Amphiphilic Triphenylene Derivatives

3.1.1. Introduction

Polycyclic aromatic triphenylene derivatives are well-known for their mesogenic behavior.$^{3,1}$ Examples of over 500 discotic liquid crystals incorporating a triphenylene core have been reported in the literature.$^{3,1c,3,2}$ The delocalized 18 $\pi$-electron system and high thermal and chemical stabilities$^{3,3}$ of triphenylenes make them well-suited as components in optoelectronic,$^{3,4}$ photoconductive,$^{3,5}$ and electroluminescent$^{3,6}$ materials, with potential applications as liquid crystalline semiconductors.$^{3,7}$ Typically, mesogenic triphenylenes are
functionalized with alkyl groups at their periphery to facilitate columnar phase assembly through a combination of aliphatic van der Waals interactions and aromatic $\pi-\pi$ stacking of triphenylene cores.\textsuperscript{3,1,3,3a,3.8} In particular, triphenylene assembly is enhanced by the six-fold substitution of medium length alkyloxy chains at the 2, 3, 6, 7, 10, and 11 positions.\textsuperscript{3.9} Synthetic routes toward six-fold substituted triphenylenes are well-established,\textsuperscript{3,3b,3.10} and symmetric triphenylenes have been prepared with a variety of substituents, including alkyl chains,\textsuperscript{3.1c} esters,\textsuperscript{3,2a,3.11} thioesters,\textsuperscript{3,7a,3.12} and benzyl ether\textsuperscript{3,2b,3.13} moieties. Most commonly, symmetric hexa-substituted triphenylenes have been prepared by the alkylation of 2,3,6,7,10,11-hexahydroxytriphenylene, which is prepared from the demethylation of 2,3,6,7,10,11-hexamethoxytriphenylene (Scheme 3.1).\textsuperscript{3.1}

![Scheme 3.2](image)

**Scheme 3.2:** Common retrosynthetic route to symmetrically substituted triphenylene mesogens: (i) alkylation, (ii) O-demethylation, (iii) oxidative trimerization.

While synthetic routes to symmetric triphenylenes are well established, there are few reliable and scalable synthetic routes to asymmetric or mixed-substituent triphenylene derivatives that are not complicated by the formation of closely related byproducts. This is despite the fact that such compounds are increasingly desirable as varying the substituents at precise locations on the triphenylene core can affect their mesogenic behavior and lead to new and unique materials properties.\textsuperscript{3,14} Synthetic routes reported to produce mixed-substituent 2, 3, 6, 7, 10, 11 substituted triphenylenes typically rely on oxidative trimerization, dimerization,\textsuperscript{3,15} or annulation\textsuperscript{3,16} of substituted aryl systems (Table 3.1). Originally, mixed substituent or asymmetric triphenylenes were prepared by oxidative trimerization of substituted catechols using chloranil and acid,\textsuperscript{3,10b,3.15} but the low yields of desired products prompted the development of new methods. Oxidative Scholl annihilations of differently substituted catechols (Table 3.1, entry A) or catechols and biphenyls (Table 3.1, entry B) using agents such as FeCl$_3$ and MoCl$_5$ have provided routes to mixed-substituent triphenylenes.\textsuperscript{3,17,3.18} These pathways, however, require a large stoichiometric excess of oxidant and often result in undesirable side products that can be difficult or impossible
to separate. Tricyclic ortho-terphenyl precursors (Table 3.1, entry C) eliminate triphenylene-based side products and require fewer equivalents of oxidant,\textsuperscript{3,4a,3,18} making them attractive target compounds for asymmetric triphenylene synthesis. Ortho-terphenyl precursors of mixed-substituent triphenylene derivatives, however, typically require a greater number of synthetic steps to prepare.

**Table 3.1**: Summary of general synthetic routes to mixed-substituent triphenylene derivatives including oxidative trimerization of different catechol derivatives (entry A), oxidative dimerization of a catechol derivative with substituted biphenyls (entry B), and oxidative annulation of ortho-terphenyl derivatives bearing different substituents (entry C)\textsuperscript{a}

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\textsuperscript{a} Oxidative trimerization and dimerization reactions are commonly carried out using oxidants such as chloranil or Lewis acids such as FeCl\textsubscript{3}, MoCl\textsubscript{5}, VoCl\textsubscript{3}, etc. The annulation of ortho-terphenyl derivatives has been carried out using these transition metal oxidants or anion-catalyzed TBAF ring closure.

An alternative route to mixed triphenylene derivatives can involve the selective alkylation of triphenylene poly-ols in a manner analogous to the synthesis of symmetric triphenylene derivatives from triphenylene hexaol as shown in Scheme 3.1. To that end, selectively
substituted triphenylene mono and poly-ols are valuable precursors to mixed-substituent triphenylenes. Care must be taken to design appropriate synthetic routes to triphenylene poly-ols as catechol protecting groups must be both stable to oxidative conditions used in the construction of the central triphenylene core, and easily and orthogonally removed to reveal the desired triphenylene poly-ol. As such, examples of routes to non-saturated triphenylene poly-ols are limited in scope and methodology. Mono-, di-, and tri-ols have been reported, but many have been synthesized through non-selective means.\textsuperscript{3,19} Ringsdorf and co-workers, for example, have prepared penta-substituted triphenylene mono-ols by the partial cleavage of alkoxy groups from hexa-substituted triphenylenes using 9-Br-BBN.\textsuperscript{3,20} The alkyl cleavage, however, was non-selective. Bushby and Lu reported a rational route to mono- and di-hydroxy triphenylenes by using isopropyl substituents to mask hydroxyl groups in the FeCl\textsubscript{3}-oxidized dimerization of selectively substituted catechols and biphenyls.\textsuperscript{3,21} Another selective route reported by Kumar and Manickam relied upon bromocatecholborane to cleave one, two, or three pentyl substituents from hexakis(pentyloxy) triphenylene resulting in the desired mono-, di-, and tri-ol products but yields were variable (17–70\%) and the authors noted difficult purifications.\textsuperscript{3,22} In general, it is evident that the synthetic methods used to produce unsaturated triphenylene poly-ols tend to be harsh and non-selective, making the controlled synthesis of triphenylene tetra-ols particularly challenging. A reliable, controlled, scalable route to prepare rationally designed triphenylene poly-ol compounds is needed to fully explore the full variability and utility of mixed-substituent mesogenic triphenylene materials.

Our interest in the synthesis of triphenylene tetra-ols arose from our desire to prepare triphenylene derivative 3.1 (Figure 3.1) for use in dynamically assembled boronate ester materials. The dynamic self-assembly of catechol derivatives with boronic acids to form boronate esters has recently received increasing attention due to the development of structurally precise, highly porous covalent organic frameworks (COFs).\textsuperscript{3,23} Along similar lines we have sought to design and self-assemble a variety of discrete, soluble analogues of COFs.\textsuperscript{3,24} Such analogues would allow us to investigate the mechanism of COF assembly in solution and the properties of boronate ester mesogens. Triphenylene tetra-ol 3.1, for example, can serve as a precursor to a discrete analogue of the widely studied COF-5 framework.\textsuperscript{3,25} In developing a convenient synthetic route to 3.1 it became evident that similar synthetic routes could be used to prepare a variety of differently substituted triphenylene tetra-ols. Herein we report the reliable
synthesis of three isomers of tetra(hydroxy) triphenylene derivatives (3.1–3.3) as well as their functionalization with monomethyl di(ethylene glycol) chains to give three new amphiphilic, mixed substituent triphenylenes (3.4–3.6), which provide an opportunity to investigate the influence of regioisomerism on the thermal properties of mixed substituent triphenylene derivatives.

![Chemical structures](image)

**Figure 3.1:** Chemical structures of target bis(hexyloxy)-tetra(hydroxy) triphenylene derivatives 3.1–3.3 and their corresponding amphiphilic derivatives 3.4–3.6, which have been functionalized with monomethyl di(ethylene glycol) substituents.

### 3.1.2. Development of Synthetic Route

Initial attempts at the synthesis of 3.1 involved the oxidative dimerization of symmetric and asymmetric substituted biphenyl compounds with functionalized catechols, employing a variety of protecting groups, transition metal oxidants, and reaction conditions. In all cases the desired product was either not observed or obtained in low yield and purification was complicated by the prevalence of undesired byproducts. Attention was therefore turned to the synthesis of ortho-terphenyl compounds that would likely undergo more selective and controlled annulation to desired triphenylene derivatives. Toward this end ortho-terphenyl derivative 3.9 was prepared by Suzuki–Miyaura coupling of 4,5-dibromo-1,2-bishexyloxy benzene 3.7 and bis(tert-butyldimethylsilyl) (TBDMS) protected aryl pinacolborane 3.8 (Scheme 3.2). Precursors 3.7 and 3.8 were prepared from 4,5-dibromoveratrole and 4-bromoveratrole in two and three steps, respectively.
Scheme 3.3: Synthesis of ortho-terphenyl 3.9 from the palladium-catalyzed cross-coupling of bis(hexyloxy)-substituted benzene dibromide 3.7 and bis(tert-butyldimethylsilyl) protected aryl pinacolborane 3.8.

Kumar and coworkers have previously reported that treatment of a related methoxy-substituted ortho-terphenyl derivative with tetra-butyl ammonium fluoride (TBAF) results in the sequential deprotection of the TBDMS moieties and subsequent annulation to give tetra(hydroxy) triphenylene derivatives.\textsuperscript{3,27} Attempts to adapt this TBAF-promoted deprotection/annulation, while promising at preparative scales and when hexyloxy chains were replaced with methoxy substituents, were unsuccessful when run at larger scales or when applied to compound 3.9. Alternative conditions for oxidative annulation were then explored. Rathore and others have shown that oxidative cyclodehydrogenation of various Scholl precursors can be carried out efficiently and in high yields using a mixture of dichlorodicyano-p-benzoquinone (DDQ) and an acid.\textsuperscript{3,28} Indeed, reacting ortho-terphenyl compound 3.9 and stoichiometric DDQ in a 10 : 1 mixture of dichloromethane/TFA gave annulated triphenylene derivative 3.10 in good yield (Scheme 3.3). Subsequent deprotection of the four TBDMS groups at positions 6, 7, 10, and 11 with KF and HBr resulted in the desired 2,3-bis(hexyloxy)-6,7,10,11-tetrahydroxy triphenylene 3.1. The overall synthetic route to triphenylene tetra-ol 3.1 outlined in Schemes 3.2 and 3.3 has several notable advantages over previous routes to triphenylene poly-ols, namely (i) it avoids the production of alternative triphenylene byproducts, (ii) the number and location of
hydroxyl functionalities in the product are controlled precisely, and (iii) the route can be easily and reliably scaled to gram quantities.

**Scheme 3.3:** Successful annulation of ortho-terphenyl derivative 3.9 to triphenylene 3.10 followed by subsequent TBDMS deprotection to give triphenylene tetra-ol 3.1.

Given the reliability of the synthetic route to triphenylene tetra-ol 3.1 it became apparent that the synthesis could be readily adapted to the preparation of additional triphenylene tetra-ol isomers 3.2 and 3.3 (Figure 3.1). The key synthetic intermediates along the routes to tetra-ols 3.2 and 3.3 are uniquely substituted ortho-terphenyl derivatives, which can be similarly prepared from Suzuki–Miyaura couplings of aryl pinacolboranes and aryl dihalides that are different variations of compounds 3.7 and 3.8 (Scheme 3.2). The choice of substituents in the pinacolborane and dihalide precursors precisely determines the substituent pattern in their final triphenylene tetra-ols. Scheme 3.4 summarizes the synthetic routes to the three synthetic precursor compounds 3.14, 3.18, and 3.19. Aryl pinacolboranes 3.14 and 3.18 are isomers of each other that differ only in the placement of their hexyloxy and tert-butyldimethylsilyloxy (OTBDMS) groups: in compound 3.14 the hexyloxy and OTBDMS substituents are meta and para to the pinacolborane, respectively, while in compound 3.18 the hexyloxy substituent is para to the pinacolborane and the OTBDMS is meta. The synthesis of compound 3.14 (Scheme 3.4a) requires statistical alkylation of catechol (3.11) followed by bromination (3.12), protection with TBDMS (3.13), and ultimately borylation using conditions developed by Buchwald. Compound 3.18 was synthesized along a related but slightly different route (Scheme 3.4b), starting with the alkylation of 5-bromosalicylaldehyde to give 3.15, Baeyer–Villiger rearrangement to give the alcohol 3.16, protection with TBDMS to provide 3.17, and finally borylation. The third key precursor shown in Scheme 3.4c is di(t-butyldimethylsilyloxy) dibromide 3.19, which is easily prepared in two steps from
Scheme 3.4: Synthetic routes to two isomeric aryl pinacolboranes 3.14 (a) and 3.18 (b), each of which are catechol derivatives possessing one hexyloxy substituent and one tert-butyldimethylsilyloxy group. Shown in (c) is the synthesis of bis(tert-butyldimethylsilyloxy) dibromide 3.19.

With compounds 3.14, 3.18, and 3.19 at hand the preparation of triphenylene tetra-ols 3.2 and 3.3 (Scheme 3.5) follows the same general method as the preparation of isomeric triphenylene tetra-ol 3.1. Suzuki–Miyaura coupling of 3.14 and 3.19 gives ortho-terphenyl 3.20. Oxidative annulation of 3.20 with DDQ in the presence of TFA results in tetra(tert-butyldimethylsilyloxy) triphenylene derivative 3.21, which is subsequently deprotected with KF in HBr to provide 2,7-bis(hexyloxy)-3,6,10,11-tetrahydroxy triphenylene 3.2. Likewise, palladium-catalyzed coupling of 3.18 and 3.19 gives ortho-terphenyl derivative 3.22. DDQ oxidation of 3.22 in TFA/dichloromethane gives annulated tetra(tert-butyldimethylsilyloxy)
product \textbf{3.23}. The TBDMS protecting groups of \textbf{3.23} are deprotected with KF and HBr to give 3,6-bis(hexyloxy)-2,7,10,11-tetrahydroxy triphenylene \textbf{3.3}. While the syntheses of isomeric triphenylene tetra-ols \textbf{3.1–3.3} each require 8 linear synthetic steps the reactions proceed, with one exception,\textsuperscript{3,33} in good to excellent yields (59–99\%) and are completely selective, providing highly controlled synthetic routes to precisely functionalized triphenylene tetra-ols.

\begin{center}
\textbf{Scheme 3.5:} Synthesis of isomeric triphenylene tetra-ols \textbf{3.2} and \textbf{3.3} from precursors \textbf{3.14} and \textbf{3.19} or \textbf{3.18} and \textbf{3.19}, respectively, following the synthetic route involving Suzuki–Miyaura coupling, oxidative annulation, and TBDMS deprotection.
\end{center}

Triphenylene tetra-ols \textbf{3.1–3.3} are able to serve as versatile platforms for the preparation of mixed-substituent triphenylene derivatives. As representative examples of the ease with which hydroxyl functionalities of compounds \textbf{3.1–3.3} can be functionalized we have prepared mixed-substituent amphiphilic triphenylene derivatives \textbf{3.4–3.6} (Scheme 3.6). In each case, all four hydroxyl groups were successfully substituted with di(ethylene glycol) monomethyl ether tosylate\textsuperscript{3,34} in moderate yields. The versatility of the synthetic route presented herein should be reiterated, as any substituent with suitably electrophilic character could be used at this stage to provide libraries of mixed-substituent triphenylene derivatives. With rational routes to amphiphilic triphenylenes \textbf{3.4–3.6} the relative locations of hexyl and monomethyl di(ethylene glycol) substituents along the triphenylene core are completely controlled. Di(ethylene glycol) substituents were chosen because they are known to crystallize less readily than comparable length alkyl substituents. By substituting triphenylene cores with two substituents that favor crystallization (\textit{i.e.} hexyloxy) and four that disfavor crystallization (\textit{i.e.} monomethyl di(ethylene glycol)) amphiphilic triphenylene derivatives can exhibit low temperatures of crystallization.
glycol)) we are able to investigate how the thermal and physical properties of mixed-substituent triphenylenes vary between different regioisomers.

**Scheme 3.6:** Functionalization of triphenylene tetra-ols 3.1–3.3 with hydrophilic monomethyl di(ethylene glycol) substituents to give mixed-substituent triphenylene derivatives 3.4–3.6.

### 3.1.3. Spectroscopic Characterization

The key step in our synthesis of triphenylene tetra-ols 3.1–3.3 is the oxidative annulation of *ortho*-terphenyl derivatives to their corresponding triphenylene derivatives by DDQ in the presence of acid (TFA). This transformation is easily observed by $^1$H NMR spectroscopy as diagnostic proton signals in the aromatic region of the spectra of *ortho*-terphenyl compounds 3.9, 3.20, and 3.22 shift substantially downfield upon annulation to triphenylene derivatives 3.10, 3.21, and 3.23, respectively. Figure 3.2 provides a representative example of these spectral changes highlighting the spectroscopic shifts observed upon annulation of *ortho*-terphenyl 3.9 to triphenylene 3.10. Singlet H$_a$ of the dihexyloxy ring shifts downfield from 6.85 ppm in *ortho*-terphenyl derivative 3.9 to 7.74 ppm in triphenylene derivative 3.10. Proton signals H$_b$ and H$_c$ of the di(tert-butyldimethylsilyloxy) rings, which overlap in the region from 6.60–
6.67 ppm in 3.9, separate into two distinct singlets at 7.79 and 7.83 ppm in annulated product 3.10. Lastly, the doublet at 6.54 ppm that corresponds to proton H_d of *ortho*-terphenyl derivative 3.9 is no longer present in the annulated triphenylene derivative. Accurate mass APCI mass spectrometric analysis further supports the loss of two hydrogen atoms upon annulation: \( m/z = 951.6180 \) [M+H]^+ for *ortho*-terphenyl 3.9 and 949.6027 [M+H]^+ for triphenylene 3.10 (\( \Delta m/z \) 3.9–3.10 = 2.0153) compared with calculated values of 951.6200 and 949.6044 (\( \Delta m/z \) = 2.0156), respectively. Cleavage of the four TBDMS protecting groups of triphenylene derivative 3.10 with KF and HBr (Scheme 3.3) is accompanied by the loss of peaks at 0.98, 0.94, 0.19 and 0.08 ppm as well as a significant change in compound solubility: the deprotected triphenylene tetra-ol 3.1 displays very limited solubility in chloroform but is well solvated in more polar solvents such as acetone and tetrahydrofuran. Accurate mass APCI mass spectrometric analysis of triphenylene tetra-ol 3.1 reveals an [M+H]^+ signal at \( m/z = 493.2575 \), which is in agreement with the calculated value of 493.2585 and commensurate with the loss of four TBDMS groups. Similar changes in the \(^1\)H NMR spectra and APCI mass spectra accompany the oxidative annulation and KF deprotection of *ortho*-terphenyl 3.20 to TBDMS-protected triphenylene 3.21 and ultimately tetra-ol 3.2, as well as from regioisomeric *ortho*-terphenyl 3.22 to TBDMS-protected triphenylene 3.23 and tetra-ol 3.3.

![Figure 3.4: Representative partial \(^1\)H NMR spectrum (300 MHz, CDCl\(_3\), 298 K) of *ortho*-terphenyl derivative 3.9 (top) and TBDMS-protected triphenylene derivative 3.10 (bottom) indicating characteristic shifts of aromatic signals upon oxidative annulation.](image)

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While proton signals in the $^1$H NMR spectra of 3.10, 3.21, and 3.23 support the successful formation of triphenylene derivatives, the three regioisomers cannot be distinguished by proton spectra alone. Similarly, mass spectroscopic analyses of the three TBDMS-protected triphenylene derivatives are, within error, identical ($m/z = 946.6027$, 949.6031, and 949.6034 [M + H]$^+$ for 3.10, 3.21, and 3.23, respectively). $^{13}$C NMR spectroscopy, however, does provide a means of distinguishing between the three different isomers. As shown in Figure 3.3, the nine carbon signals in the aromatic region of 3.10, 3.21, and 3.23 can be grouped into three clusters of three peaks each. The quaternary carbons of the central six-member ring of each triphenylene, labeled C$_1$–C$_3$ in Figure 3.3, are the farthest downfield (144–150 ppm) due to greater deshielding in this central ring. The peripheral quaternary carbon atoms (C$_4$–C$_6$ in Figure 3.3) fall within a tighter range of 123–125 ppm. Lastly, the methine carbons (C$_7$–C$_9$ in Figure 3.3) are found between 106–114 ppm.

**Figure 3.5:** Partial $^{13}$C NMR spectrum (75 MHz, CDCl$_3$, 298 K) of TBDMS-protected triphenylene derivatives 3.23 (top), 3.21 (middle), and 3.10 (bottom) highlighting the differences in chemical shift that distinguish each regioisomer.
As can be seen in Figure 3.3, the carbon signals C₁–C₃ of triphenylene derivatives 3.21 and 3.23 are highly similar while those of 3.10 are more distinct. This distinction comes from the fact that carbon C₁ of compound 3.10 at 148.7 ppm is contained within an aryl ring bearing two hexyloxy substituents, a feature not present in any of the aryl rings of isomers 3.21 or 3.23. Furthermore, carbons C₂ and C₃ of compound 3.10 both appear at 146.6 ppm as they occupy almost identical positions within aryl rings bearing two OTBDMS groups. Three distinct signals are observed for carbon atoms C₁–C₃ of compounds 3.21 and 3.23: one assigned to a carbon atom within a di(OTBDMS) ring, one assigned to a carbon atom proximal to the hexyloxy group of a mixed hexyloxy/OTBDMS ring, and one assigned to a carbon atom proximal to the OTBDMS group of a mixed hexyloxy/OTBDMS ring. Given this similarity between isomers 3.21 and 3.23 the signals for carbons C₁–C₃ appear almost indistinguishable.

In the middle cluster of signals, corresponding to carbon atoms C₄–C₆, isomer 3.10 again displays a distinct pattern while isomers 3.21 and 3.23 are significantly more similar. Carbon signals for compound 3.10 in this region appear at two chemical shifts: one isolated peak corresponding to C₄ at 123.2 ppm and two overlapping peaks corresponding to carbon atoms C₅ and C₆ at 124.0 ppm. Carbon atom C₄ is distinct as it is substituted with hexyloxy groups whereas C₅ and C₆, while symmetrically inequivalent, are both substituted with an OTBDMS group and are observed at the same chemical shift. Isomers 3.21 and 3.23 again display three distinct peaks for C₄–C₆ following the same reasons as discussed above for distinguishing their C₁–C₃ signals. Lastly, isomers 3.21 and 3.23 can be distinguished from each other by the shifts of methine carbon signals in the region spanning 106–114 ppm. Within this region the carbon atom alpha to a hexyloxy-substituted peripheral carbon is found farthest upfield and at a unique chemical shift: 106.8 for C₇ of 3.10, 105.8 for C₈ of 3.21, and 106.2 for C₉ of 3.23. Furthermore, in compound 3.23, methine carbon atoms C₇ and C₈ are in subtly distinct chemical environments such that their signals appear close (114.2 and 113.9, respectively) but do not overlap. For isomers 3.10 and 3.21, however, signals for the methine carbon atoms alpha to OTBDMS-substituted peripheral carbon atoms are sufficiently similar that they do overlap and cannot be resolved. Collectively, the nine aromatic carbon signals in the $^{13}$C NMR spectra of triphenylene isomers 3.10, 3.21, and 3.23 provide a means of distinguishing each isomer.
Functionalization of triphenylene tetra-ols 3.1–3.3 to give amphiphilic, mixed-substituent triphenylenes 3.4–3.6 was confirmed by the disappearance of hydroxyl peaks and concomitant appearance of ethylene glycol peaks in the region extending from 3.4 to 4.5 ppm of the $^1$H NMR spectra of each species. Functionalization with monomethyl di(ethylene glycol) chains was also accompanied by a notable increase in the solubility of each compound and a phase change from high melting solid materials to low melting solids (3.4 and 3.6) and one liquid (3.5). Mass spectroscopic analysis confirmed the addition of four monomethyl di(ethylene glycol) substituents to compounds 3.1–3.3, revealing [M+Na]$^+$ signals at $m/z = 923.5148$, 923.5137, and 923.5153 for mixed-substituent triphenylene derivatives 3.4–3.6, respectively, compared to the calculated value of 923.5127.

### 3.1.4. Optical and Thermal Properties

The three triphenylene tetra-ols 3.1–3.3 and amphiphilic triphenylenes 3.4–3.6 were also characterized by UV/Vis spectroscopy. Spectra of all six compounds display nearly identical absorption maxima ($\lambda_{\text{max}} = 345 \pm 1$ nm) with extinction coefficients ranging from $\varepsilon = 3.2–4.9 \times 10^4$ M$^{-1}$ cm$^{-1}$ (Appendix III.3, Figures A.III.3 and A.III.4, p.A66). These absorption characteristics closely mirror those of fully symmetric hexakis(hexyloxy) triphenylene ($\lambda_{\text{max}} = 346$ nm, $\varepsilon = 5.2 \times 10^4$ M$^{-1}$ cm$^{-1}$), hexa(hydroxy) triphenylene ($\lambda_{\text{max}} = 346$ nm, $\varepsilon = 4.0 \times 10^4$ M$^{-1}$ cm$^{-1}$), and hexakis(monomethyl di(ethylene glycol)) triphenylene ($\lambda_{\text{max}} = 345$ nm, $\varepsilon = 4.0 \times 10^4$ M$^{-1}$ cm$^{-1}$).

Lastly, the thermal properties of new amphiphilic triphenylene derivatives 3.4–3.6 were investigated by differential scanning calorimetry (DSC) and compared to symmetric control compounds hexakis(hexyloxy) triphenylene (3.25) and hexakis(monomethyl di(ethylene glycol)) triphenylene (3.26). As noted earlier, monomethyl di(ethylene glycol) substituents were chosen because ethylene glycol chains are less crystalline than comparable length alkyl chains. Indeed, DSC analysis of hexakis(hexyloxy) triphenylene 3.25 reveals a sharp crystallization at 51 °C whereas crystallization is suppressed for hexakis(monomethyl di(ethylene glycol)) triphenylene 3.26 (See Appendix III.4, Figures A.III.5 and A.III.6, p. A68). Furthermore, alkyl-
substituted 3.25 exhibits a mesophase between 56 and 64 °C, in good agreement with the reported formation of a columnar hexagonal (Col\textsubscript{h}) liquid crystalline phase.\textsuperscript{3,35} Hexakis(monomethyl di(ethylene glycol))-substituted 3.26, by contract, becomes isotropic at 47 °C with no evidence of mesophase formation. The thermal properties of amphiphilic triphenylenes 3.4–3.6 may be expected to vary between those of triphenylenes 3.25 and 3.26, and provide a means of assessing the influence of alkyl \textit{versus} ethylene glycol regiochemistry on triphenylene phase behavior.

Table 3.2: Phase transition temperatures (°C) of substituted triphenylenes. Transition temperatures are based on the 1\textsuperscript{st} cooling run (5°C/min) and 2\textsuperscript{nd} heating run (10°C/min). T\textsubscript{M} = Transition to mesophase, T\textsubscript{I} = clearing temperature (isotropic melt).

<table>
<thead>
<tr>
<th>Compound</th>
<th>T\textsubscript{M}</th>
<th>T\textsubscript{I}</th>
<th>Mesophase</th>
<th>a</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
<td>56</td>
<td>64</td>
<td>Col\textsubscript{h}</td>
<td></td>
</tr>
<tr>
<td>3.4</td>
<td>37</td>
<td>55</td>
<td>(6)</td>
<td></td>
</tr>
<tr>
<td>3.5</td>
<td>(-6)</td>
<td>28</td>
<td>Col\textsubscript{h}</td>
<td>a</td>
</tr>
<tr>
<td>3.6</td>
<td>33</td>
<td>44</td>
<td>Col\textsubscript{h}</td>
<td></td>
</tr>
<tr>
<td>3.26</td>
<td>-</td>
<td>47</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Compound 3.5 exhibits a broad mesophase between (-6) and 28 °C. Dissimilarity from the characteristic columnar hexagonal mesophase prevents conclusive mesophase characterization other than a possible ordered nemetic phase.

Shown in Table 3.2 are the phase transitions of triphenylene derivatives 3.4–3.6 and 3.25–3.26. Also shown in Table 3.2 are schematic representations of each triphenylene derivative that aid in understanding how substituent regiochemistry in amphiphilic triphenylenes influences thermal phase transitions. Of the three amphiphilic triphenylenes studied, compound 3.4, bearing hexyloxy substituents at positions 2 and 3, was found to behave most similar to hexakis(hexyloxy) triphenylene 3.25. Compound 3.4 shows a sharp crystallization at a lower temperature than all-hexyloxy 3.25 (39 °C \textit{versus} 51 °C) and similarly transitions to isotropic at a lower temperature than compound 3.25 (57 °C \textit{versus} 64 °C), as would be expected with the introduction of monomethyl di(ethylene glycol) chains. It is interesting to note that amphiphilic triphenylene 3.4 exhibits a broader mesophase (37–57 °C) than all-hexyloxy
triphenylene \textbf{3.25} (56–64 °C). By contrast, amphiphilic triphenylene derivative \textbf{3.5}, with hexyloxy substituents at the 2 and 7 positions, does not show a sharp melt (or crystallization) but rather a broad transition around −6 °C. A second transition is observed at 28 °C, likely indicating the formation of a nematic mesophase rather than a columnar phase more typical of compound \textbf{3.25}. Lastly, compound \textbf{3.6} with hexyloxy substituents at positions 3 and 6 exhibits a narrower mesophase between 33 and 44 °C. Compound \textbf{3.6}, therefore, becomes isotropic at a temperature below triphenylene derivatives \textbf{3.4}, \textbf{3.25}, and \textbf{3.26} yet above derivative \textbf{3.5}. Similar to hexakis(monomethyl di(ethylene glycol)) triphenylene \textbf{3.26}, no distinct crystallization could be observed for amphiphilic triphenylene derivative \textbf{3.6}.

The results presented in Table 3.2 clearly show that the relative placement of hexyloxy chains in amphiphilic triphenylene derivatives \textbf{3.4–3.6} significantly influences their phase behavior. Given the observed results, we hypothesize that the primary factor influencing phase behavior in compounds \textbf{3.4–3.6} is the relative spacing of their two hexyloxy substituents. Alkyl chains are known to promote crystallinity and long-range order in triphenylene mesogens.\textsuperscript{3.1–3.3} As such, placement of the two hexyloxy chains as close to each other as possible – \textit{i.e.} 2,3-bis(hexyloxy) derivative \textbf{3.4} – results in the amphiphilic derivative with the highest clearing temperature of 55 °C along with a well-defined crystallization (Appendix III.4). The clearing temperature of the amphiphilic 2,6-bis(hexyloxy) derivative \textbf{3.6}, with its hexyloxy substituents spaced slightly further apart than in compound \textbf{3.4}, is observed 11 °C lower at 44 °C. Amphiphilic derivative \textbf{3.5} is notably different than derivatives \textbf{3.4} and \textbf{3.6} because its hexyloxy substituents are almost diametrically opposed at positions 2 and 7. As such, monomethyl di(ethylene glycol) substituents fully segregate the two hexyloxy substituents from each other (as indicated by dashed curves in Table 3.2) whereas hexyloxy substituents are not similarly segregated from each other in derivatives \textbf{3.4} and \textbf{3.6}. This greater separation of hexyloxy substituents further inhibits crystallization and depresses the clearing temperature of derivative \textbf{3.5} to 28 °C. Further investigation of mixed hexyloxy and monomethyl di(ethylene glycol) substituted triphenylenes that vary in both the stoichiometry (1 : 5 through 5 : 1) and relative positioning of the different substituents will be necessary to determine if this preliminary trend is more broadly applicable. Such investigations are currently underway.
3.2. Expanded Triphenylenes as Macrodiscotic Liquid Crystals

3.2.1. Introduction

Mesogenic triphenylene compounds and their polycyclic aromatic derivatives are desirable for their applications in conductive materials,\textsuperscript{3.5a,c} electroluminescence,\textsuperscript{3.6d,e} and optoelectronics.\textsuperscript{3.1f,3.4b} In particular, substituted triphenylene compounds have been widely studied as it is well-known that six-fold peripheral substitution of medium-length alkyl chains promotes their liquid crystalline behavior.\textsuperscript{3.1a,3.9} Larger mesogenic planar hydrocarbons with polycyclic aromatic or porphyrin cores such as hexabenzocoronenes\textsuperscript{3.40} and triphenylenepthalocyanines\textsuperscript{3.41} have also attracted considerable attention in the materials science community. When functionalized with alkoxy substituents, these so-called ‘macrodiscotic’ molecules demonstrate high carrier charge mobilities and broad liquid crystalline phases.\textsuperscript{3.41b,3.3a,3.8}

Despite the widespread interest in discotic and macrodiscotic materials, there are notable synthetic gaps in the preparations of compounds that lie structurally in between substituted triphenylenes (3.27) and larger macrodiscotics (Figure 3.4).

\textbf{Figure 3.4:} General chemical structures of the polycyclic aromatic cores of triphenylene (3.28) and expanded triphenylene (3.29-3.31) macro-discotic compounds.
Williams and co-workers synthesized hexaalkoxybenzo[b]triphenylene 3.28, a mono-naphthyl di-phenyl triphenylene derivative that demonstrates mesogenic behavior when hexa-substituted with decaloxy chains.\textsuperscript{3,43} In a larger extended triphenylene system, Maly and Lynett developed a cyclotrimerization route to hexaalkoxy trinaphthylene compounds (3.29), which do not exhibit liquid crystalline phases when symmetrically substituted with hexyloxy or octyloxy chains.\textsuperscript{3,44} Notably absent is the dinaphthyl, monophenyl extended triphenylene, i.e. substituted derivatives of benzo[h]pentaphene (3.30, Figure 3.4). It would stand to reason that the study of this compound can elucidate the relative influence of π-π interactions versus alkyl chain length on the liquid crystallinity of expanded triphenylene-based compounds with high π-surface area. Moreover, the introduction of mixed-substituent variations in this class of polycyclic aromatic macrodiscotic materials may reveal the influence that regio-specific chain length substitution can have on aggregation. Herein we report the first synthesis of four variations of symmetric and mixed substituent benzo[h]pentaphene derivatives along with analysis of the optical and thermal properties of these expanded triphenylene materials.

Previously, in section 3.1, we developed a method for the synthesis of rationally-designed, mixed-substituent triphenylene derivatives and investigated the impact of regioisomerism on the phase properties of the resulting materials.\textsuperscript{3,45} Our versatile and high-yielding synthetic route enables the facile synthesis of a wide range of designer, mixed-substituent triphenylene-based materials. As the key step in our route, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is employed as a mild oxidant to annulate rationally designed ortho-terphenyl compounds. In the case of substituted benzo[h]pentaphenes, hexyloxy and octyloxy chains were chosen as substituents to prepare a series of expanded benzo[h]pentaphene derivatives that are either symmetrically substituted (3.32a and 3.32b) or bear two different length alkoxy substituents (3.33a and 3.33b). By changing the position of longer and shorter chains relative to the regions of higher and lower π-surface area, the influence of chain length versus π-surface on mesogenic properties can be investigated.
Figure 3.5: Schematic representations of benzo[b]pentaphene derivatives \(3.32a-b\) and \(3.33a-b\). For clarity, hexyloxy-substituted aryl moieties are colored red while octyloxy-substituted aryl moieties are colored blue.

**3.2.2. Synthesis**

Two synthetic pathways were employed to obtain compounds \(3.32a,b\), and \(3.33a,b\) (Scheme 3.7). Three alkoxy-substituted naphthalene derivatives were prepared and functionalized with a pinacolborane moiety following iridium(I)-catalyzed C-H activation conditions developed by Brimble and co-workers.\(^3\,46\) Expanded ortho-terphenyl derivatives \(3.36a-c\) were prepared by the Suzuki coupling of naphthalene pinacol esters \(3.35a-c\) with either 4,5-dibromo-1,2-octyloxybenezene \((3.34a)\), 4,5-dibromo-1,2-hexyloxybenzene \((3.34b)\), or dibromoveratrole \((3.34c)\). Asymmetrically substituted compounds \(3.33a\) and \(3.33b\) were synthesized from the oxidative annulation of rationally designed ortho-naphthyl benzene derivatives \(3.36a\) and \(3.36b\) in 88% and 94% yield, respectively (Scheme 3.7a). Symmetrically substituted compounds \(3.32a\) and \(3.32b\) were synthesized from a common starting material, hexamethoxy-ortho-dinaphthyl benzene \(3.36c\). The annulation of \(3.36c\) using DDQ, followed by demethylation and alkylation afforded substituted benzopentaphenes \(3.32a\) and \(3.32b\) in good yields (Scheme 3.7b). Symmetrically substituted benzopentaphene derivatives \(3.32a\) and \(3.32b\) may also be synthesized from the coupling of \(3.34a\) with \(3.35a\) or \(3.34b\) with \(3.35b\), respectively, by following the route.
shown in Scheme 3.7a (see Scheme 3.8, Section 3.4). This synthetic route can be expanded even further to the preparation of other di- and tri-substituted benzopentaphenes, further illustrating the versatility and modularity of the synthesis presented herein.

**Scheme 3.7:** Synthesis of benzo[h]pentaphene derivatives 3.32a, 3.32b, 3.33a, and 3.33b. To distinguish different substituents, hexyloxy and octyloxy chains colored in red and blue, respectively.

### 3.2.3. Spectroscopic Characterization

The formation of compounds 3.32a, 3.32b, 3.33a, and 3.33b is observed and supported by $^1$H NMR spectroscopy. Figure 3.6 shows a representative example of the distinct changes that are observed in the region extending from 7.2-8.7 ppm upon annulation of compound 3.36c to benzopentaphene derivative 3.37. These chemical shift changes reflect the dramatic physical transition between “open” and flexible tricyclic derivative 3.36c and the “closed,” more rigid polycyclic aromatic derivative 3.37. Most notable is the de-convolution of overlapping aromatic peaks $H_c$, $H_d$, and $H_e$ upon annulation, coincident with the loss of aromatic proton $H_f$. Aromatic signals $H_a$, $H_b$, and $H_c$ collectively shift downfield as they become deshielded upon increased conjugation, with naphthyl proton $H_e$ (the proton most influenced by the aromatization of the central ring) demonstrating the most significant shift of 0.9 ppm. Signals from the methoxy substituents are also observed to shift upon annulation, with the overlapping $H_g$-$i$ peaks of 3.36c separating into three distinct singlets in compound 3.37. Analogous shifts are observed for the
conversion of compounds 3.36a and 3.36b into benzopentaphene derivatives 3.33a and 3.33b (See Appendix III.1, Figures A.III.1 and A.III.2, p. A34).

Benzopentaphene formation was further supported by $^{13}$C NMR spectroscopy, and confirmed by accurate mass ESI/APCI, which indicated a peak of $m/z = 929.6648$ [MH]$^+$ for 3.32a (compared to a calculated value of 929.6654), $m/z = 1097.8533$ [MH]$^+$ for 3.32b (compared to 1097.8532), $m/z = 985.7270$ [MH]$^+$ for 3.33a (compared to 985.7280), and $m/z = 1041.7899$ [MH]$^+$ for 3.33b (compared to 1041.7906) (Appendix III.2.2).

**3.2.3. Optical and Thermal Properties**
The optical properties of compounds 3.32a-b and 3.33a-b were further investigated by UV-Vis and fluorescence spectroscopies. The absorption of the four benzo[h]pentaphene derivatives have maxima in the range of 325-340 nm (Figure 3.7a) with extinction coefficients of $\varepsilon_{5a} = 4.5 \times 10^4$,
ε₅b = 2.7×10⁴, ε₆a = 4.2×10⁴, and ε₆b = 3.4×10⁴ M⁻¹cm⁻¹. All four compounds exhibit large stokes-shifts ranging from 121-103 nm with strong emission centered in the violet region of the spectrum. This effect is visible to the naked eye: when solvated compounds 3.32a-b and 3.33a-b have a distinct violet glow under ambient light as compared to the yellow-orange color of their solutions when not illuminated. Such optical properties suggest benzopentaphene derivatives 3.32a-b and 3.33a-b may have potential as air and light stable violet-emitters for organic light emitting diode applications (Figure 3.7b).

![Figure 3.7](image)

**Figure 3.7.** (a) Absorption (solid lines) and normalized fluorescence (dashed lines) spectra of 6,7-benzopentaphene derivatives 3.32a, 3.32b, 3.33a, and 3.33b. All spectra were recorded in CH₂Cl₂ (1.0×10⁻⁵ M). Excitation wavelength for fluorescence spectra: λₑₓ = 330 nm. (b) Optical image of the violet-blue emission of benzopentaphene derivatives when excited at 365 nm (1.0×10⁻⁵ M in CH₂Cl₂).

UV-Vis and fluorescence also served to illustrate the effects of increased conjugation upon annulation, reinforcing the dramatic physical changes previously reflected in the ¹H NMR spectra of pre-annulated and annulated compounds. Upon aromatization the absorption maxima...
of benzopentaphenes 3.33a and 3.33b are red shifted by 55 cm⁻¹ relative to ortho-naphthyl benzene derivatives 3.36a and 3.36c (see Appendix III.3, Figure A.III.5, p. A67). Analogous changes were observed in the fluorescence emission spectra of pre-annulated ortho-terphenyl derivative 3.36c compared to fully annulated benzopentaphene derivatives 3.32a and 3.32b.

The phase properties of di-naphthyl-mono-phenyl benzopentaphene derivatives 3.32a-b and 3.33a-b are of particular interest given that their smaller analogue (di-phenyl-mono-naphthyl triphenylene derivative 3.29) is a mesogen while their larger analogue (trinaphthylene derivative 3.30) is not. The phase behavior of compounds 3.32a-b and 3.33a-b was investigated by differential scanning calorimetry (Table 3.3), and mesophase textures were observed by polarizing optical microscopy. This preliminary DSC analysis reveals that benzopentaphene derivatives 5b and 6b may be mesogenic whereas derivatives 5a and 6a show only isotropic melts (Table 3.3 and Appendix III.4, Figures A.III.8-11, pp. A69-A71).

Table 3.3: Thermal phase behavior of substituted benzo[h]pentaphene derivatives 3.32a, 3.32b, 3.33a, and 3.33b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_M</th>
<th>T_I</th>
<th>Mesophase</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.28</td>
<td>56 °C</td>
<td>64 °C</td>
<td>Col_h</td>
<td>3.47</td>
</tr>
<tr>
<td>3.29</td>
<td>35 °C</td>
<td>85 °C</td>
<td>Col_h</td>
<td>3.43</td>
</tr>
<tr>
<td>3.30</td>
<td>–</td>
<td>152 °C</td>
<td>–</td>
<td>3.44</td>
</tr>
<tr>
<td>3.30</td>
<td>–</td>
<td>122 °C</td>
<td>–</td>
<td>3.44</td>
</tr>
<tr>
<td>3.32a</td>
<td>–</td>
<td>80 °C</td>
<td>–</td>
<td>e</td>
</tr>
<tr>
<td>3.32b</td>
<td>63 °C</td>
<td>77 °C</td>
<td>Col_h</td>
<td>e</td>
</tr>
<tr>
<td>3.33a</td>
<td>–</td>
<td>82 °C</td>
<td>–</td>
<td>e</td>
</tr>
<tr>
<td>3.33b</td>
<td>77 °C</td>
<td>79 °C</td>
<td>Col_h</td>
<td>e</td>
</tr>
</tbody>
</table>

Transition temperatures were determined by DSC at a scan rate of 10°C min⁻¹. T_I = clearing temperature (isotropic melt), T_M = transition to mesophase. b_R=C₆H₁₃. c_R=C₁₀H₂₁. d_R=C₈H₁₇. e_This work._

The symmetrically substituted hexakis(octyloxy) benzopentaphene derivative 3.32b exhibits a narrow mesophase from 63–77 °C. A much narrower mesophase (77-79 °C) is observed for mixed-substituent bis(hexyloxy)-tetrakis(octyloxy) derivative 3.33b. By comparison, hexakis(hexyloxy) triphenylene (Figure 3.4, compound 3.28, R=C₆H₁₃) exhibits a columnar...
mesophase between 56-64 °C. The observation that 3.32b exhibits a broader mesophase at higher temperatures than hexakis(hexyloxy) triphenylene may extend from a combination of the greater π-surface area of its benzopentaphene core relative to that of triphenylene and its slightly longer octyloxy chains. The similar temperature but narrower mesophase of 3.33b is believed to result from greater disorder stemming from its mixture of hexyloxy and octyloxy substituents. The observation that benzopentaphene derivatives 3.32a and 3.33a are non-mesogenic suggests that the higher π-surface area of their naphthyl moieties must be balanced by longer alkyloxy chains to promote liquid crystallinity in these macrodiscotic compounds. It’s interesting to note, however, that hexyloxy and octyloxy trinaphthalene derivatives (Figure 3.4, compound 3.30, R=C₆H₁₃ or C₈H₁₇) are both non-mesogenic, though they do show evidence of dimerization in solution.³⁴ It’s possible that the greater π-surface area of a trinaphthalene core relative to a benzophentaphene core would require even longer alkoxy substituents to promote mesogenic behavior. Overall, the results presented herein suggest that subtle differences in the balance of alkoxy chain length, π-surface area, and substituent regiochemistry can significantly impact the phase behavior of macrodiscotic mesogens. However, these preliminary results, while supportive of regio-dependent liquid crystallinity, are not quantitative proof of mesophase identity. Small angle x-ray scattering and temperature-controlled polarized optical microscopy will be utilized to characterize the mesophase and gain insight into the long range order of these macrodiscotic compounds.

3.3. Conclusions

The synthesis of hydroxy-functionalized triphenylene derivatives via oxidative annulation of ortho-terphenyl compounds is reliable, facile, scalable, and opens innumerable routes to the synthesis of structurally precise mixed-substituent triphenylene derivatives. In the current study, three isomers of rationally-designed tetrahydroxy triphenylene derivatives were synthesized. The good to excellent yields and straightforward purifications of the synthetic route presented herein offer a valuable alternative to the current harsh, non-selective methods that are typical of triphenylene poly-ol syntheses. The tetrahydroxy triphenylene derivatives provide a versatile platform for further synthetic modifications, as demonstrated here by their functionalization with monomethyl di(ethylene glycol) chains to provide three regioisomers of amphiphilic triphenylenes bearing two hexyloxy and four monomethyl di(ethylene glycol) substituents.
Furthermore, the importance of regioisomerism on the physical properties of triphenylene mesogens was demonstrated in differences in the thermal properties of the three amphiphilic triphenylene isomers as compared to each other and to hexakis(hexyloxy) triphenylene and hexakis(monomethyl di(ethylene glycol)) triphenylene.

The adaptability of the synthetic routes presented herein is evident in the precursor design: functional groups and their regiochemistry may be easily varied by small changes in precursor substituent patterns. Similarly, multiple different functionalities can be introduced at several points in the synthesis, providing facile routes to mixed triphenylene derivatives with two – or more – types of substituents. The synthetic routes demonstrated herein can likely be adapted to the preparation of heterocyclic triphenylene derivatives such as azatriphenylenes, which are known to exhibit different electronic and physical properties than triphenylene derivatives but their development has been limited by the current use of toxic and costly transition metal catalysts in their synthesis.

Additionally the adaptability of the synthetic routes presented, has allowed us to develop and optimize a high yielding synthetic route to a new class of polycyclic aromatic macrodiscotic compounds. Four variations of benzo[h]pentaphenes were prepared and their optical and phase properties investigated. Some of the compounds (3.32b and 3.33b) show potential for use in applications such as stable, liquid crystalline violet emitters, which are particularly sought-after for applications in organic light emitting diodes and other optoelectronic materials. Furthermore, differences in the mesogenic properties of benzo[h]pentaphene derivatives that vary subtly in their alkyl chain length and substituent regiochemistry open the possibility for developing a more rigorous understanding of the influence of chain length versus π-surface area on liquid crystalline behavior. We are actively expanding and investigating a broader range of macrodiscotic and macrocyclic mesogens to further enhance our understanding of the structure-function relationships that underlie the aggregation of discotic liquid crystals and their potential materials applications. In general, we anticipate triphenylene derivatives will continue to play vital roles in the development of multifunctional mesogens with implications in such areas as organic electronic and photovoltaic materials, and rational routes to multifunctional triphenylene
derivatives, such as those described, will allow the full potential of these unique compounds to be explored and applied.

3.4. Experimental Methods

Materials. Chemicals were obtained from commercial sources and used as received. Reagent-grade solvents were used as obtained from commercial sources. Anhydrous solvents were dried using an Innovative Technologies SPS-400-5 solvent purification system.

Instrumentation. $^1$H and $^{13}$C NMR spectra were recorded with a Varian Mercury (300 MHz and 75 MHz, respectively) spectrometer using residual solvent as the internal standard. All chemical shifts are quoted using the $\delta$ scale and all coupling constants are expressed in Hertz (Hz). UV/Vis spectroscopy was recorded on a Varian Cary 100 Bio UV-Visible spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q20. The DSC is equipped with an RCS90 cooling system. DSC traces were acquired at rates of 10 °C min$^{-1}$ (heating) and 5 °C min$^{-1}$ (cooling) in the temperature range of (−50)–100 °C. ESI/APCI and APCI-MS analysis was carried out at the University of California, Riverside, Mass Spectrometry Facility.

3.4.1. Compounds from Section 3.1

Compounds 3.7, 3.8, 3.11, 3.12, 3.15, 3.19, and 3.24 were prepared according to literature procedures.$^{3,48-3.51, 3.27a, 3.31, 3.1c}$

Compound 3.13: Under an inert atmosphere, Compound 3.12 (1.5 g, 5.49 mmol) was dissolved in dimethylformamide (5.5 mL) and diisopropylethylamine (1.5 mL, 8.79 mmol) was added dropwise. The solution was stirred for 15 minutes, tertbutyldimethylsilylchloride (1.2 g, 8.24 mmol) was added, and the solution stirred overnight. Water was added (20 mL) and the crude product extracted with hexanes (3x15mL). The combined organic extracts were washed with brine (30mL), dried over MgSO4, and concentrated under reduced pressure. The crude material was purified by column chromatography, eluting with 10% dichloromethane in hexanes, to afford the pure product (1.5 g, 70%) as a colorless oil. El/GCMS (m/z) [M]$^+$ calculated for C$_{18}$H$_{31}$O$_2$SiBr, 386.1271; found 386.1282. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.03-6.92 (m, 2H),
6.73 (d, J = 8.5 Hz, 1H), 3.92 (t, J = 6.45 ppm, 2H), 1.87-1.78 (m, 2H), 1.58-1.43 (m, 2H), 1.43-1.30 (m, 4H), 1.03 (s, 9H), 0.94 (t, J = 5.7, 3H), 0.18 (s, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 151.41, 144.15, 123.23, 122.00, 116.06, 113.44, 68.61, 31.58, 29.21, 2580, 25.64, 25.55, 22.60, 18.31, 14.03, −4.70 ppm.

**Compound 3.16:** To a solution of 3.15 (2.3 g, 8.01 mmol) in dichloromethane (52 mL) was added meta-chloroperoxybenzoic acid (2.6 g, 14.9 mmol) in small portions, and the solution stirred at 40°C overnight. A 2M solution of ammonia in methanol (12.1 mL) was added, and the mixture was stirred for 2 hours. Saturated sodium bicarbonate was added (30 mL), and the product was extracted with diethyl ether (3 x 30 mL). The combined organic layers were washed with saturated sodium bicarbonate (100 mL) and brine (100 mL), dried over MgSO$_4$, and concentrated in vacuo to afford the pure product, isolated as an off-white solid (2.2 g, 99%). Mp = 41.8-42.6°C. El/GCMS (m/z) [M]$^+$ calculated for C$_{12}$H$_{17}$O$_2$Br, 272.0406; found 272.0339. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.08 (d, J = 2.4 Hz, 1H), 6.95 (dd, J = 8.7, 2.5 Hz, 1H), 6.71 (d, J = 8.8 Hz, 1H), 5.67 (s, 1H), 4.02 (t, J = 6.7, 2H), 1.86-1.77 (m, 2H), 1.49-1.40 (m, 2H), 1.38-1.30 (m, 4H), 0.92 (t, J = 7.3 Hz, 3H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 146.86, 145.49, 122.97, 117.97, 113.25, 112.96, 69.42, 31.77, 29.32, 25.88, 22.83, 14.28 ppm.

**Compound 3.17:** Under an inert atmosphere, 3.16 (541 mg, 1.98 mmol) was dissolved in dimethylformamide (2 mL) and diisopropylethylamine (0.54 mL, 3.17 mmol) was added dropwise. The solution was stirred for 15 minutes, tertbutylidemethylsilylchloride (448 mg, 2.97 mmol) was added, and the solution stirred overnight. Water was added (10 mL) and the crude product extracted with hexanes (3x10 mL). The combined organic extracts were washed with brine (20 mL), dried over MgSO$_4$, and concentrated under reduced pressure. The crude material was subjected to high vacuum to remove volatiles and afford the pure product (725 mg, 95%) as a yellow oil. El/GCMS (m/z) [M]$^+$ calculated for C$_{18}$H$_{31}$O$_2$SiBr, 386.1271; found 386.1258. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 6.96 (d, J = 2.5 Hz, 1H), 6.91 (dd, J = 8.2, 2.4 Hz, 1H), 6.70 (d, J = 8.5, 1H), 3.90 (t, J = 7.0 Hz, 2H), 1.85-1.76 (m, 2H), 1.52-1.42 (m, 2H), 1.36-1.28 (m, 4H), 1.00 (s, 9H), 0.89 (t, J = 7.6 Hz, 3H), 0.15 (s, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 150.03, 145.83, 124.37, 124.01, 113.93, 111.94, 68.61, 31.61, 29.28, 25.78, 25.62, 22.61, 18.33, 14.04, −4.70 ppm.
General procedure to prepare aryl pinacolboranes from aryl halides.

A mixture of aryl halide, bis(acetonitrile)dichloropalladium (II) (1 mol%), and Sphos Buchwald ligand (4 mol %) was prepared in a pressure flask, and immediately subjected to a vacuum/N₂ cycle (3x). To the solids was added dry 1,4-dioxane (1.7M with respect to aryl halide), and dry triethylamine (1.5 equivalents) under N₂. Last, pinacolborane (1.5 equivalents) was added quickly and the flask capped tightly. The mixture was stirred at 100°C until the reaction mixture darkened and thickened (around 3 hours). The mixture was allowed to cool, diluted with diethyl ether, and filtered over a pad of Celite. The filtrate was concentrated under reduced pressure, and the crude material purified by column chromatography.

**Compound 3.14**: Reaction scale: Compound 3.13 (1.5 g, 3.87 mmol). The product eluted from the column with 20% dichloromethane in hexanes, and was isolated as a yellow oil (1.28 g, 76%). ESI/APCI (m/z) [MH]⁺ calculated for C₂₄H₄₄₁₁BO₄Si, 435.3096; found 435.3110. ¹H NMR (CDCl₃, 300 MHz): δ 7.32-7.27 (m, 1H), 6.35 (d, J = 7.9 Hz, 1H), 3.99 (t, J = 6.9, 1H), 1.90-1.76 (m, 2H), 1.51-1.45 (m, 2H), 1.34 (s, 12H), 1.31-1.18 (m, 4H), 1.01 (s, 9H), 0.91 (t, J = 6.9 Hz, 3H), 0.17 (s, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 150.20, 147.94, 128.00, 120.63, 118.48, 83.53, 68.33, 31.65, 29.48, 25.84, 25.70, 25.67, 24.86, 22.62, 18.42, 14.07, -4.61 ppm.

**Compound 3.18**: Reaction Scale: Compound 3.17 (355 mg, 0.916 mmol). The product eluted from the column with 30% dichloromethane in hexanes, and was isolated as a yellow solid (312 mg, 78%). Mp = 69.2 - 71.1°C. ESI/APCI (m/z) [MH]⁺ calculated for C₂₄H₄₄₁₁BO₄Si, 435.3096; found 435.3104. ¹H NMR (CDCl₃, 300 MHz): δ 7.38 (dd, J = 8.1, 1.6 Hz, 1H), 7.27-7.24 (m, 1H), 6.84 (d, J = 8.2 Hz, 1H), 3.96 (t, J = 6.7 Hz, 2H), 1.87-1.76 (m, 2H), 1.52-1.42 (m, 2H), 1.33 (s, 12H), 1.30-1.23 (m, 4H), 1.01 (s, 9H), 0.91 (t, J = 6.6 Hz, 3H), 0.17 (s, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 159.29, 144.16, 129.20, 126.90, 111.85, 83.38, 68.15, 31.62, 29.28, 25.78, 25.73, 25.71, 24.81, 22.59, 18.36, 14.03, -4.59 ppm.

**General ortho-terphenyl preparation.** To a heavy-walled glass reaction vessel was added aryl dihalide (1 eq.), aryl pinacolborane (3 eq.), and potassium phosphate (4 eq.). The vessel was flushed with nitrogen, and SPhos Buchwald ligand (4 mol%) and palladium acetate (2 mol%) were added in that order. The vessel was further evacuated and backfilled with nitrogen (3x), and
degassed 10 : 1 toluene–water mixture was added. The vessel was quickly sealed with a Teflon screw cap and was heated to 100 °C overnight. The dark reaction mixture was allowed to cool, diluted with ether, and passed through a pad of Celite. The filtrate was concentrated under reduced pressure and purified by column chromatography to afford pure product.

**Compound 3.9.** Reaction scale: compound 3.7 (1.5 g, 3.44 mmol). The pure product eluted from the column with 20% dichloromethane in hexanes, and was isolated as a pale yellow oil (3.0 g, 92%). APCI-MS (m/z) [MH]⁺ calculated for C₅₄H₉₅O₆Si₄, 951.6200: found 951.6180. ¹H NMR (300 MHz, CDCl₃): δ 6.85 (s, 2H), 6.61–6.67 (m, 4H), 6.52–6.57 (dd, J = 8.8, 2.6 Hz, 2H), 4.04 (t, J = 6.6 Hz, 4H), 1.79–1.90 (m, 4H), 1.42–1.53 (m, 4H), 1.31–1.39 (m, 8H), 0.98 (m, 18H), 0.94 (s, 18H), 0.90 (t, J = 5.3 Hz, 6H), 0.19 (s, 12H), 0.08 (s, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 147.9, 146.1, 145.3, 135.1, 132.7, 122.8, 122.5, 120.2, 116.1, 69.3, 31.6, 29.3, 26.1, 25.9, 25.7, 22.6, 18.4, 14.1, −4.1, −4.2 ppm.

**Compound 3.20.** Reaction scale: compound 3.19 (144 mg, 0.291 mmol). The pure product eluted from the column with 10% dichloromethane in hexanes, and was isolated as a white solid (199 mg, 72%). Mp = 146.0–147.8 °C. ESI/APCI (m/z) [MH]⁺ calculated for C₅₄H₉₅O₆Si₄, 951.6200: found 951.6200. ¹H NMR (CDCl₃, 300 MHz): δ 7.67 (s, 2H), 7.11 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 7.9 Hz, 2H), 6.89 (s, 2H), 4.00 (t, J = 6.5 Hz, 4H), 2.11–2.02 (m, 4H), 1.83–1.74 (m, 4H), 1.75–1.66 (m, 8H), 1.43 (s, 18H), 1.40 (s, 18H), 1.31 (t, J = 6.5 Hz, 6H), 0.66 (s, 12H), 0.54 (s, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 149.6, 145.6, 143.2, 135.1, 133.6, 122.8, 121.5, 120.2, 115.1, 68.2, 31.6, 29.3, 26.0, 26.0, 25.7, 25.7, 22.6, 18.4, 14.1, −4.0, −4.7 ppm.

**Compound 3.22.** Reaction scale: compound 3.19 (110 mg, 0.223 mmol). The pure product eluted from the column with 10% dichloromethane in hexanes, and was isolated as a colorless semi-solid (124 mg, 59%). ESI/APCI (m/z) [MH]⁺ calculated for C₅₄H₉₅O₆Si₄, 951.6200: found 951.6196. ¹H NMR (CDCl₃, 300 MHz): δ 6.81 (s, 2H), 6.67–6.57 (m, 6H), 3.89 (t, J = 6.5 Hz, 4H), 1.83–1.74 (m, 4H), 1.51–1.43 (m, 4H), 1.36–1.28 (m, 8H), 1.02 (s, 18H), 0.96 (s, 18H), 0.92 (t, J = 7.0 Hz, 6H), 0.25 (s, 12H), 0.07 (s, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 149.1, 145.5, 144.1, 134.1, 133.2, 123.0, 122.4, 112.3, 68.3, 31.7, 29.5, 26.0, 25.7, 22.6, 18.4, 14.1, −4.0, −4.7 ppm.
**General triphenylene preparation.** Two methods were used to prepare tetra(hydroxy) triphenylene derivatives from their appropriate ortho-terphenyl precursors. In a two-step procedure (Method A) tetra-TBDMS protected triphenylene intermediates 3.10, 3.21, and 3.23 were isolated and purified prior to TBDMS deprotection to allow full characterization of the tetra-TBDMS protected triphenylene derivatives. Alternatively, a one-step procedure (Method B) can be used wherein the intermediate is not isolated but rather carried directly through to deprotection following annulation. Method B was observed to both maximize the yield of the desired tetra-ol product and simplify the synthesis of 3.1–3.3.

**Method A.** General annulation procedure: to a 0.01 M solution of ortho-terphenyl in dry dichloromethane was added neat trifluoroacetic acid (10% with respect to volume of solvent), and the solution stirred for 30 minutes at room temperature. Oxidant 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.1 equivalents) was added at 0 °C, and the solution was allowed to return slowly to room temperature over 3 hours; accompanied by a color change from pale lime green to emerald. Water was added slowly, and the crude product was extracted with dichloromethane (3×). The combined red or purple organic layers were washed with saturated sodium bicarbonate (3×) and brine, dried over MgSO₄, and concentrated *in vacuo*. The resulting material was purified through a short pad of silica, eluting with 2.5% ethyl acetate in hexanes to afford the pure triphenylene derivatives.

**Compound 3.10.** Reaction scale, ortho-terphenyl 3.9 (700 mg, 0.736 mmol). The organic extracts were red, and the product was isolated as a pale pink semi-solid (323 mg, 46%). APCI-MS (m/z) [MH]⁺ calculated for C₅₄H₉₃O₆Si₄, 949.6044: found 949.6027. ¹H NMR (300 MHz, CDCl₃): δ 7.83 (s, 2H), 7.79 (s, 2H), 7.74 (s, 2H), 4.22 (t, J = 6.4 Hz, 4H), 1.99–1.88 (m, 4H), 1.33–1.26 (m, 12H), 1.08 (s, 18H), 1.07 (s, 18H), 0.93 (t, J = 6.74 Hz, 6H), 0.31 (s, 12H) 0.31 (s, 12H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 148.7, 146.6, 124.0, 123.2, 114.0, 106.8, 69.3, 31.7, 29.2, 26.1, 26.1, 25.9, 25.8, 22.7, 18.7, 14.1, −4.0, −4.1 ppm.

**Compound 3.21.** Reaction scale, ortho-terphenyl 3.20 (199 mg, 0.209 mmol). The organic extracts were a ruby red, and the product was isolated as a pale yellow solid (56 mg, 29%). Mp = 132.7–134.2 °C. ESI/APCI (m/z) [MH]⁺ calculated for C₅₄H₉₃O₆Si₄, 949.6044: found
949.6031. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.86 (s, 2H), 7.80 (s, 2H), 7.71 (s, 2H), 4.16 (t, $J = 6.5$ Hz, 4H), 1.98–1.89 (m, 4H), 1.63–1.53 (m, 4H), 1.44–1.34 (m, 8H), 1.10 (s, 18H), 1.08 (s, 18H), 0.95 (t, $J = 5.6$ Hz, 6H), 0.32 (s, 12H), 0.27 (s, 12H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 150.2, 146.5, 144.9, 124.2, 123.8, 123.2, 114.1, 105.8, 68.6, 31.7, 29.4, 26.1, 25.9, 25.8, 22.7, 18.7, 14.1, –4.0, –4.1 ppm.

**Compound 3.23.** Reaction scale, ortho-terphenyl 3.22 (200 mg, 0.210 mmol). The organic extracts were deep purple, and the product was isolated as a violet grey solid (144 mg, 72%). Mp = 131.4–133.6 °C. ESI/APCI ($m/z$) [MH]$^+$ calculated for C$_{54}$H$_{93}$O$_6$Si$_4$, 949.6044: found 949.6034. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 7.80 (s, 2H), 7.79 (s, 2H), 7.76 (s, 2H), 4.19 (t, $J = 6.5$ Hz, 4H), 1.87–1.99 (m, 4H), 1.65–1.56 (m, 4H), 1.44–1.35 (m, 8H), 1.09 (s, 18H), 1.07 (s, 18H), 0.95 (t, $J = 6.3$ Hz, 6H), 0.32 (s, 12H), 0.26 (12H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 150.3, 146.6, 145.0, 124.1, 123.7, 123.3, 114.2, 113.9, 106.2, 68.8, 31.7, 29.5, 26.1, 25.8, 22.7, 18.5, 14.1, –4.1, –4.6 ppm.

**General deprotection procedure.** To a 0.1 M solution of TBDMS-protected triphenylene derivatives 3.10, 3.21, and 3.23 in 1:2 dimethylformamide–tetrahydrofuran was added potassium fluoride (8 equivalents), and aqueous hydrogen bromide (0.12 equivalents). The solution was stirred overnight with periodic monitoring by TLC. Aqueous potassium carbonate (1 M) was added, and the mixture stirred for an hour. The solution was slowly acidified with aqueous hydrochloric acid (1 M), and extracted with diethyl ether (3×). The combined organic layers were washed with brine, dried over MgSO$_4$, and concentrated *in vacuo*. The crude material was purified by column chromatography, affording pure triphenylene tetra-ol derivatives 3.1–3.3.

**Compound 3.1.** Reaction scale: TBDMS-protected triphenylene derivative 3.10 (245 mg, 0.258 mmol). The crude product was purified by column chromatography, eluting with ethyl acetate, to afford the pure product as a lavender solid (101 mg, 79%). Mp = >200 °C. ESI/APCI ($m/z$) [MH]$^+$ calculated for C$_{30}$H$_{37}$O$_6$, 493.2585: found 493.2575. $^1$H NMR (300 MHz, acetone-d): $\delta$ 8.35 (s, 2H) 8.17 (s, 2H) 7.94 (s, 2H), 7.87 (s, 2H), 7.85 (s, 2H), 4.25 (t, $J = 6.5$ Hz, 4H), 1.84–1.96 (m, 4H), 1.55–1.67 (m, 4H), 1.34–1.48 (m, 8H), 0.91–0.98 (m, 6H) ppm. $^{13}$C NMR
Compound 3.2. Reaction scale: TBDMS-protected triphenylene derivative 3.21 (70 mg, 0.074 mmol). The crude product, while isolated as a relatively pure solid, was further purified by column chromatography eluting with 100% diethyl ether to obtain a pale orange solid (33 mg, 92%). Mp = 157 °C. ESI/APCI (m/z) [MH]+ calculated for C_{30}H_{37}O_6, 493.2585: found 493.2583. ^1H NMR (300 MHz, acetone-d): δ 8.26 (s, 2H), 7.99 (s, 2H), 7.89 (s, 2H), 7.83 (s, 2H), 7.79 (s, 2H), 4.28 (t, J = 6.5 Hz, 4H), 1.84–1.93 (m, 4H), 1.50–1.62 (m, 4H), 1.32–1.44 (m, 8H), 0.92 (t, J = 6.2 Hz, 6H) ppm. ^13C NMR (acetone-d6, 75 MHz): 147.9, 147.2, 146.0, 124.4, 124.2, 123.7, 109.0, 108.7, 105.9, 69.6, 32.5, 30.4, 26.6, 23.4, 14.4 ppm.

Compound 3.3. Reaction scale: TBDMS-protected triphenylene derivative 3.23 (140 mg, 0.147 mmol). The crude product, while isolated as a relatively pure solid, was further purified by column chromatography eluting with 100% diethyl ether to give a violet solid (38 mg, 52%). Mp = 130 °C. ESI/APCI (m/z) [MH]+ calculated for C_{30}H_{37}O_6, 493.2585: found 493.2584. ^1H NMR (300 MHz, acetone-d6): δ 8.18 (s, 2H), 7.95 (s, 2H), 7.88 (s, 2H), 7.87 (s, 2H), 7.80 (s, 2H), 4.31 (t, J = 6.4 Hz, 4H), 1.85–1.96 (m, 4H), 1.51–1.64 (m, 4H), 1.32–1.45 (m, 8H), 0.93 (t, J = 6.5 Hz, 6H) ppm. ^13C NMR (acetone-d6, 75 MHz): 147.5, 147.0, 146.0, 124.4, 123.8, 123.4, 108.7, 108.6, 106.1, 69.5, 32.4, 26.4, 23.1, 14.2 ppm.

Method B. To a 0.01 M solution of ortho-terphenyl derivatives 3.9, 3.20, and 3.22 in dry dichloromethane was added neat trifluoroacetic acid (10% with respect to volume of solvent), and the solution stirred for 30 minutes at room temperature. Oxidant DDQ (1.1 equivalents) was added at 0 °C, and the solution allowed to return slowly to room temperature over 3 hours. Water was added slowly, and the intermediate extracted with dichloromethane (3×). The combined organic layers were washed with saturated sodium bicarbonate (3×) and brine, dried over MgSO_4, and concentrated in vacuo. To a 0.1 M solution of the resulting residue in 1:1 dimethylformamide–tetrahydrofuran was added potassium fluoride (8 equivalents), and aqueous hydrogen bromide (0.12 equivalents). The solution was stirred overnight. Aqueous potassium carbonate (1 M) was added, and the mixture stirred for one hour. The solution was slowly
acidified with aqueous hydrochloric acid (1 M), and extracted with diethyl ether (3×). The combined organic layers were washed with brine, dried over MgSO$_4$, and concentrated in vacuo. The crude material was purified by column chromatography, or by recrystallization in ether–hexanes, affording pure triphenylene tetra-ol derivatives 3.1–3.3.

**Compound 3.1.** Reaction scale: *ortho-*terphenyl 3.9 (500 mg, 0.525 mmol). The pure product was isolated by recrystallization from diethyl ether and hexanes (171 mg, 66%). This reaction has also been run at larger scales up to 2.8 grams of *ortho-*terphenyl 3.9, giving tetraol 3.1 in similar yields. Characterization matched the data provided for compound 3.1 as synthesized using the two-step procedure (Method A).

**Compound 3.2.** Reaction scale: *ortho-*terphenyl 3.20 (848 mg, 0.891 mmol). The pure product was isolated by column chromatography eluting with 10% acetone in dichloromethane (332 mg, 76%). Characterization matched the data provided for compound 3.2 as synthesized using the two-step procedure (Method A).

**Compound 3.3.** Reaction scale: *ortho-*terphenyl 3.22 (718 mg, 0.754 mmol). The pure product was isolated by column chromatography eluting with 10% acetone in dichloromethane (251 mg, 67%). Characterization matched the data provided for compound 3.3 as synthesized using the two-step procedure (Method A).

**General procedure for the preparation of amphiphilic triphenylenes.** To a 0.1 M solution of triphenylene tetra-ol in dimethylformamide, was added 2-(2-methoxy-ethoxy)-ethyl-toluenesulphonate$^{3,33}$ (6 equivalents), potassium carbonate (8 equivalents), catalytic lithium bromide, and 18-crown-6 under inert conditions. The system was purged with nitrogen again, and the reaction stirred at 80 °C overnight. The solution was allowed to cool, water was added, and the crude product was extracted with diethyl ether (3×). The combined ethereal extracts were washed with aqueous hydrochloric acid (1 M) and brine, and the combined aqueous layers back-extracted again with ether. The combined organic layers were dried over MgSO$_4$, concentrated under reduced pressure, and purified by column chromatography, eluting with 10% acetone in dichloromethane.
**Compound 3.4.** Reaction scale: compound 3.1 (65 mg, 0.132 mmol). Pure product was isolated as a brown oil that gradually solidified (70 mg, 59%). Mp = 37 °C. ESI/APCI (m/z) [MNa]+ calculated for C_{50}H_{76}O_{14}Na, 923.5127: found 923.5148. $^1$H NMR (300 MHz, CDCl3): $\delta$ 7.91 (s, 2H), 7.89 (s, 2H), 7.82 (s, 2H), 4.40–4.44 (m, 8H), 4.23 (t, $J = 6.5$ Hz, 4H), 3.98–4.02 (m, 8H), 3.78–3.83 (m, 8H), 3.60–3.63 (m, 8H), 3.42 (s, 12H), 1.90–2.00 (m, 4H), 1.55–1.61 (m, 4H), 1.37–1.45 (m, 8H), 0.94 (t, $J = 6.6$ Hz, 6H) ppm. $^{13}$C NMR (CDCl3, 75 MHz): 149.1, 148.5, 123.8, 123.4, 108.2, 107.8, 106.9, 71.9, 70.7, 69.9, 69.8, 69.5, 69.1, 69.0, 59.0, 31.6, 25.8, 22.6, 14.0 ppm.

**Compound 3.5.** Reaction scale: compound 3.2 (121 mg, 0.246 mmol). Pure product was isolated as a brown oil (132 mg, 60%). ESI/APCI (m/z) [MNa]+ calculated for C_{50}H_{76}O_{14}Na, 923.5127: found 923.5137. $^1$H NMR (300 MHz, CDCl3): $\delta$ 7.95–7.88 (m, 4H), 7.83 (s, 2H), 4.42 (t, $J = 4.9$ Hz, 8H), 4.23 (t, $J = 6.5$ Hz, 4H), 3.98–4.04 (m, 8H), 3.79–3.85 (m, 8H), 3.59–3.65 (m, 8H), 3.41 (s, 12H), 1.89–1.98 (m, 4H), 1.53–1.62 (m, 4H), 1.37–1.45 (m, 8H), 0.95 (t, $J = 6.5$ Hz, 6H) ppm. $^{13}$C NMR (CDCl3, 75 MHz): 149.5, 149.0, 145.9, 123.4, 123.9, 108.3, 107.6, 72.02, 70.88, 70.80, 69.88, 69.56, 69.30, 69.15, 59.08, 31.67, 29.39, 25.82, 22.64, 14.04 ppm.

**Compound 3.6.** Reaction scale: compound 3.3 (93 mg, 0.189 mmol). Pure product was isolated as a brown oil that gradually solidified (97 mg, 57%). Mp = 33 °C. ESI/APCI (m/z) [MNa]+ calculated for C_{50}H_{76}O_{14}Na, 923.5127: found 923.5153. $^1$H NMR (300 MHz, CDCl3): $\delta$ 7.90 (s, 2H) 7.88 (s, 2H) 7.82 (s, 2H), 4.42 (t, $J = 4.2$ Hz, 8H), 4.22 (t, $J = 6.5$ Hz, 4H), 3.88–4.03 (m, 8H), 3.78–3.84 (m, 8H), 3.59–3.63 (m, 8H), 3.41 (s, 12H), 1.89–2.00 (m, 4H), 1.53–1.64 (m, 4H), 1.34–1.46 (m, 8H), 0.94 (t, $J = 6.6$ Hz, 6H) ppm. $^{13}$C NMR (CDCl3, 75 MHz): 149.0, 148.5, 124.0, 123.7, 123.4, 108.3, 107.3, 106.7, 72.0, 71.9, 70.8, 69.9, 69.8, 69.4, 69.3, 69.1, 59.0, 31.6, 29.4, 25.8, 22.6, 14.0 ppm.

**Compound 26:** Hexakis(monomethyl di(ethylene glycol)) triphenylene: To a mixture of 2,3,6,7,1011-hexahydroxytriphenylene (105 mg, 0.324 mmol), potassium carbonate (447 mg, 3.24 mg), and catalytic 18-C-6 was added dimethylformamide (3.2 mL) and di(ethylene glycol) monomethyl ether tosylate (710 mg, 2.59 mmol) under nitrogen. The reaction solution was
stirred at 80°C overnight. The solution was allowed to cool, and water was added. Excess di(ethylene glycol) monomethyl ether tosylate was extracted from the aqueous layer with diethyl ether (2x). The combined ethereal extracts were washed with aqueous hydrochloric acid (1M), and the aqueous layers combined. The product was extracted from the aqueous phase with ethyl acetate (3x), and the ethyl acetate phase washed with brine, dried over MgSO₄, and concentrated under reduced pressure to afford analytically pure product (183 mg, 30%). The product was isolated as a dark oil which gradually solidified. ESI/APCI (m/z) [MNa]⁺ calculated for C₄₈H₇₂O₁₈Na, 959.4611; found 959.4634. ¹H NMR (300 MHz, CDCl₃): δ 7.88 (s, 6H), 4.42 (t, J = 4.6 Hz, 12H), 4.01 (t, J = 4.4 Hz, 12H), 3.80-3.83 (m, 12H), 3.61-3.63 (m, 12H), 3.41 (s, 18H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 148.41, 123.62, 107.61, 71.76, 70.54, 69.64, 68.89, 58.81 ppm.

3.4.2. Compounds from Section 2

Compounds 3.38c, 3.34a-b, 3.35c, and 3.35c were prepared according to literature procedures.

**Scheme 3.8**: a) Full synthesis of precursors 3.34b,c, 3.35a-c, and ortho-terphenyls 3.36a-c. b) Alternative method for the synthesis of 3.32a.

**Compound 3.38a**: To a mixture of 2,3-dihydroxynapthalene (1.0 g, 6.24 mmol), potassium carbonate (3.4 g, 25.0 mmol), and catalytic 18-crown-6 was added dimethylformamide (10 mL)
and 1-bromooctane (3.3 mL, 18.7 mmol) under N₂ and stirred overnight at 80°C. The mixture was allowed to cool and water was added (50 mL). The crude product was extracted with hexanes (3x25 mL), and washed with water (100 mL). The combined organic layers were dried over MgSO₄, filtered, and the solvent removed under reduced pressure. The crude material was purified by column chromatography, eluting with 10% dichloromethane in hexanes, affording the pure product 3.38a as a white solid (2.1 g, 88%). Mp = 47-48°C. ESI/APCI (m/z) [MH⁺] calculated for C₂₆H₄₁O₂, 385.3101; found 385.3114. ¹H NMR (CDCl₃, 300 MHz): δ 7.69-7.66 (m, 4H), 7.34-7.31 (m, 4H), 7.14 (s, 2H), 4.13 (t, J = 6.6 Hz, 4H), 1.97-1.88 (m, 4H), 1.57-1.49 (m, 4H), 1.43-1.35 (m, 16H), 0.92 (t, J = 6.7 Hz, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 149.4, 129.2, 126.2, 123.9, 107.8, 68.8, 31.8, 29.3, 29.1, 26.1, 22.7, 14.1 ppm.

**Compound 3.38b.** To a mixture of 2,3-dihydroxynaphthalene (1.0 g, 6.24 mmol), potassium carbonate (3.4 g, 25.0 mmol), and catalytic 18-crown-6 was added dimethylformamide (10 mL) and 1-bromohexane (2.6 mL, 18.7 mmol) under N₂ and stirred overnight at 80°C. The mixture was allowed to cool and water was added (50 mL). The crude product was extracted with hexanes (3x25 mL), and washed with water (100 mL). The combined organic layers were dried over MgSO₄, filtered, and the solvent removed under reduced pressure. The crude material was purified by column chromatography, eluting with 10% dichloromethane in hexanes, affording the pure product 3.38b as a white solid (1.5 g, 75%). Characterization matched reported literature values.⁴

**Compound 3.35a.** A sample of compound 3.38a (906 mg, 2.36 mmol) was subjected to high vacuum at 85°C for 15 minutes in a heavy walled pressure vessel. The vessel was flushed with N₂, and 4,4′-di-tert-butyl-2,2′-dipyridyl (38 mg, 0.142 mmol) and (1,5-Cyclooctadiene)(methoxy)iridium(I) dimer (47 mg, 0.071 mmol) were added in that order. Dry tetrahydrofuran (1.6 mL) was added under N₂, and the solution was degassed for 15 minutes. Pinacolborane (1.7 mL, 11.8 mmol) was added quickly, and the reaction sealed, and stirred at 80°C for 120 hours. The mixture was allowed to cool and filtered over Celite, eluting with dichloromethane. The filtrate was condensed under reduced pressure and purified via column
chromatography. The pure product eluted with 1:1 dichloromethane:hexanes, affording pure 3.35a (200 mg, 17%) as a white semi-solid. ESI/APCI (m/z) [MH]^+ calculated for C_{32}H_{52}^{11}\text{BO}_4, 511.3953; found 511.3943. $^1$H NMR (CDCl$_3$, 300 MHz): δ 8.20 (s, 1H), 7.66 (d, $J = 6.2$, 2H), 7.16 (s, 1H), 7.10 (s, 1H), 4.14-4.07 (m, 4H), 1.95-1.85 (m, 4H), 1.55-1.47 (m, 4H), 1.38 (s, 12H), 1.34-1.24 (m, 16H), 0.93-0.86 (m, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 150.5, 149.2, 134.5, 131.2, 128.6, 125.3, 108.5, 107.4, 83.6, 68.8, 31.6, 29.4, 26.1, 24.9, 22.7, 22.6, 14.0 ppm.

**Compound 3.35b.** A sample of compound 3.38b (700 mg, 2.13 mmol) was subjected to high vacuum at 85°C for 15 minutes in a heavy walled pressure vessel. The vessel was flushed with N$_2$, and 4,4′-di-tert-butyl-2,2′-dipyridyl (34 mg, 0.128 mmol) and (1,5-Cyclooctadiene)(methoxy)iridium(I) dimer (42 mg, 0.064 mmol) were added in that order. Dry tetrahydrofuran (1.5 mL) was added under N$_2$, and the solution was degased for 15 minutes. Pinacolborane (1.6 mL, 10.7 mmol) was added quickly, and the reaction sealed, and stirred at 80°C for 96 hours. The mixture was allowed to cool and filtered over Celite, eluting with dichloromethane. The filtrate was condensed under reduced pressure and purified via column chromatography. The pure product eluted with 25% dichloromethane in hexanes, affording pure 3.38b (551 mg, 57%) as a white semi-solid. ESI/APCI (m/z) [MH]^+ calculated for C$_{28}$H$_{44}^{11}$BO$_4$, 455.3327; found 455.3336. $^1$H NMR (CDCl$_3$, 300 MHz): δ 8.20 (s, 1H), 7.67 (d, $J = 6.2$, 2H), 7.17 (s, 1H), 7.11 (s, 1H), 4.15-4.07 (m, 4H), 1.96-1.85 (m, 4H), 1.58-1.47 (m, 4H), 1.39 (s, 12H), 1.38-1.44 (m, 8H), 0.95-0.89 (m, 6H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 150.8, 149.6, 134.9, 131.6, 128.9, 125.7, 108.8, 107.7, 84.0, 69.1, 32.0, 29.4, 26.1, 25.3, 23.0, 14.5 ppm.

**Compound 3.36a.** Toluene and deionized water were degassed separately for 15 minutes. Compound 3.34a (43 mg, 0.088 mmol) and compound 3.35b (100 mg, 0.220 mmol) were subjected to high vacuum at 80°C for 15 minutes in a heavy-walled pressure vessel, and the flask flushed with N$_2$. Potassium phosphate (56 mg, 0.264 mmol), Sphos Buchwald ligand (1.5 mg 0.004 mmol), and palladium acetate (1.2 mg, 0.002 mmol) were added in that order, and the flask flushed with N$_2$ again. Degassed toluene (0.2 mL) and deionized water (0.02 mL) were added, the heavy-walled vessel sealed, and the reaction stirred at 100°C for 24 hours. The black reaction
mixture was allowed to cool and filtered over Celite, eluting with dichloromethane. The filtrate was concentrated under reduced pressure, and the crude residue purified by column chromatography, eluting with 30% dichloromethane in hexanes, affording compound **3.36a** (50 mg, 59%) as a colorless oil. ESI/APCI (m/z) [MH]^+ calculated for C\textsubscript{66}H\textsubscript{99}O\textsubscript{6}, 987.7436; found 987.7473. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): δ 7.61 (s, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.06-6.94 (m, 4H), 4.12-4.05 (m, 12H), 1.92-1.83 (m, 12H), 1.54-1.45 (m, 32H), 0.93-0.87 (m, 18H) ppm. \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): 149.8, 149.6, 148.7, 138.0, 133.7, 129.5, 128.0, 127.0, 126.8, 125.9, 117.4, 108.4, 108.1, 69.9, 69.2, 32.3, 32.0, 29.8, 29.5, 26.5, 26.1, 23.0, 14.5 ppm.

**Compound 3.36b.** Toluene and deionized water were degassed separately for 15 minutes. Compound **3.34b** (37 mg, 0.085 mmol) and compound **3.35a** (109 mg, 0.213 mmol) were subjected to high vacuum at 80\textdegree C for 15 minutes in a heavy-walled pressure vessel, and the flask flushed with N\textsubscript{2}. Potassium phosphate (54 mg, 0.255 mmol), Sphos Buchwald ligand (1.4 mg 0.003 mmol), and palladium acetate (1.1 mg, 0.002 mmol) were added in that order, and the flask flushed with N\textsubscript{2} again. Degassed toluene (0.2 mL) and deionized water (0.02 mL) were added, the heavy-walled vessel sealed, and the reaction stirred at 100\textdegree C for 24 hours. The black reaction mixture was allowed to cool and filtered over Celite, eluting with dichloromethane. The filtrate was concentrated under reduced pressure, and the crude residue purified by column chromatography, eluting with 30% dichloromethane in hexanes, affording compound **3.36b** (83 mg, 94%) as a colorless oil. ESI/APCI (m/z) [MH]^+ calculated for C\textsubscript{70}H\textsubscript{107}O\textsubscript{6}, 1043.8062; found 1043.8105. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): δ 7.62 (s, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.06-6.95 (m, 4H), 4.13-4.03 (m, 12H), 1.94-1.82 (m, 12H), 1.56-1.45 (m, 12H), 1.44-1.27 (m, 40H), 0.96-0.86 (m, 18H) ppm. \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): 149.4, 149.2, 148.3, 137.6, 133.3, 129.1, 127.6, 126.9, 126.5, 125.4, 116.6, 107.9, 107.6, 69.4, 68.8, 31.8, 31.6, 29.4, 29.1, 26.1, 25.7, 22.7, 14.1 ppm.

**Compound 3.36c.** Toluene and deionized water were degassed separately for half an hour. Compound **3.35c** (461 mg, 1.47 mmol) and 4,5-dibromoveratrole (173 mg, 0.587 mmol) were
subjected to high vacuum at 80°C for 15 minutes in a heavy-walled pressure vessel, and the flask was flushed with N₂. Potassium phosphate (498 mg, 2.35 mmol), Sphos Buchwald ligand (19 mg 0.047mmol), and palladium acetate (16 mg, 0.023 mmol) were added in that order, and the flask flushed with N₂ again. Degassed toluene (1.17 mL) and deionized water (0.12 mL) were added, and the reaction mixture degassed for 10 minutes. The heavy-walled vessel was sealed and the reaction stirred at 100°C for 48 hours. The black reaction mixture was allowed to cool and filtered over Celite, eluting with dichloromethane. The filtrate was concentrated under reduced pressure, and the crude residue purified by column chromatography, eluting with 5% acetone in dichloromethane, affording compound 3.36c (244 mg, 82%) as a white solid. Mp = 110-111°C. ESI/APCI (m/z) [MH]⁺ calculated for C₃₂H₃₁O₆, 511.2115; found 511.2126. ¹H NMR (CDCl₃, 300 MHz): δ 7.67 (s, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.07-6.09 (m, 4H), 4.00 (s, 6H), 3.99 (s, 6H), 3.98 (s, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 149.8, 149.6, 148.4, 138.0, 133.4, 129.4, 127.9, 127.3, 126.9, 114.3, 106.6, 106.3, 56.4, 56.1, 56.0 ppm.

**Compound 3.37.** To a stirring solution of compound 3.36c (240 mg, 0.470 mmol) in dichloromethane (47 mL) was added trifluoroacetic acid (4.7 mL), and the solution was allowed to stir at room temperature for 15 minutes. The reaction was cooled to 0°C, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (117 mg, 0.517 mmol) was added, inducing a dramatic color change from pale yellow to dark green. The reaction solution was allowed to warm to room temperature over 3 hours. Water was added (100 mL), and the organic layer was isolated. The organic layer was washed with sodium bicarbonate (3x100 mL), taking care to slowly neutralize the first water layer as the aqueous layers were combined. The aqueous phase was back-extracted with dichloromethane, and the combined organic layers dried over MgSO₄ and concentrated under reduced pressure, affording pure compound 3.37 (190 mg, 79%) as a yellow solid. Mp = 110°C. ESI/APCI (m/z) [MH]⁺ calculated for C₃₂H₂₉O₆, 509.1959; found 509.1956. ¹H NMR (CDCl₃, 300 MHz): δ 8.50 (d, J = 9.1 Hz, 2H), 8.05 (s, 2H), 7.96 (d, J = 8.8 Hz, 2H), 7.48 (s, 2H), 7.29 (s, 2H), 4.18 (s, 6H), 4.08 (s, 6H), 3.54 (s, 6H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 149.3, 148.6, 147.8, 128.0, 127.6, 126.2, 125.8, 124.6, 124.1, 119.0, 110.3, 106.7, 104.1, 56.0, 55.4 ppm.

**Compound 3.32a.** Compound 3.37 (70 mg, 0.138 mmol) was dissolved in dry dichloromethane (1.1 mL) under N₂. Boron tribromide (1M in dichloromethane, 1.65 mmol) was added dropwise
at 0°C under N₂, and the reaction was allowed to warm slowly to room temperature over 3 hours. Water (15 mL) was slowly added to quench the reaction, and the mixture concentrated under reduced pressure. The intermediate product was extracted with diethyl ether (3x25 mL) and the combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure, affording pure intermediate product (hexa-hydroxy-6,7-benzopentaphene) as a green solid (56 mg). To this residue was added potassium carbonate (219 mg, 1.59 mmol), and the reaction vessel flushed with N₂. Dimethylformamide (1.7 mL) and 1-bromohexane (0.2 mL, 1.59 mmol) was added in that order, and the reaction was allowed to stir overnight at 80°C. Water was added (50 mL), and the crude product extracted with dichloromethane (3x25 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by column chromatography, eluting with 1:1 hexanes:dichloromethane, affording pure product **3.32a** (83 mg, 65% overall) as a yellow solid. Mp = 80°C. ESI/APCI (m/z) [MH]+ calculated for C₆₂H₈₉O₆, 929.6654; found 929.6648. 

\[ \text{H NMR (CDCl₃, 300 MHz): } \delta 8.42 (d, J = 9.1 \text{ Hz}, 2\text{H}), 8.04 (s, 2\text{H}), 7.89 (d, J = 8.5 \text{ Hz}, 2\text{H}), 7.42 (s, 2\text{H}), 7.26 (s, 2\text{H}), 4.28 (t, J = 6.2 Hz, 4\text{H}), 4.17 (t, J = 6.7 Hz, 4\text{H}), 3.59 (t, J = 6.2 Hz, 4\text{H}), 2.02-1.88 (m, 12\text{H}), 1.66-1.56 (m, 12\text{H}), 1.48-1.34 (m, 12\text{H}), 1.30-1.21 (12\text{H}), 0.99-0.87 (m, 18\text{H}) \text{ ppm.} \]

\[ \text{13C NMR (CDCl₃, 75 MHz): } 149.3, 148.6, 148.1, 127.8, 127.5, 126.1, 124.8, 124.1, 119.0, 118.6, 111.7, 108.3, 106.5, 69.4, 69.0, 68.5, 31.7, 31.4, 29.3, 29.1, 29.0, 25.8, 25.6, 22.7, 14.0 \text{ ppm.} \]

**Compound 3.32b.** Compound **3.37** (118 mg, 0.232 mmol) was dissolved in dry dichloromethane (2.0 mL) under N₂. Boron tribromide (1M in dichloromethane, 2.78 mmol) was added dropwise at 0°C under N₂, and the reaction was allowed to warm slowly to room temperature over 3 hours. Water (15 mL) was slowly added to quench the reaction, and the mixture concentrated under reduced pressure. The intermediate product was extracted with diethyl ether (3x25 mL) and the combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure, affording pure intermediate product (hexa-hydroxy-6,7-benzopentaphene) as a green solid (82 mg). To this residue was added potassium carbonate (320 mg, 2.32 mmol), and the reaction vessel flushed with N₂. Dimethylformamide (2.5 mL) and 1-bromo-octane (0.4 mL, 2.32 mmol) was added in that order, and the reaction was allowed to stir overnight at 80°C.
Water was added (50 mL), and the crude product extracted with dichloromethane (3x25 mL). The combined organic layers were washed with brine, dried over MgSO₄, and concentrated under reduced pressure. The crude residue was purified by column chromatography, eluting with 1:1 hexanes:dichloromethane, affording pure product **3.32b** (117 mg, 46% overall) as a yellow solid. Mp = 77°C. ESI/APCI (m/z) [MH]+ calculated for C₇₄H₁₁₃O₆, 1097.8532; found 1097.8533.¹H NMR (CDCl₃, 300 MHz): δ 8.42 (d, J = 8.8 Hz, 2H), 8.04 (s, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.42 (s, 2H), 7.26 (s, 2H), 4.28 (t, J = 6.2 Hz, 4H), 4.17 (t, J = 6.6 Hz, 4H), 3.60 (t, J = 6.5 Hz, 4H), 2.03-1.88 (m, 12H), 1.66-1.51 (m, 12H), 1.43-1.20 (m, 48H), 0.96-0.86 (m, 18H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 155.0, 151.9, 148.8, 148.4, 126.7, 123.5, 123.3, 121.7, 119.0, 119.6, 67.5, 31.5, 31.3, 29.3, 29.1, 28.9, 28.7, 25.2, 22.2, 13.6 ppm.

**Compound 3.33a.** To a stirring solution of compound **3.36a** (33 mg, 0.033 mmol) in dichloromethane (3.3 mL) was added trifluoroacetic acid (0.33 mL), and the solution was allowed to stir at room temperature for 15 minutes. The reaction was cooled to 0°C, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (8.2 mg, 0.036 mmol) was added, inducing a dramatic color change from pale yellow to dark green. The reaction solution was allowed to warm to room temperature over 3 hours. Water was added (50 mL), and the organic layer was isolated. The organic layer was washed with sodium bicarbonate (3x50 mL), taking care to slowly neutralize the first water layer as the aqueous layers were combined. The aqueous phase was back-extracted with dichloromethane, and the combined organic layers dried over MgSO₄ and concentrated under reduced pressure. The crude material was purified via column chromatography, eluting with 5% diethyl-ether in hexanes, affording pure compound **3.33a** (29 mg, 88%) as a yellow solid. Mp = 82°C. ESI/APCI (m/z) [MH]+ calculated for C₆₆H₉₇O₆, 985.7280; found 985.7270.¹H NMR (CDCl₃, 300 MHz): δ 8.40 (d, J = 8.8 Hz, 2H), 8.04 (s, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.42 (s, 2H), 7.26 (s, 2H), 4.27 (t, J = 6.0 Hz, 4H), 4.17 (t, J = 6.6 Hz, 4H), 3.59 (t, J = 6.6 Hz, 4H), 2.01-1.88 (m, 12H), 1.66-1.56 (m, 12H), 1.42-1.20 (m, 32H), 0.96-0.86 (m, 18H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 148.9, 148.1, 147.7, 127.4, 127.1, 125.7, 124.3, 123.7, 118.2, 111.3, 108.0, 106.1, 68.0, 31.4, 31.2, 28.9, 28.7, 25.7, 25.1, 22.2, 13.5 ppm.

**Compound 3.33b.** To a stirring solution of compound **3.36b** (36 mg, 0.035 mmol) in dichloromethane (3.5 mL) was added trifluoroacetic acid (0.35 mL), and the solution was
allowed to stir at room temperature for 15 minutes. The reaction was cooled to 0°C, and 2,3-
dichloro-5,6-dicyano-1,4-benzoquinone (8.6 mg, 0.038 mmol) was added, inducing a dramatic
color change from pale yellow to dark green. The reaction solution was allowed to warm to
room temperature over 3 hours. Water was added (50 mL), and the organic layer was isolated.
The organic layer was washed with sodium bicarbonate (3x50 mL), taking care to slowly
neutralize the first water layer as the aqueous layers were combined. The aqueous phase was
back-extracted with dichloromethane, and the combined organic layers dried over MgSO₄ and
concentrated under reduced pressure. The crude material was purified via column
chromatography, eluting with 5% diethyl-ether in hexanes, affording pure compound 3.33b (34
mg, 94%) as a yellow solid. Mp = 79°C. ESI/APCI (m/z) [MH]+ calculated for C₇₀H₁₀₅O₆,
1041.7906; found 1041.7899. ¹H NMR (CDCl₃, 300 MHz): δ 8.43 (d, J = 8.8 Hz, 2H), 8.05 (s,
2H), 7.89 (d, J = 9.1 Hz, 2H), 7.43 (s, 2H), 7.28 (s, 2H), 4.28 (t, J = 5.9 Hz, 4H), 4.18 (t, J = 6.6
Hz, 4H), 3.60 (t, J = 6.5 Hz, 4H), 2.00-1.89 (m, 12H), 1.67-1.52 (m, 12H), 1.42-1.20 (m, 40H),
0.98-0.83 (m, 18H) ppm. ¹³C NMR (CDCl₃, 75 MHz): 149.3, 148.6, 148.1, 127.8, 127.5, 126.1,
124.8, 124.1, 118.7, 111.6, 108.4, 106.5, 69.4, 69.0, 68.5, 31.9, 31.7, 29.5, 29.3, 26.1, 25.8,
22.7, 14.1 ppm.

Compound 3.39 (Synthesis of 3.32a as shown in Scheme 3.8b). Toluene and deionized water
were degassed separately for 15 minutes. Compound 3.34b (77 mg, 0.177 mmol) and compound
3.35b (200 mg, 0.441 mmol) were subjected to high vacuum at 80°C for 15 minutes in a heavy-
walled pressure vessel, and the flask flushed with N₂. Potassium phosphate (113 mg, 0.531
mmol), Sphos Buchwald ligand (2.9 mg 0.007 mmol), and palladium acetate (2.4 mg, 0.004
mmol) were added in that order, and the flask flushed with N₂ again. Degassed toluene (0.35
mL) and deionized water (0.04 mL) were added, the heavy-walled vessel sealed, and the reaction
stirred at 100°C for 24 hours. The black reaction mixture was allowed to cool and filtered over
Celite, eluting with dichloromethane. The filtrate was concentrated under reduced pressure, and
the crude residue purified by column chromatography, eluting with 30% dichloromethane in
hexanes, affording compound 3.39 (98 mg, 60%) as a colorless oil. ESI/APCI (m/z) [MH]+
calculated for C₆₂H₉₁O₆, 931.6810; found 931.6831. ¹H NMR (CDCl₃, 300 MHz): δ 7.61 (s,
2H), 7.34 (d, J = 8.5 Hz, 2H), 7.06-6.94 (m, 4H), 4.15-4.05 (m, 12H), 1.95-1.83 (m, 12H), 1.56-
1.46 (m, 12H), 1.42-1.30 (m, 24H), 0.94-0.90 (m, 18H) ppm. $^{13}$C NMR (CDCl$_3$, 75 MHz): 149.0, 148.8, 147.8, 137.1, 132.9, 128.7, 127.1, 126.5, 126.1, 125.0, 116.1, 107.4, 107.2, 69.0, 68.4, 31.2, 28.9, 28.6, 25.3, 22.2, 13.6 ppm.

**Compound 3.32a** (Synthesis of 3.32a as shown in Scheme 3.8b). To a stirring solution of compound 3.39 (28 mg, 0.032 mmol) in dichloromethane (3.2 mL) was added trifluoroacetic acid (0.32 mL), and the solution was allowed to stir at room temperature for 15 minutes. The reaction was cooled to 0°C, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (8.0 mg, 0.036 mmol) was added, inducing a dramatic color change from pale yellow to dark green. The reaction solution was allowed to warm to room temperature over 3 hours. Water was added (50 mL), and the organic layer was isolated. The organic layer was washed with sodium bicarbonate (3x50 mL), taking care to slowly neutralize the first water layer as the aqueous layers were combined. The aqueous phase was back-extracted with dichloromethane, and the combined organic layers dried over MgSO$_4$ and concentrated under reduced pressure. The crude material was purified via column chromatography, eluting with 5% diethyl-ether in hexanes, affording pure compound 3.32a (26 mg, 93%) as a yellow solid. Characterization was consistent with values reported for the synthesis of compound 5a using Method ‘b’ from Scheme 3.7.
3.5. References and Notes


3.33. The only reaction reported herein that proceeds in a low yield is the mono-alkylation of catechol to form compound 3.11 (30% yield). We do not envision this to be a prohibitive problem given that catechol and hexyl bromide are both readily available and inexpensive. Furthermore, this single low yielding reaction is the first step in a synthetic sequence, which helps negate product loss.


3.43. Lau, K.; Foster, J.; Williams, V. Chem. Commun. 2003, 17, 2172-2173.


Chapter 4 – Framework Materials in Pedagogy

Preparation and Analysis of Cyclodextrin-Based Metal-Organic Frameworks (CD-MOFs): Laboratory Experiments Adaptable for High School through Advanced Undergraduate Students.
This Chapter is based on the following article:


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4.6. References and Notes
4.0. Abstract

\(\gamma\)-Cyclodextrin, a plant-derived renewable resource, can assemble in the presence of KOH or RbOH into metal-organic frameworks (CD-MOFs) with applications in gas adsorption and environmental remediation. Crystalline CD-MOFs are grown by vapor diffusion and their reversible adsorption of \(\text{CO}_2(\text{g})\) is analyzed both qualitatively, by a pH-responsive color change in the presence of methyl red indicator, and quantitatively, by direct calculation of the mass increase of CD-MOF samples upon \(\text{CO}_2(\text{g})\) adsorption. The experiment can be tailored to high school through advanced undergraduate laboratories and engages students in several areas of fundamental chemistry (crystallization, chemical equilibria, acid-base reactions, gas laws), advanced materials (MOFs), and broader impacts of chemistry (renewable resources and environmental chemistry).

4.1. Introduction

As discussed in previous chapters, highly porous materials\(^4.1\) such as zeolites\(^4.2\) and activated carbon\(^4.3\) have played several prominent roles throughout the chemical, materials, and petroleum industries for over a century. Interest in porous materials stems from their varied applications, including catalysis\(^4.2c,4.3b\), chemical separations and purifications\(^4.2b,4.3d\), and the selective uptake of small molecules\(^4.2d,4.3c\). Recently, metal-organic frameworks\(^4.4\) (MOFs) have generated significant attention for their synthetic tunability and exceptionally high porosity. These crystalline framework solids are composed of transition metals ions or clusters coordinated to rigid, polyfunctional organic ligands. In many cases MOFs are stable to the evacuation of solvents, leaving behind permanently porous molecular scaffolds with surface areas that commonly exceed 1,000 \(\text{m}^2/\text{g}\) and have been observed as high as 7,140 \(\text{m}^2/\text{g}\)\(^4.5\). One especially attractive aspect of synthetic MOFs is the modularity of their design as afforded by the multitude of available transition metal “nodes” and polyfunctional organic “linkers.” This modularity provides significant, though not absolute, control over the size, shape, and functionality of the pores within MOFs that, in turn, aids in tailoring their structure to specific functions.

While interest in MOFs has increased substantially in both industrial and academic settings, there are currently few experimental protocols\(^4.6-4.8\) suitable for introducing MOFs to undergraduates.
in a laboratory setting. Furthermore, we are unaware of any laboratory experiments incorporating MOFs that are suitable for advanced high school students. This can likely be attributed to the fact that the synthesis of MOFs commonly requires hazardous solvents, high reaction temperatures, and/or expensive starting materials. Similarly, high school and undergraduate laboratories often lack student access to the instrumentation commonly used to characterize MOFs; e.g. powder X-ray diffraction (PXRD), single-crystal X-ray crystallography, and gas sorption equipment for surface area analysis.

The laboratory experiment we describe herein details the facile synthesis\(^4,9\) of crystalline MOFs from benign starting materials as well as straightforward methods for observing and measuring their uptake of CO\(_2\)(g). A particularly appealing aspect of the laboratory experiment is its use of γ-cyclodextrin (Figure 4.1A-C), a renewable raw material that is a natural degradation product of corn and potato starch, as the polyfunctional organic linker.

![Figure 4.1](image.png)

**Figure 4.1.** Three different representations of the chemical structure of γ-cyclodextrin: condensed (A), expanded (B), and space-filling (C). Crystallization of γ-cyclodextrin in the presence of RbOH or KOH results in coordination between the alkali metal cations and γ-cyclodextrin (D), giving rise to porous metal-organic frameworks (CD-MOFs) as shown in (E) and (F). Metal cations are colored purple in (D)–(F). Individual γ-cyclodextrin macrocycles are colored in (F) only to aid in visualizing their relative locations.
We anticipate that the environmental implications of using a renewable resource (γ-cyclodextrin) to prepare advanced framework materials (MOFs) capable of capturing a common greenhouse gas (CO₂) will be of particular interest to students. Furthermore, we describe three different formats for the preparation and analysis of cyclodextrin-based MOFs (CD-MOFs, Figure 4.1D-E), allowing the experiment to be tailored to the laboratory skills of different students and to the institutional resources of various high schools and colleges/universities. The experiment combines a variety of fundamental and contemporary concepts in chemistry that instructors can utilize in both laboratory and lecture contexts: e.g. crystal growth and crystal structures, coordination chemistry, ideal gas laws, chemisorption and physisorption, porous materials and MOFs, and environmental chemistry.

4.2. Experimental Overview

The preparation and investigation of CD-MOFs can be divided into three sections: (4.2.1) crystal growth, (4.2.2) crystal activation, and (4.2.3) analysis. Each of these three sections can be modified and tailored to particular laboratory environments and available instrumentation. The completion of this laboratory experiment can be carried out in one extended laboratory period (4-5 hr, Appendix IV.1.3), however the results are both more reproducible and more pronounced when carried out over two lab periods that are ideally separated by 3 (or more) days (Appendix IV.1.1-2).

4.2.1. Crystal Growth

The first section of the experiment involves the preparation and growth of CD-MOF crystals from aqueous alkaline solutions of γ-cyclodextrin. Students prepare an aqueous mixture of γ-cyclodextrin and either KOH or RbOH such that the following conditions are met: the concentration of γ-cyclodextrin in the solution is 0.05 M and the molar ratio of γ-cyclodextrin to hydroxide is 1:8. Crystals grown in the presence of KOH lead to CD-MOF-1 while those grown in the presence of RbOH give CD-MOF-2. Growth of CD-MOF crystals is achieved by vapor diffusion with the conditions for crystal growth (solvent, time, temperature) determined by the time available to carry out the lab. Small CD-MOF-1 crystals, suitable for further analysis and visible to the naked eye, can be grown within 1-1.5 hours by vapor diffusion of acetone into a KOH solution of γ-cyclodextrin at 40 °C. Notably larger and more robust crystals of CD-MOF-2
can be grown within 72-96 hours by vapor diffusion of methanol into a RbOH solution of γ-cyclodextrin at room temperature. Shown in Figures 4.2 and 4.3 are time-lapse photos of the growth of CD-MOF crystals by vapor diffusion of methanol into 0.5 M aqueous solutions of γ-cyclodextrin containing 8 molar equivalents of RbOH (Figure 4.2) or KOH (Figure 4.3).

![Figure 4.2](image)

**Figure 4.2.** Typical growth of CD-MOF-2 crystals by vapor diffusion of methanol. While small microcrystals are typically visible when viewed under an optical microscope by day 2, single crystals of CD-MOF-2 are visible to the naked eye by 3 days of growth. We have found that 3-4 days of growth yields sufficient quantities of CD-MOF-2 crystals for analysis, however extending the growth period beyond 4 days results in a greater yield of CD-MOF-2 crystals.

![Figure 4.3](image)

**Figure 4.3.** Typical growth of CD-MOF-1 crystals by vapor diffusion of methanol. Crystals of CD-MOF-1 grow slightly faster, becoming visible to the naked eye by day 2. For sequential lab sections separated by 2-3 days we suggest the growth and analysis of CD-MOF-1 crystals because of their faster growth. For sequential lab sections separated by more than 4 days we recommend the growth and analysis of CD-MOF-2 crystals because of their greater long-term stability.
Many undergraduate laboratory experiments introduce students to crystal growth by either sublimation or cooling of saturated solutions. The use of vapor diffusion provides instructors an opportunity to discuss the variety of factors that influence crystal growth, such as the relative solubilities of reagents and products, solvent vapor pressures and miscibilities, crystal growth rates, and how each of these factors influence crystal size and quality. Students may also prepare a control sample by simply grinding a 1:8 molar ratio of $\gamma$-cyclodextrin and the appropriate alkali hydroxide using a mortar and pestle. The resulting powder will have the same composition as their respective CD-MOFs, however they will not exhibit the same porous crystalline framework.

4.2.2. Crystal Activation

The second section of the experiment requires students to activate their newly grown CD-MOF crystals. The activation process is necessary to remove residual water and/or starting materials from the pores of their crystals. Activation is achieved by removal of the solution phase surrounding the CD-MOF crystals and re-immersion of the crystals in either dichloromethane (preferred, though more hazardous) or diethyl ether (less preferred, though less hazardous). This process is repeated three times to ensure effective activation. Students complete the activation of their CD-MOF crystals by either placing them under high vacuum ($<$10$^{-1}$ torr) or in an oven at 120 °C for 30 minutes (or longer, if possible). Students also have the option of activating their CD-MOF crystals in a dichloromethane solution containing 0.10 M methyl red indicator. Under this activation procedure, methyl red will be incorporated into the pores of CD-MOF crystals$^{4,9b}$ and provide a means of visually analyzing their uptake of CO$_2$ via colorimetric acid/base chemistry.

4.2.3. Analysis

The third section of this laboratory experiment involves analysis of the CD-MOFs. Students are asked to quantify the amount of CO$_2$(g) that can be absorbed within the pores of their CD-MOF crystals. This is achieved by placing the crystals in a CO$_2$(g)-rich atmosphere, which can be easily achieved by placing a vial containing a known amount of CD-MOF inside a larger vial containing a few small pieces of solid CO$_2$. Upon sublimation of some of the CO$_2$(s) (approximately 5-10 minutes) students quickly remove their CD-MOF containing vials and record the mass increase resulting from CO$_2$(g) adsorption. Quantitative calculation of the CO$_2$(g)
uptake within CD-MOF samples requires that students consider several factors, including: the mass of the crystal sample, the crystal density, CD-MOF adsorption isotherms, and the ideal gas law. Worksheets detailing the calculation of CO$_2$$_{(g)}$ uptake are provided in the Appendix (A.IV.2). For samples that have been activated in the presence of methyl red indicator, the adsorption of CO$_2$$_{(g)}$ can be observed visually: the color of CD-MOF crystals containing methyl red changes from yellow in the absence of CO$_2$$_{(g)}$ to red upon exposure to CO$_2$$_{(g)}$. The adsorption and desorption of CO$_2$$_{(g)}$, and accompanying color change, is reversible and can be repeated several times, providing opportunities for instructors to engage students in discussions of equilibrium, Le Chatlier’s principle, and chemisorption and physisorption processes.

Several additional analytical studies can be carried out depending on the instrumentation available. Thermogravimetric analysis (TGA) provides a direct means of quantifying both the thermal stability of CD-MOFs as well as the extent of their activation. Powder X-ray diffraction (PXRD) provides fairly rapid structural analysis of the lattice parameters in CD-MOF crystallites. Single-crystal X-ray diffraction will provide full analysis of the solid-state arrangement and packing of γ-cyclodextrin and alkali cations (K$^+$ or Rb$^+$) in crystalline CD-MOF samples. Lastly, gas adsorption analysis can be carried out to directly quantify the amount of CO$_2$$_{(g)}$ adsorbed within samples of CD-MOFs at a given temperature and pressure, to investigate the reversibility of CO$_2$$_{(g)}$ adsorption and desorption, and to calculate the internal surface area of CD-MOF samples according to Langmuir or Brunauer-Emmett-Teller (BET) theory. This range of techniques that can be used to analyze the structure and properties of CD-MOFs allows this experiment to be tailored to a variety of different introductory through advanced laboratory curricula.$^{4,12}$

4.2.4. Hazards

One especially appealing aspect of this experiment is its safety and simplicity. The bulk of sample preparations involve aqueous solutions of generally nonhazardous materials. Flammable or otherwise hazardous solvents are used only in small quantities (<10 mL). The solid crystalline CD-MOF products are stable and nonhazardous.$^{4,13}$

Personal protective equipment (e.g. gloves, safety goggles, and lab coats) should be worn during all chemical and solvent manipulations and transfers. γ-Cyclodextrin and methyl red are
nonhazardous according to the Global Harmonized System (GHS) of classification and labeling of chemicals, however general precautions should still be taken to avoid ingestion, inhalation, and contact with the eyes and skin. Alkali hydroxides such as KOH and RbOH can be irritating to the eyes, skin, and mucous membranes. Methanol, acetone, diethyl ether, and dichloromethane are all flammable solvents and should be handled in a fume hood. Furthermore, methanol is irritating to the eyes, may cause moderate skin irritation, and may be fatal or cause blindness if swallowed. Acetone is a flammable solvent that can be moderately irritating to the skin and should not be inhaled or ingested. Diethyl ether is highly flammable, should be used in a fume hood, and must be kept away from any ignition sources. Dichloromethane is a flammable, carcinogenic solvent. Solid CO$_2$ should be handled using forceps to avoid skin damage by frostbite. All glass vials should be inspected for cracks prior to exposure to high vacuum to avoid risk of implosion. Heat-resistant gloves or forceps should be used when transferring vials into or out of ovens. MSDS sheets for all chemicals should be available to students and instructors should encourage students to read them prior to starting the experiment.

4.3. Results

Shown in Figure 4.4 are representative pictures of CD-MOF crystals grown quickly (1 hour, CD-MOF-1, Figure 4.4A), slowly (3 days, CD-MOF-2, Figure 4.4B), and activated with methyl red indicator (Figure 4.4C).

![Figure 4.4. Representative images of KOH-based CD-MOF-1 crystals after 1 hour of growth (A), RbOH-based CD-MOF-2 crystals after 3 days of growth (B), and RbOH-based CD-MOF-2 crystals after activation with methyl red indicator (C).](image-url)
This experiment has been carried out at Wesleyan University with students ranging from sophomores through seniors as well as with a group of students from Middletown High School in Middletown, CT. In all cases students were able to grow X-ray quality single crystals of CD-MOFs using both “fast growth” (1-1.5 hours) and “slow growth” (from 2 up to 7 days) procedures.

Following activation the most common method of analysis was measuring the uptake of CO$_2$(g) upon sublimation of dry ice into vials containing CD-MOF samples. While gas adsorption within the pores of most MOFs is driven by physisorption, CD-MOF crystals adsorb CO$_2$(g) by a combination of both physisorption and chemisorption.$^{4,9b,4,14}$ At standard temperature and pressure, crystals of CD-MOF-1 and CD-MOF-2 adsorb 58.3 cm$^3$ and 57.5 cm$^3$ of CO$_2$(g), respectively, per gram of material. Given that CD-MOF-1 crystals have a density of 0.942 g/mL, a 1.0 mL vial filled with CD-MOF-1 can adsorb up to 55 times the amount of gaseous CO$_2$ at STP than the same 1.0 mL vial when empty. The quantities of materials recommended for this lab experiment, however, are insufficient to provide enough material$^{4,15}$ to fill an entire 1.0 mL vial, and absolute amounts of CO$_2$(g) will vary with both the size of the CD-MOF sample and the size of the vial used. Students must take into consideration not only CO$_2$(g) adsorption by CD-MOF crystals but also the increase in mass that arises from displacement of air within the headspace above their specific CD-MOF sample by more massive CO$_2$(g). Worksheets detailing these calculations are provided in the Appendix (A.IV.2). Students following this lab procedure grew and activated CD-MOF crystals in 1-dram (3.7 mL) vials that yielded, on average, 50 mg samples of activated, crystalline CD-MOFs. Upon exposure of these samples to a CO$_2$(g)-rich atmosphere, their mass increased by an average of 7.2 mg as compared to an ideal increase of 7.5 mg. Mechanically ground control samples averaged a mass increase of 3.4 mg, less than half that of crystalline CD-MOF samples, and their mass uptake can be attributed almost entirely to displacement of air by CO$_2$(g) within the vial headspace.

Shown in Figure 4.5 is the reversible adsorption and desorption of CO$_2$(g) by CD-MOFs along with representative examples of the reversible color change of CD-MOF-1 activated with methyl red upon exposure to CO$_2$(g).
Figure 4.5. Reversible adsorption and desorption of CO$_2$(g) by CD-MOFs induces a color change from yellow (A) to red (b) when the CD-MOFs have been activated in the presence of methyl red indicator. This process is represented structurally, with schematic space-filling models, and with pictures of student-obtained results. Metal cations are represented in purple and CO$_2$ and carbonate esters are represented in green. It should be noted that the framework itself does not change color as shown, rather the color change results from protonation and deprotonation of the methyl red indicator (not shown). Chemical structures and space-filling models are only colored to correlate with the pictured results.

In the absence of CO$_2$(g) the CD-MOF crystals are yellow in color, indicating deprotonation of the methyl red upon its incorporation and (partial) anion methathesis with hydroxide counterions in the frameworks. Exposure of these yellow CD-MOF crystals to dry ice induces a color change from yellow (pH > 6.2) to red (pH < 4.4) as the CO$_2$(g) is known to chemisorb into the framework by reacting with a hydroxyl group of γ-cyclodextrin.$^{4,9b}$ This chemisorption process, which partially accounts for the high adsorption of CO$_2$(g) by CD-MOFs, results in the formation of a
carbonate ester and liberation of a proton, which then protonates the methyl red indicator. Removal of the CD-MOF sample from a CO$_2$(g)-rich atmosphere results in reversion back to its yellow color. Students are encouraged to repeat this process several times to witness the reversibility of this acid-base reaction caused by CO$_2$(g) adsorption and desorption.

Students with access to more advanced instrumentation are encouraged to investigate their CD-MOF samples by TGA, PXRD, and with gas adsorption apparatus. The measurement of mass loss as a function of temperature provided by TGA allows students to evaluate how well their CD-MOF crystals have been activated and to investigate the thermal stability of the porous CD-MOF frameworks. Diffraction patterns obtained by powder X-ray or single crystal X-ray analysis of CD-MOF crystallites provide students an opportunity to assess the crystallinity of their samples. Measurements of gas adsorption isotherms allow students to directly quantify the amount of CO$_2$(g) (or other gases) their CD-MOF crystals will adsorb as a function of temperature and pressure, and offers a means of calculating their surface areas. Instructors can use these more advanced analytical studies to engage students in discussions of (and deviations from) the ideal gas law, reversible and irreversible processes, Le Chatleir’s principle, crystal lattices and Miller indices.

4.4. Summary

The crystallization, activation, and analysis of CD-MOFs is a safe and reliable way to introduce students not only to the structures, properties, and applications of MOFs but also to incorporate several pedagogically relevant topics into a single laboratory experiment. The experiment can be carried out within one extended laboratory period or over the course of two laboratory periods, and the materials used render the synthesis of CD-MOFs safe enough for advanced high school students. Furthermore, the analysis of CD-MOFs can range from the simple and qualitative (observation of a reversible color change based on acid-base reactions upon adsorption/desorption of CO$_2$), to more quantitative (measurement of the adsorption of sublimed CO$_2$), and finally to advanced (analysis by TGA, PXRD, X-ray crystallography, or gas adsorption isotherms, where available). Students at all levels can therefore have the opportunity to grow and analyze new and advanced CD-MOF materials. Lastly, and very importantly, this
laboratory experiment directly engages students in topics of renewable resources and environmental remediation. Chemistry has played and will continue to play a central role in these areas, and the sooner students are engaged in discussions of the impacts chemistry can have on the environment (both positive and negative) the better. Please refer to Appendix IV for sample student laboratory protocols (A.VI.1), CO2 adsorption worksheet (A.VI.2), and answers to post-lab questions (A.IV.3).
4.5. Laboratory Experimental Details

4.5.1. Notes to the Instructor

This laboratory experiment has been carried out with students ranging from advanced high school students through undergraduate chemistry majors in their junior and senior years. Following the optimization of the experimental protocol, especially with regards to the scale and solvents used to grow CD-MOF crystals by vapor diffusion, the experiment has proven to be very reliable with all students able to grow and analyze CD-MOF crystals. That said, we would like to offer some suggestions for ensuring a successful and informative laboratory experiment.

Tips for success:

[1] The student laboratory procedures were designed for a laboratory course with an enrollment of 8-10 students working in pairs but can be easily scaled to other courses with larger enrollment. Similarly, the procedures themselves can be modified to fit a variety of different laboratory schedules (e.g. the number of days between lab periods, the amount of time CD-MOF crystals are submerged in an activating solvent, the amount of time activated CD-MOF crystals are desolvated can all be adjusted).

[2] For quantitative analysis of the CO$_2$(g) adsorption within activated CD-MOF crystals it is necessary to use an analytical balance with a resolution of at least ±0.1 mg. An analytical balance with a resolution of ±0.01 mg, if available, is preferred. The increase in mass upon CO$_2$(g) adsorption will typically be on the order of 3-10 mg (depending on sample size), therefore balances with lower resolution will introduce too much error to be considered quantitative.

[3] It is important that students label their sample vials and keep them organized through the three phases of the experiment (crystal growth, activation, and analysis). Sample vials used for vapor diffusion cannot be labeled with permanent marker because such labels are solvated by methanol and acetone. We have found that labeled test tube racks are very useful for keeping sample vials organized. We have also has success using label tags. Proper labeling and
organization is necessary because the mass of 1-dram vials recommended in this experiment can vary by >50 mg. Mixing up different sample vials will lead to inaccurate and potentially unphysical results.

[4] During activation, dichloromethane may be replaced with diethyl ether for crystal activation if less hazardous solvent is preferred, although the activation will not be as complete. For the growth of CD-MOF-1 crystals, we do not recommend allowing the crystals to grow for more than 4 days as they are not as stable over time as the CD-MOF-2 crystals. For the activation of CD-MOF crystals grown by vapor diffusion of methanol, an instructor or TA may need to activate the crystals depending on student access to laboratory space.

[5] Be sure to have something on hand, such as a hammer, to crush pieces of solid CO₂. Students may improvise if a suitable tool is not made available to them.

Suggestions for increased student engagement:

Each laboratory procedure will have moments of “down time,” e.g. during activation or drying of CD-MOF crystals, during crystal growth, etc. We have found that these offer opportunities to give students a greater understanding of the structural aspects of CD-MOFs. To this end we have included different formats of coordinate files that instructors can use to display and manipulate the solid-state structures of CD-MOF-2. Coordinate files of both an extended section (see Figure 4.1e) and a smaller section (see Figure 4.1d) of the solid-state packing of CD-MOF-2 are available as .pdf, .mol2, and .xyz files. Crystallographic .cif files for each CD-MOF are available free of charge from the Cambridge Crystallographic Data Center: CCDC 773709 (CD-MOF-1) and CCDC 773710 (CD-MOF-2). If computers and appropriate software are available to students then they can view and manipulate the 3-dimensional structures of CD-MOF-2 themselves or in groups. We have found that having the ability to rotate, translate, and zoom in or out of the solid-state structures of CD-MOFs is both fun for students and greatly enhances their understanding of the structures of these porous frameworks.

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“Down time” in the lab also offers a good pedagogic opportunity to discuss other aspects of this chemistry in more detail. Possible topics include green chemistry, renewable resources, CO$_{2(g)}$ sequestration, chemisorption versus physisorption, and the indicator pH chemistry occurring in the CD-MOF pores.

Instructors may want to preemptively prepare stock samples of CD-MOF-2 crystals that have been activated with methyl red indicator. This stock sample can then be used either in lab or during lecture to demonstrate the reversible color change upon CO$_{2(g)}$ adsorption. As noted, crystals of CD-MOF-2 are stable over extended periods of time (e.g. months if not longer) whereas crystals of CD-MOF-1 are less stable and therefore not recommended for long-term demonstrations.

The students we worked with were generally excited to see the clear, well-formed CD-MOF crystallites under a microscope. Some used their camera phones to take pictures of the crystals before and after activation, and before and after CO$_2$-induced color changes in methyl red activated crystals. Students then incorporated the images into their lab reports, which offered a good means of demonstrating their individual successes.
4.5.2. Student Procedure

(Note: Please See Appendix VI for full series of Student Procedures)

PREPARATION AND ANALYSIS OF CYCLODEXTRIN-BASED METAL ORGANIC FRAMEWORKS

Introduction

Highly porous materials, such as naturally occurring zeolites, have generated significant interest for nearly a century because they have a variety of applications throughout the chemical, materials, and petroleum industries. Zeolites are, for example, used to break down crude oil into smaller petrochemicals and hydrocarbons in a process called fluid catalytic cracking (FCC). Porous materials are also used in chemical catalysis, separations, and the selective uptake and storage of small molecules and gases.

Metal-organic frameworks (MOFs) are a new class of specialized nanoporous crystalline solids. They are composed of transition metals coordinated to rigid organic ligands that form infinitely repeating molecular “scaffolds” that have very high surface areas per unit volume. Their unique structural properties allow MOFs to display exceptional gas uptake and storage properties. In this experiment we will grow single crystalline solid samples of a nanoporous cyclodextrin-based metal-organic framework (CD-MOF) composed of β-cyclodextrin (CD) and an alkali hydroxide, in this case rubidium hydroxide (RbOH). Upon growing CD-MOF crystals we will investigate their ability to adsorb a common greenhouse gas, CO$_2$. We will also prepare control samples that are composed of the same chemical components but lack any regularly repeating nanoporous structure and we will compare their ability to absorb CO$_2$ with that of the CD-MOFs. Lastly, we will absorb a pH indicator, methyl red, into the pores of one sample so we can visually investigate the adsorption of CO$_2(g)$ by a reversible color change of the crystalline material from yellow to red.
Each group will prepare multiple samples for analysis, so it is especially important that each sample is properly labeled and all of your samples are well organized throughout the experiment.

**Materials**

*Chemicals*

$\gamma$-cyclodextrin (C$_{48}$H$_{80}$O$_{40}$): CAS 17465-86-0

Rubidium hydroxide (RbOH): CAS 1310-82-3

Methyl red (C$_{15}$H$_{15}$N$_3$O$_2$): CAS 493-52-7

Deionized water (H$_2$O): CAS 7732-18-5

Methanol (CH$_3$OH): CAS 67-56-1

Dichloromethane (CH$_2$Cl$_2$): CAS 75-09-2

Carbon Dioxide (CO$_2$): 124-38-9

*Equipment*

Volumetric flasks

Glass vials

Syringes and syringe filters

Thermometers

Test tube or vial rack

Balances and weighing paper

Drying oven / Vacuum Oven

Optical microscope
Mortar and pestle

Label Tags

**Hazards**

γ-Cyclodextrin is nonhazardous, however general precautions should still be taken to avoid ingestion, inhalation, and contact with the eyes and skin. Rubidium hydroxide can be irritating to the eyes, skin, and mucous membranes. Methanol is irritating to the eyes, may cause moderate skin irritation, and may be fatal or cause blindness if swallowed. Dichloromethane is a flammable, carcinogenic solvent. Personal protective equipment (e.g. gloves, lab coat, fume hood, etc.) should be used when handling dichloromethane and all forms of contact should be avoided (i.e. inhalation, ingestion, skin contact, etc.). Dry ice (CO$_2$(s)) is extremely cold and should be handled with forceps to avoid frostbite.

**Experimental Procedure: Lab period 1**

*Stock Sample and Solution Preparation:* The following three samples or solutions need to be prepared. Groups may evenly divide stock sample preparations.
**Solution A.** RbOH/ $\gamma$-CD$_{\text{aq.}}$: Weigh out 778 mg of $\gamma$-CD and 492 mg of RbOH and add both to a small beaker or glass vial. To this solid mixture add 12 mL of DI H$_2$O, resulting in a 0.05 M solution of $\gamma$-CD. This stock solution will provide enough material for 5-6 groups to grow CD-MOF crystals.

**Solution B.** Methyl red indicator: Weigh out 13.5 mg of methyl red indicator powder and add to a 50 mL volumetric flask. Dilute to the mark with dichloromethane, providing more than enough indicator solution for 5-6 groups.

**Sample C.** Mechanically ground control samples: Weigh out 250 mg of $\gamma$-CD in a mortar and add 158 mg of RbOH. Mechanically grind the mixture with a pestle resulting in a non-crystalline control sample with the same composition as the crystalline CD-MOF samples you will be growing. Each group should collect $\geq$50 mg of “crushed” RbOH/ $\gamma$-CD in a 1-dram glass vial.

**Sample Preparation**

Each group is going to prepare 3 samples. One sample will be used as a “control” and will consist of the mechanically ground mixture of RbOH and $\gamma$-CD. The other two samples will be used to grow crystalline CD-MOFs, one of which will be activated in the absence of methyl red indicator and the other will be activated in the presence of methyl red indicator:

- **CD-MOF:** Crystalline samples of CD-MOF grown from Solution A from above.
- **Indicator:** Crystalline samples of CD-MOF grown from Solution A from above and activated in the presence of methyl red indicator (Solution B from above).
- **Control:** Mechanically ground mixture of RbOH and $\gamma$-CD (Sample C from above).

Each group should be careful to label and organize their samples so that they do not get mixed up. Data for each sample should be recorded in each student’s notebook and/or the worksheet provided on the following page.
Worksheet 1: Experimental and Calculated Results

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mass Vial</td>
<td>Mass Vial + Activated Crystals (after CO₂)</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD-MOF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Indicator</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Crystallization by Vapor Diffusion*

Vapor diffusion is a common technique used to grow crystals. A variety of factors influence crystal growth, including the relative solubilities of reagents and products, solvent vapor pressures and miscibilities, and growth rates. In vapor diffusion, a miscible binary solvent system is chosen of liquids with different vapor pressures. The liquid with the lower vapor pressure (the solvent) contains the dissolved solutes of interest; in our case the aqueous solution of γ-CD and RbOH. The solutes are insoluble in the higher vapor pressure (the precipitant); in this case, methanol. A closed system of solution and precipitant is constructed, and the precipitant is allowed to vapor diffuse into the solution. As the concentration of precipitant slowly increases in the solvent, the solutes gradually become less soluble, encouraging well-ordered crystal growth. In this experiment CD-MOF crystals will begin to appear within 3-4 days of growth, and can continue to grow beyond 4 days.

*CD-MOF Crystal Growth*

Obtain two 1-dram glass vials, pre-weigh them on an analytical balance with a resolution of at least ±0.1 mg, and record the weight of the vials in your Worksheet. Then draw up ~1.5-2.0 mL
of the RbOH/γ-CD<sub>(aq.)</sub> solution (Solution A) in a disposable syringe. Cap the syringe with a PTFE syringe filter and then add 0.75 mL of the solution to each of your 1-dram glass vials. [Note: the syringe filter retains a small volume of solution as it filters so be sure the filter is dripping before measuring out the 0.75 mL]. Label your vials with label tags. These will become the CD-MOF and Indicator samples.

Pipette several mL of methanol into 2 separate large vials. Both 11-dram glass vials and 20-mL scintillation vials are well sized to encompass 1-dram glass vials containing the RbOH/γ-CD solution. The methanol level in the large vials should be higher than the level of RbOH/γ-CD solution in each of your smaller vials. Use forceps to carefully place the uncapped CD-MOF and Indicator vials inside the large, methanol-containing vials, tightly cap and parafilm the large outer vials, label each outer vial so you know which sample it is, and leave the crystallization systems to sit undisturbed for 3–4 days.

CO<sub>2</sub> Absorption – Control Samples (Lab period 1)

Record the mass of your Control sample in its respective vial without the cap. Now you should have both the mass of the empty vial as well as its mass with mechanically ground control sample, allowing you to calculate the mass of the sample itself.

Add small chunks of CO<sub>2</sub>(s) (dry ice) to a large glass vial and, using forceps, place your Control sample vial into the larger vial. The setup is analogous to that used in vapor diffusion. As the CO<sub>2</sub>(s) sublimes the resulting CO<sub>2</sub>(g) may be absorbed into the solid sample. Let the system sit for 5-10 minutes.

Working quickly but carefully, remove the sample vial from its CO<sub>2</sub> chamber, remove condensation with a Kimwipe, and take the mass of the vial. Enter the vial mass in your Worksheet as Control “Mass Vial + Activated Crystals (after CO<sub>2</sub>).”
Activation of CD-MOF and Indicator Samples (between Lab periods 1 and 2)

As mentioned above, allow your CD-MOF crystal samples (CD-MOF, Indicator) to grow, undisturbed, for 3-4 days. After this time, you will observe CD-MOF crystals within each of sample vials. The crystals will be visible without magnification, however you should also view them under an optical microscope. Make note of their general shape and color. While the crystals are well formed they will still contain varying amounts of solvents and starting materials both within their pores and in the solution around them. To remove these excess solvents and starting materials we need to activate the crystals according to the following procedures:

**CD-MOF sample.** Following 3-4 days of crystal growth, using a pipette, carefully remove the aqueous solution from your vial while leaving the solid crystals behind. Then add enough dichloromethane to submerge your CD-MOF crystals. Allow your crystals to soak in dichloromethane for 1 to 24 hours (depending on the times available for student or teaching assistant access to the lab). Repeat this process two more times.

**Indicator sample.** While activating your above CD-MOF samples, you’ll also begin incorporating methyl red indicator into your Indicator sample. Use a pipette to remove the solvent from Indicator sample vial and carefully submerge your crystals in the methyl red indicator solution (i.e. Solution B from above). Let these crystals soak in the indicator solution for 1 to 24 hours. Repeat this process once more with the methyl red indicator solution and then one last time with fresh dichloromethane.

To complete the activation step, and following removal of the last wash with dichloromethane, both the CD-MOF and Indicator samples should be dried by either placing them in an oven at ~120 °C or under high vacuum (≤10⁻¹ Torr) for 30 minutes (or longer, if possible) to remove any trace solvent.
**CO₂ Absorption (Lab period 2)**

Record the mass of your CD-MOF and Indicator samples in their respective vials but without their caps. Now you should have both the mass of each empty vial as well as its mass with activated crystals, allowing you to calculate the mass of the crystalline samples themselves.

Add small chunks of CO₂(s) (dry ice) to 2 separate large glass vials and, using forceps, place your CD-MOF sample into one and your Indicator sample into the other. As the CO₂(s) sublimes the resulting CO₂(g) will be adsorbed into the pores of each solid sample. Let the crystals adsorb CO₂ for 5-10 minutes.

Working quickly but carefully, remove the sample vials from their CO₂ chambers one at a time and take the mass of each vial. Enter each vials mass in your Worksheet as “Mass Vial + Activated Crystals (after CO₂).” For your Indicator sample make note of any color change; the absorption of CO₂(g) will induce a color change from yellow crystals to orange-red crystals. It is likely that the Indicator won’t absorb as much CO₂(g) because of methyl red incorporated in their pores. Its primary use is as a colorimetric means of observing the adsorption of CO₂(g).

**Analysis**

Fill out the remaining cells of your Worksheet for your samples. Determine the absolute mass of CO₂(g) uptake and percent mass difference of CO₂(g) uptake for each sample. In order to quantitatively determine the amount of CO₂(g) uptake in your CD-MOF sample you will need to take into account the volume of your vial occupied by CD-MOF crystals, the amount of CO₂(g) your CD-MOF is capable of absorbing at 298 K and 1.0 atm pressure, and the displacement of air in your vial by more massive CO₂(g). A worksheet from your instructor can be provided to aid in this calculation.
**Post-Lab Questions**

[1] What’s the difference between *absorption* and *adsorption*?

[2] What’s the difference between *chemisorption* and *physisorption*?

[3] Two very useful properties of metal-organic frameworks (MOFs) include their ability to adsorb gases and their exceptionally high surface area per volume. How is the high surface area per volume of MOFs related to their ability to adsorb gasses?

[4] Most MOFs adsorb gases only by physisorption, but CD-MOFs adsorb CO$_2$(g) by both physisorption and chemisorption. How does the color change experiment with methyl red indicator indicate that CO$_2$(g) is chemisorbed by the CD-MOFs?

[5] If you could prepare enough CD-MOF-1 to completely fill a 1.0 L bottle, how many grams of CO$_2$(g) could that bottle contain at 298 K and 1.0 atm pressure? Compare your answer to the number of grams of CO$_2$(g) the same 1.0 L bottle could contain?
4.6. References and Notes


4.10. For selected reviews of environmental applications of MOFs, particularly with regards to CO2 capture and sequestration, see: (a) Morris, R. E.; Wheatley Angew. Chem. Int. Ed. 2008,

4.11. If screw caps are used care should be taken not to completely seal vials containing solid CO₂ so as to avoid the build up of pressure and potential rupture of the vial. As an alternative, appropriately sized rubber septa, pierced with a disposable needle to vent excess pressure, can be used to cap the vials.

4.12. Representative examples of TGA, PXRD, and gas adsorption isotherm data can be found in the supporting online information of references 9a and 9b. Crystallographic .cif files for CD-MOF-1 and CD-MOF-2 are available free of charge from the Cambridge Crystallographic Data Center with deposition numbers CCDC 773709 and CCDC 773710, respectively.

4.13. As a dramatic example of nonhazardous nature of CD-MOF crystals, it is has been reported⁴.⁹a that CD-MOFs can be prepared entirely from food-grade ingredients (γ-cyclodextrin, potassium benzoate, water, and the spirit Everclear (95% EtOH)), rendering them safe to eat. We would like to reiterate here, however, that the procedure described in this article does not use food-grade materials and students should never be advised to ingest anything in the laboratory.


4.15. Significantly larger samples of CD-MOF-2 crystals can be grown by scaling up the starting materials and using larger containers (e.g. test tubes or beakers) for crystallization by vapor diffusion. It has been our observation, however, that the time required for crystal growth scales with sample size. With a significant increase in reaction scale the growth of CD-MOF-2 crystals takes prohibitively long (>2 weeks) for the experiment to be run as an undergraduate laboratory experiment. The laboratory protocols detailed in the Supplementary Information provide a useful balance of crystal yield and time required for crystal growth.