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Syntheses and Structures of Functionalized Cycloparaphenylenes and Fused Cycloparaphenylene Precursors

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Dissertation submitted to the Eberly College of Arts and Sciences

at West Virginia University
in partial fulfillment of the requirements
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Doctoral of Philosophy
in
Organic Chemistry

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ABSTRACT

Syntheses and Structures of Functionalized Cycloparaphenylenes and Fused Cycloparaphenylene Precursors

Changfeng Huang

A synthetic pathway of preparing functionalized [9]cycloparaphenylene ([9]CPP) bearing three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units and two macrocyclic [6]CPP precursors has been developed. The key steps included the Diels–Alder reaction between (*E,E*)-1,4-bis(4-bromophenyl)-1,3-butadiene and 1,4-benzoquinone followed by methylation to produce an L-shaped building block with two 4-bromophenyl groups *cis* to each other exclusively, the nickel-mediated homocoupling reactions to construct the macrocyclic dimers and trimers, and mild, efficient oxidative aromatization by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to furnish the functionalized [9]CPP.

A synthetic pathway for constructing fused carbon nanohoops with the two nanohoops in nanotube-like connection has also been developed. The key intermediate with all four 4-bromophenyl groups *cis* to one another in an L-shaped building block was prepared by two consecutive Diels–Alder reactions, followed by methylation. The Ni(cod)₂-mediated homocoupling reactions produced the molecules that contained either two hydrogenated [6]CPP, or two hydrogenated [9]CPPs fused through 1,4-dimethoxybenzene moieties and other bent and fused nanostructures with subunits of differing sizes of CPPs. The structure of a fused carbon nanohoop containing two hydrogenated [6]CPP units was established by X-ray structure analysis and a stepwise synthetic sequence. The structure of a molecule containing two fused carbon nanohoops

comprised of two hydrogenated [9]CPPs was also established by a similar stepwise synthesis.

In addition, a synthetic sequence to a functionalized [10]CPP has also been established. This synthetic pathway is being explored for the construction of fused carbon nanohoops containing two fully aromatized [10]CPPs.

DEDICATED TO

My wife, Hongmei Yan, My sons, Xinnan Huang, Yanis Huang

And My Parents

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Chapter 1. Syntheses and Structures of Functionalized Cycloparaphenylenes

1.1 Introduction

Carbon nanotubes have been gaining extensive attention since their first report and structural analysis by Iijima in 1991.¹ Because of their hollow cylindrical carbon nanostructures with all sp^2 carbon bonding, carbon nanotubes showed unprecedented mechanical, electronic and optical properties and high potential in the application of new nanotechnologies and materials science.^{2,3,4} Carbon nanotubes are categorized into two types: single-wall carbon nanotubes and multi-wall nanotubes. Multi-wall carbon nanotubes can be considered as a bundle of single-wall carbon nanotubes aligned together. Single-wall carbon nanotubes are classified into three kinds: armchair, zigzag, and chiral, conceptually depending on the way the graphene is rolled to make the carbon nanotube seamlessly by a pair of chiral indices (n, m) , where $n > m > 0$ (Figure 1.1). Two vector units are a_1 from carbon 1 to 3, and a_2 from carbon 1 to 5 respectively. For example if we made a carbon nanotube by rolling the graphene from the point O to O' in Figure 1.1, the resultant carbon nanotube is called chiral (4,3). Two extreme situations, one is when $n = m$, rolling angle $\theta = 30^\circ$, then it is armchair type single-wall carbon nanotube, type A on the right picture in Figure 1; the other is when $m = 0$, rolling angle $\theta = 0^\circ$ or 60° , it is called zigzag type single-wall carbon nanotube, type B on the right picture. The rest of single-wall carbon nanotubes are called chiral. One striking property of single-wall carbon nanotube is that it will shift from metallic to semi-conducting when the diameter or sidewall structure (or chirality) is slightly changed.⁴ So it is very important to produce single-wall carbon nanotubes with defined chirality and diameter if one wishes to study the structure-properties relationship and explore

Figure 1.1. Chiral index for single-wall carbon nanotubes

their potential applications. However, modern methods of preparing carbon nanotubes, including arc discharge, laser ablation, and chemical vapor deposition, always produce mixtures of carbon nanotubes.² Some catalyst manipulations^{6,7,8,9} and post synthesis purification techniques, such as the involvement of surfactant-assistant gel chromatography,¹⁰ DNA sequence,¹¹ orthogonal iterative density gradient ultracentrifugation and electrophoresis,¹² have been advanced to achieve high purity of carbon nanotubes with narrow diameter distribution. However, an effective way of producing single-chirality carbon nanotubes with predetermined type is still limited.

To address this problem, scientists proposed a bottom-up synthesis, which is a growth on template strategy. Tour and coworkers mass produced the chirality-controlled carbon nanotubes from a short pure single-wall carbon nanotube seed as a template through a complex route with Fe as catalyst.¹³ Liu and coworkers expanded this cloning strategy to grow single-wall carbon nanotubes with controlled chirality on a quartz substrate without any metal catalysts through an open-end growth mechanism using open-end single-wall carbon nanotubes as seeds.¹⁴ In this

regard, the use of template objects that mimic part of predetermined carbon nanotubes to strictly dictate the diameter and sidewall structure during the growth of carbon nanotubes holds high promise. Progress has been made even though with limited practical success. For instance, Li and co-workers grew one kind of carbon nanotube with high purity on a W and Co alloy catalyst. They attributed the selective growth to the catalysts crystals with high melting point and their unique atomic arrangement.¹⁵ Liu and co-workers generated (5,5)CNTs from fullerenedione that decomposed at high temperature and used the resulting material as a template.¹⁶ Zhou and co-workers also prepared (5,5)CNTs with extreme high purity from Scott's (5,5)CNT end-cap molecule after activated with water and air at high temperature.¹⁷ A new example of controlled synthesis of CNTs with single-chirality was reported by Amsharov, Fasel and coworkers, who used polycyclic aromatic hydrocarbon P1 as a precursor to form carbon nanotube seed through surface-catalyzed cyclodehydrogenation, followed by growth via epitaxial elongation to form a carbon nanotube on the same catalyst (Figure 1.2).¹⁸

Another type of possible template that unambiguously mimics the chirality of single-wall carbon nanotubes is called open-end templates that are taken from the middle segments of a single-wall carbon nanotube, while still keeping the full structural information of the carbon nanotube. The smallest repeating units in these carbon nanotubes are called carbon nanorings, like one single layer left after being cut perpendicular to the main axis (Figure 1.3). Figure 1.3 shows the possible templates for growing single-chirality single-wall carbon nanotubes. The smallest carbon nanorings for armchair single-wall carbon nanotubes are called cycloparaphenylenes (CPPs), in which all the benzene rings are connected at the *para*-position to form a macrocycle. The corresponding nanorings that represent zigzag type single-wall carbon

nanotubes are named cyclacenes. However there has been no report about the successful synthesis of cyclacenes.

Figure 1.2. Synthesis of carbon nanotubes from three endcaps, oxidized fullerenes, short (5,5)CNT end cap and polycyclic aromatic hydrocarbon **P1**

Carbon nanotubes

Armchair

(n,n)CNT

Zigzag

(n,0)CNT

Carbon nanorings

cycloparaphenylene (CPP)

Cyclacene

Figure 1.3. Types of single-wall carbon nanotubes, their smallest repeating units³

Not only were these beautiful templates and related growth mechanisms introduced theoretically, but their growth feasibility to produce CNTs from CPPs was confirmed experimentally. In 2013, Itami and co-workers first published the metal-free CNT growth with narrow diameter distribution from [9]CPP and [12]CPP as seeds.¹⁹ The carbon nanotubes were produced with high purity when [12]CPP was coated on C-plane of sapphire wafer with a flow of ethanol as the carbon source under high temperature and high vacuum. The average diameter of resultant CNTs was similar to that of [12]CPP seeds, which supports the growth on template mechanism.

1.2 Characteristics of different growth-on-templates strategies

A comparison of the different templates for carbon nanotubes growth in terms of supply quantity, product property, and mass production is summarized in Table 1.⁵ From Table 1 we can see that CPP has a great potential to act as a template over other templates. Another advantage of CPP as a potential template is that it is size-tunable, whereas other templates have very limited derivatives.

Table 1. Characteristics of different templates for growth of carbon nanotubes

Template types	Template supply	Description of product	Mass production
fullerene dione	Milligram scale	Wide diameter distribution	Scalable
CNT endcap	Milligram scale	Mainly semiconductive	Scalable
PAH	Milligram scale	(6,6)CNT	Difficult
CPP	Gram scale	Narrow diameter distribution	Scalable

1.3 CPP's properties and potential applications

Apart from serving as potential templates for the controlled synthesis of CNTs, CPPs themselves are aesthetically pleasing. The pursuit of synthesis of these unique, strained macrocycles will not only promote the discovery of new reactions and the development of novel methodology, but also will bring about new materials and applications.^{17,18,19,20} Inherently interesting CPPs have shown unique size-dependent optoelectronic and redox properties.²¹ The

HOMO-LUMO gaps decreases when the ring size decreases, which is opposite to that of linear oligoparaphenylenes, resulting in the longest wavelength absorption maxima and the emission maxima being red-shifted as the ring size decreases. The oxidation potentials of CPPs decrease with the decrease of ring size.^{23b}

The presence of the well-defined porous structure of CPPs makes them ideal candidates for study of host-guest interactions,²² catalysis and gas storage.²³ Furthermore, the unusual alignment of radially oriented π -conjugated systems affords great chances to probe the effect of pyramidalization of sp^2 -hybridized carbons on aromaticity,²⁴ and ring size on strain energy,²⁵ and a variety of applications in supramolecular interactions.²⁶

1.4 Organic synthesis of CPPs

Even though the CPPs' structures are relatively simple, it has been a challenge to synthesize them due to the presence of substantial strain energy in them. Early efforts include Parekh and Guha's attempted synthesis of [2]CPP in 1934 from oxidizing of 1,4-benzenedithiol to form cyclic disulfide **2** followed by copper-catalyzed desulfurization.²⁷ However the last step did not proceed to produce any of the highly strained [2]CPPs. Cyclic disulfide **2** was not formed; instead cyclic trimer **4** or tetramer was formed (Scheme 1.1).

Scheme 1.1. Parekh and Guha's attempted synthesis of [2]CPP

It was in 1993 when the synthesis of CPP was reported by Vogtle and co-workers in their preliminary publication, which was entitled On the Way to Macrocyclic Paraphenylenes.²⁸ One route involved macrocyclization to form the desired ene-yne **7** from double Wittig reactions between diphosphonium **5** and dialdehyde **6**. But the subsequent Diels–Alder reaction between **7** and diene equivalent did not take place to produce any CPP products.

Scheme 1.2. Vogtle's two routes to CPP

They also explored a different route starting from less strained *cis*-1,4-bis(4-iodophenyl)cyclohexane **8** with the hope that sp^3 -hybridized carbons in macrocycle **10** would be able to accommodate the curvature and the presence of aromaticity after aromatization of the cyclohexane moiety would compensate for the buildup of the ring strain. However double copper-mediated Kumada homocoupling reaction resulted in only linear oligomers. Similarly the

more rigid building block **9** also did not help in macrocyclization. After these attempts, he commented that the most promising pathway to make CPPs would be from 1,4-disubstituted cyclohexane building blocks.

The first successful synthesis of CPPs was achieved by Jasti and Bertozzi in 2008, almost 15 years later (Scheme 1.3).^{29a} Since then several synthetic pathways for constructing CPP with different sizes ranging from the smallest with 5 benzene units to the largest 18 benzenes were developed.²⁹ In the first successful synthesis the key intermediate iodidephenyl substituted 1,4-*cis*-dimethoxy-2,5-cyclohexadiene **11** was formed more favorably by two consecutive nucleophilic addition reactions of lithium reagents, produced from 1,4-diiodobenzene, to 1,4-benzoquinone. Then **11** was converted to borylated partner **12** for macrocyclization. The Suzuki-Miyaura cross-coupling reaction between **11** and **12** afforded a mixture of the CPP precursors, which were transformed successfully to CPPs under a reductive aromatization condition with lithium naphthalenide.

Scheme 1.3. First successful synthesis of CPPs

Later, both Jasti's group^{29f,29g,30,31} and Itami's group^{29b,29d,32,33} expanded this methodology to selective synthesis of CPP with different sizes. The differences between these groups lie in

two aspects. Jasti expanded the difunctionalized L-shaped building blocks either by taking advantage of different reactivity of aryl bromides and chlorides or by sequential oxidative dearomatization of 4-hydroxybiphenyl/nucleophilic addition, while Itami used the excess of one partner in the Suzuki-Miyaura cross-coupling reaction. Further Jasti prepared CPPs from reductive aromatization starting with diaryl substituted cyclohexadienes, whereas Itami produced CPPs with oxidative aromatization beginning with diaryl-substituted cyclohexanes. In Jasti's synthesis of [7]CPP (Scheme 1.4), he started with oxidative dearomatization of **16** by phenyliodonium diacetate (PIDA) to afford **17**, which is equivalent to one nucleophilic addition of 1,4-benzoquinone with the corresponding lithium reagent. A modified procedure was adopted to prepare the unsymmetrical L-shaped building block **19** with high diastereoselectivity, which later became the standard protocol for making this kind of *cis* L-shape building block. Compound **17** was deprotonated with NaH, followed by the nucleophilic addition of 4-chlorobenzenelithium from the side opposite to the alkoxide due to static repulsion to afford **18**, in high diastereoselectivity (*cis:trans* = 19:1). Subsequent methylation led to the unsymmetrical L-shaped building block **19**. Still a portion of **19** was borylated to yield **20**. The subsequent orthogonal Suzuki-Miyaura cross-coupling reactions provided the macrocyclic CPP precursor **22**, which was aromatized to afford [7]CPP.

Scheme 1.4. Synthesis of [7]CPP

Itami and co-workers at the same time adopted a different strategy of selectively preparing CPPs (Scheme 1.5). In their first report of selective synthesis of CPPs, they used **24a** recommended by Vogtle, as the L-shaped building block, which was synthesized from 1,4-diiodobenzene and cyclohexane-1,4-dione. They cleverly converted **23a** to borylated **23b** without protection of hydroxyl groups, which later proved a nice way for better purification. Then by using an excess of **24a** to react with **23b** in two consecutive Suzuki-Miyaura cross-coupling reactions delivered the difunctionalized **25**, which underwent another Suzuki-Miyaura cross-coupling with **23b** to furnish the macrocycle **26**. All the cyclohexane units in the macrocycle **26** were aromatized with *p*-toluenesulfonic acid (TsOH) and microwave irradiation to afford [12]CPP.

In 2011, Itami and co-workers reported a nice way of macrocyclization: shotgun synthesis of [9] and [12]CPPs through the Ni(cod)₂-mediated homocoupling reactions (Scheme 1.6).^{29e,34} This time they adopted an improved procedure to increase the diastereoselectivity and the yield of double nucleophilic addition of the lithium reagent to cyclohexane-1,4-dione with the help of cerium and lithium salts, which suppressed the monoaddition product and the formation of the *trans* isomer. In doing so the L-shaped building block **27** was prepared in 71–84% yield. The subsequent Ni(cod)₂-mediated homocoupling reactions furnished the macrocyclic trimer **28** and tetramer **29** in a one-pot operation. Improved oxidative aromatization of **28** and **29** by sodium hydrogen sulfate in *m*-xylene/water under air afforded [9]CPP and [12]CPP, respectively.

Scheme 1.5. Selective Synthesis of [12]CPP

Scheme 1.6. Concise Synthesis of [9] and [12]CPP

Another strategy of overcoming the ring strain during the synthesis of CPPs directly from benzene units was reported by Yamago^{29c} through reductive elimination (Scheme 1.7) and

Scheme 1.7. Synthesis of [8]CPP by Yamago

by Stępień^{29p} through template effect. Yamago and co-workers found that transmetalation between ditin **30** and Pt(cod)Cl₂ afforded the less strained macrocyclic Pt complex **31**.

Subsequently, the ligand exchange and reductive elimination, promoted by oxidation with bromine, afforded the [8]CPP without any aromatization step as the smallest CPP at that time.

Stępień and coworkers synthesized two nanotube endcaps through a completely different but concise approach (Scheme 1.8). Strain-free precursors **32** and **34** in which three 2,7-dibromocarbazoles or derivatives were connected by a mesitylene unit underwent three-fold nickel-mediated homocoupling reactions to deliver nanotube endcaps **33** and **35** respectively, in one step. This approach features a one step macrocyclization and very high ring strain buildup,

Scheme 1.8. Synthesis of Nanotube End-caps

which are quite different from other strategies. One can anticipate that future strategy for preparing CPPs could involve with removable tethers.

The pursuit of synthesis of CPPs gained more attention in 2014 when Jasti's group^{29m} and Yamago's group^{29l} independently published almost simultaneously the synthesis of smallest [5]CPP (Scheme 1.9). Yamago and co-workers prepared the macrocyclic [5]CPP precursor **38** through reductive elimination of a Pt complex and Ni-mediated homocoupling respectively. However, they could not proceed further to aromatize it with the widely used reductive aromatization method due to the low reactivity of methoxy groups and high ring strain. But stannane-mediated reductive aromatization took place to furnish [5]CPP when the highly reactive free hydroxyl-substituted precursor **39**, obtained by removal of the TES groups, were used. Jasti's group discovered the existence of macrocyclic precursor **41** when they tried to prepare a [10]CPP precursor through Suzuki-Miyaura cross-coupling reaction. Optimization of the reaction conditions led to the formation of **41** in 44% yield through the palladium-catalyzed homocoupling of aryl boronic esters at room temperature under air. In order to circumvent the limitation of the reductive power of sodium naphthalenide, they quenched the reaction mixture with methanol to form the partial reduced product **42**. Following the LDA induced E1cb elimination at room temperature, the desired [5]CPP was obtained.

Scheme 1.9. Synthesis of [5]CPP by Yamago and Jasti

1.5 Our synthesis of a functionalized CPP

It is apparent from the work of other research groups that the efficient synthesis of the intermediate *cis*-difunctionalized aryl-substituted cyclohexadienes or cyclohexanes, is crucial to the successful synthesis of CPPs. However, the current methods of preparing them involved multiple steps with precise sequence of addition and quantity (Scheme 1.10). In the first report of CPP synthesis *cis*-diiodide aryl-substituted cyclohexadiene **11** was prepared by two consecutive nucleophilic additions of a lithium reagent to 1,4-benzoquinone in 34% yield. Oxidative dearomatization with a hypervalent iodide compound was employed to eliminate one of the two steps of nucleophilic addition reaction. Deprotonation of free hydroxyl group greatly improved

the diastereoselectivity of the next nucleophilic addition reaction of an aryllithium reagent from 3:1 to 19:1 in favor of the desired *cis* product. This was attributed to ionic repulsion that anionic nucleophilic lithium reagent would attack from the opposite side.^{29f} This procedure was adopted as a standard method for preparing *cis*-difunctionalized aryl-substituted cyclohexadienes or cyclohexanes. Later Itami developed a procedure that used the cerium ion to coordinate with the oxygen atom of the hydroxyl group in order to block one side of the cyclohexyl system from the nucleophilic attack to achieve high diastereoselectivity with high yield.^{29e}

Scheme 1.10. Synthesis of Key Intermediate to CPP

We envisioned that the possibility of taking advantage of the inherent high stereoselectivity of the Diels–Alder reaction to form the desired CPP precursors. The first step of our approach involved the synthesis of difunctionalized dienes. The simplest difunctionalized diene would be 1,4-bis(4-bromophenyl)-1,3-butadiene. Using Davis’s procedure (Scheme

Scheme 1.12. Model Study of Diels–Alder reaction Between Diene 48 and 49

Then we turned our attention to explore the Diels–Alder reaction between 3,6-dimethoxybenzyne and diene **48**. The precursor triflate **54** to 3,6-dimethoxybenzyne was synthesized from the commercially available 2,5-dimethoxybenzaldehyde through Baeyer–Villiger oxidation, TMS protection, lithiation followed by quenching with TMSCl, deprotection, and trifluoromethylsulfonylation in high yield (Scheme 1.13). However, the following Diels–Alder reaction between diene **48** and 3,6-dimethoxybenzyne, generated from **54**, did not take place, with a variety of reaction conditions including different fluoride sources, addition sequences, temperatures, and solvents (Scheme 1.14).

Scheme 1.13. Synthesis of Benzyne Precursor 54

Scheme 1.14. Diels–Alder reaction Between Diene 48 and Benzyne Precursor 54

Then we turned to the Lewis-acid catalyzed Diels–Alder reaction between diene **48** and 1,4-benzoquinone (Scheme 1.15). Gratifyingly, the dihydronaphthene derivative **55** was achieved in 92% yield by a one-pot, two-step reaction using $\text{BF}_3 \cdot \text{OEt}_2$ to catalyze the Diels–Alder reaction between **48** and 1,4-benzoquinone, followed by methylation. A single crystal of **55** suitable for X-ray diffraction was obtained from by recrystallization from dichloromethane/hexanes. The X-ray structure analysis clearly showed that the two 4-bromophenyl substituents were situated *cis* to each other exclusively (Figure 1.4).

Scheme 1.15. Diels–Alder reaction between 48 and 1,4-Benzoquinone

Figure 1.4. X-ray crystal structure of dibromide **55**

We then used **55** to undergo the $\text{Ni}(\text{cod})_2$ -mediated homocoupling reaction in the presence of 2,2'-bipyridyl (bipy) to promote the macrocyclic ring formation (Scheme 1.16). At 5 mM concentration of **55**, the cyclic dimer *syn*-**56a** and *anti*-**56b** were produced in 21% and 6% yields, respectively. This was the first example of producing the cyclic dimers from the L-shaped building block, which was in sharp contrast to the reports in which only a trimer or a tetramer or a mixture of both was obtained from the L-shaped building blocks.^{29e,34} One year later, Yamago and co-workers reported a second example of cyclic dimer formation in 11% yield from the L-shaped building block **57** (Scheme 1.17).³⁵ More recently our group expanded the reaction scope with other dienophiles (Scheme 1.18).³⁶ The Diels–Alder reaction between diene **48** and dimethyl acetylenedicarboxylate again afforded the L-shaped building block **60** in 85% yield. The $\text{Ni}(\text{cod})_2$ -mediated homocoupling reactions produced the cyclic dimer **61** in less than 5% yield and the cyclic trimer **62** as the major product in 18% yield.

Scheme 1.16. Ni(cod)₂-mediated Homocoupling Reaction with 55

Scheme 1.17. Ni(cod)₂-mediated Homocoupling Reaction with 57

Scheme 1.18. Ni(cod)₂-mediated Homocoupling Reaction with 60

The structure of the dimer *syn*-**56a** was characterized by the ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy. In the ^1H NMR spectrum, all the aromatic proton signals in the biphenyl segments are shifted upfield to 6.6-6.7 ppm. The signal of the allylic hydrogens occurred at 5.2 ppm, while the signal of the vinylic hydrogens occurred at 6.8 ppm. Recrystallization of *syn*-**56a** from dichloromethane and hexanes provided suitable crystals for X-ray diffraction (Figure 1.5). The X-ray structure analysis not only unambiguously confirmed its structure, but also showed that the dimer is oval-shaped, and the two biphenyl segments lies close to each other within a distance ranging from ca. 3.42 to 4.10 Å. The two

Figure 1.5. X-ray crystal structure of the dimer *syn*-**56a**

phenyl rings in the biphenyl segments are twisted with a dihedral angle around 49° . This may account for the upfield shift of the aromatic proton signals in the biphenyl segments, which are located in the magnetically shielded region of the aromatic ring current of the phenyl groups on the opposite side.

Vögtle predicted that rigid building blocks would facilitate the formation of macrocyclic rings.²⁸ The X-ray structure of our L-shaped building block **55** clearly showed that the included angle between the two 4-bromophenyl groups is 73.6° in the crystal lattice, smaller than that of **23a** and **24b** at ca. 80° and similar to that of **60** at 73.5° . The conformational analysis of 1,4-cyclohexadienes by Marshall and coworkers⁵⁷ suggests that the small 3J coupling constant of 4.7 Hz between allylic protons and vinylic protons in **55** indicates that the dihydronaphthalene ring is only slightly puckered ($<10^\circ$) from planarity, with a flattened-boat structure in solution as in crystal lattice. This smaller included angle between the two 4-bromophenyl groups in **55** than in **23a** and **24b** may be responsible for channeling the second $\text{Ni}(\text{cod})_2$ -mediated homocoupling reaction toward the formation of the cyclic dimers *syn*-**56a** and *anti*-**56b** as the major products.

The allylic 1,3-strain between the methoxy groups and the two 4-bromophenyl groups in **55** may be responsible for the smaller included angle between the two 4-bromophenyl groups and thus favor dimer formation. However these interactions are not severe in **60** or in Itami and Yamago's cases. Instead, those L-shaped building blocks are more in favor of the formation of trimers under the Ni(cod)₂-mediated homocoupling condition.

We first tried to brominate the allylic hydrogens in hope of using LDA for aromatization as reported by Jasti's group in their synthesis of [5]CPP.^{29m} Although we did observe the formation of some brominated products, the LDA induced elimination did not occur. Other aromatization methods were also unsuccessful (Scheme 1.19).

Scheme 1.19. Efforts to Aromatize *syn*-56a

We also attempted to aromatize the cyclic dimers by treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) at temperatures ranging from 25 to 150 °C, but were not successful. Perhaps DDQ's oxidation power is not strong enough to overcome the developing ring strain in the functionalized [6]CPP.

We also tried to oxidize the cyclic dimer *syn*-**56a** to quinone **63**, hoping that the base-induced tautomerization would compensate for the ring strain to form the anion of the corresponding hydroquinone[6]CPP. The oxidation proceeded well with CAN in silica gel in 15 min. However, the base-induced tautomerization did not take place, and **63** was recovered.

We then turned our attention to exploring the aromatization of functionalized [9]CPPs with less ring strain by synthesizing the trimers from the Ni(cod)₂-mediated homocoupling reactions with L-shaped building block **55**. After careful and tedious flash column

Scheme 1.20. Synthesis of Trimers

chromatography of the reaction mixture of Ni(cod)₂-mediated homocoupling reaction of **55**, we are able to isolate the cyclic trimers *syn*-**64a** and *anti*-**64b** (*syn*-**64a**: *anti*-**64b** = 1:3) in a 11% combined yield. At higher 50 mM concentration of **55**, we obtained the cyclic dimers in 8% combined yield (*syn*-**56a**:*anti*-**56b** = 3:1) and the cyclic trimers in 18% combined yield (*syn*-**64a**:*anti*-**64b** = 1:3) (Scheme 1.20).

Again the structures of the cyclic trimers were characterized by the ^1H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy. With *syn*-**64a** possessing three planes of symmetry and one C_3 axis of symmetry; and *anti*-**64b** containing only one plane of symmetry, it is relatively easy to identify them from the NMR spectroscopy. Only one singlet from the methoxy groups, one set of doublets with AB pattern from the aromatic protons in the biphenyl segments, a doublet from the allylic protons and a doublet from the vinylic protons were observed in *syn*-**64a** ^1H NMR spectrum. The *anti*-**64b** ^1H spectrum showed three singlets with equal intensity for the methoxy groups, three sets of doublets with AB pattern from the aromatic protons in the biphenyl segments, one singlet and one AB pattern from the aromatic protons in the dimethoxybenzene parts, one set of two doublets and one set of ABXY spin system from the allylic and vinylic protons in the cyclohexadiene structures. These signals fall within the normal chemical shift range of these types of protons. Unlike the dimers, the aromatic signals are not shifted upfield to ca. 6.6 ppm. Another difference in chemical shifts of the ^1H NMR spectrum between the dimers and trimers is that vinylic signals of the dimers occurred at 6.8 ppm, whereas that of the trimers occurred at around 6.0 ppm.

We were delighted to observe the disappearance of the doublets for the allylic and vinylic protons in the cyclohexadiene units when the trimers were treated with DDQ for aromatization. After extensive screening of the oxidants, solvents, reaction temperature, and reaction time, we were able to aromatize the trimer with DDQ⁷⁸ cleanly in 88% yield at 70 °C in chlorobenzene for 2 hrs. It was interesting to note that both *syn*-**64a** and *anti*-**64b** underwent fully aromatization to form the functionalized [9]CPP **65** with three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units (Scheme 1.21). This mild aromatization protocol with excellent

yield is in contrast with Itami's oxidative aromatization of [9]CPP at higher temperature (150 °C) and longer time (48 h) in 24% yield.^{29c,34}

Scheme 1.21. Synthesis of 65 and Its Energy-Minimized Structure by DFT Calculations

We also conducted DFT calculations of the functionalized [9]CPP **65**. The most stable conformer indicates that the 5,8-dimethoxynaphth-1,4-diyl units cant away from the inner plane of the [9]CPP circle at an angle of 133.8° on average with two of the units tilting above the ring and the third tilting below the ring, which is similar to the X-ray structure confirmed by the crystal structure of the aromatized product of **62**.³⁶ The three biphenyl moieties of **65** have three unique torsional angles of 19.5° , 36.5° , and -37.5° . The diameter of the ring is calculated to be

12.4 Å as reported previously for the parent [9]CPP.^{29a} However, the NMR spectrum of **65** at 25 °C showed only one set of signals, including one singlet for the methoxy groups, two singlets for the hydrogens on the naphthyl systems, and one set of two coupling doublets for the hydrogens on biphenyl segments. Conducting the NMR experiment at –50 °C did not show any significant change with regard to the broadness of the signals. In conjunction with the DFT calculations, the observation of only one set of NMR signals for **65** suggests rapid arene rotations on the NMR time scales.

The UV-vis spectrum of **65** showed a major absorption maximum at 362 nm with a molecular absorption coefficient (ϵ) of $5.2 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$, which lay between those of the parent [9]CPP (340 nm) and [9]cyclo-1,4-naphthalene (378 nm). The fluorescence maximum (λ_{em}) was observed at 512 nm, indicating a red shift compared to those of the parent [9]CPP (494 nm) and [9]cyclo-1,4-naphthalene (491 nm).³⁹

1.6 Summary

In summary, we have developed an efficient pathway of preparing functionalized [9]CPP bearing three evenly spaced 5,8-dimethoxynaphth-1,4-diyl units and macrocyclic dimer [6]CPP precursors. This pathway features a key step involving a Diels–Alder reaction to construct the *cis* L-shaped building block, nickel-mediated homocoupling to build macrocycles efficiently, and mild aromatization methods with DDQ. The high stereoselectivity and versatility of the Diels–Alder reaction between a variety of readily available dienes and dienophiles bearing diverse structural features make our synthetic pathway especially attractive for the synthesis of functionalized CPPs.⁴⁰ Moreover, the presence of 5,8-dimethoxynaphth-1,4-diyl units in **65** affords additional handles for subsequent synthetic elaborations.⁴

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Chapter 2. Syntheses and Structures of Bent and Fused Cycloparaphenylene Precursors

2.1. Introduction

In his pioneering paper, Itami conceptually demonstrated the first diameter-controlled synthesis of CNTs from cycloparaphenylenes as templates without any metal catalysts.¹ It is considered a great advance toward controlled synthesis of CNTs with uniform structure and defined diameter using a bottom-up synthesis, growth-on template strategy and exemplify the synthetic potential of CPP-based templates for such purpose. In the end, he mentioned that for perfect diameter and sidewall structure control, robust substrates and modified equipment are needed. Toward this end, a number of substituted or π -extended CPP derivatives have been prepared, such as Itami's [9]cyclo-1,4-naphthalene,² Jasti's tetraphenyl substituted [12]CPP,³ Swager's naphthalene-spaced [12]CPP,⁴ Müllen's 3D π -extended polyphenylene cylinders,⁵ Wegner's substituted [8]CPP,⁶ and Yamago's [4]cyclo-2,7-pyrenylene.⁷ However, if one reexamines the growth mechanism of CNTs, other issues need to be resolved before the bottom-up synthetic strategy becomes practical in producing CNTs.

In addition to the hypothesis by Irle and Morokuma from DFT calculations that CNTs growth can be induced by ethynyl radical addition on CPP substrates,⁸ there are two popular mechanisms on the CNT growth. The first was put forward by Scott, suggesting that repetitive Diels–Alder reactions between the substrate's bay area and acetylene or acetylene equivalents, followed by aromatization by release of H₂ at that thermal conditions could regenerate bay area for the next Diels–Alder reactions for tube growth (Scheme 2.1).^{9–13} Clearly this method will only elongate the substrate, keeping the growing CNTs with the same structure as the substrate. However it is well known and experimentally established that CPP substrates will not undergo

Diels–Alder reaction with dienophiles in the bay area,^{14,15,16} similar to the observation that biphenyl or terphenyl will not take part in any Diels–Alder reaction. One possible solution to this problem, suggested by Scott, was to use longer PAH segments, such as hisanthene or perylene with suitable dienophiles,⁹⁻¹³ which were proved to be reactive by Jasti's group.¹⁴⁻¹⁵ A straightforward method to incorporate the longer PAH segments in those aryl-substituted CPPs is through Scholl reaction. However, halogenation,¹⁶ structural rearrangement¹⁷ including 1,2-phenyl shift^{16,18} or strain release ring opening¹⁶ in these strained macrocycles is always a concern. It is still a challenge to synthesize these larger π -extended CPP derivatives^{19,20} and no reports about larger fully π -extended CPPs such as **66** have been published. Also no experimental conditions to demonstrate the growth of CNTs through this mechanism have been reported.

Scheme 2.1. Growth Mechanism Through Diels–Alder Reaction and Rearomatization

A second carbon nanotubes growth mechanism with CPPs as the growth templates was proposed by Itami through CPP radicals under chemical vapor deposition (CVD) method with carbon sources.¹ At high temperature, CPP radicals, generated from homolytic C-H bond cleavage, annulated with unsaturated C2 species from ethanol as the carbon source to produce CNTs. Because the bond dissociation energies of aryl C-H bond (113 kcal/mol) and aryl C-C bond (114 kcal/mol) are almost the same, it is likely that at high temperature both aryl C-H bond cleavage and aryl C-C bond cleavage will take place, thus destroying the CPP template. This

may account for the formation of oligophenylenes, multi-wall CNTs, low yield of the process, and the imperfect diameter distribution of the resulting CNTs. However if the template is longer with fully π -extended CPP such as **66**, even though one layer of the CPP is broken, the whole template is not totally destroyed and there is still opportunity for recombination. From both aspects of growth mechanisms, Jasti proposed that the π -extended CPP may be important for generating CNTs in high yield by using CVD method.¹⁶ The simplest of the π -extended CPPs would be CPP dimers. So far there are only two reports of the synthesis of CPP dimers.^{21,22}

The first synthesis of arene-bridged CPP dimer was reported by Jasti group in 2012 (Scheme 2.2).²¹ The synthetic sequence used the *cis*-bromo-containing diiodide **72**, prepared from two consecutive nucleophilic additions of lithium reagent to a bromo-containing protected dieneone, as a key intermediate. The coupling partner, diboronic ester **73**, was obtained in large quantity during the exploration of the synthesis of [6]CPP²³ and the large-scale synthesis of [8] and [10]CPPs²⁴ by the oxidative dearomatization/addition sequence. Suzuki-Miyaura cross-coupling reactions between the bromo-containing diiodide **72** and **73** effectively delivered the bromo-containing macrocyclic [8]CPP precursor **74** in 30% yield. The subsequent Suzuki-Miyaura cross-coupling reaction between **74** and 1,4-bisborylbenzene, 1,5-diborylnaphthalene afforded the arene-bridged CPP dimer precursors **75** and **76**, respectively. Lastly reductive aromatization by sodium naphthalenide furnished the arene-bridged CPP dimers, which according to DFT calculations adopted the *cis* conformation in the gas phase and in solution, but *trans* conformation in solid phase. To form the nanotube-like structures, additional carbon-carbon bond connection to form the fixed *cis* structure will be needed.

Scheme 2.2. Synthesis of Arene-Bridged [8]CPP Dimer

Itami group later published the synthesis of the directly connected [10]CPP dimer **84** through a single C-C bond by the nickel-mediated homocoupling through a chloro-containing [10]CPP **83**, which was produced from the acid-mediated oxidative aromatization of chloro-

containing [10]CPP precursor **82**.²² Triangle-shaped chloro-containing **82** was prepared by a 9+1-type cyclization between **81** and the C-shaped **80** (Scheme 2.3).

Scheme 2.3. Synthesis of Directly-Connected [10]CPP Dimer

Compound **80** was prepared from two L-shaped building blocks **27b** and **79** using well established procedures for the selective synthesis of [9]-[11] and [13]CPP.²⁵ The chloro-containing linear unit **81** was synthesized by the palladium-catalyzed borylations of 1,4-dibromo-2-chlorobenzene.²⁶ They showed that the stable conformation of **84** is the structure in which one CPP unit sits directly above the other CPP unit.

2.2. Our synthesis of a nanotube-like dimer, trimer and related bent and fused carbon nanohoops

As these CPP dimers are connected through a single C-C bond, there are always problems of free rotation and conformational conversion. So they are not considered as ideal templates for CNT growth according to the analysis from above two growth mechanisms. However, our functionalized CPPs and precursors can be easily oxidized to quinone forms and act as good dienophiles. If the second Diels–Alder reaction takes place on the same side as the macrocycles, then after a second nickel-mediated homocoupling reaction, the nanotube-like structures could be constructed, which can serve as potential templates for the CNTs growth.

2.2.1. First route to construct nanotube-like structures

The idea that the second Diels–Alder reaction may proceed to form an adduct with all four 4-bromophenyl groups *cis* to each other was first observed by Yiwei Huang²⁷ during our pursuit to find an efficient Lewis acid-catalyzed Diels–Alder reaction. In compound **85**, all the four 4-bromophenyl groups are located on the same side (Scheme 2.4). The structure of **85** was established by X-ray structure analysis. However the Ni(cod)₂-mediated homocoupling reaction of **85** did not produce any discernable products.

Scheme 2.4. Synthesis of Tetrabromide Ketone 85

2.2.2 Second route to construct nanotube-like structures

Scheme 2.5. Attempted Synthesis of Nanotube-like Structures from Cyclic Dimer

With the idea that the second Diels–Alder reaction may form the all *cis* product, we explored the possibility of using the oxidized cyclic dimer 63 for the second Diels–Alder reaction with diene 48 promoted by $\text{BF}_3 \cdot \text{OEt}_2$ (Scheme 2.5). The second Diels–Alder reaction

went smoothly to afford the DA adduct **86** in 75% yield. However, the following methylation reaction did not proceed well, producing the methylated product **87** in only 10% yield. We suspect that **86** may have the *anti* structure, which is more difficult for methylation because the resulting methoxyl groups suffer from more severe steric interactions with either the 4-bromophenyl groups or the biphenyl bridges. Further indication of the *anti* structure came from the fact that no intramolecular homocoupling product from the Ni(cod)₂-mediated homocoupling reaction was obtained.

2.2.3. Third route to construct nanotube-like structures

We then turned our attention to investigating how the second Diels–Alder reaction took place. As we increase the amount of diene **48** in the Diels–Alder reaction with 1,4-benzoquinone in the presence of BF₃•OEt₂, no double DA adducts were observed. However, when 1,4-hydrobenzoquinone **88** was oxidized to 1,4-benzoquinone **89**, it underwent the second Diels–Alder reaction to deliver, after methylation, the *syn*-tetrabromide **90** as the major product in 68% yield and the *anti*-tetrabromide **91** as the minor product (*syn*-tetrabromide **90**:*anti*-tetrabromide **91** = 8:1) (Scheme 2.6). The structure of *anti*-tetrabromide **91** was unambiguously established by X-ray structure analysis. We also grew crystals of *syn*-tetrabromide **90** from dichloromethane/hexanes, although an X-ray structure of **91** was obtained (Figure 2.1), the quality of the X-ray structure of **90** was poor. Fortunately, we were able to obtain crystals suitable for X-ray structure analysis, when *syn*-tetrabromide **90** was converted to the corresponding *syn*-tetraiodide **92** (Scheme 2.7). The X-ray structure of **92** (Figure 2.2) clearly indicates that the four 4-iodophenyl groups are on the same side exclusively and are in close

proximity to each other, resulting in upfield shift of the ^1H NMR signals of phenyl protons to less than 7.0 ppm.

Scheme 2.6. Synthesis of *syn*-Tetrabromide 70

Figure 2.2. X-ray crystal structure of the *syn*-tetraiodide **92**

With large quantity of the *syn*-tetrabromide **90** at hand, we applied the same protocol of the Ni(cod)₂-mediated homocoupling reaction of *syn*-tetrabromide **90** in the presence of 2,2'-bipyridyl (Schemes 2.8 and 2.9). We were able to isolate the macrocyclic dimers **73** and **74** in 5% and 1% yield, respectively, when the reaction was run at 1 mM concentration. The structure of **93** was established by X-ray structure analysis (Figure 2.3). It is very interesting to note that dimer **93** has a nanotube-like structure in which two [6]CPP precursors are fused through two 1,4-dimethoxybenzene units. The structure of **93** represents the first example of fusing two nanohoops together with the holes facing each other in a nanotube-like arrangement. The dimer **94** contains a bent [12]CPP precursor which is fused within itself with two 1,4-

dimethoxybenzene units. Dimer **93** and **94** display similar chemical shifts and splitting patterns as one-layer dimer *syn*-**56a**, one upfield AB pattern for the aromatic protons, one downfield pseudo quartet with equal intensity for the vinylic protons, and a downfield “hump” for allylic protons. The high-resolution MS spectra also indicate that **93** and **94** are dimers.

Scheme 2.8. Synthesis of Macrocyclic Dimers **93 and **94** at Low Concentration**

HRMS (ESI) calcd for $\text{C}_{80}\text{H}_{60}\text{O}_4$ (M^+) 1084.4486, found 1084.4520 HRMS (ESI) calcd for $\text{C}_{80}\text{H}_{60}\text{O}_4$ (M^+) 1084.4486, found 1084.4474

Figure 2.3. X-ray crystal structure of fused nanohoops **93**

In addition, we were also able to purify and identify three (**95a**, **95b**, and **95c**) of the four possible trimers by NMR and high-resolution MS techniques when the homocoupling reaction were carried out at 50 mM concentration. It is worth noting that **95a** contains two fused [9]CPP precursors in a nanotube-like structure, **95b** contains a bent [18]CPP precursor macrocyclic ring, and **95c** contains fused [12]CPP and [6]CPP precursors (Scheme 2.9).

Scheme 2.9. Synthesis of Macrocyclic Trimers 95a, 95b, and 95c at Higher Concentration

On the basis of the NMR analysis, we were also able to differentiate the three trimers from the ¹H NMR spectra. It is easiest to discern **95a**, which has a *D*_{3h} symmetry and shows only one AB pattern for the aromatic protons, a set of two doublets coupled to each other for the vinylic protons and allylic protons, and a singlet for the methoxy protons. The most obvious difference between **95b** and **95c** is that **95b** exhibits three singlets of equal intensity for the three different types of methoxy groups, whereas **95c** exhibits two singlets in 2:1 ratio for the two different types of methoxy groups. In addition **95b** has one set of vinylic protons and allylic protons that show a pseudo quartet with equal intensity and a “hump” respectively, but **95c** has two sets of those spin systems. Moreover, **95b** has an ABXY spin system in which H³, H⁴, H⁵,

H⁶ are chemical nonequivalent and four distinct signals were observed, whereas **95c** does not. Unfortunately we were not able to isolate the trimer **95d**, which would be expected to show upfield shifted aromatic signals as observed in the spectrum of **93**.

2.3. Structural elucidation of nanotube-like dimer **93**

Before the X-ray structure became available for **93**, we undertook the development of a stepwise synthesis of **93** to allow the elucidation of its structure. First we prepared the dibromide diboronic ester **97** that has a coupling partner on each side. It was anticipated that the Suzuki-Miyaura cross-coupling reactions of two molecules of **97** could lead to dimer **93**. The Diels-Alder reaction between dibromide **89** and diboryl diene **96**, which was prepared by the palladium-catalyzed borylation of diene **48** in excellent yield with Buchwald's catalyst system,²⁸ afforded, after methylation, the *syn*-dibromide diboronic ester **97** in 55% yield.

Scheme 2.10. First Attempt to Synthesize Fused Nanohoops **93**

However, the subsequent Suzuki-Miyaura cross-coupling reaction between two molecules of **97** did not produce the desired dimer **93** (Scheme 2.10), as we did not observe any upfield-shifted signals around 6.4-6.8 ppm.

Then we switched to another strategy, with a stepwise synthetic sequence for **93** by constructing one ring first followed by an intramolecular ring formation for the second ring. It is

well known aryltrimethylsilanes can act as masked aryl halides,^{27,28} and they do not interfere with the nickel-mediated homocoupling reaction. So we started with the synthesis of the trimethylsilyl (TMS)-protected diene **101** (Scheme 2.11).

Scheme 2.11. Synthesis of TMS-Protected Diene 101

We tried two routes to make TMS-protected diene **101**. The first route made use of the palladium catalyzed homocoupling reaction of vinylic stannane **100** assisted by copper,²⁹ which was prepared from 2,2'-azobis(2-methylpropionitrile) (AIBN)-mediated alkyne hydrostannylation under air with alkyne **99**.³⁰ The terminal alkyne **99** was prepared from monolithiation of 1,4-dibromobenzene, silylation with TMSCl, Sonogashira coupling with (trimethylsilyl)ethyne, and desilylation of the terminal acetylenic silane. However vinylic stannane **100** was not stable on a silica gel column and was easily hydrolyzed.

We then tried another route starting with hydroboration of terminal alkyne **99**, followed by base-induced iodination afforded alkenyl iodide **103**,³¹ which underwent the Ni(cod)₂-mediated homocoupling reaction to produce the desired TMS-protected diene **101**.

With TMS-protected diene **101** in hand, we performed the Diels–Alder reaction between quinone dibromide **89** and diene **101** using AlCl_3 as the catalyst instead of $\text{BF}_3 \cdot \text{OEt}_2$ to avoid any desilylation induced by fluoride, followed by methylation. This one-pot sequence successfully provided the desired *syn*-TMS-protected dibromide **104** in 55% yield (Scheme 2.12). The $\text{Ni}(\text{cod})_2$ -mediated homocoupling reaction of **104** at low concentration produced cyclic dimers *syn*-**105** in 30% yield and *anti*-**106** in 30% yield. Both **105** and **106** were treated with ICl to form the corresponding iodides, which were treated with $\text{Ni}(\text{cod})_2$ for homocoupling reactions at low concentration. As can be expected only **105** produced **93** in 8% yield from **104**. The ^1H NMR spectrum of **93** from this procedure matches exactly with that of **93** obtained from tetrabromide **90**. This stepwise synthetic sequence further confirmed the structure of **93** apart from its X-ray structure.

2.4. Structural elucidation of nanotube-like trimer **95a**

The structure of **95a** was further elucidated by a similar stepwise synthetic pathway developed for structural clarification of **93**. We designed two ways for preparing the key intermediates, *syn*- and *anti*-macrocyclic trimers **110** and **111**. The first step of the stepwise pathway involved selective Suzuki–Miyaura cross-coupling reactions between TMS-protected diboronic ester **107** and TMS-protected monochloroiodide **108** to produce **109**, followed by the intramolecular $\text{Ni}(\text{cod})_2$ -mediated homocoupling reaction of **109** to form *syn*-trimer **110** and *anti*-trimer **111** (Scheme 2.13).

Scheme 2.12. Elucidation of Structure of Fused Nano hoops 93

Compound **107** was prepared by borylation of **104** and compound **108** was made by a procedure similar to that of **104** but by starting from 1-(4-chlorophenyl)-4-(4-iodophenyl)-1,3-butadiene.

Later we developed a concise pathway to *syn*- and *anti*- macrocyclic trimers **110** and **111** from a shotgun approach (Scheme 2.14). At a 50 mM concentration, TMS-protected dibromide **104** also underwent the $\text{Ni}(\text{cod})_2$ -mediated homocoupling reactions to produce trimers **110** and **111** (*syn*-trimer **110**:*anti*-trimer **111** = 1:3). Trimer **110** was treated with ICl to produce the

Scheme 2.13. Stepwise Synthesis of Trimers 110 and 111 and Subsequent Transformations

Scheme 2.14. Shotgun Synthesis of Trimer 110 and 111 and Subsequent Transformations

corresponding hexaiodide, which on exposure to Ni(cod)_2 in the presence of bipy produce trimer **95a**, because the crude ^1H NMR spectrum had identical peaks as in that of **95a** obtained in Scheme 2.9.

However attempts to perform oxidative aromatization of **95a** with DDQ at temperatures ranging from ambient temperature to 70°C failed to produce the fully aromatized product. But we do observe partial removal of the allylic hydrogens in **95a** initially. Forcing the reaction to go to completion resulted in decomposition.

2.5. Ongoing project

As larger rings should have less ring strain, we began to develop a synthetic pathway for the functionalized [10]CPP and the corresponding fused two-nanohoop system by using the pathway developed for stepwise synthesis of **93**. Compared to the synthesis of functionalized [9]CPP, the functionalized [10]CPP can be prepared from aromatization of the dimer of the L-shaped building block **113** with an extended biphenyl system prepared from dibromide **55** (Scheme 2.15). The synthesis started with borylation of the L-shaped building block *syn*-dibromide **55** with the Pd₂(dba)₃/X-Phos catalyst to produce **112** in excellent yield. However, the next step for the extension of one benzene ring with normal procedures,^{21,26} afforded the desired product either in low yield or a mixture that was hard to isolate the desired product. After extensive screening, we were able to prepare the one phenyl ring extended L-shaped building block **113** in 76% yield with the Pd(PPh₃)₄/Ag₂CO₃ in refluxing tetrahydrofuran (THF) for a longer time.³² The same Ni(cod)₂-mediated homocoupling reactions of **113** in dilute condition yielded the desired dimer **114** in 10% yield. We did not know the exact stereochemistry of the isolated dimer at this stage. However, based on the observation during the silica gel column purification of *syn*-**56a** and *anti*-**56b**, the *syn*-isomer was eluted first from the column, and so we suspect that the obtained sample is the *syn*-isomer depicted in **114**. It was very surprising to observe that the attempted aromatization by DDQ at 70 °C did not deliver any of the desired

product **115**. Only **114** was recovered. However, upon increasing the reaction temperature to 150 °C, the fully aromatized **115** having a functionalized [10]CPP structure was obtained in 65% yield.

Scheme 2.15. Synthesis of Functionalized [10]CPP

With the model study of the functionalized [10]CPP **115** being accomplished, we targeted our next goal to the preparation of fused nano hoops containing two units of the [10]CPP precursor. First we tried the shotgun approach used previously for the synthesis of fused two layer nano hoops **93**. Using the same sequences, including borylation and one phenyl ring extension, compound **117** was prepared in 42% yield in two steps from tetrabromide **90** (Scheme 2.16). However, we did not observe any dimer products upon the $Ni(cod)_2$ -mediated homocoupling reactions.

Scheme 2.16. Attempted Shotgun Synthesis of Fused [10]CPP Precursors

Then we turned to the stepwise sequence to try to construct a molecule containing two fused [10]CPP precursors (Scheme 2.17). As the solubility of the desired benzene extended dibromide diene is very poor, we proceeded with one benzene extended TMS-protected diene **118** by the Suzuki-Miyaura cross-couplings between **96** and **98**. The AlCl_3 -catalyzed Diels–Alder reaction between **118** and quinone dibromide **89**, afforded, after methylation, **119** in 60% yield. Borylation, followed by one-benzene extension produced the TMS-protected dibromide **120** in 54% yield. The $\text{Ni}(\text{cod})_2$ -mediated homocoupling reactions of **120** under dilute concentration formed the expected *syn*-dimer **121** in 15% yield and *anti*-dimer **122** in 15% yield. Iodination followed by the $\text{Ni}(\text{cod})_2$ -mediated homocoupling with a small amount of *syn*-dimer **121** provided very encouraging results. We observed a set of doublets ^1H NMR signals in the upfield-shifted region around 6.4–6.8 ppm, suggesting that intramolecular homocoupling

Scheme 2.17. Stepwise Synthesis toward Fused [10]CPP Precursors

occurred to form a molecule that contained two units of the [10]CPP precursor. Unfortunately, we need more materials to finish the project for the subsequent oxidative aromatization. Nevertheless, this effort provides the foundation for the construction of a structure containing two fused and fully aromatized [10]CPP units.

2.6. Summary

We have developed pathways for preparing fused two-layer [6] and [9]CPP precursors in a nanotube-like arrangement either via shotgun synthesis or via stepwise synthesis. The shotgun synthesis involved Ni(cod)₂-mediated homocoupling reaction of all *syn*-tetrabromide building blocks. The stepwise pathway, in which the rings were constructed consecutively, not only confirmed the structures of the isomers from shotgun synthesis, but also improved the overall yield of **93** containing two [6]CPP precursors and it provides possibilities of preparing two-layer CPP precursors with different sizes. These nanotube-like structures may serve as potential templates for the controlled growth of armchair type single-wall carbon nanotubes.

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Chapter 3. Experiment Section

General Experimental Methods

All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) was distilled from benzophenone ketyl prior to use. Commercial available chemicals were of reagent grade and were used as received without further purification. Purification by column chromatography was performed using 32-65 μm silica gel. Melting points were uncorrected. High resolution mass spectra were obtained on a hybrid linear ion trap Fourier transform mass spectrometer system equipped with an ion source. The UV-vis absorption spectrum was recorded on a Shimadzu UV-1800 spectrophotometer with a 1-nm resolution, and the baseline was corrected with a solvent filled square quartz cell. The fluorescence spectrum was recorded on a Shimadzu Rf-5301PC spectrofluorophotometer with a 2-nm resolution. (*E,E*)-1,4-Bis(4-bromophenyl)-1,3-butadiene (**48**) was prepared according to the reported procedure.^{S1}

Experimental Procedure for 2,5-Dimethoxyphenol 51. To an ice-cold solution of 19.7 g of 70% *m*-chloroperbenzoic acid in 100 mL of dichloromethane was added dropwise a solution of 10.2 g of 2,5-dimethoxybenzaldehyde (61.4 mmol) in 50 mL of dichloromethane. After the addition was finished, the ice bath was removed and the reaction mixture was stirred for 4 h at room temperature. Then the reaction mixture was washed consecutively with aqueous saturated sodium bicarbonate (3 × 30 mL) and 100 mL of 10% sodium thiosulfate. The organic layer was concentrated and dissolved in methanol, and stirred with excess 10% aqueous sodium hydroxide for 30 min. The reaction mixture was acidified to pH 1 with 3N HCl solution and extracted with ethyl acetate (3 × 60 mL). The organic layers were collected, dried and concentrated via high vacuo to give 7.80 g of **51** (82%) as yellow liquid: ¹H NMR (CDCl₃, 400 MHz) δ 6.74 (1 H, d, *J* = 8.4 Hz), 6.63 (1 H, d, *J* = 3.2 Hz), 6.42 (1 H, br), 6.39 (1 H, dd, *J* = 8.8, 3.2 Hz), 3.75 (3 H, s), 3.72 (3 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 154.1, 146.2, 140.9, 111.4, 103.8, 101.7, 56.0, 55.0.

Experimental Procedure for Silane 52. To the mixture of 1.90 ml of hexamethyldisilazane (9.06 mmol) and 4.82g of LiClO₄ (4.53 mmol) was added 1.37 g of **51** (8.88 mmol) and the reaction mixture was stirred at room temperature for 4 h under an inert atmosphere. Then the reaction mixture was diluted with dichloromethane, filtered and concentrated under high vacuum to yield 1.88 g of **52** (8.30 mmol, 93%) as yellow liquid: ¹H NMR (CDCl₃, 400 MHz) δ 6.76 (1 H, d, *J* = 8.8 Hz), 6.50 (1 H, d, *J* = 3.2 Hz), 6.44 (1 H, dd, *J* = 9.2, 3.2 Hz), 3.74 (3 H, s), 3.70 (3 H, s), 0.27 (9 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 153.9, 145.1, 145.0, 112.7, 108.0, 105.4, 55.8, 55.1, 0.04.

Experimental Procedure for Silane 53. To the solution of 1.88 g of **52** (8.30mmol) in 30 mL THF at -78 °C was added 5.4 mL of 2M LDA (10.8 mmol) solution dropwise. After the reaction

mixture was kept at $-78\text{ }^{\circ}\text{C}$ for 2 h, 1.6 mL of trimethylsilyl chloride (12.5 mmol) was added dropwise at this temperature. Then the reaction mixture was allowed to warm to room temperature for overnight. Water was added and extracted with diethyl ether. The organic layers was collected, dried and concentrated. The residue was purified by a short silica gel column chromatography to give 2.35 g of **53** (7.87 mmol, 94%) as yellow liquid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.01 (1 H, d, $J = 8.8$ Hz), 6.62 (1 H, d, $J = 8.4$ Hz), 3.97 (3 H, s), 3.94 (3 H, s), 0.68 (9 H, s), 0.61 (9 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.6, 150.0, 143.6, 118.0, 112.3, 102.4, 55.0, 54.5, 1.68, 1.55.

Experimental Procedure for Triflate 54. To the solution of 2.35g of **53** (7.87 mmol) in 50 mL of diethyl ether at $0\text{ }^{\circ}\text{C}$ was added 5.90 mL of 1.6M *n*-BuLi (9.44 mmol) in hexanes dropwise. The reaction mixture was stirred at $0\text{ }^{\circ}\text{C}$ for 30 min, then 2.7 mL of triflate anhydride (15.8 mmol) was added to the reaction mixture. After it was allowed to warm to room temperature for two more hours, it was quenched with NaHCO_3 solution (50 mL) and extracted with diethyl ether (3×40 mL). The combined organic layers were dried, concentrated and purified by silica gel column chromatography to afford 2.44 g of **54** (6.81mmol, 86%) as yellow liquid: ^1H NMR (CDCl_3 , 400 MHz) δ 6.96 (1 H, d, $J = 9.2$ Hz), 6.78 (1 H, d, $J = 9.2$ Hz), 3.80 (3 H, s), 3.77 (3 H, s), 0.38 (9 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.1, 145.1, 142.6, 123.7, 120.5, 117.3, 114.1, 110.0, 55.9, 55.7, 0.66.

Experimental Procedure for CPP Precursor Dibromides 55. To a mixture of 1.000 g of diene **48** (2.75 mmol) and 0.360 g of 1,4-benzoquinone (3.33 mmol) in 150 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 0.61 mL of boron trifluoride diethyl etherate (4.94 mmol). The reaction mixture was stirred at room temperature for 20 h. Distilled water (20 mL) was added slowly, and the organic layer was separated. The

aqueous layer was back extracted with 40 mL of dichloromethane. The combined organic layers were dried over sodium sulfate and concentrated to afford a brown/yellow solid. The crude solid was used without further purification.

To the brown/yellow solid and 5.315 g of potassium carbonate (38.5 mmol) in 200 mL of anhydrous acetone under a nitrogen atmosphere was added 2.6 mL of dimethyl sulfate (27.5 mmol) by using a syringe, and the reaction mixture was heated under reflux for 18 h. Distilled water (40 mL) was added and the reaction mixture was extracted with ethyl acetate (3 × 40 mL) and then dichloromethane (40 mL). The combined organic layers were dried over sodium sulfate and concentrated. The solid residue was purified by flash column chromatography (silica gel/ethyl acetate:hexanes = 1:5) to produce 1.248 g of **55** (2.49 mmol, 91% yield) as a white solid: mp 203–204 °C; IR 1483, 1257, 811 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 7.33 (4 H, d, *J* = 7.8 Hz), 7.05 (4 H, d, *J* = 8.4 Hz), 6.73 (2 H, s), 5.95 (2 H, d, *J* = 3.0 Hz), 4.83 (2 H, d, *J* = 3.0 Hz), 3.61 (6 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 151.2, 143.7, 131.0, 129.9, 127.7, 127.0, 119.5, 109.2, 55.7, 40.6; HRMS (ESI) calcd for C₂₄H₂₀Br₂O₂ (M⁺) 497.9825, 499.9804, 501.9784, found 497.9818, 499.9798, 501.9777. Recrystallization of **55** from chloroform/hexanes produced a single crystal suitable for X-ray structure analysis.

Experimental Procedure for Cyclic Dimers *syn*-56a and *anti*-56b and Cyclic Trimers *syn*-64a and *anti*-64b. To a 500 mL-flask were added 0.650 g of **55** (1.30 mmol) and 0.490 g of 2,2'-bipyridyl (3.14 mmol). The flask was flushed with nitrogen and placed in a glovebox under a nitrogen atmosphere before 0.870 g of Ni(cod)₂ (3.16 mmol) was added. The flask was fitted with a condenser, rubber septa, and then removed from the glovebox before 260 mL of THF was introduced via cannula. The reaction mixture was heated at reflux for 48 h before it was allowed to cool to room temperature. Then the reaction mixture was passed through a short pad of silica

gel and eluted with ethyl acetate (200 mL) and dichloromethane (200 mL). The combined eluents were concentrated, and the residue was purified by flash column chromatography (silica gel/ dichloromethane:hexanes = 1:5 to 1:1) to produce 0.091 g of *syn-56a* (0.134 mmol, 21% yield) as a white solid, 0.025 g of *anti-56b* (0.037 mmol, 6% yield) as a white solid, and 0.050 g of a mixture of *syn-64a* and *anti-64b* (0.049 mmol, 11% combined yield, *syn-64a:anti-64b* = 1:3) as a white solid. A small fraction of the mixture of *syn-64a* and *anti-64b* was further purified by preparative TLC to afford pure samples of *syn-64a* and *anti-64b* for structural elucidation. At 50 mM concentration of **55**, the cyclic dimers *syn-56a* and *anti-56b* were isolated in 8% combined yield (*syn-56a:anti-56b* = 3:1), and the cyclic trimers *syn-64a* and *anti-64b* were isolated in 18% combined yield (*syn-64a:anti-64b* = 1:3). *syn-56a*: mp > 310 °C; IR 1483, 1253 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 6.90 (4 H, s), 6.78 (4 H, dd, *J* = 4.4, 2.4 Hz), 6.67 (8 H, d, *J* = 8.4 Hz), 6.60 (8 H, d, *J* = 7.6 Hz), 5.17 (4 H, m), 3.84 (12 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 150.9, 140.2, 138.4, 133.3, 131.4, 127.4, 125.9, 108.5, 55.9, 37.3; HRMS (ESI) calcd for C₄₈H₄₀O₄ (M⁺) 680.2921, found 680.2923. Recrystallization of *syn-56a* from dichloromethane/hexanes produced a single crystal suitable for X-ray structure analysis. *anti-56b*: IR 1488, 1260 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 6.91 (4 H, s), 6.77 (4 H, dd, *J* = 4.4, 2.6 Hz), 6.67 (8 H, d, *J* = 8.5 Hz), 6.60 (8 H, d, *J* = 7.9 Hz), 5.17 (4 H, m), 3.85 (12 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 151.0, 140.3, 138.4, 133.2, 131.4, 127.4, 125.9, 108.6, 55.9, 37.3; HRMS (ESI) calcd for C₄₈H₄₀O₄ (M⁺) 680.2921, found 680.2926. *syn-64a*: IR 1476, 1256 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 7.50 (12 H, d, *J* = 8.5 Hz), 7.29 (12 H, d, *J* = 8.4 Hz), 6.73 (6 H, s), 5.97 (6 H, d, *J* = 3.1 Hz), 4.91 (6 H, d, *J* = 2.9 Hz), 3.60 (18 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 151.5, 143.7, 137.9, 128.5, 127.7, 127.6, 126.2, 109.1, 55.8, 40.9; HRMS (ESI) calcd for C₇₂H₆₀O₆ (M⁺) 1020.4384, found 1020.4356. *anti-64b*: IR 1477, 1255 cm⁻¹; ¹H NMR (CDCl₃,

600 MHz) δ 7.54 (4 H, d, J = 8.4 Hz), 7.430 (4 H, d, J = 8.4 Hz), 7.426 (4 H, d, J = 8.4 Hz), 7.34 (4 H, d, J = 7.8 Hz), 7.27 (4 H, d, J = 8.4 Hz), 7.25 (4 H, d, J = 8.4 Hz), 6.76 (2 H, d, J = 8.9 Hz), 6.74 (2 H, s), 6.73 (2 H, d, J = 8.9 Hz), 6.10 (2 H, ddd, J = 9.8, 4.8, 1.0 Hz), 6.00 (2 H, d, J = 3.0 Hz), 5.96 (2 H, ddd, J = 9.8, 4.7, 1.2 Hz), 4.95 (2 H, t, J = 4.5 Hz), 4.933 (2 H, d, J = 3.0 Hz), 4.928 (2 H, t, J = 4.5 Hz), 3.72 (6 H, s), 3.63 (6 H, s), 3.57 (6 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 151.47, 151.45, 151.43, 143.8, 143.4, 143.0, 138.7, 138.6, 137.5, 129.0, 128.43, 128.34, 128.2, 128.1, 127.8, 127.58, 127.56, 127.0, 126.6, 126.5, 126.1, 109.1, 108.9, 55.81, 55.75, 40.86, 40.83, 40.77; HRMS (ESI) calcd for $\text{C}_{72}\text{H}_{60}\text{O}_6$ (M^+) 1020.4384, found 1020.4379.

Experimental Procedure for Quinone 63. To a 100-mL flask were added 600 mg silica gel and a solution of 275 mg of ceric ammonium nitrate (5.07 mmol) in 5 mL H_2O was added dropwise while stirring. After 5 min, 20 mL of dichloromethane was added to the mixture. Then a solution of 56 mg of *syn*-**56a** (0.082 mmol) in 15 mL of dichloromethane was added to the reaction mixture. 15 min later the whole reaction mixture was filtered and washed with 100 mL of dichloromethane. The combined solvents were concentrated and the residue was purified by silica gel column chromatography (hexanes:dichloromethane:diethyl ether = 10:3:3) to give 45 mg of **63** (0.072 mmol, 88%) as orange solid: ^1H NMR (CDCl_3 , 400 MHz) δ 6.95 (4 H, s), 6.71 (4 H, m), 6.70 (8 H, d, J = 8.4 Hz), 6.57 (8 H, d, J = 7.2 Hz), 5.02 (4 H, m); ^{13}C NMR (CDCl_3 , 150 MHz) δ 187.0, 146.0, 138.9, 137.8, 136.3, 131.9, 127.2, 126.4, 36.9.

Experimental Procedure for the Functionalized [9]CPP 65. To a 200-mL flask were added 0.076 g (0.074 mmol) of a mixture of **64a** and **64b** and 0.255 g (1.12 mmol) of DDQ. The flask was flushed with nitrogen at 0 °C and then 30 mL of chlorobenzene was introduced by using a syringe. The reaction mixture was heated to 70 °C. After 2 h at 70 °C, the reaction mixture was allowed to cool to room temperature, diluted with 100 mL of dichloromethane and immediately

passed through a basic aluminum oxide column (4 cm high, 2.5 cm in diameter). The column was eluted with an additional 300 mL of dichloromethane. The combined eluents were concentrated in vacuo immediately to afford **65** (0.066 g, 0.065 mmol, 88% yield) as a yellow solid: IR 1459, 1255 cm^{-1} ; ^1H NMR (CDCl_3 , 600 MHz) δ 7.45 (12 H, d, $J = 8.7$ Hz), 7.24 (12 H, d, $J = 8.7$ Hz), 6.99 (6 H, s), 6.97 (6 H, s), 3.81 (18 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 150.8, 142.9, 137.4, 135.8, 132.5, 127.5, 126.0, 124.6, 107.1, 56.0; HRMS (ESI) calcd for $\text{C}_{72}\text{H}_{54}\text{O}_6$ (M^+) 1014.3915, found 1014.3940.

Experimental Procedure for DA Adduct 86. To a mixture of 45 mg of diene **48** (0.12 mmol) and 22 mg of quinone **63** (0.035 mmol) in 10 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 0.10 mL of boron trifluoride diethyl etherate (0.8 mmol). The reaction mixture was stirred at room temperature for 20 h. Distilled water (20 mL) was added slowly, and the organic layer was separated. The aqueous layer was back extracted with 40 mL of dichloromethane. The combined organic layers were dried and concentrated. The residue was purified by silica gel column chromatography (hexanes:dichloromethane:diethyl ether = 10:2:2) to give 36 mg of **86** (0.027 mmol, 75%) as white solid: ^1H NMR (CDCl_3 , 600 MHz) δ 7.37 (8 H, d, $J = 7.8$ Hz), 7.11 (8 H, d, $J = 7.2$ Hz), 6.55 (8 H, d, $J = 8.4$ Hz), 6.28 (12 H, m), 6.18 (4 H, m), 4.45 (4 H, m), 4.00 (4 H, d, $J = 6.0$ Hz), 3.96 (4 H, d, $J = 6.0$ Hz); ^{13}C NMR (CDCl_3 , 150 MHz) δ 138.9, 138.7, 137.8, 131.2, 130.7, 130.5, 128.7, 126.8, 126.3, 121.3, 41.4, 36.9, 29.7.

Experimental Procedure for Tetrahydride 87. To 23 mg of potassium carbonate (0.17 mmol) and 36 mg of **86** (0.027) in 20 mL of anhydrous acetone under a nitrogen atmosphere was added 0.012 mL of dimethyl sulfate (0.13 mmol) by using a syringe, and the reaction mixture was heated under reflux for 18 h. Distilled water (40 mL) was added and the reaction mixture was

extracted with dichloromethane (3 × 40 mL). The combined organic layers were dried over sodium sulfate and concentrated. The solid residue was purified by flash column chromatography (silica gel/ dichloromethane:hexanes = 1:4) to produce 4 mg of **87** (0.003 mmol, 10% yield) as a white solid: ¹H NMR (CDCl₃, 600 MHz) δ 7.39 (8 H, d, *J* = 8.4 Hz), 7.17 (8 H, d, *J* = 8.4 Hz), 6.80 (4 H, m), 6.64 (8 H, d, *J* = 8.4 Hz), 6.60 (8 H, d, *J* = 7.8 Hz), 6.01 (4 H, d, *J* = 3.0 Hz), 5.05 (8 H, m), 3.26 (12 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 152.3, 144.1, 139.9, 138.6, 134.9, 133.2, 131.5, 130.2, 130.0, 127.8, 126.1, 120.1, 61.5, 41.6, 38.3.

Experimental Procedure for Dibromide 89. To a mixture of 3.64 g of diene **48** (10.0 mmol) and 1.30 g of 1,4-benzoquinone (12.0 mmol) in 200 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 1.00 mL of boron trifluoride diethyl etherate (8.10 mmol). The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was then passed through a short silica gel column, washed with dichloromethane, and concentrated to afford a brown/yellow solid. The crude solid was used without further purification.

To the brown/yellow solid and 2.78 g of silver oxide (12.0 mmol) under a nitrogen atmosphere was added 100 mL of anhydrous diethyl ether. The reaction mixture was stirred overnight and passed through a short silica gel column, washed with diethyl ether, and concentrated. The residue was recrystallized from diethyl ether to afford 3.76 g of **89** (8.0 mmol, 80% yield) as a brown solid. ¹H NMR (CDCl₃, 600 MHz) δ 7.43 (4 H, d, *J* = 8.4 Hz), 7.15 (4 H, d, *J* = 8.4 Hz), 6.60 (2 H, s), 5.91 (2 H, d, *J* = 2.7 Hz), 4.72 (2 H, d, *J* = 2.7 Hz); ¹³C NMR (CDCl₃, 150 MHz) δ 186.0, 141.6, 140.2, 136.4, 131.8, 130.2, 126.5, 121.0, 40.0; HRMS (ESI) calcd for C₂₂H₁₄Br₂O₂ (M⁺) 467.9355, found 467.9342.

Experimental Procedure for Tetrabromides *syn*-90 and *anti*-91. To a mixture of 3.64 g of diene **48** (10.0 mmol) and 4.70 g of dibromoquinone **89** (10.0 mmol) in 200 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 1.00 mL of boron trifluoride diethyl etherate (8.10 mmol). The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was passed through a short silica gel column, washed with dichloromethane, and concentrated to afford a yellow solid. The crude solid was used without further purification. To the yellow solid and 5.52 g of potassium carbonate in dry acetone (200 mL) was added 2.40 mL of dimethyl sulfate (25.4 mmol) via a syringe, and the reaction mixture was heated at reflux for 3 h. The reaction mixture was then allowed to cool to rt and concentrated. Distilled water (100 mL) was added, and the reaction mixture was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over sodium sulfate and concentrated. Recrystallization of the crude solid from chloroform produced 5.86 g of the methylated tetrabromide *syn*-**90** (6.80 mmol, 68% yield) as a white solid and *anti*-**91** (NMR yield 8.5%) as white solid. *syn*-**90**: mp: 174–176 °C; IR 1703, 1668, 1484, 817 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 7.22 (8 H, d, *J* = 8.4 Hz), 6.81 (8 H, d, *J* = 8.4 Hz), 6.09 (4 H, d, *J* = 2.8 Hz), 4.81 (4 H, d, *J* = 3.2 Hz), 3.53 (6 H, s); ¹³C NMR (CDCl₃, 150 MHz) δ 152.1, 142.6, 131.2, 129.2, 128.1, 119.9, 60.4, 40.4; HRMS (ESI) calcd for C₄₀H₃₀Br₄O₂ (M⁺) 859.8953, 861.8933, 863.8912, found 859.8940, 861.8930, 863.8901. *anti*-**91**: ¹H NMR (CDCl₃, 400 MHz) δ 7.36 (8 H, d, *J* = 8.8 Hz), 7.06 (8 H, d, *J* = 8.8 Hz), 5.86 (4 H, d, *J* = 2.8 Hz), 4.82 (4 H, d, *J* = 2.8 Hz), 2.97 (6 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 152.7, 143.6, 131.5, 131.0, 129.6, 127.3, 120.1, 60.2, 41.0.

Experimental Procedure for Tetraiododie 92. To 1.01 g of Tetrabromide *syn*-**90** (1.17 mmol) in 50 mL dry THF at -78 °C was added dropwise 3.2 mL of a 1.6 M solution of *n*-butyllithium (5.12

mmol) in hexanes. After 2 h at $-78\text{ }^{\circ}\text{C}$, a solution of 1.48 g of iodine (5.83 mmol) in 50 mL of THF was added dropwise. Then the reaction mixture was stirred at room temperature overnight. Distilled water (100 mL) was added, and the reaction mixture was extracted with diethyl ether ($3 \times 50\text{ mL}$) and dichloromethane (100 mL). The combined organic layers were dried over magnesium sulfate and concentrated. The crude residue was purified by flash column chromatography (silica gel/ dichloromethane:hexanes = 1:4) to produce 0.86 g of **92** (0.82 mmol, 70%). Recrystallization of the residue from dichloromethane/hexanes produced a single crystal of **92** suitable for X-ray structure analysis: ^1H NMR (CDCl_3 , 400 MHz) δ 7.42 (8 H, d, J = 8.8 Hz), 6.67 (8 H, d, J = 8.4 Hz), 6.06 (4 H, d, J = 3.6 Hz), 4.77 (4 H, d, J = 2.8 Hz); ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.1, 143.3, 137.1, 131.0, 129.5, 128.0, 91.4, 60.4, 40.5.

Experimental Procedure for Fused Nanostructures Dimers 93 and 94 and Trimers 95a, 95b and 95c. To an oven-dried 2 L-flask was added 1.26 g of tetrabromide *syn*-**90** (1.46 mmol) and 1.00 g of 2,2'-bipyridyl (6.42 mmol). Then the flask was flushed with nitrogen and moved into a glove box, where 1.64 g of bis(1,5-cyclooctadiene)nickel(0) (6.42 mmol) was added. The flask was fitted with a condenser, rubber septa, and then removed from the glove box before 1500 mL of THF was transferred via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 h. After the reaction mixture was allowed to cool to room temperature, it was passed through a short silica gel column and eluted with dichloromethane. The combined eluents were concentrated, and the residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:5 to 2:1) to produce 0.039 g of **93** (0.036 mmol, 5% yield) as a white solid, and 0.008 g of **94** (0.007 mmol, 1% yield) as a white solid. At 50 mM concentration, 1.96 g of tetrabromide *syn*-**90** produced 6 mg of **95a** (0.004 mmol, 0.5% yield) as a white solid, 12 mg of **95b** (0.007 mmol, 1% yield) as a white solid, and 14 mg of **95c** (0.009 mmol, 1%

yield) as a white solid were isolated. **93**: ^1H NMR (CDCl_3 , 400 MHz) δ 6.94 (8 H, m), 6.68 (16 H, d, $J = 8.0$ Hz), 6.54 (16 H, d, $J = 8.0$ Hz), 5.17 (8 H, m), 3.83 (12 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.4, 139.8, 139.7, 134.0, 132.1, 127.7, 126.8, 62.0, 38.3; HRMS (ESI) calcd for $\text{C}_{80}\text{H}_{60}\text{O}_4$ (M^+) 1084.4486, found 1084.4509. Recrystallization of **93** from dichloromethane/hexanes produced a single crystal suitable for X-ray structure analysis. **94**: ^1H NMR (CDCl_3 , 400 MHz) δ 6.71 (8 H, m), 6.50 (16 H, d, $J = 8.4$ Hz), 6.44 (16 H, d, $J = 8.4$ Hz), 5.09 (8 H, m), 3.86 (12 H, s); HRMS (ESI) calcd for $\text{C}_{80}\text{H}_{60}\text{O}_4$ (M^+) 1084.4486, found 1084.4494. **95a**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.24 (12 H, d, $J = 8.0$ Hz), 6.92 (12 H, d, $J = 8.0$ Hz), 6.11 (12 H, d, $J = 2.4$ Hz), 4.79 (12 H, d, $J = 2.4$ Hz), 3.71 (18 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.7, 142.8, 138.3, 130.7, 127.8, 127.4, 126.5, 60.2, 40.5; HRMS (ESI) calcd for $\text{C}_{120}\text{H}_{91}\text{O}_6$ (MH^+) 1627.6810, found 1627.6895. **95b**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.33 (8 H, d, $J = 8.0$ Hz), 7.14 (8 H, d, $J = 8.4$ Hz), 7.05 (8 H, d, $J = 8.4$ Hz), 6.91 (8 H, d, $J = 8.0$ Hz), 6.88 (8 H, d, $J = 8.4$ Hz), 6.87 (8 H, d, $J = 8.0$ Hz), 6.84 (4 H, m), 6.05 (8 H, t, $J = 3.2$ Hz), 5.24 (4 H, m), 4.73 (8 H, t, $J = 2.4$ Hz), 3.75 (12 H, s), 3.61 (6 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.9, 152.8, 151.3, 143.2, 142.8, 140.6, 138.0, 137.8, 137.5, 133.9, 132.9, 130.8, 129.9, 127.8, 127.7, 127.6, 127.5, 126.4, 126.3, 126.2, 125.8, 61.8, 60.6, 59.7, 40.8, 40.6, 38.8; HRMS (ESI) calcd for $\text{C}_{120}\text{H}_{91}\text{O}_6$ (MH^+) 1627.6810; found 1627.6744. **95c**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.20 (8 H, d, $J = 8.4$ Hz), 7.09 (8 H, d, $J = 8.4$ Hz), 6.91 (8 H, d, $J = 7.2$ Hz), 6.89 (8 H, d, $J = 8.4$ Hz), 6.88 (8 H, d, $J = 8.4$ Hz), 6.83 (16 H, m), 5.98 (4 H, d, $J = 2.4$ Hz), 5.25 (4 H, m), 5.23 (4 H, m), 4.68 (4 H, d, $J = 2.4$ Hz), 3.73 (12 H, s), 3.66 (6 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.9, 151.6, 143.4, 140.6, 140.4, 138.6, 137.7, 137.4, 134.2, 133.8, 133.0, 130.4, 127.70, 127.65, 127.58, 127.23, 126.8, 126.2, 126.1, 125.6, 61.9, 60.0, 40.9, 38.8, 38.7; HRMS (ESI) calcd for $\text{C}_{120}\text{H}_{91}\text{O}_6$ (MH^+) 1627.6810 found 1627.6744.

Experimental Procedure for Boronic Ester 96. To a mixture of 3.64 g of diene **48** (10 mmol), 6.09 g of bis(pinacolato)diboron (24mmol), 5.89 g of potassium acetate (60 mmol), 310 mg of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (0.3 mmol) and 238 mg of XPhos (0.5 mmol) under a Argon atmosphere was added 300 mL of anhydrous dioxane. Then the reaction mixture was heated at 80 °C for 12 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a short pad of silica gel, washed with diethyl ether 100 mL. The combined organic solvents were collected and concentrated via high vacuo. The solid was washed with hexanes and to give 4.22 g of boronic ester **96** (9.2 mmol, 92%) as grey solid: ¹H NMR (CDCl₃, 400 MHz) δ 7.79 (4 H, d, *J* = 8.0 Hz), 7.45 (8 H, d, *J* = 8.0 Hz), 7.03 (2 H, m), 6.70 (2 H, m), 1.36 (24 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 139.9, 135.1, 133.3, 130.1, 125.7, 83.7, 24.8.

Experimental Procedure for Diboronic ester 97. To a mixture of 4.58 g of **96** (10.0 mmol) and 4.72 g of dibromoquinone **89** (10.0 mmol) in 200 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 1.00 mL of boron trifluoride diethyl etherate (8.10 mmol). The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was passed through a short silica gel column, washed with dichloromethane, and concentrated to afford a yellow solid. The crude solid was used without further purification. To the yellow solid and 5.52 g of potassium carbonate in dry acetone (200 mL) was added 2.40 mL of dimethyl sulfate (25.4 mmol) via a syringe, and the reaction mixture was heated at reflux for 3 h. The reaction mixture was then allowed to cool to rt and concentrated. Distilled water (100 mL) was added, and the reaction mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over sodium sulfate and concentrated. Recrystallization of the crude solid from ether produced 5.25 g of **97** (5.50 mmol, 55% yield) as yellow solid: ¹H

NMR (CDCl₃, 400 MHz) δ 7.61 (4 H, d, J = 8.0 Hz), 7.18 (4 H, d, J = 8.4 Hz), 7.06 (4 H, d, J = 8.4 Hz), 6.78 (4 H, d, J = 8.4 Hz), 6.12 (2 H, d, J = 3.6 Hz), 6.03 (2 H, d, J = 2.8 Hz), 4.87 (2 H, d, J = 2.8 Hz), 4.82 (2 H, d, J = 2.8 Hz), 3.46 (6 H, s), 1.34 (24 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 152.3, 147.3, 142.5, 134.7, 131.4, 131.1, 131.0, 129.2, 128.4, 127.6, 126.9, 119.7, 83.5, 60.5, 41.5, 40.2, 24.9, 24.8.

Experimental Procedure for Vinyl Iodide 103. To a mixture of 3.48 g of 4-trimethylsilylphenylacetylene (20.0 mmol) and in 20 mL of anhydrous THF under a nitrogen atmosphere was added by using a syringe 24.0 mL of catecholborane. The reaction mixture was stirred for 12 h at 70 °C. Then the reaction mixture was concentrated under high vacuum. Distilled water (20 mL) was added to the solid residue. After the reaction mixture was stirred at 90 °C for 2 h, it was filtered and washed with cold water. Then the solid residue was dissolved in 50 mL of diethyl ether and cooled to 0 °C. 20 mL of 3 M aqueous NaOH solution was added to the mixture, followed by addition of 6.10 g of iodine in 150 mL of diethyl ether. After 2 h, the reaction mixture was added 100 mL of water and extracted with diethyl ether (3 $\times$ 40 mL). The combined organic layers were washed with water, dried over sodium sulfate and concentrated. The residue was purified with silica gel column chromatography (hexanes as eluents) to give 4.23 g of vinyl iodide **103** (14 mmol, 70%) as yellow liquid: ¹H NMR (CDCl₃, 400 MHz) δ 7.64 (2 H, d, J = 8.4 Hz), 7.57 (1 H, d, J = 14.8 Hz), 7.39 (2 H, d, J = 8.0 Hz), 6.99 (1 H, d, J = 14.8 Hz), 0.45 (9 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 144.9, 140.7, 137.8, 133.6, 125.2, 77.2, -1.13.

Experimental Procedure for TMS-Protected Diene 101. To a 500 mL-flask were added 4.23 g of **103** (14.0 mmol) and 2.94 g of 2,2'-bipyridyl (16.8 mmol). The flask was flushed with nitrogen and placed in a glovebox under a nitrogen atmosphere before 4.62 g of Ni(cod)₂ (16.8 mmol) was added. The flask was fitted with a condenser, rubber septa, and then removed from

the glovebox before 150 mL of THF was introduced via cannula. The reaction mixture was heated at reflux for 48 h before it was allowed to cool to room temperature. Then the reaction mixture was passed through a short pad of silica gel and eluted with dichloromethane (200 mL). The combined eluents were concentrated, and the residue was purified by flash column chromatography (silica gel/hexanes), and then recrystallized with hexanes to produce 2.10 g of **101** (6.0 mmol, 85% yield) as a white solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.51 (4 H, d, J = 8.0 Hz), 7.43 (8 H, d, J = 8.0 Hz), 7.00 (2 H, m), 6.69 (2 H, m), 0.29 (18 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.0, 137.7, 133.7, 132.9, 129.5, 125.7, -1.1.

Experimental Procedure for Dibromide 104. To a mixture of 3.50 g of diene **101** (10.0 mmol), 4.70 g of dibromoquinone **89** (10.0 mmol) and 0.34 g of anhydrous AlCl_3 (2.5 mmol), 200 mL of anhydrous dichloromethane was added in glove box. The reaction mixture was stirred at room temperature for 20 h. The whole mixture was passed through a short pad of silica gel, washed with dichloromethane and concentrated to afford a yellow solid. The crude solid was used without further purification. To the yellow solid and 5.52 g of potassium carbonate (40 mmol) in 200 mL of dry acetone was added 2.4 mL of dimethyl sulfate (25.4 mmol) via a syringe, and the reaction mixture was heated under reflux for 3 h. After that the reaction mixture was allowed to cool to room temperature and concentrated. Then distilled water (100 mL) was added and the reaction mixture was extracted with dichloromethane (3×100 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified carefully by flash column chromatography (silica gel, dichloromethane:hexanes = 1:4 to 1:2) to produce 4.67 g of **104** (5.5 mmol, 55% yield) as a yellow solid: mp 96.6–97.9 °C; ^1H NMR (CDCl_3 , 600 MHz) δ 7.26 (4 H, d, J = 8.0 Hz), 7.17 (4 H, d, J = 8.8 Hz), 6.95 (4 H, d, J = 8.0 Hz), 6.79 (4 H, d, J = 8.4 Hz), 6.11 (2 H, d, J = 3.6 Hz), 6.02 (2 H, d, J = 3.2 Hz), 4.81 (2 H, d, J = 2.8 Hz), 4.80 (2 H,

d, $J = 2.8$ Hz), 3.54 (6 H, s), 0.23 (18 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.3, 144.6, 142.7, 137.4, 133.1, 131.4, 131.0, 130.6, 129.2, 128.2, 127.7, 119.7, 60.3, 41.2, 40.2;

Experimental Procedure for Stepwise Synthesis of Fused Nanotube-like Dimer 93. To an oven-dried 1000 mL flask was added 0.57 g of Dibromide **104** (0.67 mmol) and 0.25 g of 2,2'-bipyridyl (0.44 mmol). Then the whole flask was flushed with nitrogen and moved into a glove box, where 0.44 g of bis(cyclooctadiene)nickel(0) (1.60 mmol) was added and a water condenser was fitted. Outside of the glove box, 700 mL of THF was transferred under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 hours. After the mixture was allowed to cool to room temperature, the reaction mixture was passed through a short pad of silica gel and flushed with dichloromethane. The combined solvents were concentrated and the residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:6 to 1:3) to produce 0.220 g of **105** mixture contaminated with a few trimers as a white solid, 0.137 g of **106** (0.0074 mmol, 30.0% yield) as a white solid. One third of **105** mixture contaminated with trimers was dissolved in 20 mL of dichloromethane under a nitrogen atmosphere and cooled to -78°C . To the solution at -78°C , 0.2 mL of a solution of 1M ICl in dichloromethane was added dropwise. After 5 min at -78°C , the solution was quenched with a saturated sodium thiosulfate solution and diluted with 30 mL of water. The mixture was extracted with dichloromethane (3×20 mL), dried over sodium sulfate and concentrated. To the crude mixture was added 0.41 g of 2,2'-bipyridyl (0.26 mmol) in a 250 mL-flask. Then the whole flask was flushed with nitrogen and moved into a glove box, where 0.73 g of bis(cyclooctadiene)nickel(0) (0.26 mmol) was added and a water condenser was fitted. The flask was then removed from the glove box and 100 mL of THF was added via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 hours. After the mixture was allowed to cool to

room temperature, the reaction mixture was passed through a short silica gel column and eluted with dichloromethane. The combined eluents were concentrated, and the residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:5) to produce 9 mg of **93** (8.3 % yield from **104**). **106**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.48 (8 H, d, J = 8.0 Hz), 7.32 (8 H, d, J = 8.0 Hz), 6.85 (4 H, m), 6.64 (8 H, d, J = 8.4 Hz), 6.50 (8 H, d, J = 7.6 Hz), 6.00 (4 H, d, J = 2.8 Hz), 5.00 (4H, m), 4.94 (4 H, d, J = 2.4 Hz), 4.80 (2 H, d, J = 2.8 Hz), 3.54 (6 H, s), 0.25 (18 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 151.8, 145.8, 139.9, 138.5, 137.6, 134.2, 133.4, 133.1, 130.6, 127.4, 127.0, 126.0, 60.9, 42.0, 38.2, 0.97; **105**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.47 (8 H, d, J = 8.0 Hz), 7.34 (8 H, d, J = 8.0 Hz), 6.83 (4 H, m), 6.67 (8 H, d, J = 8.8 Hz), 6.54 (8 H, br), 5.97 (4 H, d, J = 2.4 Hz), 5.02 (4H, m), 4.95 (4 H, d, J = 2.0 Hz), 3.46 (6 H, s), 0.25 (18 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.0, 145.9, 140.0, 138.6, 137.6, 134.2, 133.5, 133.3, 130.7, 127.4, 127.0, 126.1, 61.0, 42.1, 38.4, 0.84.

Experimental Procedure for Diboronic ester 107. To a mixture of 2.71 g of dibromide **104** (3.2 mmol), 1.79 g of bis(pinacolato)diboron (7.0 mmol), 1.90 g of potassium acetate (7.0 mmol), 30 mg of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (0.03 mmol) and 46 mg of XPhos (0.09 mmol) under a Argon atmosphere was added 200 mL of anhydrous dioxane. Then the reaction mixture was heated at 80 °C for 12 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a short silica gel column, washed with 100 mL of diethyl ether. The combined organic solvents were collected and concentrated via high vacuo. The solid was washed with hexanes to give 2.72 g of boronic ester **107** (2.9 mmol, 90%) as white solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (4 H, d, J = 8.0 Hz), 7.24 (4 H, d, J = 8.0 Hz), 7.01 (4 H, d, J = 8.0 Hz), 6.96 (4 H, d, J = 8.0 Hz), 6.08 (2 H, d, J = 3.6 Hz), 6.07 (2 H, d, J = 3.6 Hz), 4.86 (2 H, d, J = 2.8 Hz), 4.84 (2 H, d, J = 2.8 Hz),

3.48 (6 H, s), 1.30 (24 H, s), 0.22 (18 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.5, 147.3, 144.5, 137.1, 134.7, 133.1, 131.3, 130.8, 128.0, 127.8, 126.8, 83.4, 60.4, 41.2, 41.1, 24.9, 24.8, -1.0.

Experimental Procedure for Unsymmetrical Quinone. To a mixture of 3.67 g of 1-(4-chlorophenyl)-4-(4-iodophenyl)-1,3-butadiene (10.0 mmol) and 1.30 g of 1,4-benzoquinone (12.0 mmol) in 200 mL of anhydrous dichloromethane under a nitrogen atmosphere was added by using a syringe 1.00 mL of boron trifluoride diethyl etherate (8.10 mmol). The reaction mixture was stirred at room temperature for 20 h. The reaction mixture was then passed through a short silica gel column, washed with dichloromethane, and concentrated to afford a brown/yellow solid. The crude solid was used without further purification.

To the brown/yellow solid and 2.78 g of silver oxide (12.0 mmol) under a nitrogen atmosphere was added 100 mL of anhydrous diethyl ether. The reaction mixture was stirred overnight and passed through a short silica gel column, washed with diethyl ether, and concentrated. The residue was recrystallized from diethyl ether to afford 3.54 g of unsymmetric quinone (7.50 mmol, 75% yield) as a brown solid: ^1H NMR (CDCl_3 , 600 MHz) δ 7.63 (2 H, d, $J = 8.4$ Hz), 7.28 (2 H, d, $J = 8.4$ Hz), 7.23 (2 H, d, $J = 8.4$ Hz), 7.05 (2 H, d, $J = 8.4$ Hz), 6.68 (2 H, s), 5.91 (2 H, d, $J = 2.4$ Hz), 4.75 (1 H, dm, $J = 2.4$ Hz), 4.72 (1 H, dm, $J = 1.8$ Hz); ^{13}C NMR (CDCl_3 , 150 MHz) δ 185.8, 141.5, 141.3, 140.8, 139.6, 137.6, 136.27, 136.25, 132.7, 130.3, 129.7, 128.7, 126.5, 126.3, 92.4, 40.0, 39.7.

Experimental Procedure for Disilane 108: To a mixture of 1.65 g of diene **101** (4.7 mmol), 1.85 g of the unsymmetrical quinone (3.9 mmol) and 0.13 g of anhydrous AlCl_3 (1.0 mmol), 100 mL of anhydrous dichloromethane was added in glove box. The reaction mixture was stirred at room temperature for 20 h. The whole mixture was passed through a short pad of silica gel, washed with dichloromethane and concentrated to afford a yellow solid. The crude solid was used without further purification. To the yellow solid and 2.15 g of potassium carbonate (15.5 mmol) in 200 mL of dry acetone was added 0.9 mL of dimethyl sulfate (9.5 mmol) via a syringe, and the reaction mixture was heated under reflux for 3 h. After that the reaction mixture was allowed to cool to room temperature and concentrated. Then distilled water (100 mL) was added and the reaction mixture was extracted with dichloromethane (3×100 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified carefully by flash column chromatography (silica gel, dichloromethane:hexanes = 1:4 to 1:2) to produce 1.75 g of **108** (2.15 mmol, 55% yield) as a yellow solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.39 (2 H, d, $J = 8.4$ Hz), 7.283 (2 H, d, $J = 8.0$ Hz), 7.279 (2 H, d, $J = 8.0$ Hz), 7.03 (2 H, d, $J = 8.4$ Hz), 6.96 (4 H, d, $J = 7.6$ Hz), 6.86 (2 H, d, $J = 8.4$ Hz), 6.69 (2 H, d, $J = 8.4$ Hz), 6.12 (2 H, d, $J = 3.6$ Hz), 6.04 (2 H, d, $J = 2.8$ Hz), 4.83 (2 H, d, $J = 2.8$ Hz), 4.81 (1H, m), 4.80 (1H, t, 3.6 Hz), 3.551 (3 H, s), 3.547 (3 H, s), 0.256 (9 H, s), 0.243 (9 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.3, 144.61, 144.59, 143.5, 142.2, 137.41, 137.39, 137.0, 133.15, 133.14, 131.54, 131.49, 131.4, 130.7, 130.5, 129.6, 128.8, 128.3, 128.1, 128.0, 127.70, 127.67, 126.75, 126.74, 91.1, 60.3, 41.18, 41.16, -0.94, -1.0.

Experimental Procedure for Stepwise Synthesis of Fused Nanotube-like Trimer 95a. To an oven-dried 200 mL-flask was added 1.42 g of dibromide **104** (1.67 mmol) and 0.57 g of 2,2'-bipyridyl (3.68 mmol). Then the flask was flushed with nitrogen and moved into a glove box,

where 1.01 g of bis(1,5-cyclooctadiene)nickel(0) (3.68 mmol) was added. The flask was fitted with a condenser, a rubber septa, and then removed from the glove box before 30 mL of THF was transferred via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 h. After the reaction mixture was allowed to cool to room temperature, it was passed through a short silica gel column and flushed with dichloromethane. The combined eluents were concentrated, and the residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:5 to 1:1) to produce 132 mg of **106** (0.096 mmol, 12% yield) as a white solid, 0.090 g of **105** (0.066 mmol, 8% yield) as a white solid, 0.140 g of **111** (0.068 mmol, 13% yield) as a white solid and **110** (4% NMR yield) as a white solid. The whole **110** mixture was dissolved in 20 mL of dichloromethane under a nitrogen atmosphere and cooled to $-78\text{ }^{\circ}\text{C}$. To the solution at $-78\text{ }^{\circ}\text{C}$, 0.15 mL of a solution of 1 M ICl in dichloromethane was added dropwise. After 5 min at $-78\text{ }^{\circ}\text{C}$, the solution was quenched with a saturated sodium thiosulfate solution and diluted with 30 mL of water. The mixture was extracted with dichloromethane ($3 \times 20\text{ mL}$), dried over sodium sulfate, and concentrated. To the crude mixture was added 30 mg of 2,2'-bipyridyl (0.19 mmol) in a 250 mL-flask. Then the whole flask was flushed with nitrogen and moved into a glovebox, where 50 mg of bis(1,5-cyclooctadiene)nickel(0) (0.19 mmol) was added and a water condenser was fitted. The flask was then removed from the glove box and 100 mL of THF was added via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 hours. After the mixture was allowed to cool to room temperature, the reaction mixture was passed through a short silica gel column and eluted with dichloromethane. The combined eluents were concentrated. The crude ^1H NMR spectrum clearly showed the major product was the compound **95a**. **111**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.37 (4 H, d, $J = 8.4\text{ Hz}$), 7.34 (4 H, d, $J = 8.4\text{ Hz}$), 7.33

(4 H, d, $J = 8.4$ Hz), 7.26 (4 H, d, $J = 8.4$ Hz), 7.21 (4 H, d, $J = 8.0$ Hz), 7.13 (4 H, d, $J = 8.4$ Hz), 7.121 (4 H, d, $J = 8.0$ Hz), 7.117 (4 H, d, $J = 8.4$ Hz), 7.09 (4 H, d, $J = 8.0$ Hz), 6.08 (4 H, m), 4.90 (8 H, m), 3.57 (6 H, s), 3.55 (6 H, s), 3.19 (6 H, s), 0.18 (18 H, s); 0.077 (18 H, s); 0.009 (18 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 152.9, 152.6, 152.5, 144.6, 144.5, 144.4, 143.5, 142.98, 142.96, 138.6, 138.5, 138.0, 137.1, 137.06, 133.10, 133.06, 133.04, 131.8, 131.6, 131.55, 131.2, 130.7, 130.5, 129.0, 128.8, 128.3, 128.1, 128.0, 127.8, 127.7, 127.0, 126.9, 126.7, 126.62, 126.59, 126.4, 61.1, 60.8, 60.5, 41.6, 40.9, 40.7, -1.00, -1.04, -1.09; HRMS (ESI) calcd for $\text{C}_{138}\text{H}_{145}\text{O}_6\text{Si}_6(\text{MH}^+)$ 2065.9651, found 2065.9627. **110**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.44 (12 H, d, $J = 8.4$ Hz), 7.27 (12 H, d, $J = 8.4$ Hz), 7.18 (12 H, d, $J = 7.8$ Hz), 7.03 (12 H, d, $J = 8.4$ Hz), 6.08 (6H, d, $J = 3.6$ Hz), 6.00 (6H, d, $J = 3.2$ Hz), 4.99 (6H, d, $J = 2.8$ Hz), 4.96 (6H, d, $J = 3.2$ Hz), 3.22 (18 H, s), 0.08 (54 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 153.0, 144.7, 143.7, 138.2, 137.2, 133.1, 132.0, 131.4, 128.5, 128.4, 127.9, 127.2, 126.5, 61.4, 41.5, 41.4; HRMS (ESI) calcd for $\text{C}_{138}\text{H}_{145}\text{O}_6\text{Si}_6(\text{MH}^+)$ 2065.9651, found 2065.9652.

Experimental Procedure for Diboronic ester 112. To a mixture of 0.58 g of dibromide **55** (1.2 mmol), 0.71 g of bis(pinacolato)diboron (2.77 mmol), 0.72 g of potassium acetate (6.9 mmol), 12 mg of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (0.01 mmol) and 30 mg of XPhos (0.08 mmol) under a Argon atmosphere was added 100 mL of anhydrous dioxane. Then the reaction mixture was heated at 80 °C for 12 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a short silica gel column, washed with diethyl ether 100 mL. The combined organic solvents were collected and concentrated via high vacuo. The solid was washed with hexanes to give 0.65 g of boronic ester **112** (1.1 mmol, 95%) as white solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (4 H, d, $J = 8.4$ Hz), 7.23 (4 H, d, $J = 8.4$ Hz), 6.71 (2 H, s), 5.94 (2 H, d, $J = 3.2$ Hz), 4.88 (2 H, d, $J = 2.8$ Hz), 3.57

(6 H, s), 1.33 (12 H, s), 1.33 (12 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.4, 148.1, 134.6, 127.6, 127.4, 109.1, 83.5, 55.7, 41.5, 24.9, 24.8.

Experimental Procedures for Dibromide 113. To a mixture of 3.58 g of dibronic ester **112** (6.0 mmol), 10.2 g of 1-bromo-4-iodobenzene (36 mmol), 9.93 g of silver carbonate (36 mmol), 0.70 g of tetrakis(triphenylphosphine)palladium(0) (0.6 mmol) under a Argon atmosphere was added 200 mL of anhydrous THF. Then the reaction mixture was heated at reflux for 40 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a short silica gel column, washed with 100 mL of diethyl ether. The combined organic solvents were collected and concentrated via high vacuo. The residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:5) to produce 2.97 g of **113** (4.6 mmol, 76% yield) as a white solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.52 (4 H, d, J = 8.4 Hz), 7.42 (4 H, d, J = 8.4 Hz), 7.41 (4 H, d, J = 8.4 Hz), 7.29 (4 H, d, J = 8.0 Hz), 6.77 (2 H, s), 6.04 (2 H, d, J = 3.2 Hz), 4.95 (2 H, d, J = 2.8 Hz), 3.64 (6 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.4, 144.4, 140.0, 137.3, 131.7, 128.7, 128.5, 127.9, 127.5, 126.5, 121.1, 109.2, 55.8, 40.9.

Experimental Procedures for Cyclic Dimer 114. To an oven-dried 2000 mL flask was added 0.63 g of Dibromide **104** (0.97 mmol) and 0.36 g of 2,2'-bipyridyl (2.3 mmol). Then the whole flask was flushed with nitrogen and moved into a glove box, where 0.64 g of bis(cyclooctadiene)nickel(0) (2.3 mmol) was added and a water condenser was fitted. Outside of the glove box, 1000 mL of THF was transferred under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 hours. After the mixture was allowed to cool to room temperature, the reaction mixture was passed through a short silica gel column and flushed with dichloromethane. The combined solvents were concentrated and the residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:6 to 1:3) to produce 48

mg of **114** (0.05 mmol, 10% yield) as a white solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.35 (8 H, d, $J = 8.4$ Hz), 7.21 (8 H, d, $J = 8.4$ Hz), 6.99 (8 H, d, $J = 8.4$ Hz), 6.92 (4 H, s), 6.79 (8 H, d, $J = 8.0$ Hz), 6.72 (4 H, dd, $J = 4.0, 2.0$ Hz), 5.27 (4 H, m), 3.88 (6 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 150.8, 141.2, 140.0, 138.6, 137.3, 132.4, 130.8, 127.7, 127.3, 126.8, 125.9, 108.8, 56.0, 37.8. HRMS (ESI) calcd for $\text{C}_{72}\text{H}_{56}\text{O}_4$ (M^+) 984.4173, found 984.4184.

Experimental Procedure for the Functionalized [10]CPP 115. To a 20-mL sealtube were added 0.020 g (0.02 mmol) of **114** and 0.025 g (0.12 mmol) of DDQ. The flask was flushed with nitrogen at 0 °C and then 3 mL of chlorobenzene was introduced by using a syringe. The reaction mixture was heated to 150 °C. After 4 h at 150 °C, the reaction mixture was allowed to cool to room temperature, diluted with 10 mL of dichloromethane and immediately passed through a basic aluminum oxide column (4 cm high, 2.5 cm in diameter). The column was eluted with an additional 100 mL of dichloromethane. The combined eluents were concentrated in vacuo immediately to afford 0.013 g of **115** (0.013 mmol, 65% yield) as a yellow solid: ^1H NMR (C_6D_6 , 600 MHz) δ 7.49 (8 H, d, $J = 8.4$ Hz), 7.45 (16 H, t, $J = 8.4$ Hz), 7.37 (8 H, d, $J = 8.4$ Hz), 7.00 (4 H, s), 6.70 (4 H, s), 3.45 (12 H, s); ^{13}C NMR (C_6D_6 , 150 MHz) δ 151.0, 143.8, 139.2, 138.2, 137.6, 136.2, 132.8.0, 127.2, 126.7, 124.9, 106.7, 55.1; HRMS (ESI) calcd for $\text{C}_{72}\text{H}_{52}\text{O}_4$ (M^+) 980.3860, found 980.3878.

Experimental Procedure for Tetraboronic Ester 116. To a mixture of 1.50 g of tetrabromide **90** (1.74 mmol), 2.12 g of bis(pinacolato)diboron (8.35 mmol), 2.05 g of potassium acetate (20.9 mmol), 32 mg of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (0.035 mmol) and 83 mg of XPhos (0.17 mmol) under a Argon atmosphere was added 150 mL of anhydrous dioxane. Then the reaction mixture was heated at 80 °C for 12 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a

short silica gel column, washed with 100 mL of diethyl ether. The combined organic solvents were collected and concentrated via high vacuo. The solid was washed with hexanes to give 1.55 g of boronic ester **116** (1.48 mmol, 85%) as a white solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.59 (8 H, d, J = 8.4 Hz), 7.09 (8 H, d, J = 8.4 Hz), 6.05 (4 H, d, J = 3.2 Hz), 4.92 (4 H, d, J = 2.8 Hz), 3.25 (6 H, s), 1.32 (48 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.7, 147.4, 134.8, 131.4, 128.0, 127.0, 83.4, 60.9, 41.5, 24.84, 24.81.

Experimental Procedure for Tetrabromide 117. To a mixture of 1.19 g of dibronic ester **116** (1.13 mmol), 3.84 g of 1-bromo-4-iodobenzene (13.6 mmol), 3.74 g of silver carbonate (13.6 mmol), 0.26 g of tetrakis(triphenylphosphine)palladium(0) (0.23 mmol) under an argon atmosphere was added 200 mL of anhydrous THF. Then the reaction mixture was heated at reflux for 40 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a short silica gel column, washed with 100 mL of diethyl ether. The combined organic solvents were collected and concentrated via high vacuo. The residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:5 to 1:3) to produce 0.92 g of **117** (0.79 mmol, 70% yield) as a white solid: ^1H NMR (CDCl_3 , 400 MHz) δ 7.42 (8 H, d, J = 8.8 Hz), 7.25 (8 H, d, J = 8.0 Hz), 7.24 (8 H, d, J = 8.4 Hz), 7.04 (8 H, d, J = 8.0 Hz), 6.15 (4 H, d, J = 2.8 Hz), 4.90 (4 H, d, J = 2.8 Hz), 3.64 (6 H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 152.5, 143.6, 139.7, 137.3, 131.7, 131.1, 128.4, 128.04, 127.97, 126.4,, 121.1, 60.4, 40.7. HRMS (ESI) calcd for $\text{C}_{64}\text{H}_{46}\text{Br}_4\text{O}_2$ (M^+) 1164.0205, 1165.0239, 1166.0185, 1167.0218, found 1164.0239, 1165.0191, 1166.0219, and 1167.0242.

Experimental Procedures for Diene 118. To a mixture of 1.52 g of dibronic ester **96** (3.32 mmol), 1.70 g of bromide **98** (7.42 mmol), 2.00 g of potassium carbonate (14.6 mmol), 0.12 g of tetrakis(triphenylphosphine)palladium(0) (0.10 mmol) under a Argon atmosphere was added 150

mL of anhydrous THF and 50 mL of degased H₂O . Then the reaction mixture was heated at reflux for 40 h. After the reaction was complete, the hot reaction mixture was quickly filtered. 100 mL of diethyl ether and 50 mL of H₂O was added to the mixture. Then the mixture was partitioned and extracted with 50 mL of diethyl ether and 100 mL of dichloromethane. The combined organic solvents were collected and concentrated via high vacuo. The residue was washed with water, diethyl ether and air dried to produce 1.17 g of **118** (2.32 mmol, 70 % yield) as a yellow solid: ¹H NMR (CDCl₃, 400 MHz) δ 7.61 (8 H, s), 7.60 (4 H, d, *J* = 8.8 Hz), 7.52 (4 H, d, *J* = 8.4 Hz), 7.03 (2 H, m), 6.73 (2 H, m), 0.31 (18 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 141.0, 140.2, 139.4, 136.5, 133.9, 132.4, 129.4, 127.3, 126.8, 126.2, -1.1.

Experimental Procedures for Dibromide 120. To a mixture of 1.37 g of diene **118** (2.72 mmol), 1.21 g of quinone **89** (2.56 mmol) and 0.085 g of anhydrous AlCl₃ (0.64 mmol), 100 mL of anhydrous dichloromethane was added in glovebox. The reaction mixture was stirred at room temperature for 20 h. The whole mixture was passed through a short pad of silica gel, washed with dichloromethane and concentrated to afford a yellow solid. The crude solid was used without further purification. To the yellow solid and 1.41 g of potassium carbonate (10.2 mmol) in 200 mL of dry acetone was added 0.6 mL of dimethyl sulfate (6.4 mmol) via a syringe, and the reaction mixture was heated under reflux for 3 h. After that the reaction mixture was allowed to cool to room temperature and concentrated. Then distilled water (100 mL) was added and the reaction mixture was extracted with dichloromethane (3 $\times$ 100 mL). The combined organic layers were dried over sodium sulfate and concentrated. The residue was purified carefully by flash column chromatography (silica gel, dichloromethane:hexanes = 1:4 to 1:3) to produce 1.54 g of **119** (1.54 mmol, 60% yield) as a yellow solid. To a mixture of 1.54 g of dibromide **119** (1.54 mmol), 0.80 g of bis(pinacolato)diboron (3.16 mmol), 0.91 g of potassium acetate (9.24

mmol), 40 mg of tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (0.03 mmol) and 60 mg of XPhos (0.15 mmol) under an argon atmosphere was added 100 mL of anhydrous dioxane. Then the reaction mixture was heated at 80 °C for 12 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a short silica gel column, washed with 100 mL of diethyl ether. The combined organic solvents were collected and concentrated via high vacuo. The residue was washed with hexanes to give the crude diboronic ester as a white solid. The crude solid was used without further purification. To a mixture of the crude diboronic ester, 2.61 g of 1-bromo-4-iodobenzene (9.24 mmol), 2.56 g of silver carbonate (9.24 mmol), 0.35 g of tetrakis(triphenylphosphine)palladium(0) (0.3 mmol) under an argon atmosphere was added 200 mL of anhydrous THF. Then the reaction mixture was heated at reflux for 40 h. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and filtered through a short silica gel column, washed with 100 mL of diethyl ether. The combined organic solvents were collected and concentrated via high vacuo. The residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:5) to produce 0.96 g of **120** (0.83 mmol, 54 % yield) as a white solid: ¹H NMR (CDCl₃, 400 MHz) δ 7.49 (4 H, d, J = 8.0 Hz), 7.40 (4 H, d, J = 8.4 Hz), 7.39 (4 H, d, J = 8.4 Hz), 7.29 (4 H, d, J = 8.4 Hz), 7.27 (4 H, d, J = 8.4 Hz), 7.26 (4 H, d, J = 7.8 Hz), 7.04 (4 H, d, J = 8.4 Hz), 7.03 (4 H, d, J = 8.4 Hz), 6.18 (2 H, d, J = 3.2 Hz), 7.15 (2 H, d, J = 2.8 Hz), 7.39 (4 H, d, J = 8.4 Hz), 4.90 (4 H, t, J = 2.8 Hz), 3.64 (6 H, s), 0.32 (18 H, s); ¹³C NMR (CDCl₃, 100 MHz) δ 152.5, 143.7, 143.2, 141.2, 139.8, 138.8, 138.4, 137.3, 133.7, 131.7, 131.2, 130.9, 128.5, 128.0, 127.96, 127.90, 126.6, 126.5, 126.2, 121.0, 60.4, 40.73, 40.69, -1.0.

Experimental Procedures for Cyclic Dimer 121 and 122: To an oven-dried 1000 mL-flask was added 0.96 g of dibromide **120** (0.83 mmol) and 0.29 g of 2,2'-bipyridyl (1.83 mmol). Then

the flask was flushed with nitrogen and moved into a glovebox, where 0.50 g of bis(1,5-cyclooctadiene)nickel(0) (1.83 mmol) was added. The flask was fitted with a condenser, a rubber septa, and then removed from the glovebox before 830 mL of THF was transferred via cannula under a nitrogen atmosphere. Then the reaction mixture was heated at reflux for 15 h. After the reaction mixture was allowed to cool to room temperature, it was passed through a short silica gel column and eluted with dichloromethane. The combined eluents were concentrated, and the residue was purified by flash column chromatography (silica gel, dichloromethane:hexanes = 1:5 to 1:2) to produce 0.126 g of **122** (0.063 mmol, 15% yield) as a white solid, and 0.120 g of **121** (0.060 mmol, 15% yield) as a white solid. Cyclic dimer **122**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.56 (16 H, s), 7.53 (8 H, d, $J = 8.4$ Hz), 7.37 (8 H, d, $J = 8.4$ Hz), 7.34 (8 H, d, $J = 7.8$ Hz), 7.22 (8 H, d, $J = 8.4$ Hz), 6.94 (8 H, d, $J = 8.4$ Hz), 6.80 (4 H, dd, $J = 4.2, 1.8$ Hz), 6.67 (8 H, d, $J = 7.8$ Hz), 6.13 (4 H, d, $J = 2.4$ Hz), 5.13 (4 H, m), 5.05 (4 H, d, $J = 3.0$ Hz), 3.61 (12 H, s), 0.28 (36 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 151.7, 144.1, 141.4, 140.8, 139.7, 138.9, 138.8, 138.6, 137.2, 133.8, 133.7, 132.2, 130.9, 128.1, 127.79, 127.73, 127.3, 127.1, 126.7, 126.4, 125.8, 61.1, 41.5, 38.6, -1.1. Cyclic Dimer **121**: ^1H NMR (CDCl_3 , 600 MHz) δ 7.56 (16 H, m), 7.54 (8 H, d, $J = 8.4$ Hz), 7.38 (8 H, d, $J = 8.4$ Hz), 7.33 (8 H, d, $J = 8.4$ Hz), 7.22 (8 H, d, $J = 8.4$ Hz), 6.94 (8 H, d, $J = 8.4$ Hz), 6.80 (4 H, dd, $J = 4.8, 2.4$ Hz), 6.67 (8 H, d, $J = 7.8$ Hz), 6.13 (4 H, d, $J = 3.0$ Hz), 5.12 (4 H, m), 5.05 (4 H, d, $J = 3.0$ Hz), 3.61 (12 H, s), 0.28 (36 H, s); ^{13}C NMR (CDCl_3 , 150 MHz) δ 151.7, 144.2, 141.4, 140.8, 139.6, 138.9, 138.8, 138.6, 137.2, 133.9, 133.7, 132.2, 130.9, 128.1, 127.80, 127.74, 127.3, 127.1, 126.7, 126.4, 125.8, 61.1, 41.5, 38.6, -1.08.

Figure S1. ORTEP Drawing of the Crystal Structure of Dibromide **55**.

Perspective view of the molecular structure of **55** ($C_{24}H_{20}Br_2O_2$) with the atom labeling scheme provided for the non-hydrogen atoms. The thermal ellipsoids are scaled to enclosed 30% probability.

independent molecule 1

independent molecule 2

independent molecule 3

Figure S2. ORTEP Drawing of the Crystal Structure of the Cyclic Dimer *syn*-**56a**.

Perspective view of the molecular structure of *syn*-**56a** ($C_{48}H_{40}O_4$, three independent molecules) with the atom labeling scheme. The thermal ellipsoids are scaled to enclose 30% probability.

Figure S4. ORTEP Drawing of the Crystal Structure of *syn*-tetraiodide **92**.

Perspective view of the molecular structure of *syn*-tetraiodide **92** ($\text{C}_{40}\text{H}_{30}\text{I}_4\text{O}_2 \cdot \text{CH}_2\text{Cl}_2$) with the atom labeling scheme for the independent non-hydrogen atoms. The thermal ellipsoids are scaled to enclose 30% probability.

Computational Details.

Spin-restricted density functional theory (RDFT) calculations were performed with the Gaussian 03 (G03) program.^{S2} Geometry optimization and normal mode analyses were performed using the B3LYP functional and the 6-31G(d) basis set.^{S3, S4} This functional–basis set combination was utilized in related studies,^{31g,9} and reproduces the geometries of two X-ray crystallographic species characterized in the present study with reasonable accuracy (Table S1 and S2). The identified stationary points met or exceeded all default G03 convergence criteria. Normal-modes were calculated for each optimized structure to confirm the absence of negative eigenvalues.

Metrical Comparison of X-Ray and DFT Structure.

Table S1. Comparison of Experimental and Computational Metrical Parameters for the CPP Precursor Dibromide 55.

	EXP (X-ray)	DFT (B3LYP/6-31G(d))
C3-C4 (Å)	1.382(4)	1.40
C4-C5 (Å)	1.383(3)	1.39
C1-C6 (Å)	1.390(3)	1.40
C6-C7 (Å)	1.520(3)	1.52
C7-C8 (Å)	1.507(3)	1.51
C8-C9 (Å)	1.309(3)	1.33
C7-C19 (Å)	1.525(3)	1.54
C7-C8-C9 (°)	125.2(2)	124.2
C6-C7-C19 (°)	115.0(2)	114.5
C8-C7-C19 (°)	108.8(2)	109.6
C6-C7-C19-C20 (°)	30.1(2)	25.7
C1-C10-C13-C14 (°)	-58.2(2)	-68.2

Table S2. Comparison of Experimental and Computational Metrical Parameters for the Cyclic Dimer *syn*-56a

	EXP (X-ray)	DFT (B3LYP/6-31G(d))
C2-C3 (Å)	1.383(5)	1.40
C3-C4 (Å)	1.363(5)	1.39
C5-C6 (Å)	1.386(5)	1.39
C5-C7 (Å)	1.504(5)	1.53
C7-C8 (Å)	1.510(5)	1.52
C8-C9 (Å)	1.308(5)	1.34
C7-C42 (Å)	1.534(4)	1.55
C40-C41 (Å)	1.386(4)	1.40
C36-C39 (Å)	1.464(4)	1.49
C7-C8-C9 (°)	120.6(4)	121.4
C5-C7-C42 (°)	111.9(3)	112.8
C8-C7-C42 (°)	111.2(3)	111.9
C6-C7-C19-C20 (°)	36.2(4)	40.0
C1-C10-C13-C14 (°)	-13.4(4)	-6.8
C13-C14-C17-C22 (°)	-37.7(4)	-39.0
C35-C38-C39-C40 (°)	-38.5(4)	-39.0

Analyses of the Functionalized [9]CPP 65 and the Cyclic Trimer *anti*-64b.

Figure S6. Ball-and-stick model for the functionalized [9]CPP **65** derived from DFT with all aryl-aryl torsions on the top face noted. For clarity, hydrogen atoms were deleted.

Figure S7. Ball-and-stick model for the cyclic trimer *anti*-**64b** derived from DFT with relevant metrical parameters highlighted.

A **B**

Figure S8. Aerial view of ball-and-stick models for **1** (A) and *anti*-**64b** (B) derived from DFT with aryl-aryl torsions noted. For clarity, hydrogen atoms were deleted. The dimethoxynaphthyl moieties cant away from the circle at angles of 133.8° and 112.5° on average for **65** and *anti*-**64b**, respectively.

Computational Coordinates and Energetic Details:

Dibromide 55

C	-6.017920	-0.343981	6.834634
C	-8.349956	0.009098	5.315013
C	-6.774244	0.816287	6.996434
C	-6.409726	-1.331637	5.933392
C	-7.573169	-1.147529	5.180791
C	-7.934197	0.980189	6.236820
H	-6.467836	1.576211	7.707043
H	-5.821276	-2.235860	5.821481
H	-7.884156	-1.930444	4.495831
H	-8.528268	1.880721	6.375300
C	-6.522988	-2.096947	-0.745155
C	-8.651200	-1.016565	0.725521
C	-6.348757	-1.812167	0.608768
C	-7.737653	-1.844462	-1.379663
C	-8.792518	-1.307451	-0.636771
C	-7.412947	-1.268754	1.331471
H	-5.396047	-2.001447	1.091260
H	-7.861649	-2.064304	-2.434533
H	-9.744090	-1.122427	-1.126957
H	-7.264758	-1.025439	2.378565
C	-9.609662	0.266559	4.471982
H	-10.318395	0.761783	5.151068
C	-9.810581	-0.388510	1.516745
H	-10.611758	-0.219636	0.784978
C	-9.285880	1.238563	3.359783
C	-9.384367	0.952449	2.060726
H	-8.938198	2.221326	3.671371
H	-9.113796	1.701156	1.318908
C	-10.295347	-0.990242	3.961967
C	-11.675822	-3.297056	3.142776
C	-10.388046	-1.296866	2.599101
C	-10.911698	-1.840799	4.913178
C	-11.579930	-2.990655	4.507207
C	-11.102405	-2.453203	2.197357
H	-12.044915	-3.653278	5.226982
H	-12.213878	-4.188431	2.844194
O	-10.806875	-1.436149	6.219617
O	-11.198456	-2.650495	0.842850
C	-11.376476	-2.251397	7.233351
H	-12.463413	-2.344993	7.109906

Calculation results at DFT-optimized geometry:

Total Energy— -6219.80154331 AU

SCF Convergence— 0.2578E-08

Three lowest frequencies (cm⁻¹): 12.4, 23.8, 29.5

Cyclic Dimer syn-64a

C	-6.034648	-1.397777	1.320344
C	-5.933567	1.391161	1.496529
C	-5.537049	-0.647822	0.232873
C	-6.466337	-0.754239	2.477557
C	-6.413208	0.641599	2.568010
C	-5.499517	0.746564	0.318527
H	-6.849716	-1.318248	3.320003
H	-6.754058	1.121211	3.478222
O	-6.058002	-2.762766	1.150240
O	-5.851632	2.761172	1.491600
C	-6.281693	3.461656	2.643464
H	-7.345075	3.282264	2.854426
H	-6.131291	4.520857	2.425359
H	-5.690532	3.187686	3.528082
C	-6.615591	-3.557840	2.180426
H	-6.047568	-3.466720	3.116354
H	-6.560867	-4.589458	1.827019
H	-7.664721	-3.294151	2.371653
C	-5.107480	-1.342827	-1.060308
H	-5.666006	-2.284292	-1.122597
C	-5.033753	1.571571	-0.873259
C	-5.443580	0.864143	-2.155971
C	-5.488268	-0.466207	-2.237128
H	-5.703229	1.480465	-3.013937
H	-5.774980	-0.956533	-3.165259
H	-5.551382	2.537187	-0.827909
C	-3.601586	-1.702816	-1.071058
C	-0.791188	-2.174325	-1.011698
C	-2.795401	-1.434542	-2.183468
C	-2.987043	-2.292058	0.044666
C	-1.612007	-2.516300	0.076534
C	-1.421953	-1.667921	-2.157049
H	-3.229773	-0.977895	-3.066052
H	-3.586481	-2.560319	0.908250
H	-1.164769	-2.951872	0.966758
H	-0.820011	-1.379348	-3.014195
C	-3.517417	1.866599	-0.853720
C	-0.690587	2.209297	-0.930599
C	-2.877788	2.379515	-1.992545
C	-2.726008	1.610737	0.270783
C	-1.343087	1.778203	0.233704
C	-1.494824	2.544337	-2.033431
H	-3.461547	2.624537	-2.876418
H	-3.182693	1.221075	1.174074
H	-0.753005	1.499227	1.102282
H	-1.029153	2.922879	-2.939953
C	0.791188	2.174325	-1.011698
C	3.601586	1.702816	-1.071058
C	1.612007	2.516300	0.076534
C	1.421954	1.667921	-2.157049
C	2.795401	1.434542	-2.183468
C	2.987043	2.292058	0.044666
H	1.164769	2.951873	0.966758
H	0.820011	1.379348	-3.014195
H	3.229773	0.977894	-3.066052
H	3.586481	2.560319	0.908250
C	0.690587	-2.209297	-0.930598
C	3.517417	-1.866599	-0.853719
C	1.343087	-1.778203	0.233704
C	1.494824	-2.544338	-2.033430
C	2.877788	-2.379515	-1.992544
C	2.726008	-1.610737	0.270783
H	0.753005	-1.499226	1.102282
H	1.029153	-2.922879	-2.939953
H	3.461547	-2.624537	-2.876418
H	3.182693	-1.221074	1.174074
C	5.107480	1.342827	-1.060308
H	5.666006	2.284292	-1.122597

C	5.033753	-1.571571	-0.873259
H	5.551382	-2.537187	-0.827909
C	5.488268	0.466206	-2.237128
C	5.443580	-0.864143	-2.155971
H	5.774980	0.956533	-3.165259
H	5.703229	-1.480465	-3.013937
C	5.499517	-0.746564	0.318528
C	6.466337	0.754240	2.477557
C	5.537049	0.647822	0.232874
C	5.933567	-1.391161	1.496530
C	6.413207	-0.641599	2.568010
C	6.034648	1.397777	1.320344
H	6.754057	-1.121211	3.478223
H	6.849716	1.318248	3.320004
O	5.851632	-2.761172	1.491600
O	6.058002	2.762766	1.150240
C	6.281693	-3.461656	2.643465
H	6.131290	-4.520857	2.425360
H	5.690532	-3.187686	3.528082
H	7.345075	-3.282264	2.854426
C	6.615591	3.557840	2.180426
H	6.047568	3.466720	3.116354
H	6.560867	4.589458	1.827019
H	7.664720	3.294151	2.371654

Calculation results at DFT-optimized geometry:

Total Energy= -2153.98051611 AU

SCF Convergence= 0.3572E-08

Three lowest frequencies (cm⁻¹): 20.4, 22.1, 29.9

Functionalized [9]CPP 65

C	3.518389	5.396719	2.078322
C	4.524148	4.429280	2.062281
C	4.713752	3.585033	0.951908
C	3.956143	3.881783	-0.198809
C	2.973194	4.860779	-0.193280
C	2.673251	5.584960	0.973408
C	0.713076	7.034147	0.062442
C	1.326642	6.216322	1.074170
C	0.509077	5.712400	2.075021
C	-0.889164	5.718594	1.950403
C	-1.517320	6.243277	0.829901
C	-0.724204	7.061665	-0.050558
C	-3.800350	5.322600	1.451999
C	-2.834277	5.638852	0.481442
C	-2.996284	5.068870	-0.794461
C	-3.973610	4.112850	-1.036759
C	-4.843645	3.678870	-0.019071
C	-4.783414	4.363436	1.207521
C	-6.040534	1.961153	-1.449133
C	-6.347708	0.620307	-1.677101
C	-6.205651	-0.340978	-0.662228
C	-5.901363	0.126692	0.628812
C	-5.589778	1.461997	0.854237
C	-5.573494	2.397899	-0.196985
C	-5.122633	-2.070890	-1.981587
C	-4.423378	-3.285462	-2.029247
C	-4.602325	-4.266850	-1.065179
C	-5.739474	-4.137935	-0.191621
C	-6.455741	-2.885671	-0.138929
C	-6.025627	-1.789477	-0.966384
C	-1.361064	-6.107498	-1.720799
C	-0.735935	-6.009364	-0.465395
C	-1.543964	-5.629003	0.622941
C	-2.858405	-5.219322	0.441353
C	-3.431489	-5.162079	-0.841583
C	-2.679685	-5.691417	-1.904516
C	3.419756	-5.265638	0.289853
C	2.868955	-5.067920	-0.988697
C	1.558688	-5.437355	-1.269762
C	0.738844	-6.031741	-0.291735
C	1.350383	-6.389412	0.922580
C	2.661397	-6.010972	1.208390
C	4.956774	-2.401834	2.052033
C	5.950623	-1.949758	1.194853
C	6.474587	-2.894089	0.240709
C	5.757236	-4.122285	-0.011893
C	4.558105	-4.407679	0.729781
C	4.283718	-3.610362	1.831826
C	5.688435	1.660041	2.256668
C	6.025752	0.310197	2.320748
C	6.137398	-0.472031	1.158099
C	6.094397	0.213778	-0.070030
C	5.782858	1.566139	-0.131653
C	5.468578	2.305937	1.025839
C	7.715352	-2.669737	-0.446598
C	8.172431	-3.571079	-1.384569
C	7.457639	-4.757877	-1.651602
C	6.294102	-5.047416	-0.970972
O	5.608677	-6.220338	-1.114168
O	8.411046	-1.555590	-0.069198
C	9.642722	-1.277046	-0.706453
C	6.098059	-7.184885	-2.026009
C	1.490366	7.854478	-0.823695
C	0.873668	8.631893	-1.781082
C	-0.533548	8.672136	-1.879961
C	-1.321503	7.928878	-1.026565
O	2.840497	7.840297	-0.615831
C	3.662010	8.636951	-1.447610

O	-2.6886161	7.995276	-1.006548
C	-3.337613	8.832919	-1.942068
C	-7.606006	-2.786402	0.715588
C	-7.989784	-3.851414	1.502623
C	-7.291761	-5.076477	1.448431
C	-6.210047	-5.234166	0.608159
O	-5.554085	-6.420533	0.436687
C	-5.980811	-7.544368	1.182373
O	-8.296577	-1.609331	0.650009
C	-9.458075	-1.459572	1.443717
H	3.354373	5.978379	2.982165
H	5.131178	4.297289	2.953608
H	4.055795	3.265209	-1.085689
H	2.349205	4.990249	-1.072644
H	0.954050	5.114774	2.865243
H	-1.467139	5.116971	2.645315
H	-3.747813	5.791346	2.431538
H	-2.274260	5.295757	-1.572659
H	-3.985553	3.607713	-1.998299
H	-5.481811	4.107043	2.000205
H	-6.111620	2.668018	-2.271945
H	-6.644974	0.304225	-2.673926
H	-5.797842	-0.586584	1.440845
H	-5.237225	1.759970	1.837709
H	-4.798704	-1.266602	-2.634924
H	-3.586206	-3.368214	-2.715566
H	-0.794121	-6.463012	-2.577527
H	-1.099389	-5.538632	1.609844
H	-3.414082	-4.830144	1.288935
H	-3.113185	-5.723353	-2.901025
H	3.434380	-4.511290	-1.730072
H	1.125982	-5.148513	-2.223461
H	0.774908	-6.916881	1.679074
H	3.080982	-6.239307	2.184975
H	4.550428	-1.723514	2.795195
H	3.397596	-3.819066	2.423050
H	5.497696	2.187135	3.186567
H	6.121043	-0.162306	3.294881
H	6.215667	-0.340796	-0.994847
H	5.711804	2.033431	-1.109125
H	9.108061	-3.404454	-1.904836
H	7.867074	-5.455578	-2.372220
H	10.003695	-0.347471	-0.262408
H	9.517701	-1.137111	-1.789070
H	10.377857	-2.074688	-0.531487
H	5.398534	-8.021490	-1.977639
H	7.102459	-7.532106	-1.746936
H	6.126566	-6.794926	-3.052747
H	1.456080	9.256705	-2.447427
H	-0.980530	9.329660	-2.615848
H	4.685530	8.460709	-1.111577
H	3.423698	9.704927	-1.347629
H	3.571940	8.347690	-2.503711
H	-4.406193	8.717216	-1.751477
H	-3.119279	8.533471	-2.976369
H	-3.055149	9.886222	-1.807303
H	-8.858537	-3.780379	2.145911
H	-7.650236	-5.901654	2.051872
H	-5.319014	-8.362696	0.892658
H	-7.019628	-7.814241	0.947090
H	-5.892081	-7.371781	2.263800
H	-9.836469	-0.457993	1.231036
H	-9.231282	-1.541222	2.515661
H	-10.224221	-2.202585	1.182489

Calculation results at DFT-optimized geometry:

Total Energy= -3227.36894548 AU

SCF Convergence= 0.1565E-08

Three lowest frequencies (cm⁻¹): 16.5, 18.1, 18.3

Cyclic Trimer anti-64b

C	6.556577	-2.205917	1.061697
C	6.799340	0.793677	1.474291
C	7.108125	-1.278007	-0.008760
C	6.405658	-1.511586	2.396168
C	6.521680	-0.196260	2.577449
C	7.239503	0.101608	0.182736
C	7.560026	-1.864475	-1.216003
C	7.847290	0.881580	-0.832229
C	8.265379	0.297807	-2.022394
C	8.117651	-1.080548	-2.218496
O	7.419338	-3.225602	-1.294824
O	8.007577	2.212936	-0.543805
C	8.552262	3.056731	-1.540371
H	9.581662	2.770582	-1.796944
H	8.554651	4.062484	-1.115146
H	7.940550	3.051559	-2.452520
C	7.805985	-3.872356	-2.492484
H	7.235894	-3.499946	-3.354334
H	7.585867	-4.931698	-2.346477
H	8.879514	-3.749059	-2.692447
H	6.373299	0.229490	3.568333
H	6.167206	-2.157147	3.239609
H	8.720043	0.892344	-2.805825
H	8.457369	-1.519008	-3.149489
C	5.589447	1.727272	1.278091
C	3.359996	3.442774	0.834843
C	5.744706	3.118419	1.227751
C	4.292719	1.212561	1.153039
C	3.203136	2.049688	0.926800
C	4.654392	3.959849	1.011174
H	6.735094	3.547165	1.348782
H	4.131046	0.142741	1.228761
H	2.218319	1.612076	0.788275
H	4.807672	5.035788	0.991508
C	5.232154	-2.890363	0.690150
C	2.716862	-4.124108	0.209066
C	4.956385	-4.179627	1.162443
C	4.242935	-2.242085	-0.058621
C	3.006781	-2.843029	-0.287579
C	3.725169	-4.789459	0.924389
H	5.713777	-4.712913	1.733839
H	4.444216	-1.261270	-0.477902
H	2.258986	-2.320341	-0.878374
H	3.530001	-5.781665	1.323561
C	1.379618	-4.733911	-0.002584
C	-1.199345	-5.862709	-0.394982
C	0.213841	-3.985895	0.229189
C	1.227818	-6.064690	-0.422721
C	-0.039120	-6.614125	-0.618767
C	-1.049813	-4.541996	0.045087
H	0.301339	-2.963765	0.588177
H	2.111661	-6.667559	-0.616280
H	-0.126703	-7.647231	-0.949363
H	-1.929798	-3.946207	0.265714
C	2.201500	4.318408	0.528162
C	-0.047216	5.912369	-0.190110
C	2.341341	5.446386	-0.298668
C	0.916077	4.032392	1.016202
C	-0.184848	4.812046	0.663240
C	1.240720	6.226469	-0.644407
H	3.318623	5.694266	-0.704067
H	0.776488	3.194615	1.694104
H	-1.161816	4.566163	1.068603
H	1.383432	7.085996	-1.296805
C	-2.582260	-6.473015	-0.668927
C	-4.974494	-4.759427	-1.406502
C	-3.642030	-6.076212	0.346443
C	-3.015416	-6.179839	-2.086995

C	-4.078435	-5.442791	-2.409188
C	-4.757722	-5.302046	0.009647
C	-3.504956	-6.577654	1.663788
C	-5.748130	-5.064655	0.995169
C	-5.591358	-5.543519	2.290818
C	-4.462884	-6.298539	2.630219
O	-2.394174	-7.349662	1.885061
O	-6.855956	-4.371301	0.576434
C	-7.865113	-4.078733	1.524122
H	-7.478996	-3.466917	2.350423
H	-8.313976	-4.993878	1.934275
H	-8.629398	-3.514017	0.986081
C	-2.171100	-7.846915	3.190762
H	-2.975293	-8.524166	3.510700
H	-2.076089	-7.032938	3.922108
H	-1.231033	-8.400242	3.144884
H	-4.313955	-5.259925	-3.456246
H	-2.390075	-6.604621	-2.870349
H	-6.340086	-5.352240	3.050302
H	-4.363181	-6.669739	3.643404
C	-1.243957	6.732866	-0.700827
C	-3.809126	5.431833	-1.671824
C	-2.492019	6.647030	0.162319
C	-1.517793	6.350330	-2.138659
C	-2.644656	5.781658	-2.564141
C	-3.675338	6.049942	-0.283891
C	-2.453642	7.245772	1.445399
C	-4.816674	6.061464	0.554933
C	-4.758907	6.630750	1.821597
C	-3.572270	7.224527	2.269967
O	-1.262783	7.836187	1.780708
O	-5.947112	5.500429	0.019304
C	-7.104360	5.415825	0.828756
H	-7.477930	6.410399	1.109861
H	-6.917670	4.832394	1.740485
H	-7.857374	4.906371	0.224145
C	-1.141167	8.422149	3.062853
H	-0.121613	8.808164	3.121494
H	-1.294377	7.682982	3.860852
H	-1.850900	9.249871	3.199955
H	-2.753083	5.507209	-3.611872
H	-0.708523	6.539807	-2.841215
H	-5.625838	6.635843	2.471817
H	-3.549244	7.671807	3.256891
C	-4.004944	3.907667	-1.651782
C	-4.343651	1.080738	-1.668316
C	-5.156503	3.320242	-2.187417
C	-3.017409	3.059028	-1.136975
C	-3.187811	1.677849	-1.134402
C	-5.322032	1.935762	-2.202771
H	-5.936634	3.956128	-2.599199
H	-2.102801	3.480958	-0.732751
H	-2.418457	1.052213	-0.690992
H	-6.215604	1.513403	-2.654482
C	-4.816428	-3.227577	-1.510420
C	-4.514496	-0.393858	-1.650551
C	-3.557458	-2.637816	-1.686839
C	-5.927316	-2.374718	-1.457396
C	-5.779984	-0.989933	-1.517110
C	-3.408796	-1.254642	-1.753709
H	-2.681275	-3.267886	-1.794224
H	-6.918244	-2.800485	-1.341855
H	-6.661700	-0.360780	-1.428878
H	-2.418295	-0.838460	-1.914683
H	-2.448368	-7.560651	-0.580387
H	-6.018348	-4.973701	-1.672611
H	-4.722272	5.846290	-2.120981
H	-0.913845	7.782062	-0.686620
H	7.630163	1.439111	1.790668
H	7.286205	-3.019135	1.187032

Calculation results at DFT-optimized geometry:
Total Energy— -3231.0035049 AU
SCF Convergence— 0.3536E-08
Three lowest frequencies (cm⁻¹): 11.6, 12.3, 15.5

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Experimental (a) and calculated (b) splitting patterns

Control ^1H NMR spectrum (a);
DPFGSENOE subspectrum (b)

Selective excitation of H1/H4

Control ^1H NMR spectrum (a);
DPFGSENOE subspectrum (b)

Selective excitation of H2/H3

^{13}C NMR spectrum in CDCl_3 (a)

Expanded portion of the ^1H - ^{13}C gHMBCAD spectrum (b)

^{13}C NMR spectrum in CDCl_3 (a)

Expanded portion of the ^1H - ^{13}C gHMBCAD spectrum (b)

Expanded portions of the ^1H - ^{13}C gHMBCAD spectrum

One-bond correlations $^1\text{H} - ^{13}\text{C}$
gHSQCAD spectrum

syn-56a

anti-56b

NOESY

^{13}C NMR spectrum in CDCl_3

Adiabatic version of gradient selected

^1H - ^{13}C gHSQCAD spectrum

Observed three bond ($^3J_{\text{HC}}$)
gHMBCAD correlations

Experimental (a) and calculated (b) splitting patterns

Experimental (a) and calculated (b) splitting patterns

(mix = 0.8s, relaxation delay = 2s)

Expanded portions of the NOESY spectrum

Observed key nOe's confirm cyclic structure

Expanded portion of the **NOESY** spectrum

Differentiation of CH₃O groups

One bond correlation ($^1J_{C-H}$)

HETCOR

Expanded portion of the one-bond correlation
($^1J_{CH}$) **HETCOR** spectrum

Key long-range ($^3J_{\text{HC}}$) gHMBCAD correlations
confirm cyclic structure

H25
H7

H12

C4/C14/C17

Adiabatic version of the
gHMBCAD
spectrum

Adiabatic version of gHSQCAD

one-bond correlations

Experimental (a) and calculated (b) splitting patterns
for H12, H13, H15, and H16

Control ^1H NMR spectrum (a)
 1D NOESY (DPFGSENOE) spectrum (b)
 Selective excitation of OCH_3

ROESYAD spectrum (a); expanded of portions of the ROESYAD spectrum (b,c)

¹³C NMR chemical shifts (δ/ppm)

1/4-OCH ₃	55.97
C2/C3	107.11
C5/C10	124.62
C6/C9	135.80
C7/C8	132.45
C11	142.89
C12/C16	127.54
C13/C15	126.03
C14	137.44

One-bond correlations ($^1J_{\text{HC}}$)

gHSQCAD

$^2J_{\text{HC}}$ and $^3J_{\text{HC}}$ gHMBCAD correlations

UV-Vis/Fluorescence Spectra

Spectra a) : UV-vis absorption spectrum of **65** at a concentration of 5×10^{-7} M in degassed CH_2Cl_2 . At absorption maximum $\lambda_{\text{abs}} = 362$ nm, $\epsilon = 5.2 \times 10^4 \text{ M}^{-1} \text{ CM}^{-1}$.

Spectra b): Fluorescence spectrum of **65** at a concentration of 5×10^{-7} M in degassed CH_2Cl_2 upon excitation at 362 nm. Fluorescence maximum $\lambda_{\text{em}} = 512$ nm.

The UV-vis spectrum of **65** in CH_2Cl_2 (5×10^{-7} M) exhibited the absorption maximum (λ_{abs}) at 362 nm with a molecular absorption coefficient (ϵ) of $5.2 \times 10^4 \text{ M}^{-1} \text{ CM}^{-1}$, which lay between that of the parent [9] CPP (340 nm) and [9] CN (378 nm), but much red shifted compared with arene-substituted [9] CPP (310nm, 320nm). However the fluorescence maximum (λ_{em}) was observed at 512 nm, which showed significant red-shift to that of [9] CPP (494 nm), [9] CN (491 nm) and arene-substituted [9] CPP (405 nm, 400 nm).

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ROESY

gHSQCAD ($^1J_{H-C}$)

gHMBCAD ($^3J_{H-C}$)

gHMBCAD ($^3J_{H-C}$)

¹H NMR chemicals shifts (δ/ppm, at -20°C)

¹³C chemical shifts (-20°C)

C1/C1'	150.96
1/1'-OCH ₃	61.80
C2/C2'	133.71
C3/C3'	38.41
C4/C4'	132.72
C5	140.31
C6/C6'	127.66
C7/C7'	125.71
C8	137.78
C9	137.11
C10/C10'	126.61
C11/C11'	127.39
C12	142.53
C13	40.06
C14	126.15
C15	127.61
C16	40.49
C17	130.40
C18	129.70
C19	152.69
19-OCH ₃	61.11
C20	152.58
20-OCH ₃	59.93
C21	142.98
C22/C22'	127.24
C23/C23'	126.36
C24	137.76

¹H NMR spectrum in CDCl₃ (-20°C)

^{13}C NMR spectrum in CDCl_3 (-20°C)

^1H NMR spectra at - 20°C and +25°C

^1H NMR spectrum, Double Resonance at 4.73 ppm, at +25 °C.

¹H NMR spectrum, Double Resonance at 5.24 ppm, at +25 °C.

^1H NMR spectrum, Double Resonance at 6.05 ppm, at +25 °C.

¹H NMR spectrum, Double Resonance at 4.75 ppm, at +60 °C.

^1H NMR spectrum, Double Resonance at 5.21 ppm, at +60 °C.

^1H NMR spectrum, Double Resonance at 6.05 ppm, at +60 °C.

¹H NMR spectrum, Double Resonance at 6.8 ppm, at +60 °C.

NOESY spectrum

at -20°C

Chemical shift assignments of OCH₃ groups

Aromatic portion of the NOESY spectrum (-20°C)

gHMBCAD (+25°C)

gHSQCAD (¹J_{H-C})

gHMBCAD (-20°C)

One bond correlations ---gHSQCAD

Three bond ($^3J_{H-C}$)
correlations confirm
between rings

gHMBCAD
connections

gHSQCAD

gHMBCAD

gHMBCAD correlations

gHMBCAD

(-20°C)

gHMBCAD

(+25°C)

¹³C NMR spectra

-20°C

+25°C

Expanded portions of the ^{13}C NMR spectra

-20°C

+25°C

Expanded portions of the ^{13}C NMR spectra

-20°C

+25°C

gCOSY

Expanded portions of the 2D NMR spectra

Expanded portions of the ROESYAD spectrum

Through space correlations

ROESYAD

Through space correlations

Aromatic region

Expanded portions of the gHSQCAD ($^1J_{\text{HC}}$) spectrum

$^2J_{\text{HC}}$ and $^3J_{\text{HC}}$ HMBC correlations confirm interring linkage

^1H NMR spectrum in C_6D_6

^1H NMR spectrum in C_6D_6 , Double Resonance at 7.16 ppm, at +25 $^\circ\text{C}$

^1H NMR spectrum in C_6D_6 , Double Resonance at 4.68 ppm, at +25 $^\circ\text{C}$

^1H NMR spectrum in C_6D_6 , Double Resonance at 5.28 ppm, at +25 $^\circ\text{C}$

^1H NMR spectrum in C_6D_6 , Double Resonance at 5.34 ppm, at +25 °C

^1H NMR spectrum in C_6D_6 , Double Resonance at 6.88 ppm, at +25 °C

The Crude ^1H NMR Spectrum of Iodination of 106 with ICl

The Crude ^{13}C NMR Spectrum of Iodination of 106 with ICl

The Crude ^1H NMR Spectrum of Iodination of 105 with ICl

The Crude ^{13}C NMR Spectrum of Iodination of 105 with ICl

The Crude ^1H NMR Spectrum of the $\text{Ni}(\text{cod})_2$ -mediated homocoupling reaction with the crude sample from Iodination of 105 with ICl.

Unsymmetrical Quinone

The Crude ^1H NMR Spectrum of $\text{Ni}(\text{cod})_2$ -Mediated Homocoupling Reaction of 110 after Treated with ICl

^1H NMR spectrum in C_6D_6

1D NOESY spectra (b-c)

Expanded portion of the gHSQCAD spectrum

Expanded portion of the ^{13}C NMR spectrum in CD_2Cl_2

Long-range gHMBCAD correlations

**Syntheses and Structures of Functionalized Cycloparaphenylenes and Fused
Cycloparaphenylene Precursors**

Changfeng Huang

**Dissertation submitted to the Eberly College of Arts and Sciences
at West Virginia University in partial fulfillment of the requirements
for the degree of**

Doctor of Philosophy in Organic Chemistry

C. Eugene Bennett Department of Chemistry

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