ACCOUNTS of chemical research

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Syntheses of the Smallest Carbon Nanohoops and the Emergence of Unique Physical Phenomena

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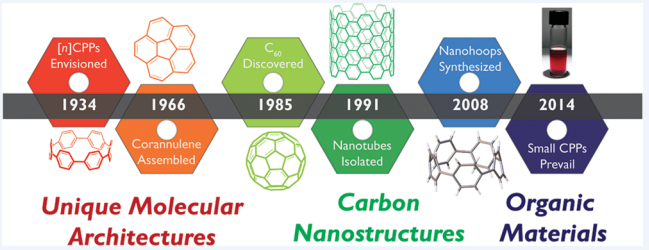
CONSPECTUS: The design and construction of non-natural products have fascinated and perplexed organic chemists for years. Their assembly, akin to what has been accomplished for the total synthesis of natural products, has stretched the limits of what can be prepared in the laboratory. Unlike many natural products, however, carbon-rich structures often lack heteroatoms, further complicating their construction. Consider some of the classical molecules in this genre: cubane and dodecahedrane. While highly symmetric, their assembly is far from trivial. These fascinating hydrocarbon targets have fueled the development of carbon−carbon bond-forming reactions, as new methods are needed to access these types of compounds. Among these carbon-rich structures, polycyclic aromatics such as helicenes, fullerenes, and some fullerenes share common ground due to the distortion of one or more aromatic rings out of planarity. Recently added to this group are the [*n*]cycloparaphenylenes ([*n*]CPPs), "carbon nanohoops". Here, a linear string of benzene rings connected at the para positions is wrapped back upon itself to form a cyclic structure. Clearly a simple linear *p*-oligophenylene cannot be cyclized in this manner without extremely harsh reaction conditions. In order to access these structures using solution-phase organic chemistry, clever synthetic strategies that can compensate for this severe distortion are required.



Although cycloparaphenylenes can be considered the smallest possible fragment of an armchair carbon nanotube (CNT), they were envisioned as synthetic targets long before CNTs were discovered in 1991. CPP synthesis was first attempted in 1934, almost 70 years before Iijima's first report on CNTs. The long-forgotten targets reemerged in 1993 with a report from Vögtle, though he ultimately was unsuccessful in achieving their synthesis. More than a decade later, in 2008, CPPs succumbed to total synthesis by Jasti and Bertozzi, allowing access to three different-sized carbon nanohoops in milligram quantities. Since then, the Jasti group has embraced the smallest CPPs as inspiring synthetic targets, challenging us to develop new methodology to construct increasingly strained macrocycles.

Having recently synthesized [5]-, [6]- and [7]CPP, the three smallest nanohoops synthesized to date, we have been able to realize a variety of new physical phenomena unique to these structures. Perhaps most significantly, unlike linear *p*-phenylenes and inorganic quantum dots, the HOMO−LUMO gaps of the CPPs narrow with decreasing CPP size. The smallest CPPs discussed in this Account illustrate this feature exceptionally well, as their HOMO−LUMO gaps become narrower than those of even the longest *p*-polyphenylenes.

The smaller CPPs are fascinating from a structural standpoint as well because of the high amount of distortion in each benzene ring. From the synthesis of [7]CPP (84 kcal/mol of strain energy) to that of [5]CPP (119 kcal/mol of strain energy), our laboratory has been able to test the boundaries of synthetic and physical organic chemistry. In this Account, we detail how these challenging macrocycles were synthesized and the unique properties these structures possess.

INTRODUCTION

Aesthetically pleasing molecules have long captivated the interests of synthetic chemists.[1] Such targets, often displaying high degrees of symmetry, push the limits of organic synthesis despite their apparently simple structures.[2] In the transformation of complex intermediates into the striking Platonic hydrocarbons cubane[3] and dodecahedrane[4] (Figure 1), new boundaries were established for the assembly of molecules with atomic-level precision. Like many classical natural products targeted throughout the mid-to-late 1900s,[5−7] these geometric beauties highlighted that our imagination is truly the only limit to what is available via organic synthesis.[8] The pursuit of structurally unique *non-natural* products has driven the discovery of novel reactions and methodology and, perhaps most importantly, opened the door to molecules with new properties.

Several aromatics, prized for their distortion from planarity and targeted by organic chemists, fall into this category as well. The [*n*]cycloparaphenylenes ([*n*]CPPs),[9−11] composed of benzene rings linked at the para positions end-to-end, exemplify the challenges faced when targeting highly strained molecules. Although initially probed in the 1930s (vide infra),[12] these perplexing macrocycles did not succumb to total synthesis until

Received: November 25, 2014
Published: February 17, 2015

DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566

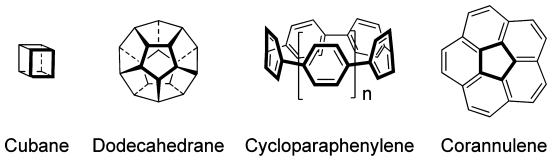


Figure 1. Challenging hydrocarbons that have been tackled by organic synthesis.

recent years.[13] Over 30 years after [*n*]CPPs were first explored, the synthesis of bowl-shaped corannulene[14−16] marked yet another milestone. Unbeknownst to scientists at the time, these two targets would later gain additional accolades as fundamental fragments of carbon nanotubes (CNTs)[17,18] and buckminsterfullerene (C_{60}),[19,20] respectively. Interestingly, it was not until the late 1980s and early 1990s, decades after the aforementioned synthetic endeavors, that these carbon allotropes were actually discovered.[17,19] Hence, the recent resurgence of these classical structures has been fueled by the prospect of a "bottom-up" organic synthesis of uniform carbon nanostructures (Figure 1).[9,10,21−25] What started as a quest to stretch the confines of synthesis has led us into a fascinating region of science—the merger of organic synthesis and materials science.[26]

As an initial foray into [*n*]CPP chemistry, Parekh and Guha first reported the synthesis of macrocyclic *p*,*p*′-diphenylene disulfide (**1**) in 1934.[12] Unfortunately, heating with copper led only to partially desulfurized compounds rather than the strained target molecule [2]cycloparaphenylene (Figure 2a, **2**). Setting their sights on less-strained macrocycles, Vögtle and coworkers proposed several more targets nearly 60 years later.[27] Analogous to the methodology pursued by Parekh and Guha, pyrolysis of aryl sulfide macrocycle **3** also failed to furnish any [6]CPP (Figure 2b). In addition, Vögtle attempted a Cu-mediated Kumada macrocyclization of *syn*-1,4-diarylcyclohexane **4** and a Wittig macrocyclization between diphosphonium **5** and dialdehyde **6**. While the former reaction led only to polymeric byproducts (Figure 2c),[28] the latter afforded the desired ene−yne macrocycle **7** (Figure 2d). Unfortunately, intermolecular Diels−Alder reactions with **7** to access [*n*]CPPs were ineffective. Although conversion of **8** to [5]CPP precursor **9** was detected by mass spectrometry (Figure 2e),[27] no successful dehydrogenation conditions of **9** were reported. Although elegant synthetic strategies had been developed to access a "picotube"[29,30] and cyclophenacene,[31,32] as of 2008 the synthesis of the [*n*]cycloparaphenylenes was still an unsolved problem.[33]

With hopes of completing the first successful [*n*]CPP synthesis over 70 years after the seminal attempt, Jasti and Bertozzi targeted macrocycles containing 1,4-*syn*-dimethoxy-2,5-cyclohexadiene units[34] as masked aromatic rings. Lithium−halogen exchange with *p*-diiodobenzene followed by a twofold nucleophilic addition reaction with 1,4-benzoquinone (1,4-BQ) allowed the facile construction of *syn*-cyclohexadiene moiety **10**. Borylation of a portion of this material generated **11**, the necessary partner for the subsequent macrocyclization. Under Suzuki−Miyuara cross-coupling conditions, macrocycles **12**−**14** were generated, albeit unselectively and in low yields (Scheme 1).

As in Vögtle's "shotgun" approach,[27] while intermolecular coupling to form linear oligomeric byproducts dominated, high dilution and the rigid geometry (i.e., fewer degrees of freedom) of the initial "building blocks" resulted in a small amount of the desired intramolecular closure product. Advantageously, the carbon framework was established in just four steps.

Conversion of macrocycles **12**−**14** to their corresponding cycloparaphenylenes proved challenging because of the high strain energy that needed to be overcome as well as the propensity for these systems to undergo molecular rearrangements. Following precedents for aromatization of similar systems, reductive conditions such as Stephen's reagent and low-valent titanium were extensively screened but failed to furnish [*n*]CPPs.[35] Under these conditions, formation of carbocation **15** followed by a rapid concomitant aryl shift to give **16** ultimately produces undesired meta-substituted **17** (Scheme 2). The formation of [*n*]CPPs was finally achieved in modest yield by treating **12**−**14** with lithium naphthalide at −78 °C.[36] Single-electron reduction of a C−O bond, presumably to form radical **18**, followed by a second reduction event leaves the penultimate intermediate **19** in the correct oxidation state for the final elimination of lithium methoxide (Scheme 2). Impressively under these low-temperature

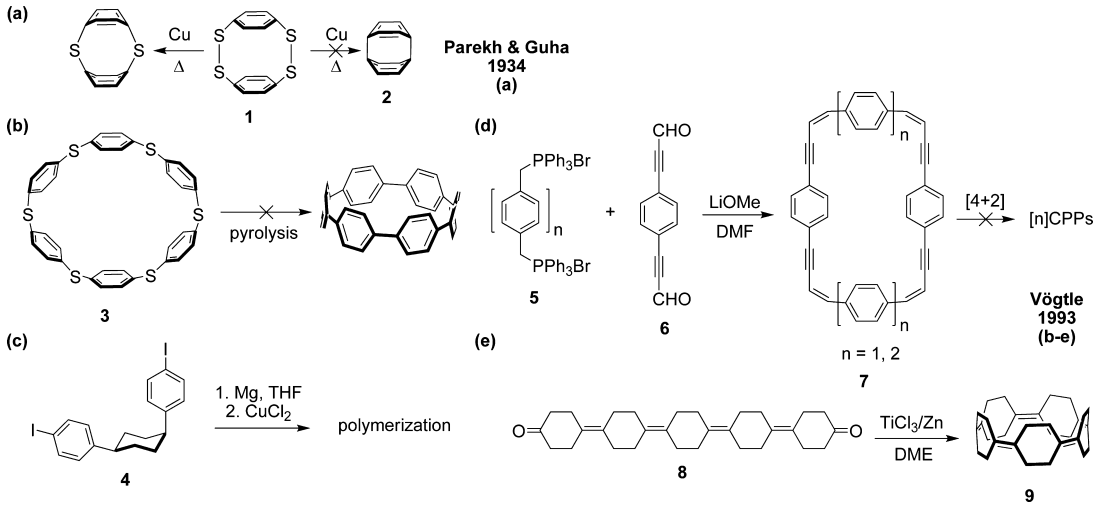
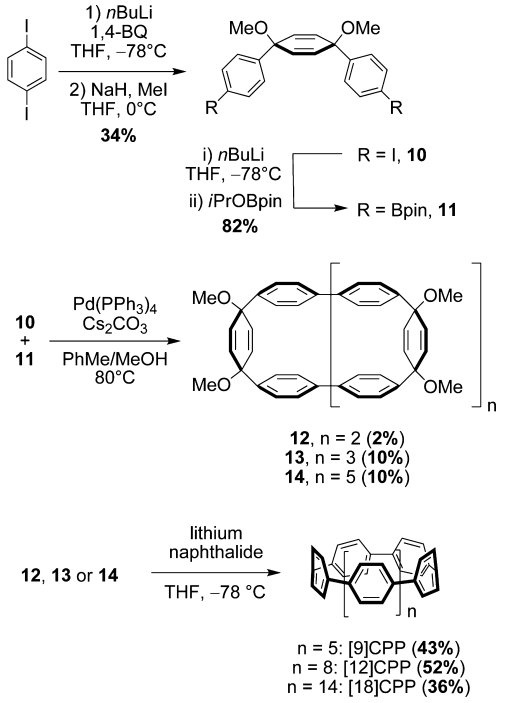


Figure 2. (a) Parekh and Guha's attempts toward [2]cycloparaphenylene (**2**). (b) Attempted pyrolysis of macrocyclic aryl sulfide **3** to obtain [6]cycloparaphenylene. (c) Attempted "shotgun" Kumada macrocyclization of diiodide **4**. (d) "Shotgun" Wittig macrocyclization reaction followed by failed intermolecular Diels−Alder reaction. (e) Intramolecular McMurry coupling of dione **8** to provide trace amounts of macrocycle **9**.

DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566

Scheme 1. Synthesis of [9]-, [12]-, and [18]CPP by Jasti and Bertozzi



conditions, highly strained [9]CPP can be accessed, as well as [12]- and [18]CPP.[13,37] With these molecules in hand for the first time, the structures were characterized using UV–vis and fluorescence spectroscopy. Surprisingly, these three CPPs had virtually identical absorption maxima, but their fluorescence maxima red-shifted with decreasing size. Preliminary computational studies indicated that the HOMO–LUMO gap of the CPPs narrowed with decreasing size, exactly opposite to what is expected for linear *p*-phenylenes.[38,39] Clearly, the novel architecture of these structures led to optoelectronic properties that were unique and as of yet unexplored.

Since this pivotal report in 2008,[13] our group[40−47] and the groups of Itami[48,49] and Yamago[37,50,51] have made significant contributions to cycloparaphenylene research. In 2009, the Itami group reported the first selective synthesis of [12]CPP.[52] Shortly thereafter, in 2010, Yamago synthesized the smallest CPP at the time: [8]CPP.[50] In a follow-up paper, Yamago and co-workers prepared [8]–[13]CPP and characterized these structures electrochemically.[37] These experimental results corroborated the computational results indicating that smaller CPPs have narrower HOMO–LUMO gaps. Moreover, computational results indicated that CPPs have narrower band gaps than even the very longest linear paraphenylenes, rendering them as new motifs in conjugated materials (Figure 3a). Dramatic electronic structural changes from benzenoid to

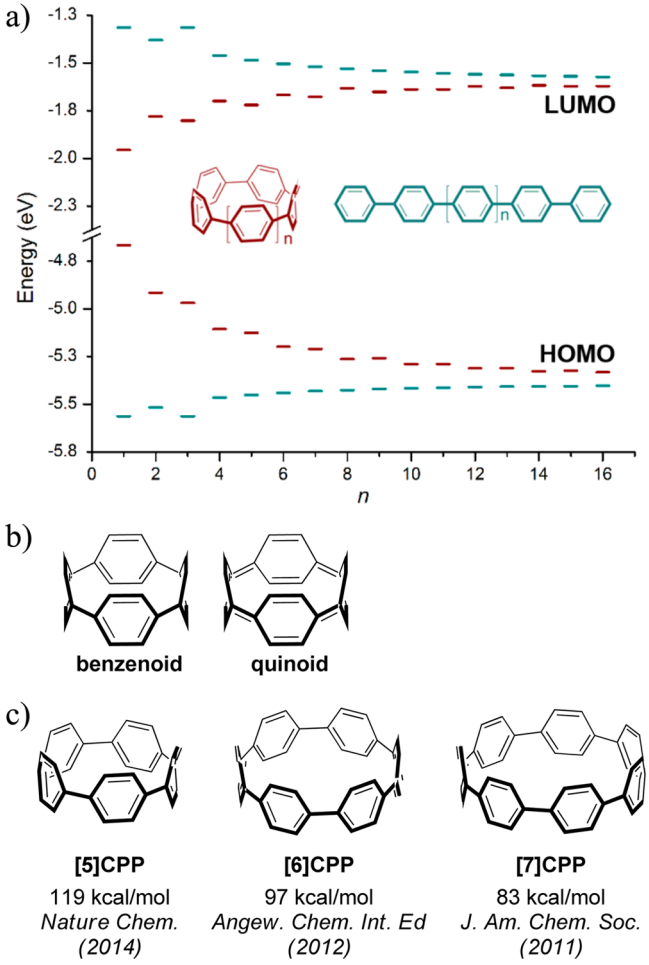
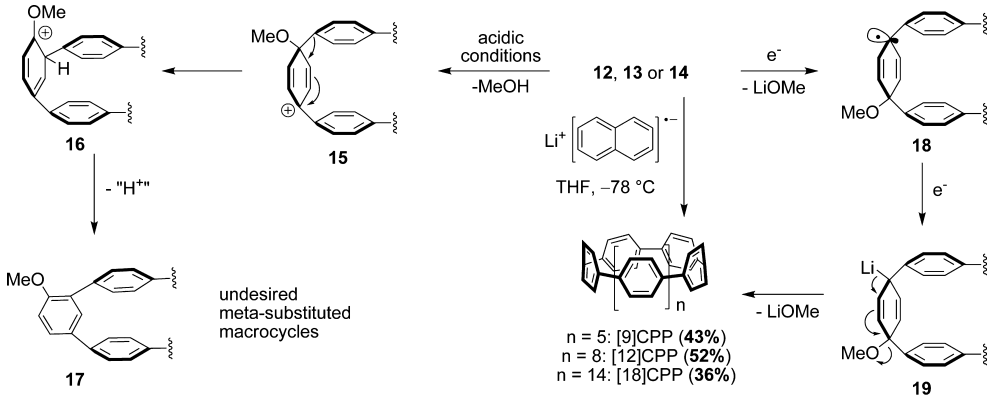


Figure 3. (a) Calculated HOMO and LUMO levels of cyclic (red) and acyclic (blue) p-phenylenes (B3LYP/6-31G*).[37] (b) Benzenoid and quinoid electronic structures of [4]CPP. (c) Strained macrocycles accessed by the Jasti laboratory in recent years.

Scheme 2. Reductive Aromatization Mechanism and Potential Decomposition Pathway



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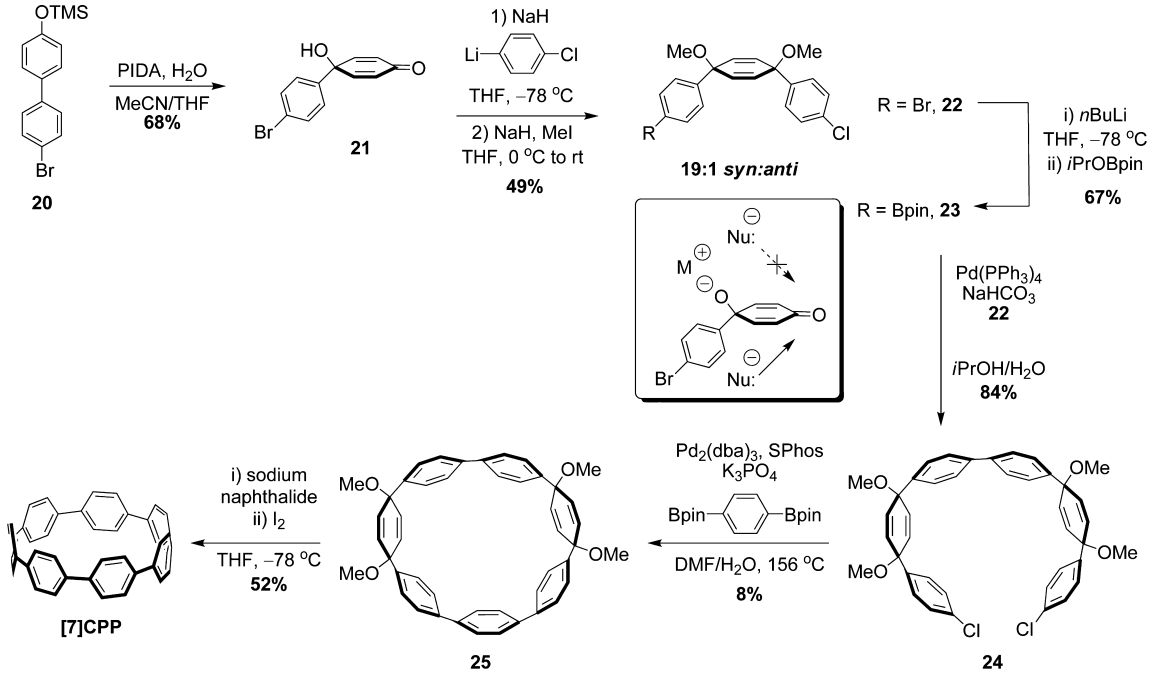
Scheme 3. Synthesis of [7]Cycloparaphenylene



quinoid were also predicted computationally for the smaller CPPs, whereby either [5]-[53] or [6]CPP[38,54] was foreseen as the "turning point" (Figure 3b). To further explore these hypotheses and glean insight into the behavior of the smaller [*n*]CPPs, we set out to apply our synthetic prowess to these challenging macrocyclic targets (Figure 3c).[55,56] In particular, [5]−[7]CPP not only represented extremely challenging synthetic targets but also would help address the new phenomena that were predicted and observed for these new carbon nanohoops.[40,43,47]

[7]CYCLOPARAPHENYLENE

In order to access [7]CPP, we aimed to incorporate some pivotal aspects of the original Jasti and Bertozzi synthesis, namely, the use of appropriately substituted cyclohexadiene rings to alleviate strain during a key macrocyclization step and a reductive aromatization reaction to unveil the hidden aromatic structure in the cyclohexadiene moieties. Modification of both the construction and reactivity of these cyclohexadiene-based monomeric units, however, was essential to our approach. Oxidative dearomatization of biphenyl **20** using aqueous phenyliodine(III) diacetate afforded quinol **21**, which allowed for the synthesis of unsymmetric monomeric unit **22** via the nucleophilic addition of (4-chlorophenyl)lithium (Scheme 3). Unlike the twofold nucleophilic additions employed by Jasti in 2008,[13] we designed a system that overwhelmingly favors the syn isomer over the anti isomer as a result of electrostatic control of the incoming anionic nucleophile.[57] Deprotonation of **21** with sodium hydride led to the greatest stereoselectivity (>19:1) via a sodium alkoxide. The selectivity was diminished (13:1), however, when the reaction proceeded through a lithium alkoxide upon the addition of excess aryllithium reagent. Low selectivity (3:1) was observed upon methylation of **21**, further supporting our hypothesis of electrostatic control (Scheme 3 inset). Thus, the more ionic the O−R bond is, the less favorable the approach of the nucleophile to the same face as the oxygen becomes (NaO > LiO > MeO).

With unsymmetric **22** in hand, a portion of the material was borylated via lithium−halogen exchange conditions followed by an (isopropoxy)pinacolborane quench to afford **23**. As aryl chlorides do not undergo lithium−halogen exchange under these conditions, the aryl bromide was able to be selectively transformed. After both coupling partners **22** and **23** had been accessed, a Suzuki−Miyuara cross-coupling reaction employing $Pd(PPh_3)_4$ allowed us to access the advanced dichloride intermediate **24**. Importantly, the aryl chlorides remained intact under these catalytic conditions, reinforcing the orthogonality we sought in this synthesis. Switching to a more reactive, electron-deficient catalyst system (Pd−SPhos[58]) allowed for facile oxidative insertion into the aryl chloride bonds, setting us up for the key macrocyclization step with 1,4-benzenediboronic acid bis(pinacol) ester as the coupling partner. Despite only an 8% isolated yield of macrocycle **25** upon building in 16 kcal/mol of strain energy, we were finally in a position to test the limits of our reductive aromatization conditions. To our delight, treatment of **25** with sodium naphthalide afforded [7]CPP as an orange solid in 52% yield. Impressively, the reaction was able to build in 67 kcal/mol of strain at −78 °C, allowing us to construct the smallest [*n*]CPP known at the time in 0.72% overall yield from **20** (Scheme 3).

In accordance with all other [*n*]CPPs, [7]CPP exhibits a major optical transition at 339 nm due to a combination of HOMO−1 → LUMO and HOMO → LUMO+1 transitions. The HOMO → LUMO transition is barely visible with a weak absorption at 410 nm, while the maximum emission shifts to 592 nm. Concurrent with the red shift in the emission is a dramatic decrease in quantum yield: [12]CPP has a quantum yield of 0.81, while those of [8]CPP and [7]CPP are 0.10 and 0.007, respectively. Interestingly, despite the decrease in quantum efficiency, [7]- and [8]CPP have similar molar extinction coefficients (Figure 4). This dramatic effect on the emission wavelength and quantum yield gives experimental support for size-dependent structural changes, such as increased planarization to relieve excited-state strain[59] and electronic

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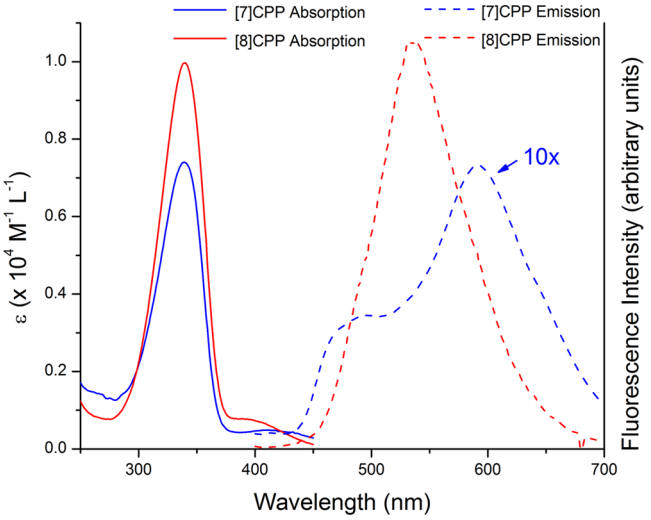


Figure 4. Absorption and emission spectra of [7]- and [8]CPP. It should be noted that while [7]CPP is a much weaker emitter than [8]CPP, its emission spectrum has been enhanced 10-fold to allow all of the features to be shown at an appropriate scale.

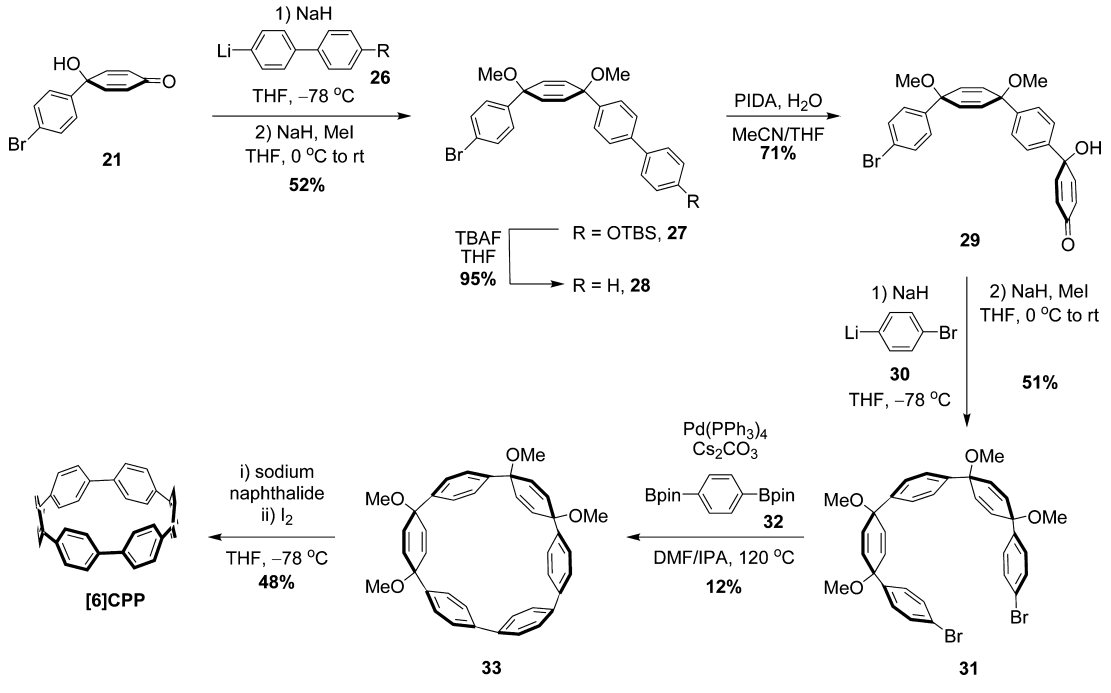
effects such as vibronic coupling[60] and exciton localization.[61] Electrochemical measurements in tetrahydrofuran revealed an $E^{ox}_{1/2}$ of 0.53 V vs Fc/Fc^+ and an $E^{red}_{1/2}$ of −2.57 V vs Fc/Fc^+,[62] which is consistent with the predicted trend of a narrowing HOMO−LUMO gap with decreasing [*n*]CPP size.[37] Intrigued with our initial findings, we sought to determine whether the syntheses of [6]- and [5]CPP would shine additional light on these phenomena.

[6]CYCLOPARAPHENYLENE

With the synthesis of [7]cycloparaphenylene accomplished, we next set out to test the limits of our synthetic tactics. At the time, no other syntheses of [7]CPP,[63] let alone smaller, more challenging targets, had been reported in the literature. Our initial strategy toward [6]CPP, encompassing 97 kcal/mol of strain (4.9 kcal/mol per benzene ring greater than that of [7]CPP),[37,43] first involved replacing the biphenyl unit with a phenyl unit in [7]CPP macrocyclic precursor **25**. In doing so, target macrocycle **33** appeared, at least at first glance, to be more suitable for the geometric constraints necessary to access [6]CPP. Thus, our route commenced with a stereoselective addition of lithiated biphenyl **26** to quinol **21**. Desilylation of TBS-protected phenol **27** followed by oxidative dearomatization of **28** with aqueous $PhI(OAc)_2$ afforded highly functionalized quinol **29**. Subsequent addition of lithiated arene **30** led to the five-ring macrocylic precursor **31** containing alternating arene and cyclohexadiene units. Gratifyingly, a Suzuki−Miyaura macrocyclization reaction implementing $Pd(PPh_3)_4$ as the catalyst and 1,4-benzenediboronic acid bis(pinacol) ester (**32**) as the coupling partner furnished macrocycle **33** in 12% yield. Reductive aromatization of this strained macrocycle with sodium naphthalide, as in our [7]CPP synthesis, gave the target cycloparaphenylene as an orange solid in 48% yield (Scheme 4). Before the fascinating properties of [6]CPP are addressed, it is worth noting that advanced intermediate **31** has become a staple compound in our laboratory and was recently used for the first gram-scale syntheses of [8]- and [10]CPP.[42] In doing so, our lab recently has accessed dimeric,[44] anionic,[64] and cationic[46] [8]CPP analogues.

In comparisons of [6]CPP with larger carbon nanohoops, there are several anomalous physical features that immediately stand out. Most notably, unlike any of the other [*n*]CPPs that were synthesized previously,[45] [6]CPP had no detectable fluorescence. As [7]CPP showed a dramatic reduction in quantum efficiency, we were not surprised with the continuing trend and hence the isolation of the first nonemitting cycloparaphenylene. Our findings were supported by time-dependent density functional theory calculations that assigned no oscillator strength[65] (f = 0) to the HOMO → LUMO

Scheme 4. Synthesis of [6]Cycloparaphenylene



DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566

transition.[43] The $E^{ox}_{1/2}$ of [6]CPP in dichloromethane was shown to be 0.44 V vs Fc/Fc^+, which followed in accordance with preceding work suggesting an increasing HOMO level, leading to a more facile oxidation, with decreasing nanohoop diameter. The single ^1H NMR resonance 0.16 ppm *downfield* of that observed in the case of [7]CPP (δ = 7.64 vs 7.48 ppm, respectively) further confirmed Wong's nucleus-independent chemical shift (NICS(1)) calculations[38] predicting an increase in quinoidal character (i.e., a decrease in aromaticity) per individual benzene ring in [*n*]CPPs smaller than [8]CPP. Intrigued by these solution-state results, we turned our attention to the unique behavior of [6]CPP in the crystalline state.

As in larger [*n*]CPPs, the average length of 1.490 Å for the $C_{ipso}-C_{ipso}$ bonds adjoining adjacent benzene rings in [6]CPP[43] (compared with 1.488 Å in [7]CPP[63] and 1.486 Å in [8]CPP[42]) indicates a benzenoid structure with retained single-bond character.[38,53−55] The crystal packing, however, is completely unprecedented in the [*n*]CPP literature (Figure 5).

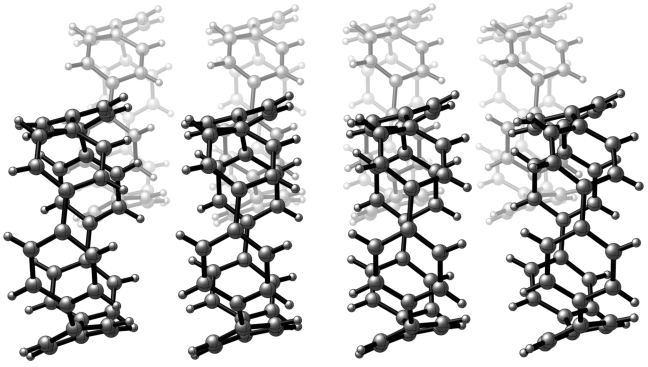


Figure 5. ORTEP drawing of [6]cycloparaphenylene (thermal ellipsoids shown at 50% probability) showing the tubular packing structure of the nanohoops in the solid state.

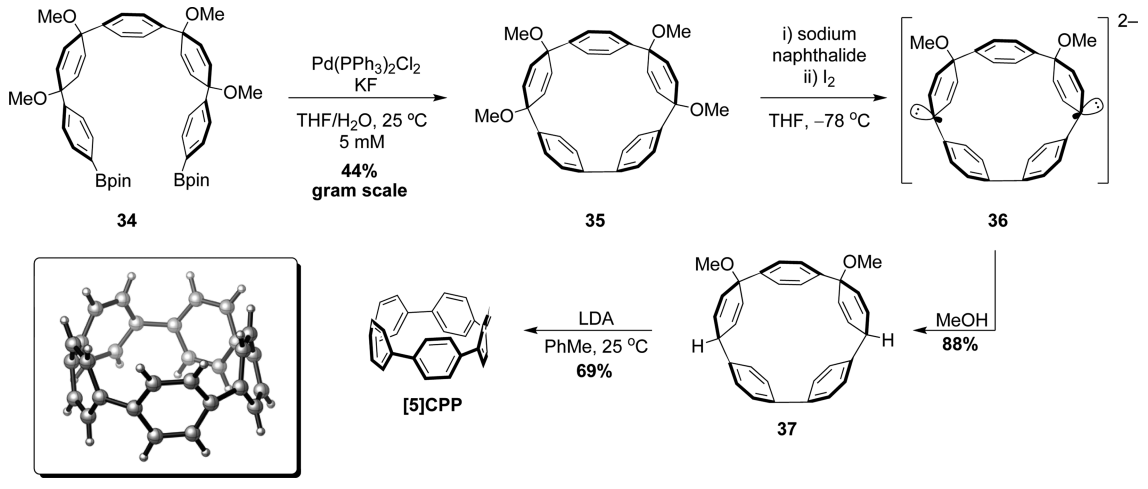
While [7]−[10]- and [12]CPP exhibit herringbone or herringbone-like packing,[42,63,66−68] [6]CPP organizes into uniform, tubular cylinders in the solid state. The predisposition for [6]CPP molecules to arrange themselves akin to how one might imagine the self-assembly of a (6,6) armchair CNT bodes well for the "bottom-up" synthesis of homogeneous carbon nanotubes and exploration of [*n*]CPP reactivity in the crystalline state. Furthermore, the uniform channels formed by [6]CPP ought to play a significant role in guest−host applications. However, we wondered whether these features are unique to [6]CPP or might be even more pronounced in smaller nanohoops. To assess these questions experimentally, our efforts naturally turned toward the synthesis of [5]CPP.

[5]CYCLOPARAPHENYLENE

Our initial foray toward accessing [5]CPP, a target with 119 kcal/mol of strain energy (23.8 kcal/mol per phenyl ring), involved a serendipitous discovery upon repetition of our synthetic route for [10]CPP.[42] Isolation of small amounts of a compound with a distinct singlet in its ^1H NMR spectrum (δ = 6.00 ppm) along with shifts similar to those previously observed in other [*n*]CPP macrocyclic precursors prompted us to pursue the identity of this byproduct. Through mass spectrometry and X-ray crystallography, we were astonished to discover that this structure was neither a linear oligomer nor a larger macrocyclic compound but rather compound **35**, the macrocyclic precursor to [5]CPP. We rationalized its formation through intramolecular boronate homocoupling of **34**, a typically undesired oxidative byproduct of Suzuki−Miyuara cross-coupling reactions. In this instance, however, we chose to exploit facile and mild carbon−carbon bond construction methodology[69] to optimize the synthesis of **35** en route to [5]CPP.

Thus, treatment of **34**, a precursor in our selective syntheses of [8]- and [10]CPP that is easily accessed via dibromide **31**,[42] with potassium fluoride and bis(triphenylphosphine)palladium-(II) dichloride under air at room temperature afforded macrocycle **35** in 44% yield on a gram scale (Scheme 5). Here we were in a position yet again to test the limits of our reductive aromatization chemistry. To our surprise, treatment of **35** with sodium naphthalide at −78 °C effected its reduction to dianion **36**, but in this case the dianion was unable to undergo twofold elimination to afford [5]CPP. We anticipate that there was insufficient energy at this temperature to build in the remaining 87 kcal/mol of strain energy, as no more than 67 kcal/mol of strain energy had previously been overcome using this methodology.[40,43,45] Warming above −78 °C led to decomposition, as evidenced by the precipitation of insoluble brown material. Clearly having reached the limits of our

Scheme 5. Synthesis of [5]Cycloparaphenylene



DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566

reductive aromatization reaction, we instead trapped **36** with a proton source to give reduced macrocycle **37**. Finally, treatment of **37** with lithium diisopropylamide (LDA) at room temperature cleanly generated deep-red [5]CPP in 69% yield via twofold E1cB elimination (Scheme 5).[47] Yamago and co-workers also recently accessed a cyclohexadiene-incorporated macrocycle similar to **35** through intramolecular Yamamoto coupling of **31**.[70] Using modified reductive aromatization methodology ultimately allowed them to isolate [5]CPP also. Counterintuitively, [5]CPP, the smallest and most strained [*n*]CPP reported to date, is now the easiest carbon nanohoop for our laboratory to access, offering mild macrocyclization conditions without exclusion of oxygen and no steps that require heating above room temperature.

Upon analysis of [5]CPP's solid-state structure (Scheme 5 inset), we were surprised to find that [5]CPP does not pack into uniform cylinders as [6]CPP does. Rather, it adopts the herringbone packing structure observed for other reported [*n*]CPPs (*n* = 7−10, 12),[42,63,66−68] further piquing our curiosity about [6]CPP's unique behavior. Compared with the structure of [6]CPP, what truly stood out was the increased amount of distortion experienced by each benzene ring throughout the nanohoop (Table 1). The para carbons at each tertiary center are displaced by an average of 15.6° from planarity, which is more than that of the lone bent aromatic ring encountered in several natural products.[47,71,72] The distortion found in the benzene rings of [5]CPP is trumped, however, by those in the single phenyl ring of several paracyclophanes[73−75] and the pyrene moieties of [9](2,7)pyrenophane and 1,7-dioxa[7](2,7)pyreneophanes.[76,77] In addition, several other cyclophanes have been predicted computationally to have highly distorted aromatic rings, though the crystal structures of these compounds have not been obtained.[78,79]

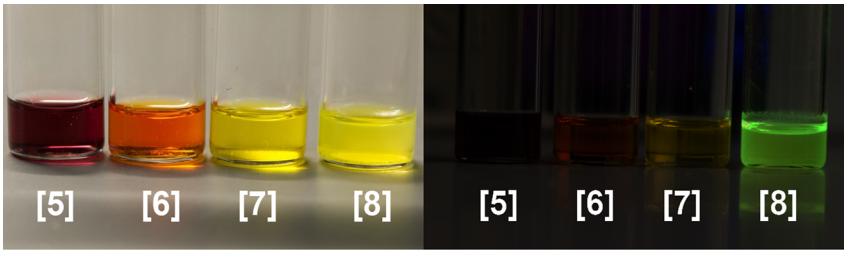
Table 1. Deviations of Benzene Rings from Planarity (α) Seen in Various Organic Targets As Determined by Crystal Structure Analysis

molecule	α (deg)
cavicularin[72]	7.9
[6]CPP[43]	12.7
haouamine A[71]	13.6
[5]CPP[47]	15.6
3-carboxy[7]paracyclophane[74]	16.8
8-carboxy[6]paracyclophane[73]	20.5
substituted [1.1]paracyclophane[75]	25

The outstanding solubility of [5]CPP compared with other cycloparaphenylenes permitted extensive solution-state characterization, providing initial insight into the newest member of the [*n*]CPP family. As was observed in the case of [6]CPP, the ^{1}H NMR spectrum of [5]CPP also shows a single resonance, which is consistent with free rotation or wobbling of the phenyl rings on the NMR time scale. Furthermore, the chemical shift of [5]CPP (δ = 7.86 ppm) is 0.24 ppm downfield from that observed for [6]CPP (δ = 7.64 ppm), providing further experimental evidence for the decrease in aromaticity seen with the smaller cycloparaphenylenes.[38] Electrochemical analysis in tetrahydrofuran revealed two quasi-reversible single-electron oxidation and reduction events ($E^{ox}_{1/2}$ = 0.25 and 0.46 V vs Fc/Fc$^+$; $E^{red}_{1/2}$ = −2.27 and 2.55 V vs Fc/Fc$^+$), rendering it the easiest [*n*]CPP to oxidize and reduce. [5]CPP is the first nanohoop that, under the experimental electrochemical conditions, showed a second oxidation wave in the solvent window. The narrowing HOMO−LUMO gap is consistent with computational data[37] and is made even more evident by the weak absorption at 502 nm. This absorption, approximately 25 nm lower in energy than that of [6]CPP,[43] again has a small oscillator strength,[65] which is responsible for the fact that [5]CPP does not have any visible fluorescence. When [5]CPP is put side-by-side with [6]−[8]CPP, the red-shifted visible absorption of the smaller CPPs becomes quite apparent (Figure 6 left). Additionally, their diminishing quantum yields are obvious under ultraviolet irradiation at 365 nm (Figure 6 right). With our ability to rapidly advance the synthesis and characterization of these highly strained hydrocarbon macrocycles, a provocative question is whether [4]CPP is accessible via organic synthesis.

CONCLUSION AND OUTLOOK

In this Account, we have summarized our strategies to access [5]−[7]CPP. By tackling these organic structures as synthetic chemists, we have developed strategies to overcome tremendous amounts of molecular strain, leaving us with startlingly distorted benzene rings strung together systematically in a nanohoop. Alongside cubane, dodecahedrane, and corannulene,



	[5]CPP	[6]CPP	[7]CPP	[8]CPP
λ_{max} =	335 nm	338 nm	339 nm	340 nm
$E^{ox}_{1/2}$ =	0.25 V, 0.46 V	0.44 V	0.53 V	0.59 V
$E^{red}_{1/2}$ =	−2.27 V, −2.55 V	not reported	−2.57 V	not reported
^{1}H δ =	7.86 ppm	7.64 ppm	7.48 ppm	7.48 ppm
Strain/phenyl ring =	23.8 kcal/mol	16.2 kcal/mol	11.9 kcal/mol	9.18 kcal/mol

Figure 6. [5]−[8]Cycloparaphenylene under (left) ambient light and (right) UV irradiation, along with a summary of selected data.[37,40,43,47,62]

DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566

now these small [*n*]CPPs can be added to the family of fascinating carbon-rich structures that have succumbed to total synthesis. Aside from their prospects to function as templates for the rational "bottom-up" synthesis of homogeneous armchair carbon nanotubes,[24,80−82] much promise lies in their ability to function as stand-alone materials. In view of their fascinating size-dependent optoelectronic properties, reports of the implementation of cycloparaphenylenes as organic semiconductors and sensors will surely follow. In addition, their radially oriented π orbitals make them ideal candidates for applications in a multitude of supramolecular interactions.[42,83] Reports of novel [*n*]CPPs and their derivatives, as well as their inclusion into devices, will follow in due course.

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Notes

The authors declare no competing financial interest.

Biographies

Matthew R. Golder was born in Natick, Massachusetts, in 1988. He received a B.S. degree from the University of Rochester in 2010 under the tutelage of Professor Patrick Holland and was a visiting student in Professor Stefan Hecht's laboratory at HU Berlin. After receiving an M.A. from Boston University in 2014, he moved to the University of Oregon and is currently a Ph.D. student with Professor Ramesh Jasti. His current research interests are focused on the synthesis and characterization of cycloparaphenylenes and related carbon-rich nanostructures.

Ramesh Jasti was born in Concord, North Carolina, in 1975. He attended the University of North Carolina at Chapel Hill as an undergraduate, working under Professor Royce Murray. He conducted his graduate education under the guidance of Professor Scott Rychnovsky at the University of California, Irvine, where his research unraveled numerous mechanistic aspects of the Prins cyclization reaction. After obtaining his Ph.D. in 2006, he started as a postdoctoral fellow at the Lawrence Berkeley National Laboratory with Professor Carolyn Bertozzi, attacking problems in nanoscience utilizing organic synthesis as an enabling tool. He began as an Assistant Professor at Boston University in 2009 and moved to the University of Oregon as an Associate Professor in 2014. Representative awards include the NSF CAREER Award, the Alfred P. Sloan Fellowship, and the Camille Dreyfus Teacher-Scholar Award.

ACKNOWLEDGMENTS

We gratefully acknowledge all members of the Jasti Laboratory, both past and present, for their significant contributions to the work discussed in this Account. This work was supported by funding from the NSF (CHE-1255219), the Sloan Foundation, the Camille and Henry Dreyfus Foundation, the University of Oregon, and Boston University. M.R.G. thanks Vertex Pharmaceuticals for a graduate research fellowship.

REFERENCES

(1) Hoffmann, R. Molecular Beauty. *J. Aesthetics Art Criticism* **1990**, *48*, 191−204.

(2) Hoffmann, R.; Hopf, H. Learning from Molecules in Distress. *Angew. Chem., Int. Ed.* **2008**, *47*, 4474−4481.

(3) Eaton, P. E.; Cole, T. W. The Cubane System. *J. Am. Chem. Soc.* **1964**, *86*, 962−964.

(4) Paquette, L. A.; Ternansky, R. J.; Balogh, D. W.; Kentgen, G. Total synthesis of dodecahedrane. *J. Am. Chem. Soc.* **1983**, *105*, 5446−5450.

(5) Woodward, R. B.; Cava, M. P.; Ollis, W. D.; Hunger, A.; Daeniker, H. U.; Schenker, K. The Total Synthesis of Styrchnine. *J. Am. Chem. Soc.* **1954**, *76*, 4749−4751.

(6) Eschenmoser, A.; Wintner, C. Natural product synthesis and vitamin B_{12}. *Science* **1977**, *196*, 1410−1420.

(7) Nicolaou, K. C.; Petasis, N. A.; Zipkin, R. E. The endiandric acid cascade. Electrocyclizations in organic synthesis. 4. "Biomimetic" approach to endiandric acids A−G. Total synthesis and thermal studies. *J. Am. Chem. Soc.* **1982**, *104*, 5560−5562.

(8) Trauner, D. Finding function and form. *Nat. Prod. Rep.* **2014**, *31*, 411−413.

(9) Jasti, R.; Bertozzi, C. R. Progress and challenges for the bottom-up synthesis of carbon nanotubes with discrete chirality. *Chem. Phys. Lett.* **2010**, *494*, 1−7.

(10) Tian, X.; Jasti, R., Synthesis of Cycloparaphenylenes: The Shortest-Possible Segments of Armchair Carbon Nanotubes. In *Fragments of Fullerenes and Carbon Nanotubes: Designed Synthesis, Unusual Reactions, and Coordination Chemistry*; Petrukhina, M. A., Scott, L. T., Eds.; Wiley: Hoboken, NJ, 2011.

(11) Hirst, E. S.; Jasti, R. Bending Benzene: Syntheses of [*n*]Cycloparaphenylenes. *J. Org. Chem.* **2012**, *77*, 10473−10478.

(12) Parekh, V. C.; Guha, P. C. Synthesis of *p,p′*-diphenylene disulfide. *J. Indian Chem. Soc.* **1934**, *11*, 95−100.

(13) Jasti, R.; Chattacharjee, J.; Neaton, J. B.; Bertozzi, C. R. Synthesis, Characterization, and Theory of [9]-, [12]-, and [18]-Cycloparaphenylene: Carbon Nanohoop Structures. *J. Am. Chem. Soc.* **2008**, *130*, 17646−17647.

(14) Barth, W. E.; Lawton, R. G. Dibenzo[*ghi,mno*]fluoranthene. *J. Am. Chem. Soc.* **1966**, *88*, 380−381.

(15) Lawton, R. G.; Barth, W. E. Synthesis of corannulene. *J. Am. Chem. Soc.* **1971**, *93*, 1730−1745.

(16) For more recent syntheses of corannulene, see: (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. Corannulene. A convenient new synthesis. *J. Am. Chem. Soc.* **1991**, *113*, 7082−7084. (b) Butterfield, A. M.; Bruno, G.; Siegel, J. S. Kilogram-Scale Production of Corannulene. *Org. Process Res. Dev.* **2012**, *16*, 664−676.

(17) Iijima, S. Helical microtubulues of graphitic carbon. *Nature* **1991**, *354*, 56−58.

(18) Prasek, J.; Drbohlavova, J.; Chomoucka, J.; Hubalek, J.; Jasek, O.; Adam, V.; Kizek, R. Methods for carbon nanotubes synthesis—Review. *J. Mater. Chem.* **2011**, *21*, 15872−15884.

(19) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. C_{60}: Buckminsterfullerene. *Nature* **1985**, *318*, 162−163.

(20) Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. A Rational Chemical Synthesis of C_{60}. *Science* **2002**, *295*, 1500−1503.

(21) Tsefrikas, V. M.; Scott, L. T. Geodesic Polyarenes by Flash Vacuum Pyrolysis. *Chem. Rev.* **2006**, *106*, 4868−4884.

(22) Scott, L. T. Polycyclic Aromatic Hydrocarbon Bowls, Baskets, Balls, and Tubes: Challenging Targets for Chemical Synthesis. *Polycyclic Aromat. Compd.* **2010**, *30*, 247−259.

(23) Steinberg, B.; Scott, L. New strategies for synthesizing short sections of carbon nanotubes. *Angew. Chem., Int. Ed.* **2009**, *48*, 5400−5402.

(24) Scott, L. T. Conjugated Belts and Nanorings with Radially Oriented p Orbitals. *Angew. Chem., Int. Ed.* **2003**, *42*, 4133−4135.

(25) For related work on the "bottom-up" synthesis of nanographene, see: (a) Yang, X.; Dou, X.; Rouhanipour, A.; Zhi, L.; Räder, H. J.; Müllen, K. Two-Dimensional Graphene Nanoribbons. *J. Am. Chem. Soc.* **2008**, *130*, 4216−4217. (b) Chen, L.; Hernandez, Y.; Feng, X.; Müllen, K. From Nanographene and Graphene Nanoribbons to Graphene Sheets: Chemical Synthesis. *Angew. Chem., Int. Ed.* **2012**, *51*, 7640−7654.

(26) Kunz, H.; Müllen, K. Natural Product and Material Chemistries—Separated Forever? *J. Am. Chem. Soc.* **2013**, *135*, 8764−8769.

DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566

(27) Friederich, R.; Nieger, M.; Vögtle, F. Auf dem Weg zu makrocyclischen *para*-Phenylenen. *Chem. Ber.* **1993**, *126*, 1723−1732.
(28) Recently, the Itami laboratory has been able to synthesize [*n*]CPPs using these types of molecules. See ref 49 and references therein.
(29) Kammermeier, S.; Jones, P. G.; Herges, R. Ring-Expanding Metathesis of Tetradehydro-anthracene—Synthesis and Structure of a Tubelike, Fully Conjugated Hydrocarbon. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2669−2671.
(30) Kammermeier, S.; Jones, P. G.; Herges, R. Beltlike Aromatic Hydrocarbons by Metathesis Reaction with Tetradehydrodianthracene. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2200−2202.
(31) Nakamura, E.; Tahara, K.; Matsuo, Y.; Sawamura, M. Synthesis, Structure, and Aromaticity of a Hoop-Shaped Cyclic Benzenoid [10]Cyclophenacene. *J. Am. Chem. Soc.* **2003**, *125*, 2834−2835.
(32) Matsuo, Y.; Tahara, K.; Sawamura, M.; Nakamura, E. Creation of Hoop- and Bowl-Shaped Benzenoid Systems by Selective Detraction of [60]Fullerene Conjugation. [10]Cyclophenacene and Fused Corannulene Derivatives. *J. Am. Chem. Soc.* **2004**, *126*, 8725−8734.
(33) For an earlier synthesis of cycloparaphenylacetylenes, see: Kawase, T.; Darabi, H. R.; Oda, M. Cyclic [6]- and [8]-Paraphenylacetylenes. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2664−2666.
(34) A similar strategy was used previously to synthesize cyclophynes. See: Srinivasan, M.; Sankararaman, S.; Hopf, H.; Varghese, B. Synthesis of Buta-1,3-diyne-Bridged Macrocycles with (*Z*)-1,4-Diethynyl-1,4-dimethoxycyclohexa-2,5-diene as the Building Block. *Eur. J. Org. Chem.* **2003**, 660−665.
(35) For earlier examples on similar system, see: (a) Alonso, F.; Yus, M. Reactivity of 3,6-dimethoxy-3,6-dimethylcyclohexa-1,4-diene. Regioselective arylation of electron-rich aromatic compounds. *Tetrahedron* **1991**, *47*, 313−316. (b) Morrow, G. W.; Schwind, B. Syntheses of *para*-Terphenyl via Reductive Deoxygenation of Quinol Derivatives. *Synth. Commun.* **1995**, *25*, 269−276.
(36) Liu, H.-J.; Yip, J.; Shia, K.-S. Reductive cleavage of benzyl ethers with lithium naphthalenide. A convenient method for debenzylation. *Tetrahedron Lett.* **1997**, *38*, 2253−2256.
(37) Iwamoto, T.; Watanabe, Y.; Sakamoto, Y.; Suzuki, T.; Yamago, S. Selective and Random Syntheses of [*n*]Cycloparaphenylenes (*n* = 8−13) and Size Dependence of Their Electronic Properties. *J. Am. Chem. Soc.* **2011**, *133*, 8354−8361.
(38) Wong, B. M. Optoelectronic Properties of Carbon Nanorings: Excitonic Effects from Time-Dependent Density Functional Theory. *J. Phys. Chem. C* **2009**, *113*, 21921−21927.
(39) Segawa, Y.; Fukazawa, A.; Matsuura, S.; Omachi, H.; Yamaguchi, S.; Irle, S.; Itami, K. Combined experimental and theoretical studies on the photophysical properties of cycloparaphenylenes. *Org. Biomol. Chem.* **2012**, *10*, 5979−5984.
(40) Sisto, T. J.; Golder, M. R.; Hirst, E. S.; Jasti, R. Selective Synthesis of Strained [7]Cycloparaphenylene: An Orange-Emitting Fluorophore. *J. Am. Chem. Soc.* **2011**, *133*, 15800−15802.
(41) Sisto, T. J.; Tian, X.; Jasti, R. Synthesis of Tetraphenyl-Substituted [12]Cycloparaphenylene: Toward a Rationally Designed Ultrashort Carbon Nanotube. *J. Org. Chem.* **2012**, *77*, 5857−5860.
(42) Xia, J.; Bacon, J. W.; Jasti, R. Gram-Scale Synthesis and Crystal Structures of [8]- and [10]CPP, and the Solid-State Structure of C_{60}@[10]CPP. *Chem. Sci.* **2012**, *3*, 3018−3021.
(43) Xia, J.; Jasti, R. Synthesis, Characterization, and Crystal Structure of [6]Cycloparaphenylene. *Angew. Chem., Int. Ed.* **2012**, *51*, 2474−2476.
(44) Xia, J.; Golder, M. R.; Foster, M. E.; Wong, B. M.; Jasti, R. Synthesis, Characterization, and Computational Studies of Cycloparaphenylene Dimers. *J. Am. Chem. Soc.* **2012**, *134*, 19709−19715.
(45) Darzi, E. R.; Sisto, T. J.; Jasti, R. Selective Syntheses of [7]−[12]Cycloparaphenylenes Using Orthogonal Suzuki−Miyaura Cross-Coupling Reactions. *J. Org. Chem.* **2012**, *77*, 6624−6628.
(46) Golder, M. R.; Wong, B. M.; Jasti, R. Photophysical and theoretical investigations of the [8]cycloparaphenylene radical cation and its charge-resonance dimer. *Chem. Sci.* **2013**, *4*, 4285−4291.
(47) Evans, P. J.; Darzi, E. R.; Jasti, R. Efficient Room-Temperature Synthesis of a Highly Strained Carbon Nanohoop Fragment of Buckminsterfullerene. *Nat. Chem.* **2014**, *6*, 404−408.
(48) Omachi, H.; Matsuura, S.; Segawa, Y.; Itami, K. A Modular and Size-Selective Synthesis of [*n*]Cycloparaphenylenes: A Step toward the Selective Synthesis of [*n*,*n*] Single-Walled Carbon Nanotubes. *Angew. Chem., Int. Ed.* **2010**, *49*, 10202−10205.
(49) Omachi, H.; Segawa, Y.; Itami, K. Synthesis of Cycloparaphenylenes and Related Carbon Nanorings: A Step toward the Controlled Synthesis of Carbon Nanotubes. *Acc. Chem. Res.* **2012**, *45*, 1378−1389.
(50) Yamago, S.; Watanabe, Y.; Iwamoto, T. Synthesis of [8]Cycloparaphenylene from a Square-Shaped Tetranuclear Platinum Complex. *Angew. Chem., Int. Ed.* **2010**, *49*, 757−759.
(51) Kayahara, E.; Iwamoto, T.; Suzuki, T.; Yamago, S. Selective Synthesis of [6]-, [8]-, and [10]Cycloparaphenylenes. *Chem. Lett.* **2013**, *42*, 621−623.
(52) Takaba, H.; Omachi, H.; Yamamoto, Y.; Bouffard, J.; Itami, K. Selective Synthesis of [12]Cycloparaphenylene. *Angew. Chem., Int. Ed.* **2009**, *48*, 6112−6116.
(53) Jagadeesh, M. N.; Makur, A.; Chandrasekhar, J. The Interplay of Angle Strain and Aromaticity: Molecular and Electronic Structures of [0_n]Paracyclophanes. *J. Mol. Model.* **2000**, *6*, 226−233.
(54) Segawa, Y.; Omachi, H.; Itami, K. Theoretical Studies on the Structures and Strain Energies of Cycloparaphenylenes. *Org. Lett.* **2010**, *12*, 2262−2265.
(55) Tahara, K.; Tobe, Y. Molecular Loops and Belts. *Chem. Rev.* **2006**, *106*, 5274−5290.
(56) Bunz, U.; Menning, S.; Martín, N. Para-Connected Cyclophenylenes and Hemispherical Polyarenes: Building Blocks for Single-Walled Carbon Nanotubes. *Angew. Chem., Int. Ed.* **2012**, *51*, 7094−7101.
(57) Wipf, P.; Jung, J.-K. Nucleophilic Additions to 4,4-Disubstituted 2,5-Cyclohexadienones: Can Dipole Effects Control Facial Selectivity? *Chem. Rev.* **1999**, *99*, 1469−1480.
(58) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. Catalysts for Suzuki−Miyaura Coupling Processes: Scope and Studies of the Effect of Ligand Structure. *J. Am. Chem. Soc.* **2005**, *127*, 4685−4696.
(59) Fujitsuka, M.; Cho, D.; Iwamoto, T.; Yamago, S.; Majima, T. Size-dependent fluorescence properties of [*n*]cycloparaphenylenes (*n* = 8−13), hoop-shaped π-conjugated molecules. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14585−14588.
(60) Reddy, V. S.; Camacho, C.; Xia, J.; Jasti, R.; Irle, S. Quantum Dynamics Simulations Reveal Vibronic Effects on the Optical Properties of [*n*]Cycloparaphenylenes. *J. Chem. Theory Comput.* **2014**, *10*, 4025−4036.
(61) Adamska, L.; Nayyar, I.; Chen, H.; Swan, A. K.; Oldani, N.; Fernandez-Alberti, S.; Golder, M. R.; Jasti, R.; Doorn, S. K.; Tretiak, S. Self-Trapping of Excitons, Violation of Condon Approximation, and Efficient Fluorescence in Conjugated Cycloparaphenylenes. *Nano Lett.* **2014**, *14*, 6539−6546.
(62) Li, P.; Sisto, T. J.; Darzi, E. R.; Jasti, R. The Effects of Cyclic Conjugation and Bending on the Optoelectronic Properties of Paraphenylenes. *Org. Lett.* **2014**, *16*, 182−185.
(63) Since our initial report, Itami has also reported on the selective synthesis of [7]CPP. See: Sibbel, F.; Matsui, K.; Segawa, Y.; Studer, A.; Itami, K. Selective synthesis of [7]- and [8]cycloparaphenylenes. *Chem. Commun.* **2014**, *50*, 954−956.
(64) Zabula, A. V.; Filatov, A. S.; Xia, J.; Jasti, R.; Petrukhina, M. A. Tightening of the Nanobelt upon Multielectron Reduction. *Angew. Chem., Int. Ed.* **2013**, *52*, 5033−5036.
(65) While all [*n*]CPPs have a negligible oscillator strength for this transition, the larger sizes are suggested to have higher quantum yields due to symmetry breaking in the excited state. See ref 61 and references therein.
(66) Segawa, Y.; Šenel, P.; Matsuura, S.; Omachi, H.; Itami, K. [9]Cycloparaphenylene: Nickel-Mediated Synthesis and Crystal Structure. *Chem. Lett.* **2011**, *40*, 423−425.

DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566

(67) Kayahara, E.; Sakamoto, Y.; Suzuki, T.; Yamago, S. Selective Synthesis and Crystal Structure of [10]Cycloparaphenylene. *Org. Lett.* **2012**, *14*, 3284−3287.
(68) Segawa, Y.; Miyamoto, S.; Omachi, H.; Matsuura, S.; Šenel, P.; Sasamori, T.; Tokitoh, N.; Itami, K. Concise Synthesis and Crystal Structure of [12]Cycloparaphenylene. *Angew. Chem., Int. Ed.* **2011**, *50*, 3244−3248.
(69) Punna, S.; Díaz, D. D.; Finn, M. G. Palladium-Catalyzed Homocoupling of Arylboronic Acids and Esters Using Fluoride in Aqueous Solvents. *Synlett* **2004**, 2351−2354.
(70) Kayahara, E.; Patel, V. K.; Yamago, S. Synthesis and Characterization of [5]Cycloparaphenylene. *J. Am. Chem. Soc.* **2014**, *136*, 2284−2287.
(71) Baran, P. S.; Burns, N. Z. Total synthesis of (±)-haouamine A. *J. Am. Chem. Soc.* **2006**, *128*, 3908−3909.
(72) Takiguchi, H.; Ohmori, K.; Suzuki, K. Synthesis and determination of the absolute configuration of cavicularin by a symmetrization/asymmetrization approach. *Angew. Chem., Int. Ed.* **2013**, *52*, 10472−10476.
(73) Tobe, Y.; Ueda, K.; Kakiuchi, K.; Odaira, Y.; Kai, Y.; Kasai, N. Synthesis, Structure and Reactivities of [6]Paracyclophanes. *Tetrahedron* **1986**, *42*, 1851−1857.
(74) Allinger, N. L.; Walter, T. J.; Newton, M. G. Synthesis, structure, and properties of the [7]paracyclophane ring system. *J. Am. Chem. Soc.* **1974**, *96*, 4588−4597.
(75) Kawai, H.; Suzuki, T.; Ohkita, M.; Tsuji, T. Kinetic Stabilization of the [1.1]Paracyclophane System: Isolation and X-ray Structural Analysis of a [1.1]Paracyclophane Derivative and Its Interconversion with the Transannular Adduct. *Chem.—Eur. J.* **2000**, *6*, 4177−4187.
(76) Bodwell, G. J.; Bridson, J. N.; Houghton, T. J.; Kennedy, J. W. J.; Mannion, M. R. 1,7-Dioxa[7](2,7)pyrenophane: The Pyrene Moiety Is More Bent than That of C_{70}. *Chem.—Eur. J.* **1999**, *5*, 1823−1827.
(77) Dobrowolski, M. A.; Cyrański, M. K.; Merner, B. L.; Bodwell, G. J.; Wu, J. I.; Schleyer, P. v. R. Interplay of π-Electron Delocalization and Strain in [*n*](2,7)Pyrenophanes. *J. Org. Chem.* **2008**, *73*, 8001−8009.
(78) Tsuji, T.; Okuyama, M.; Ohkita, M.; Kawai, H.; Suzuki, T. Functionalization and Kinetic Stabilization of the [4]Paracyclophane System and Aromaticity of Its Extremely Bent Benzene Ring. *J. Am. Chem. Soc.* **2003**, *125*, 951−961.
(79) Rice, J. E.; Lee, T. J.; Remington, R. B.; Allen, W. D.; Clabo, D. A., Jr.; Schaefer, H. F., III. [5]Paracyclophane. An important example of ring strain and aromaticity in hydrocarbon compounds. *J. Am. Chem. Soc.* **1987**, *109*, 2902−2909.
(80) Fort, E. H.; Donovan, P. M.; Scott, L. T. Diels−Alder Reactivity of Polycyclic Aromatic Hydrocarbon Bay Regions: Implications for Metal-Free Growth of Single-Chirality Carbon Nanotubes. *J. Am. Chem. Soc.* **2009**, *131*, 16006−16007.
(81) Fort, E. H.; Scott, L. T. Carbon nanotubes from short hydrocarbon templates. Energy analysis of the Diels−Alder cycloaddition/rearomatization growth strategy. *J. Mater. Chem.* **2011**, *21*, 1373−1381.
(82) Omachi, H.; Nakayama, T.; Takahashi, E.; Segawa, Y.; Itami, K. Initiation of carbon nanotube growth by well-defined carbon nanorings. *Nat. Chem.* **2013**, *5*, 572−576.
(83) Iwamoto, T.; Watanabe, Y.; Sadahiro, T.; Haino, T.; Yamago, S. Size-Selective Encapsulation of C_{60} by [10]Cycloparaphenylene: Formation of the Shortest Fullerene-Peapod. *Angew. Chem., Int. Ed.* **2011**, *50*, 8342−8344.

DOI: 10.1021/ar5004253
Acc. Chem. Res. 2015, 48, 557−566