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Bending Benzene: Syntheses of [*n*]Cycloparaphenylenes

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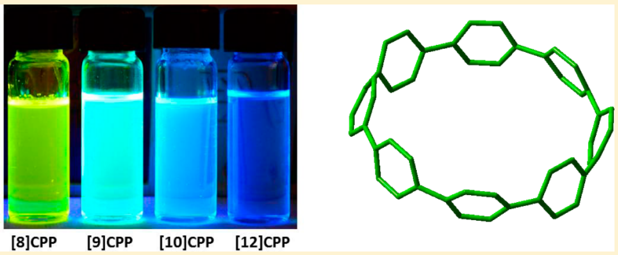
ABSTRACT: Since the first successful synthesis in 2008, methods to prepare the [*n*]cycloparaphenylenes have evolved rapidly. The aim of this synopsis is to provide an overview of recent advancements in this emerging field. The optoelectronic properties and supramolecular chemistry of these unique structures are presented as well.



The [*n*]cycloparaphenylenes ([*n*]CPPs) have long been molecules of interest for not only organic chemists but also theoreticians, materials engineers, and physicists alike.[1−4] As early as 1934, CPPs were first postulated in the literature.[5] At the time, [*n*]CPPs (where *n* represents the number of benzene rings) represented a physical organic curiosity. Comprised of cyclic all-para-linked phenyl groups, [*n*]CPPs contain a highly strained, radially oriented π-system (Figure 1).

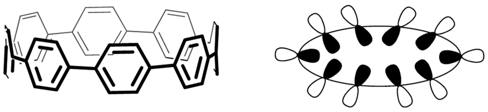


Figure 1. [8]Cycloparaphenylene (left) and a radially oriented π-system (right).

More recently, interest returned to [*n*]CPPs for their relation and possible uses in synthesizing uniform carbon nanotubes (CNTs).[6] [*n*]CPPs represent the shortest possible subunit of an armchair CNT and may be amenable to extension into structurally uniform single-walled armchair CNTs (sw-CNTs).[7−9] Pioneering work by Vögtle and co-workers in the early 1990s set important precedents in CPP chemistry.[10] With renewed interest in these molecules, CPPs were finally successfully synthesized in 2008.[11]

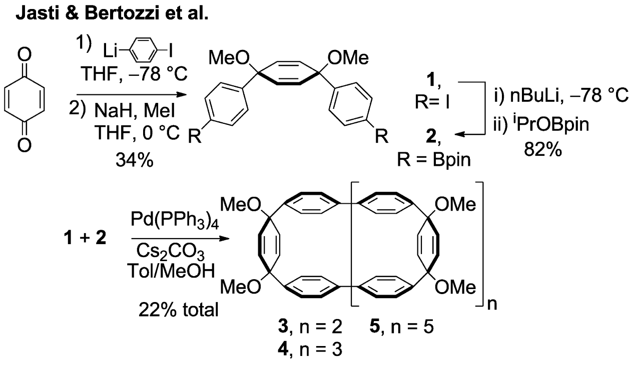
Empirical observations of [*n*]CPPs have revealed properties amenable to many uses beyond CNT synthesis. Because of their cyclic nature, the conjugation of CPPs gives rise to unique size-dependent optoelectronic properties.[11−14] With defined and rigid cavities, [*n*]CPPs are also capable of strong host−guest interactions,[15,16] and therefore are promising new supramolecular components. The aim of this synopsis is to provide an overview of recent advancements in the synthesis of [*n*]cycloparaphenylenes as well as briefly summarize their optoelectronic and supramolecular properties.

■ FIRST SYNTHESES OF [*n*]CYCLOPARAPHENYLENES

Since the first CPP synthesis in 2008,[11] the synthesis and exploration of [*n*]cycloparaphenylenes has exploded into a hot research area with important contributions from Jasti and co-workers,[6,11,16−19] Itami and co-workers,[13,20−24] and Yamago and co-workers.[12,15,25] The initial syntheses evolved from nonselective to selective, and increasingly challenged the limit of size. Following is a summary of the initial approaches to CPP synthesis.

First Syntheses of [9]-, [12]-, and [18]-Cycloparaphenylene. The first successful syntheses of cycloparaphenylenes were reported by Jasti and Bertozzi in 2008.[11] [9]-, [12]-, and [18]CPP were prepared in a nonselective fashion. The synthesis of CPPs is challenging due to the large strain associated with the bent aromatic system. To overcome this challenge, Jasti and co-workers elegantly utilized cyclohexadiene moieties as masked benzene rings to introduce curvature and alleviate strain in macrocyclic precursors **3**−**5** (Scheme 1). Macrocycles were assembled via a "shotgun" Suzuki−Miyaura reaction between fragments **1** and **2** (Scheme 1). Diiodide **1** was synthesized on multigram scale via a double addition of (4-iodophenyl)lithium to benzoquinone, followed by methylation. A portion of this material was then borylated to give coupling partner **2**.

Scheme 1. Jasti's Synthesis of [9]-, [12]-, and [18]CPP Precursors



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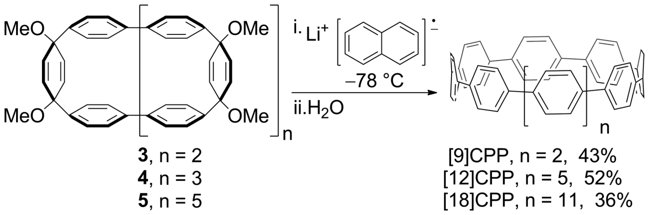
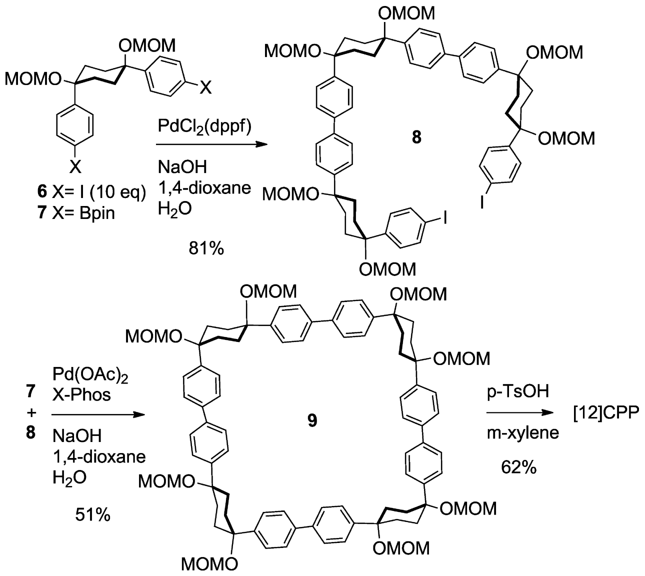
Shotgun Suzuki–Miyaura coupling led to macrocycles **3**–**5** in 22% combined yield. Conversion of the macrocycles to the final CPPs necessitated novel methodology. Standard aromatization conditions employ the use of strong acids to generate carbocations, which lead to undesired rearrangement. Lithium naphthalide was found to be an excellent solution, capable of introducing large amounts of strain energy at low temperatures. Aromatization with lithium naphthalide proceeds smoothly at −78 °C via single electron reduction to give [9]-, [12]-, and [18]cycloparaphenylenes in 36–42% yield (Scheme 2).

Scheme 2. Reductive Aromatization To Yield [9]-, [12]-, and [18]CPP



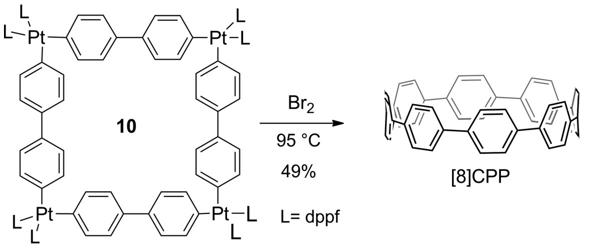
Selective and Random Synthesis of [12]- and [9]-Cycloparaphenylene. Shortly after the first synthesis, Itami reported the selective synthesis of [12]cycloparaphenylene.[20] Itami's synthesis relied on the use of *cis*-cyclohexane-1,4-diyl units as masked aromatic rings to alleviate strain while constructing the macrocyclic precursor. Construction of the [12]-macrocycle was achieved via sequential Suzuki–Miyaura cross-coupling of units **6** and **7** (Scheme 3). Aromatization of macrocycle **9** to [12]CPP was achieved in 62% yield by microwave irradiation with *p*-TsOH. In this case, aromatization proceeds via dehydration followed by oxidation. In order to increase the yield and reduce costs, Itami developed a nickel-mediated aryl–aryl coupling with Ni(cod)$_2$ and bppy to selectively synthesize [12]CPP using only a dibromide analogue of **6**. Unfortunately, the reaction proved unselective in that while the [12]CPP precursor did form in 22% yield, the [9]CPP precursor also formed concurrently in a higher 32% yield. Treatment of this macrocycle with similar aromatization conditions yielded [9]CPP in a reduced yield of 24%, presumably due to higher strain energy associated with the smaller CPP.[24]

Scheme 3. Itami's Synthesis of [12]CPP



Selective and Random Syntheses of [8]–[13Cycloparaphenylene. In 2010, Yamago and co-workers achieved the selective synthesis of [8]cycloparaphenylene, the smallest CPP at the time.[25] This synthesis utilized a novel approach to overcoming strain involving a tetranuclear platinum complex (Scheme 4). The square complexes comprised of fully aromatic oligophenylenes avoided strain by taking advantage of the inherent Pt coordination geometry. Reductive elimination of **10** to yield [8]cycloparaphenylene proceeded in 49% yield. In this regard, Yamago was able to selectively synthesize [8]CPP in three steps, without a re-aromatization step. Although the scalability is limited by the cost associated with stoichiometric platinum, the synthetic sequence is very concise. Modification of the route by inclusion of terphenyl fragments lead to the formation of [8]–[13]cycloparaphenylenes, with [8] and [12] being selectively formed when desired.[12]

Scheme 4. Yamago's Selective Synthesis of [8]CPP

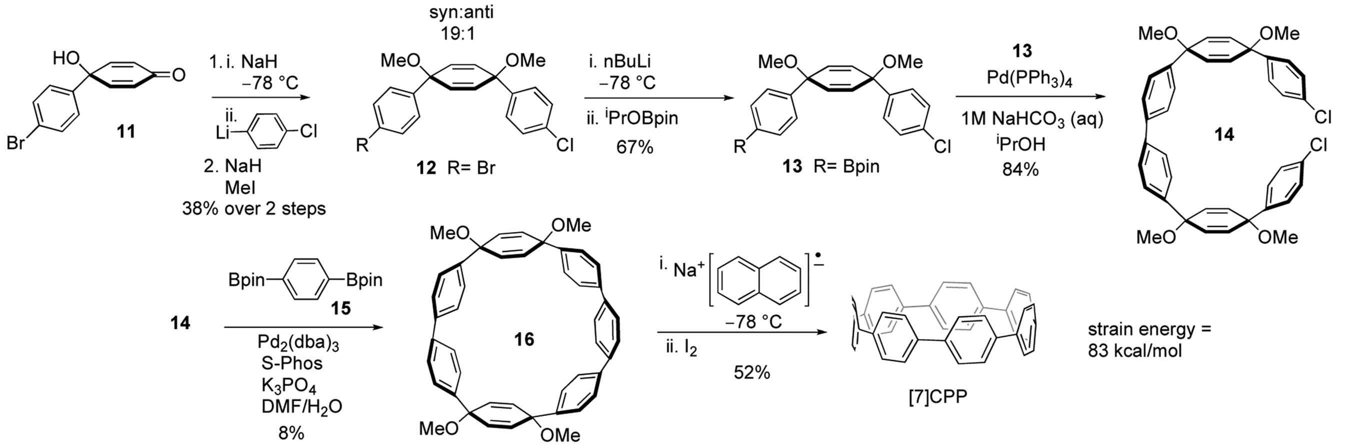


SCALING DOWN: THE QUEST FOR THE SMALLEST CYCLOPARAPHENYLENE

With the ability to synthesize a variety of CPPs, the focus turned to pushing the limits of size—what is the smallest CPP that can be prepared by synthetic organic chemistry? Computational modeling suggested that for hoops smaller than [6]CPP the six-membered rings would no longer be benzenoid but would prefer a quinoidal-type electronic structure.[26] The smaller, more strained CPPs were also predicted to have narrower band gaps,[11] which might be useful in organoelectronic applications. Synthesis of smaller CPPs was a daunting challenge due to the dramatic increase in strain energy. Synthetic strategies therefore had to be redesigned to overcome this challenge.

Selective Synthesis of [7]Cycloparaphenylene. In 2011, Jasti and co-workers reported the synthesis of the then smallest CPP: [7]cycloparaphenylene. Again utilizing cyclohexadienes as masked aromatic rings, unsymmetric fragments **12** and **13** (Scheme 5) were synthesized. The high diastereoselectivity of the addition step (**11** to **12**) is due to electrostatic repulsion of the deprotonated alcohol. Repulsion by the sodium alkoxide favors addition from the opposite face generating the *syn* product with high selectivity. Differing reactivities of aryl chlorides and bromides was exploited for orthogonality in assembling **16** in a stepwise fashion. Bromide **12** underwent an initial cross-coupling with **13** to form dichloride **14**. This dichloride then was coupled with **15** to give macrocycle **16**. The macrocycle efficiently underwent reductive aromatization in the presence of sodium naphthalide at −78 °C to yield [7]CPP in 52% yield.[17] Notably, the final aromatization builds in a calculated 67 kcal/mol of strain energy at low

Scheme 5. Jasti's Synthesis of [7]CPP

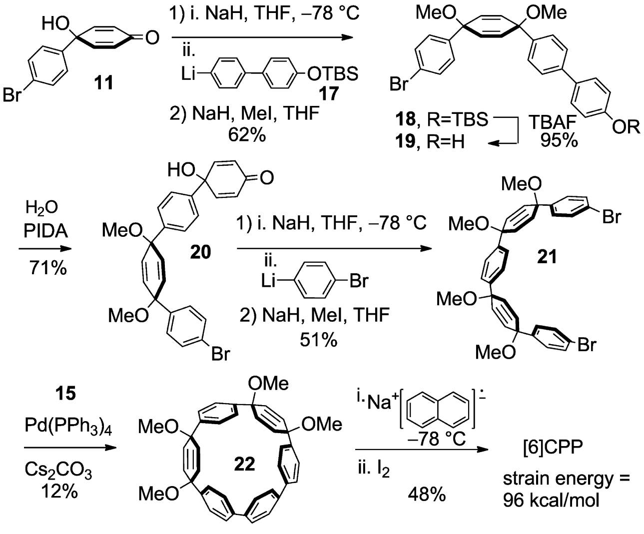


temperature. Strain energies were predicted for CPPs using model homodesmotic reactions.[17,27] It was later shown that this same methodology could be applied to the first divergent, selective synthesis of [7]−[12]CPPs.[19]

The Smallest Yet: Selective Synthesis of [6]-Cycloparaphenylene. More recently, the synthesis of CPPs was scaled down even further with the selective synthesis of [6]cycloparaphenylene.[18] Attempts to access [6]-cycloparaphenylene from intermediate **14** were unsuccessful. Presumably, the existence of two phenyl groups in between cyclohexadiene units prevents sufficient curvature for macrocycle formation.

New intermediate **21** was targeted with alternating cyclohexadiene/phenyl moieties and the more reactive aryl bromide functionality (Scheme 6). The synthesis was achieved through a sequential oxidative dearomatization/addition process. Ketone **11** underwent deprotonation with NaH, addition of TBS-protected aryl lithium **17**, and subsequent methylation to yield dimethoxy ether **18** in 52% overall. As before, sodium alkoxide formation leads to high diastereoselectivity in the addition step. TBAF deprotection reveals phenol **19** which undergoes oxidative dearomatization with PIDA in the presence of water to yield ketone **20**. A highly diastereoselective second addition of (4-bromophenyl)lithium followed by methylation gave dibromide **21**.[17] Assembly of macrocycle **22** was achieved via Suzuki coupling of dibromide **21** with **15** in 12% yield. Reductive aromatization with sodium naphthalide yielded [6]CPP, the smallest CPP to date, in 48% yield. Impressively, the reductive aromatization methodology was able to construct a molecule with 96 kcal/mol of strain energy at −78 °C.

Scheme 6. Jasti's Synthesis of [6]CPP



Characterization of [6]CPP showed novel behavior unique to the smallest sized nanohoop. NMR spectra of larger sized CPPs reveal a singlet, with shifts moving upfield with decreasing size. The NMR spectrum of [6]CPP revealed a singlet at δ7.64 ppm, 0.16 ppm downfield relative to [7]CPP.[17] The electronic properties and crystal structure were also distinctly unique from larger [*n*]CPPs (vide infra).

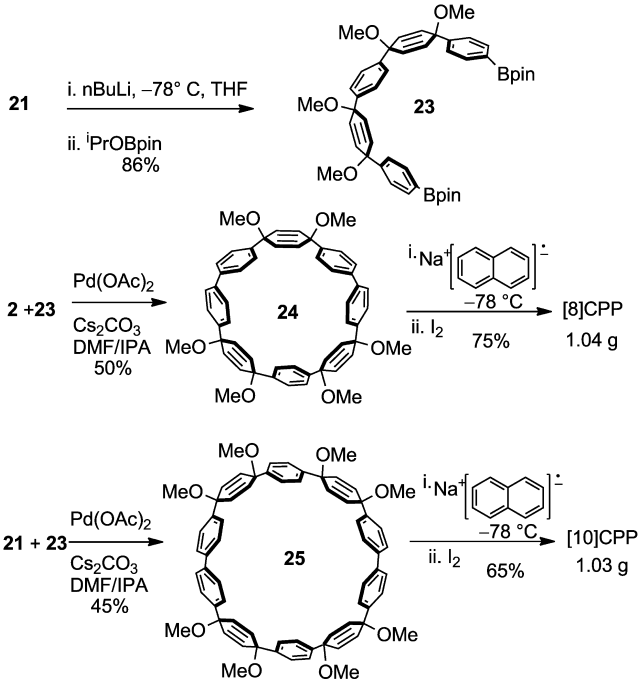
■ RECENT ADVANCES IN CYCLOPARAPHENYLENE SYNTHESIS

Although the previous synthetic routes were capable of accessing CPPs of many sizes, early syntheses of CPPs were unable to yield large amounts of product. No route led to more than 15 mg of CPP.[16] Limited availability of material hindered exploration of the properties and investigation into the reactivity of CPPs. Although [12]CPP is commercially available, the cost remains prohibitively high at $1000 (USD) per 10 mg.[28] It was therefore imperative that methods be developed that allowed for larger scale synthesis of CPPs.

Gram Scale Synthesis of [8]- and [10]CPP. Dibromide **21** used to synthesize [6]CPP presented the solution to the problem of scalability. While coupling of **21** with **15** only led to the [6]CPP precursor in 12% yield, use of **21** to access larger, less strained macrocycles proved significantly more successful.[16] Upon optimization, the route to generate **21** was maximized to 30% overall yield. Notably, greater than 20 g of material can be prepared in a single one-pot reaction using standard 2-L flasks. In addition, the number of isolated intermediates was decreased by developing an in situ methylation procedure. Dibromide **21** was also easily converted to diboronate **23** in 86% yield (Scheme 7).

Coupling of dibromide **21** with either **2** or **23** leads to the precursors for [8] and [10]CPP in 50% and 45% yields, respectively (Scheme 7). This macrocyclization is advantageous over previous syntheses in that it utilizes relatively inexpensive $Pd(OAc)_2$ under ligandless conditions. Treatment of macrocycles **24** and **25** with sodium naphthalide at −78 °C yielded 1.04 g of [8]CPP (75% yield) and 1.03 g of [10]CPP (65%

Scheme 7. Gram-Scale Synthesis of [8]- and [10]CPP



yield). This gram-scale achievement represents a 2-fold increase in the previous yields for [8]- and [10]CPP. The scalability and versatility of this oxidative dearomatization/addition sequence will allow for the large scale synthesis of novel [*n*]CPPs previously unobtainable in usable amounts.

Synthesis of Tetraphenyl-Substituted [12]CPP. With scalable and selective syntheses of CPPs developed, aspirations of using them as templates for "bottom-up" CNT growth have become more feasible. Extension of 1 mg of pure CPP would yield over 1 kg of structurally uniform, sw-CNTS 1 mm long. One approach to extending these nanohoops into full CNTs is via a metal-free Diels–Alder (DA) sequence conceptualized by Scott.[7,29] Computational studies suggest that the barrier for DA initiation is prohibitively high for CPP alone. However, addition of more phenylene rows lowers the barrier considerably to the same magnitude encountered in facile DA reactions between acetylene and bisanthene (24 kcal/mol) or perylene (30 kcal/mol).[29]

With this data in mind, efforts are underway to access elongated CPP structures for Diels–Alder extension. Utilizing methodology developed for the synthesis of [7]CPP, Jasti and co-workers synthesized a tetraphenyl-substituted [12]CPP, **26** (Figure 2).[30] Derivative **26** will serve as a model system both for cyclodehydrogenation reactions to form a fully fused side wall as in **27** and for optimization of Diels–Alder conditions for extension into a CNT. With successful methodology developed on this model system, the Jasti Group aims to prepare arylated CPP **28** which would lead to ultrashort CNT **29**.

CRYSTAL STRUCTURES AND OPTOELECTRONIC AND HOST–GUEST PROPERTIES OF CPPS

While computationally predicted to have unique optical properties and π cavities,[26] such properties of CPPs could not be explored until their synthesis was completed. Empirical study of the molecules' electronic properties has illustrated unique size-dependent properties opposite of trends encountered with other highly fluorescent nanostructures.[17] Additionally, the studies of solid state structures and host–guest capabilities were finally possible.[16,25] Interestingly, the smaller sized CPPs exhibit the most noticeable shifts in behavior.

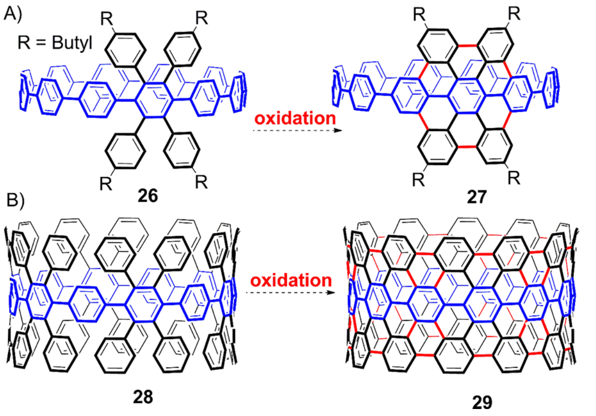


Figure 2. (A) Cyclodehydrogenation of Tetraphenyl-substituted [12]CPP to form fused structure **27**; (B) Cyclodehydrogenation of fully arylated [12]CPP to form an ultrashort CNT **29**.

Crystal Structures of CPPs. In 2011, Itami presented the first crystal structure of [12]CPP.[21] The crystal packing structure showed molecules oriented into herringbone patterns in the solid state. Along one axis, the molecules formed tubular structures with uniform cavities of 16.5 Å. Bond lengths around the aryl rings were all approximately 1.39 Å, illustrating retention of benzenoid character. Itami's crystal structure of [9]CPP revealed greater bond variation, with bonds alternating between 1.39 and 1.36 Å.[24] [9]CPP was also found to arrange in a tubular, herringbone fashion.

Jasti and co-workers later solved the crystal structures for [6]-, [8]-, and [10]CPP.[16,18] [8]- and [10]CPP pack in similar fashion to [9]- and [12]CPP, exhibiting herringbone orientation in the solid state. The pore size of the tubular channels corresponds to the diameter of [8]- and [10]CPP, 10.8 and 12.7 Å, respectively. Like the larger sizes, [6]CPP exhibited uniform bond lengths, showing retention of benzenoid character even with the high curvature. Interestingly, the crystal packing structure of [6]CPP revealed striking differences. [6]CPP was found to organize into completely linear, nanotube like structures with a diameter of 8.08 Å (Figure 3). It remains unclear as to why [6]CPP adopts such a different packing structure. Self-assembly into organized tubes could provide a means for the "bottom-up" synthesis of uniform (6,6) armchair sw-CNTs. Preassembled structures could possibly be annealed photochemically or thermally, extruding H_2 to join phenylene units.[31]

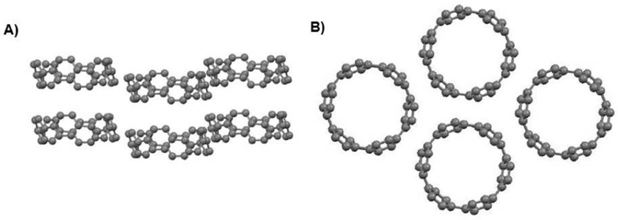


Figure 3. Crystal packing structure of [6]CPP: (A) linear packing; and (B) tubular alignment.

Host–Guest Interactions of C_{60}@[10]CPP. The nanometer-scale diameters of CPPs and their inward oriented π

cloud make them attractive candidates for size-selective encapsulation of guest molecules.[15] In 2011, the Yamago group demonstrated that [10]CPP selectively incorporates C_{60} forming peapod structure **32** (Figure 4). Formation of the C_{60}@[10]CPP was evidenced by a 0.054 ppm shift downfield in the ^{1}H NMR spectrum of [10]CPP and a 1.4 ppm shift upfield in the ^{13}C NMR spectrum of C_{60}. Quenching studies found that the association between [10]CPP and C_{60} stabilized the molecules by 38 kJ mol^{-1}.

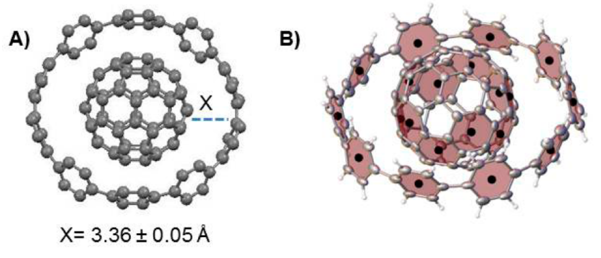


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Figure 4. (A) C_{60}@[10]CPP peapod complex and (B) $\pi-\pi$ interactions of C_{60}@[10]CPP.

In 2012, the C_{60}@[10]CPP complex was successfully crystallized (Figure 4).[16] The dihedral angles of [10]CPP in the C_{60} complex are 28.5 ± 2.5° whereas the angles in the unincorporated [10]CPP are 27.3 ± 11.7°. The smaller variance in the complex is attributable to highly favorable and efficient $\pi-\pi$ stacking. The torsional angles of [10]CPP alternate such that parallel π-stacking geometries are seen for all ten rings between [10]CPP and C_{60} (Figure 4b). The average distance between C_{60} (ring centroid) to [10]CPP (ring plane) is 3.36 ± 0.05 Å. Host−guest complexes between fullerenes and conjugated macrocycles are strongly stabilized by concave-convex interactions. The concave−convex alignment of [10]CPP onto C_{60}, with all aromatic rings participating, suggests that appropriately sized [*n*]CPPs may be better complexing agents than even the [*n*]paraphenyleneacetylenes.[4]

Size-Dependent Optoelectronic Properties of [*n*]-Cycloparaphenylenes. In similar fashion to other nanoscale materials such as quantum dots,[32] single metal nanoparticles,[33] and linear oligophenylenes,[34] [*n*]CPPs exhibit size-dependent optical properties. In contrast to these other classes of nanomaterials, [*n*]CPPs experience red-shifting emission with decreasing size. The absorption maxima is insensitive to [*n*]CPP size, with all [*n*]CPPs absorbing at approximately 340 nm.[12,17,18] DFT analysis showed that the HOMO−LUMO transition for all [*n*]CPPs is forbidden.[12,13] The maxima is attributed instead to a combination of HOMO-2 to LUMO, HOMO-1 to LUMO, HOMO to LUMO+1, and HOMO to LUMO+2. The absorption maxima are therefore size independent and unaffected by number of phenyl rings. The emission redshifts from 450 nm for [12]CPP to 592 nm for [7]CPP. Yamago and co-workers explained that this trend results from increased strain of smaller [*n*]CPPs.[12] Increasing strain energy decreases the aromatic character of the phenyl rings and increases the polyene character. Although this is a reasonable explanation, several alternative theories describing CPPs unusual optical properties have been put forth and the subject is one of current interest.[3]

The quantum yields (QY) of [*n*]CPPs also display size dependence.[19] Sizes [14]−[16]CPP display relatively uniform QYs between 0.88 and 0.90.[13] As [*n*]CPP size decreases, the QY drops accordingly with [7]CPP having a QY of 0.01 and [6]CPP having no observable fluorescence.[18,19] This behavior is not currently well understood, and additional photochemical studies are forthcoming.

Oxidation potentials of CPPs were determined by cyclic voltammetry with tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. The oxidation wave was found to be reversible for all sizes, suggesting the radical cation intermediates are stable entities.[12,18] The oxidation potential decreases with decreasing number of phenyl rings, with [6]CPP having the lowest potential of 0.44 V (vs the ferrocene/ferrocenium couple). Reduction potentials could not be observed within the electrochemical window of either dichloromethane or 1,1,2,2-tetrachloroethane and to date remain unstudied.[12,18] With larger quantities of CPPs now available, additional studies of the electronic properties of CPPs can be expected.

■ CONCLUSION

Within four short years, [*n*]cycloparaphenylenes have evolved from being theoretical suppositions to synthetically accessible molecules on gram scale. Exploration of the properties of [*n*]CPPs have added to the physical organic understanding of aromaticity and conjugation, particularly as it pertains to molecular hoops and belts. Further exploration of these molecules and synthesis of novel derivatives will open the door for exciting material applications.

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Notes

The authors declare no competing financial interest.

Biographies

Professor Jasti received his Ph.D. at UC Irvine in 2006 with Prof. Scott Rychnovsky and conducted his postdoctoral studies with Prof. Carolyn Bertozzi at UC Berkeley. Prof. Jasti joined the faculty at Boston University in 2009 where his research focuses on the synthesis and properties of carbon-based nanomaterials.

Elizabeth Hirst completed her undergraduate studies at The George Washington University before beginning her Ph.D. work as the first graduate student in the laboratory of Professor Jasti at Boston University.

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