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T H E C H E M I C A L R E C O R D

Organoplatinum-Mediated Synthesis of Cyclic π -Conjugated Molecules: Towards a New Era of Three-Dimensional Aromatic Compounds

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Dedicated to Professor Teruaki Mukaiyama on the occassion of the 40th anniversary of the Mukaiyama aldol reaction

ABSTRACT: This article describes the most recent developments in the synthesis of threedimensional π -conjugated molecules and the elucidation of their properties made by our research group. Various cycloparaphenylenes (CPPs) of different sizes and a cage-like 3D molecule were synthesized based on the platinum-mediated assembly of π -units and subsequent reductive elimination of platinum. The assembly of π -units by this method mimics the self-assembly process for the formation of supramolecular ligand–metal complexes with 3D cages and polyhedral structures. Furthermore, reductive elimination of platinum successfully took place with high efficiency, despite the high strain energy of the target molecule. Several size-dependent physical properties of CPPs, namely the photophysical, redox, and host–guest chemistries, were also clarified. These results are of use for a molecular-level understanding of CNT physical properties as well as fullerene peapods. Theoretical and electrochemical studies suggest that small CPPs and their derivatives should be excellent lead compounds for molecular electronics. **DOI 10.1002/tcr.201300035**

Keywords: cycloparaphenylenes, fullerenes, host-guest systems, nanotubes, supramolecular chemistry

1. Introduction

It is obvious that one must think logically to take research forward. However, the beginning of research is not necessarily logical, and in many instances, is actually triggered in illogical ways, such as by a serendipitous finding, an instinct, curiosity, passion, and so on. For organic chemists, molecular structure or shape is undoubtedly one of the "illogical" triggers that initiates research. Cycloparaphenylenes (CPPs) are such molecules.

CPPs are hoop-shaped π -conjugated molecules in which paraphenylene (PP) units are linked in a cyclic manner (Figure 1). CPPs are the shortest structural unit of armchair carbon nanotubes (CNTs) and are also structural constituents of fullerenes. For example, C_{60} contains [5]CPP units (the number in the brackets indicates the number of PP units constituting CPP). Because of their unique structure, CPPs have attracted the attention of theoretical, physical, and synthetic chemists for more than half a century.^[11] It is worth noting that organic chemists had instinctually recognized the impact of the CPP structure before the discovery of fullerenes and CNTs. By analogy to the huge potentials of CNTs and fullerenes in materials science and technology, especially for photo-, electro-, and photoelectronic applications,^[2] CPPs also hold significant potential as key molecular units for future materials with new and/or improved properties. In addition,



Fig. 1. Structures of a CPP, armchair CNT, and $C_{60}.$ The CPP unit is highlighted as red in the CNT and $C_{60}.$

CPPs would be a seed compound for the syntheses of structurally uniform CNTs,^[3] as CNTs are currently prepared as mixtures of varying size, helicity, and length by physical methods such as laser vaporization, arc discharge of carbon, and aromatic hydrocarbon combustion, and separated by tedious multistep procedures. Therefore, the bottom-up synthesis of structurally uniform CNTs (at least in size and helicity) from CPPs by organic synthesis would be an excellent alternative to current CNT mass-production methods. In

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addition, the cavity of CPPs offers a unique opportunity in supramolecular chemistry to study concave–convex π – π interactions^[1d] and fabricate hierarchically ordered π -materials, which mimic fullerene peapods.^[4]

Despite the potential impact of CPPs in fundamental and applied chemistry and materials science, a lack of synthetic methods for their preparation have inhibited progress in unveiling their unique properties until recently.

In 2008, Jasti, Bertozzi, and co-workers reported for the first time the synthesis of [9], [12], and [18]CPPs.^[5] A significant feature of their synthesis is the use of 3,6-*cis*dimethoxycyclohexa-1,4-diene **1** as a masked aromatic ring (Scheme 1a). The cyclohexadiene unit provided the curvature and rigidity necessary for macrocyclization leading to cyclic precursor **2** through the Pd-catalyzed Suzuki–Miyaura coupling reaction of **1a** (X = I) and **1b** (X = Bpin, pin refers to pinacolate). Subsequent reductive aromatization afforded the corresponding CPPs. Immediately after this report, Itami and co-workers reported in 2009 the selective synthesis of [12] CPP using 1,4-*cis*-cyclohexane **3** as a masked aromatic ring

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tional career, he was a visiting student in the Professor Christopher C. Cummins group at Massachusetts Institute of Technology, United States (2008). He was also a recipient of the JSPS Predoctoral Fellowship from 2008 to 2011. Since 2011, he has been an assistant professor at the Institute for Chemical Research, Kyoto University (with Prof. Shigeru Yamago). His research interests include the synthesis of new organic molecules and their applications to new organic materials on the basis of new and efficient organic reactions, organometallic reactions, and reactive intermediates.

Takahiro Iwamoto was born in Osaka, Japan, in 1986. He received his B.Sc. (2009) from Kyoto University and his M.Sc. (2011) from the same university under the supervision of Professor Shigeru Yamago. He is currently a Ph.D. student in the same group, focusing on the synthesis and supra



molecular chemistry of new cyclic π -conjugated molecules. He has been a Predoctoral Research Fellow of the JSPS since 2011. In 2012, he worked with Professor Lawrence T. Scott's group at Boston College as an exchange student.

(Scheme 1b).^[6] After stepwise macrocyclization with **3a** (X = I) and **3b** (X = Bpin) giving cyclic precursor **4**, oxidative dehydration afforded the CPP. Subsequent extension of this method by Jasti allowed for the selective synthesis of a series of [6]–[12]CPPs,^[7] as well as the gram-scale syntheses of [8] and [10]CPPs.^[8] At present, the smallest CPP able to be synthesized is [6]CPP. Itami and co-workers also extended their synthetic method for the size-selective synthesis of a series of [9]–[16]CPPs.^[9] These methods have also been applied to the synthesis of several derivatives by Jasti,^[10] Itami,^[11] and Müllen.^[12]

Our group developed a different synthetic route toward CPPs and reported the selective synthesis of [8]CPP in 2010 (Scheme 1c).^[13] The synthesis relies on the formation of "platinum square" **6**, which was prepared by the transmetalation of





Scheme 1. Synthetic routes to CPPs.

4,4'-bisstannylated biphenyl **5c** ($X = SnMe_3$) and Pt(cod)Cl₂ (cod refers to 1,5-cyclooctadiene). Reductive elimination of the platinum species from 6 afforded [8]CPP, which was the smallest CPP prepared at that time. Application of this synthetic method permitted the random synthesis of [8]-[13]CPPs,^[14] selective synthesis of [6] and [10]CPPs,^[15] and various CPP derivatives.^[16] Furthermore, an extension of the concept of the formation of 6 led us to synthesize a cage-like threedimensional π -conjugated molecule.^[17] Isobe and co-workers applied our method to the synthesis of the simplest structural unit of chiral CNTs.^[18] We further unraveled several unique properties of CPPs including size-dependent photophysical properties,^[14,19] redox properties,^[14,15b] and size-selective hostguest chemistry.^[20] The most recent developments in the synthesis of CPPs and their derivatives and the elucidation of their properties made by our group are presented in this article.

2. Molecular Design

2.1. Synthetic Planning

Our initial idea for the synthesis of CPPs came from our ongoing project toward the development of new reagents for living radical polymerization.^[21] We have already reported that organotellurium compounds are excellent agents for providing control over molecular weight and molecular weight distribution in radical polymerization.^[22] Furthermore, the organotellurium group at the living polymer end can be transformed into a variety of functional groups under anionic, cationic, and radical conditions.^[22,23] During this study, we learned that the C-Te-C bond angle of organotellurium compounds is nearly 90° (Figure 2a), since 5s and 5p orbitals do not form hybridized orbitals owing to their significant energy differences. Besides the structural uniqueness, this bond angle minimizes the activation energy of the homolytic substitution reaction between polymer-end radicals and organotellurium compounds, which is the key mechanism in controlling the molecular weight distribution in living radical polymerization.^[24] We have also demonstrated that organotellurium compounds undergo reductive elimination (ligand coupling



Fig. 2. a) In silico optimized structure of dimethyltelluride and b) a possible synthetic route to CPPs from a square-shaped precursor.

reaction) under mild conditions.^[25] These results, coupled with a continued interest directed toward curved π -conjugated molecules,^[26] ignited a new synthetic route to CPPs utilizing square-shaped organotellurium compound 7g (Y = Te) as an intermediate. Once 7g forms, subsequent reductive elimination of tellurium from 7g would give [4n]CPP (n =integer) (Figure 2b).

We immediately expected two significant challenges to arise in this synthetic route. One is the efficient formation of the desired cyclic macrocycles; that is, obtaining the desired compound in good yield and high selectivity. The precursors are not necessarily square-shaped, and any cyclic precursors of this sort would give CPPs. However, a C–Y–C bond angle of 90° would be suitable for the predictable and selective synthesis of CPPs of a certain size. The other challenge is the reductive elimination to form highly strained CPPs (see below); to the best of our knowledge, no studies exist showing reductive elimination to be applicable for the synthesis of highly strained molecules. Despite these challenges, we were optimistic in our synthetic strategy, and commenced synthesis of the "tellurium square".

Despite our optimistic expectations, however, the synthesis of tellurium square 7g was unsuccessful so far. During this study, we also learned that Stang and co-workers had already reported the synthesis of "iodonium square" 7h (Y = I⁺), in which a 4,4′-biphenyl unit (n = 2) was connected through the hypervalent iodine species.^[27] Thus, we also synthesized 7h as reported, and attempted to convert it to CPPs. However, no CPPs were detected.

We were also aware that the structure of **6** is a covalently bonded version of a palladium or platinum square which is formed by the self-assembly of 4,4'-bipyridyl with palladium and platinum (Scheme 2).^[28] Therefore, the use of platinum or palladium would be a promising strategy for the formation of 7. Since bisaryl palladium(II) species undergo reductive elimination at ambient temperature and are not expected to have a sufficient lifetime to form a square complex, we selected platinum square 7**i** as the next target.

Prior to this study, to the best of our knowledge, only two examples of the synthesis of cyclic multinuclear platinum complexes were known in which the platinum atoms are covalently connected with conjugated molecules. Youngs and co-workers reported the preparation of butadiyne-bridged cyclic tetranuclear platinum complex **8** (Figure 3).^[29] However, no attempts were reported for the reductive elimination of the platinum complex to form a cyclic hexadecayne. Bäuerle and co-workers reported the reaction of a diyne-substituted terthiophene with PtCl₂(dppp) (dppp refers to 1,3-bis (diphenylphosphino)propane) to give bisplatino-macrocycle **9** in good yield.^[30] Subsequent reductive elimination of platinum from **9** afforded the corresponding cyclodimeric terthiophenediyne in moderate yield. The diyne units were further converted to thiophene by treatment with disodium sulfide, giving cyclo[8]thiophene.

After we started our work, Bäuerle and co-workers also reported the direct synthesis of cyclic oligothiophenes mediated by cyclic platinum intermediate **10**, which was formed by the transmetalation of a bisstannylated quinquethiophene and PtCl₂(cod).^[31] While the structure of **10** was not fully characterized, reductive elimination of platinum afforded a mixture of cyclic oligothiophenes (m = 1-6). These results suggest that formation of the cyclic platinum complex having PP units analogous to the sides of a square is possible; however, it remained unclear whether reductive elimination of platinum



Scheme 2. Synthesis of $(4,4'-bipyridyl)_4M_4$ (M = Pd, Pt) complex through the self-assembly process pioneered by Fujita and co-workers.



Fig. 3. Structures of oligomeric cyclic platinum compounds prepared by Youngs and Bäuerle.

п	Diameter ^[b] (nm)	Strain energy ^[c] (kJ/mol) [kcal/mol]	HOMO energy (eV)	LUMO energy (eV)
4	5.70	602.7 [144.1]	-4.498	-1.990
5	7.05	490.5 [117.2]	-4.665	-1.955
6	8.40	406.8 [97.23]	-4.915	-1.780
7	9.77	356.5 [85.20]	-4.968	-1.802
8	11.13	307.1 [73.40]	-5.105	-1.699
9	12.49	279.6 [66.82]	-5.125	-1.720
10	13.87	246.6 [58.93]	-5.198	-1.666
11	16.61	229.4 [54.83]	-5.209	-1.677
12	16.61	205.21 [49.05]	-5.263	-1.632
13	17.99	194.33 [46.45]	-5.259	-1.651
14	19.36	176.14 [42.10]	-5.289	-1.638
15	20.74	168.33 [40.23]	-5.289	-1.638
16	22.11	153.82 [36.76]	-5.311	-1.622
17	23.49	148.27 [35.44]	-5.309	-1.630
18	24.87	136.63 [32.65]	-5.326	-1.617
19	26.23	132.76 [31.73]	-5.324	-1.622
20	27.62	122 96 [29 39]	-5 332	-1.621

Table 1. Calculated diameters and strain and HOMO/LUMO energies of [n]CPPs.^[a]

^[a]Data obtained from DFT calculations at the B3LYP/6-31G* level of theory. ^[b]Determined from the diameter of an inscribed circle containing the ipso carbons of each PP unit. ^[c]A group equivalent reaction [(n + 1) terphenyl \rightarrow [n]CPP + n biphenyl] used for Itami^[35] and Bachrach^[34] was employed.

from the complex would take place when considering the significant strain energy of the final products.

2.2. Structure, Strain Energies and HOMO/LUMO Energies of CPPs

The structure and electronic properties of [n]CPPs (n = 4-20) were estimated using density functional theory (DFT) calculations at the B3LYP/6-31G* level of theory prior to the synthesis.^[14] The most stable conformation of even-numbered [n]CPPs is an alternating zigzag orientation of PP units with nearly $D_{(n/2)h}$ point group symmetry, and that of odd-numbered CPPs has a helical arrangement of PP units. The dihedral angles between two adjacent PP units of even CPPs are 33-35° for large CPPs (n > 10), the values of which are similar to those of linear oligoparaphenylenes (35.8°).^[32] The dihedral angles become smaller as CPPs are decreased in size, and the calculated dihedral angles of [8] and [6]CPPs are 31° and 27°, respectively. These results are virtually identical to the reports from Itami and co-workers^[33] and Bachrach and Stück.^[34] Diameters, strain energies, and HOMO/LUMO energies of the CPPs are summarized in Table 1. As there is no fixed definition of the CPP diameter, we have defined it here as the diameter of a circle passing through the ipso carbons of each PP unit.

The CPP strain energies increase with a decrease in the number of PP units, and a small but distinct odd-even effect originating from the conformational differences between odd and even CPPs could be observed. [20]CPP, which was the largest and least strained CPP among the calculated CPPs, possesses 123 kJ mol⁻¹ of strain energy, a value almost the same as that of cyclopropane (117 kJ mol⁻¹).^[35] [12]CPP, which was prepared for the first time by Jasti and Bertozzi, possesses 205 kJ mol⁻¹ of strain energy, which is very close to that of cyclopropene (230 kJ mol⁻¹). The strain energies of [8]CPP, our first synthetic target, and [5]CPP, the structural unit of C₆₀, are 307 and 491 kJ mol⁻¹, respectively. These results clearly indicate that CPPs are highly strained molecules. However, considering that the highly strained hydrocarbon cubane (strain energy of 649 kJ mol⁻¹) had already been prepared, we supposed that small CPPs, such as [5]CPP, could possibly be synthesized by selecting an appropriate synthetic route and reaction conditions.

HOMO and LUMO energies of the CPPs increase and decrease, respectively, as the size of the CPP decreases. The size dependences of the HOMO/LUMO energies of CPPs are in sharp contrast to those of linear oligoparaphenylenes, for which the HOMO and LUMO energies increase and decrease, respectively, as the result of an increase in the effective conjugation when the number of PP units is increased. The conflicting results for CPPs most likely originate from the size dependence of the aromaticity of the PP units, which decrease in benzenoid character and increase in quinoid character as the number of PP units decreases.^[1e,36] Therefore, smaller CPPs have stronger polyene character than larger analogues. This size-dependent decrease in aromaticity accompanied by the structural transformation to quinoid form was recently experimentally proven by Raman spectroscopy.^[37] The HOMO/ LUMO energies of CPPs exhibit odd-even effects due to the existence of the helical conformation in the odd CPPs. However, the PP units of CPPs rotate freely at ambient temperature; accordingly, the experimentally observed physical properties of CPPs showed less pronounced odd-even effects, a result reflected by the time-averaged structure and orbital energies (see below).

The HOMO/LUMO gap for [5]CPP was calculated to be 2.71 eV, a value very close to the experimentally obtained HOMO/LUMO gap for C_{60} (2.88 eV). Since many C_{60} derivatives have been applied to charge-transporting materials in organic electronics, especially for photovoltaics,^[2c,2d] small CPPs such as [5]CPP and its derivatives would be prominent lead materials for molecular electronics.

Theoretical calculations suggest that, besides size as discussed above, a variety of factors, such as functionality, length, and helicity, influence the electronic structure of CPPs and their derivatives (Figure 4). For example, a cyclic tetramer of fluorene, similar in size to [8]CPP but containing a



Fig. 4. Structures and HOMO/LUMO energies of [8]CPP and its derivatives obtained by DFT calculations at the B3LYP/6-31G* level of theory. Structures of tubular compounds and energy values in parentheses were obtained at the B3LYP/3-21G* level of theory.



Scheme 3. Selective synthesis of [12]CPP.

dimethylmethylene bridge in the biphenyl unit of the CPP, possesses a lower LUMO energy, higher HOMO energy, and, thus, narrower HOMO/LUMO gap than that of [8]CPP. Replacement of the hydrogen atoms of a CPP with fluorine (perfluoro[8]CPP) and introduction of an electronegative nitrogen atom to a CPP (a cyclic tetramer of 2,5-connected bipyridine) act to decrease both HOMO and LUMO energies. Furthermore, tubular compounds formed by an increase in the length of a CPP possess far narrower HOMO/LUMO gaps compared to the corresponding CPP having the same diameter. These results clearly suggest the ease of orbital-energy engineering of CPPs compared to fullerenes, given that the availability and structural flexibility of fullerenes and CNTs are quite limited. Therefore, CPPs offer unique structural and electronic diversities for molecular electronics. All compounds shown in Figure 4 are our synthetic targets.

3. Synthesis of CPPs

3.1. Selective Synthesis of [8] and [12]CPPs

We chose [8]CPP as an initial target (Scheme 1c).^[13] 4,4'-Bis(trimethylstannyl)biphenyl **5c** prepared from commercially available 4,4'-dibromobiphenyl was treated with two equivalents of $PtCl_2(cod)$ to give bisplatinated biphenyl **5d**. Then, **5d** was heated with an equimolar amount of **5c** in THF, giving the square-shaped platinum complex **6e** in good yield. Alternatively, **6e** was also obtained in high yield by heating a 1 : 1 mixture of **5c** and $PtCl_2(cod)$. Precipitation of **6e** was observed during the reaction, which may shift the equilibrium toward the formation of **6e** and also reduce the transformation of **6e** into unwanted side products such as linear oligomeric compounds. The cod ligand in **6e** was substituted with dppf to give **6f**, and subsequent reductive elimination of platinum by the addition of bromine afforded [8]CPP. The overall yield of [8]CPP was 37% in our first report but has now been increased to 57% by optimization of the conditions.

[12]CPP was also selectively synthesized starting from 4,4"-bis(trimethylstannyl)terphenyl in a similar manner through platinum square **11** in 43% overall yield (Scheme 3).^[14] More than 100 mg of [12]CPP was obtained in a large-scale preparation. Several carbon- and heteroatom-bridged CPP derivatives were also successfully synthesized in our group, starting from the corresponding carbon- and heteroatom-bridged biphenyl derivatives.^[16]



Scheme 4. Synthesis of the simplest structural unit of helical CNTs by Isobe and co-workers.

Isobe and co-workers successfully applied our synthetic method to the synthesis of the simplest structural unit of helical CNTs starting from chrysene derivative 12 bearing Bpin groups (Scheme 4).^[18a] After boron-platinum transmetalation to form a platinum square, reductive elimination of platinum by the addition of triphenylphosphine afforded the desired 13 in good yield as a mixture of rotational isomers. The helical chirality of the products is preserved at ambient temperature; the products were optically resolved using HPLC equipped with a chiral stationary phase, permitting the isolation of the optically active, simplest helical CNT structural unit for the first time. Isobe and co-workers also succeeded in the synthesis and optical resolution of the simplest structural unit of zigzag single-walled CNTs (SWCNTs)^[18b] and π lengthened compounds prepared from Pigment Red 168^[18c] using the same synthetic strategy.

3.2. Random Synthesis of [n] CPPs $(n = 8-13)^{[14]}$

The above results clearly demonstrate the efficacy of the platinum-square route for the synthesis of [4m]CPPs (m = integer). However, the results also suggest that the structural diversity with respect to ring size is quite limited. To expand the synthetic versatility, we next attempted to employ different PP units as the precursors for cyclic platinum complexes. If the C–Pt–C bond-angle preference in the platinum complex is 90°, a rectangular platinum complex would selectively form. Once such a complex forms, the reductive elimination of platinum from the complex would give varieties of even CPPs.

To examine this hypothesis, a 1:1 mixture of bisplatinated biphenyl **5d** and 4,4''-bis(trimethylstannyl) terphenyl **14** was heated in 1,2-dichloroethane at 50°C for 32 h, and the resulting mixture was treated with dppf followed by bromine (Scheme 5). While we anticipated the selective formation of [10]CPP, a mixture of [8], [9], [10], [11], and [12]CPP was obtained in 2.4%, 3.2%, 5.3%, 4.7%, and



Scheme 5. Random synthesis of [8]-[13]CPPs.

2.3% overall yields, respectively, as confirmed after separation by gel-permeation chromatography (GPC) and MALDI-TOF-MS analysis. The products and their ratios were dependent on the reaction conditions employed for platinum complex formation. When **5d** and **14** were heated for 20 h under otherwise identical conditions, [9], [10], [11], [12], and [13]CPP were formed in 5.4%, 9.6%, 7.7%, 3.8%, and 0.8% yields, respectively; [8]CPP was not observed. A mixture of CPPs was also obtained by mixing **5c**, **14**, and Pt(cod)Cl₂ in a ratio of 1 : 1 : 2 at 70°C in 1,2-dichloroethane for 24 h. After ligand exchange and bromine-induced reductive elimination, [8]–[12]CPPs were obtained in 0.7%, 3.0%, 7.3%, 9.8%, and 3.7% yields, respectively.

[10]CPP is expected to form from rectangular platinum complex 16, and [8], [9], [11], and [12]CPPs should form from tetranuclear platinum complexes 6, 15, 17, and 11, respectively (Scheme 6). In order for [13]CPP to form, three terphenyl and two biphenyl units or one terphenyl and five biphenyl units must couple, indicating the formation of a penta- or hexanuclear platinum intermediate. It has already been reported that the transmetalation between arylstannanes and platinum is reversible, and that the aryl groups on the diarylplatinum complexes undergo scrambling.^[38] Therefore, the formation of unexpected platinum complexes must be due to equilibrium during the transmetalation and/or ligandexchange reactions. It is unclear at this moment whether the formation of platinum complexes is thermodynamically controlled through the self-assembly process, as platinum deposition was observed under the current conditions. Though the detailed mechanism is not fully understood, this synthetic route is attractive because it gives various CPPs, including odd CPPs, which can be easily separated using GPC depending on their molecular size.

3.3. Alternative Synthetic Route

While the above-mentioned method could produce several CPPs in reasonable overall yields, selective synthesis could only



Scheme 6. Possible synthetic precursors of [9], [10], and [11]CPPs.



Scheme 7. Selective synthesis of [10], [8], and [6]CPPs.

be achieved for [8] and [12]CPPs. Furthermore, the method could not be applied to the synthesis of CPPs smaller than [8]CPP despite their potential as molecular electronic materials. Jasti and co-workers recently succeeded in the synthesis of [6]CPP, the smallest CPP so far synthesized; however, their route requires numerous reaction steps, providing a low overall yield (0.7% over eight steps).^[7b] Therefore, a new and highyielding synthetic route for small CPPs is highly sought after.

We recently developed a new and selective route toward platinum-square formation that was effective for the size-selective synthesis of [10], [8], and [6]CPPs (Scheme 7).^[15b] The new synthetic route relied on the synthesis of platinum square **19** from U-shaped *p*-haloaryl-substituted dinuclear platinum complex **18**. Upon treatment of **18j–18l** under Yamamoto coupling conditions^[39] employing two equivalents of Ni(cod)₂ and dppf at 50°C, platinum complexes **19j–19l** were formed in 20–63% yields. [10] and [8]CPPs were obtained in 75% and 74% yields from **19j** and **19k**, respectively, using the Br₂-induced reductive elimination adopted from our previous synthesis.^[7b]

In contrast, treatment of **191** with Br_2 did not afford [6]CPP at all. However, the use of $XeF_2^{[40]}$ instead of Br_2 as an oxidant induced the desired reductive elimination, giving [6]CPP in 47% yield. Fluorine-based oxidants such as AgF, fluoride anion sources such as tetrabutylammonium fluoride,

and several neutral and electron-deficient ligands such as $P[OCH(CF_3)_2]_3$,^[41] acetonitrile, and cod, were also effective in forming [6]CPP. Under optimized conditions, [6]CPP was obtained in 8.9% overall yield from commercially available 1,4-diiodobenzene. Therefore, this new synthetic route significantly increases the availability of [6]CPP.

We also selectively synthesized [10]CPP starting from L-shaped *cis*-coordinated *p*-iodobiphenyl **20m** by applying a protocol developed by Osakada and co-workers.^[42] Thus, **20m** was treated with a stoichiometric amount of Pd(dba)₂ (dba refers to dibenzylideneacetone) and 2,2'-bipyridyl (bpy); the resulting intermediate was further treated with a stoichiometric amount of AgBF₄. Although we anticipated the formation of [8] or [16]CPP via the selective dimerization or tetramerization of **20m**, respectively, [10]CPP was exclusively formed in 13% isolated yield (Scheme 8).^[15a]

A plausible mechanism for the formation of [10]CPP from **20m** involves oxidative addition of **20m** to a Pd(dba)₂/ bpy species to afford the corresponding aryl–Pd(II) complex **20n** (L' may be cod or bpy). The cationic Pd complex generated from **20n** upon treatment with silver salt induces an aryl-coupling reaction to give trimer **21**,^[42a] from which elimination of 4,4'-bispalladium biphenyl occurs to give triangular trinuclear platinum complex **22**.^[42b,43] Finally, reductive elimination of platinum from **22** gives [10]CPP.



Scheme 8. Selective synthesis of [10]CPP from L-shaped *cis*-coordinated platinum 20m.



Fig. 5. ¹H NMR chemical shifts of [n]CPPs in CDCl₃.

3.4. NMR Spectra of CPPs

All CPPs showed a single peak in the ¹H NMR spectra in the aromatic region and two peaks in the ¹³C NMR spectra even at low temperatures such as -80°C, indicating that the paraphenylene units freely rotate on the NMR timescale. The rotational barrier of the paraphenylene unit in [12]CPP was estimated by theoretical calculations as 16 kJ mol⁻¹ by Itami and co-workers.^[33]

The ¹H NMR chemical shifts of the CPPs, including CPPs prepared by Bertozzi, Jasti, and Itami, are summarized in Figure 5. Among [8]–[19]CPPs, the proton resonances shift downfield with an increase in CPP size, reaching a maximum at \sim 7.7 ppm. In contrast, the change in proton resonances from [6] to [7]CPPs show an upfield shift with the increase in size,



Scheme 9. Self-assembly of trispyridyl ligand 23 to form cage molecule 24 reported by Fujita and co-workers.

suggesting the existence of two competing factors affecting the chemical shift. The chemical shift of the aromatic hydrogen in [n]paracyclophanes shows a lower magnetic field in smaller cyclophanes^[44] due to a decrease in aromaticity and the existence of a deshielding effect caused by an increase in ring strain. Therefore, the observed size dependence of the proton chemical shift of [6] and [7]CPPs is probably derived from ring strain, but that of larger CPPs cannot be explained by strain. Further studies are needed to clarify this unique size dependence.

3.5. Synthesis of a 3D π -Conjugated Molecule^[17]

Despite the detailed mechanism for the formation of the platinum square (e.g., 6 from 5) being unclear, the process by which complex formation occurs can be regarded as a covalent bonding version of the self-assembly of structurally related coordination complexes (Scheme 1c vs. Scheme 2). The numerous existing reports on supramolecular transitionmetal-ligand complexes with 3D cages and polyhedral structures^[45] may suggest that these complexes would be suitable precursors for novel hoop-shaped π -conjugated molecules. For example, Fujita reported that trispyridyl ligand 23 and palladium(II) or platinum(II) selectively and quantitatively formed octahedral, hexapalladium or platinum cage 24 by selfassembly involving a ligand-metal interaction (Scheme 9).^[45a] If a structurally related cage consisting solely of covalent bonds was to form, such a molecule would be a possible precursor of a 3D π -conjugated molecule.

To examine this possibility, 1,3,5-tris(*p*-trimethylstannylphenyl)benzene **25c** was first treated with three equivalents of Pt(cod)Cl₂ to afford trisplatinated **25d**, which was further treated with an equimolar amount of **25c**. A white precipitate appeared during the reaction; this solid, isolated in 81% yield, was identified as the desired octahedral-shaped, hexanuclear platinum complex **26e** (Scheme 10). Treatment of **26e** with dppf, followed by the reductive elimination of platinum from the resulting dppf complex **26f** by



Scheme 10. Synthesis of 3D π -conjugated molecule 27.

addition of XeF₂, afforded cage-like 3D molecule **27** in 21% yield. The structure of **27** was initially elucidated from ¹H and ¹³C NMR spectroscopy and MS, and was finally and unambiguously determined using single-crystal X-ray crystallographic analysis.

The calculated strain energy of **27** was 501 kJ mol⁻¹, which is higher than that of [6]CPP (407 kJ mol⁻¹) and even [5]CPP (491 kJ mol⁻¹).^[14] In contrast, precursor **26** did not exhibit significant strain because the bond angle of *cis*-substituted platinum would be close to its ideal angle of 90°. These results strongly suggest that the use of reductive elimination is an excellent strategy for synthesizing highly strained molecules.

The key steps of the synthesis are the platinum-mediated assembly of π -units by transmetalation and subsequent reductive elimination of platinum. The assembly process mimics the self-assembly of metal and ligand species that form structurally related cage-like coordination complexes. As many metal-organic frameworks with 3D structures are already known and can easily be prepared, the assembly/reductive elimination strategy described here would provide a variety of new 3D π -conjugated molecules with different structures and topologies, which are otherwise difficult to obtain using conventional synthetic methods.

4. Properties of CPPs

4.1. UV and Fluorescence Spectra of CPPs

The UV-vis absorption and fluorescence spectra of the CPPs are shown in Figure 6.^[14,19] All CPPs absorbed UV-vis light at around $\lambda_{max} \approx 340$ nm regardless of their size. The absorption coefficient (ϵ) slightly increased with an increase in the size of the CPP. This insensitivity of λ_{max} to size is because the HOMO/LUMO transition is forbidden with no or very small oscillator strengths in all cases, as suggested by the time-dependent DFT calculations.^[14,46] The strong absorption can be assigned to the sum of nearly degenerate HOMO-2 and



Fig. 6. a) UV-vis (solid lines) and fluorescence (dashed lines) spectra and b) fluorescence emission of [6], [8], [9], [10], [11], [12] and [13]CPPs in chloroform. Fluorescence spectra are normalized to the UV-vis absorption intensities.

HOMO-1 to LUMO, and HOMO to nearly degenerate LUMO+1 and LUMO+2 transitions. In sharp contrast to the size dependency of the HOMO/LUMO energies of CPPs, HOMO-1 and HOMO-2 increased and LUMO+1 and LUMO+2 decreased as the number of PP units was increased. Consequently, the energy gaps of the allowed transitions are almost the same regardless of CPP size. The small CPPs exhibited small shoulder peaks at $\lambda \approx 380-450$ nm; these absorptions are thought to be related to the HOMO/LUMO transition.

All CPPs fluoresced with the exception of [6] CPP, and the Stokes shift became larger and more red-shifted with a decrease



Fig. 7. Schematic energy diagram for the relaxation process of CPP in the excited state. Reprinted with permission from reference [19]. Copyright 2012, Royal Society of Chemistry.

in CPP size. Fluorescence quantum yields were quite high for larger CPPs (e.g., 0.72 for [13]CPP) but decreased considerably with a decrease in CPP size (e.g., 0.084 for [8]CPP).^[19] Furthermore, time-resolved fluorescence spectroscopy showed that the lifetime of the singlet excited state was dependent on the size of the CPP, and smaller CPPs had longer lifetimes compared to their larger counterparts, e.g., the lifetimes of [8] and [13]CPPs were measured as 17.6 and 2.0 ns, respectively. In addition, the polarity of the solvent, such as toluene, chloroform, and acetonitrile, did not affect the lifetime. All these results indicate the larger structural change from the Franck-Condon state to the relaxed state in smaller CPPs and the absence of intra- or intermolecular charge transfer involved at the excited state. The larger Stokes shift of the smaller CPPs is reflected by the smaller HOMO/LUMO gap compared to the larger CPPs, as discussed in Section 2.2.

The structural relaxation in the excited state as detected by the fluorescence upconversion method showed that the decay lifetimes of the initial components became shorter for smaller CPPs, e.g., 0.27 and 4.31 ps for [8] and [13]CPP, respectively. These results suggest that smaller CPPs undergo a faster but larger structural relaxation from the Franck–Condon state to the relaxed state compared to larger CPPs. Theoretical calculations suggest that the structural relaxation accompanies the planarization of each PP unit in CPP as well as the increase in the quinoidal contribution of the benzene unit, and that the structural change is more significant in smaller CPPs than larger ones (Figure 7).

4.2. Redox Properties of CPPs

All of the CPPs examined showed reversible oxidation waves as measured using cyclic voltammetry (CV) in 1,1,2,2tetrachloroethane ($C_2H_2Cl_4$) solutions containing 0.1 mol L⁻¹ Bu₄NPF₆ at room temperature (Figure 8 and Table 2).^[14,15b] This clear reversibility indicates that the oxidized intermediates



Fig. 8. Cyclic voltammogram of [8]CPP in $Bu_4NPF_6/C_2H_2Cl_4$ at room temperature.

Table 2. Half-wave oxidation potentials of [n]CPPs obtained using cyclic voltammetry.^[a]

n	E (vs. Fc/Fc ⁺)
6	0.29
8	0.59
9	0.70
10	0.74
11	0.79
12	0.83
13	0.85

 $^{[a]}V$ vs. ferrocene/ferrocenium couple; $Bu_4NPF_6~(0.1~M)$ in 1,1,2,2-tetrachloroethane; scan rate = 20 mV/s; scan range = 0–1.25 V.

are stable under ambient temperatures; indeed, we recently succeeded in isolating the radical cation and dication of [8]CPP.^[47] We initially thought that the oxidation wave observed in the CV experiments was a one-electron process, but we now believe that the wave consists of two-electron processes. Detailed studies are now in progress. Reduction wave(s) could not be observed within the potential window of this solvent.

The oxidation potential was strongly affected by the size of the CPPs, with [6]CPP exhibiting the lowest half-wave oxidation potential of 0.29 V (vs. the ferrocene/ferrocenium couple). The oxidation potential was observed to increase with larger CPP sizes, reaching a plateau around 0.85 V with an increase in the number of PP units. This trend is in good agreement with the trend observed for CPP HOMO energies, and the oxidation potential is likely to reflect the time-averaged HOMO energy of the dynamic structures of the CPPs.



Scheme 11. a) Size-selective encapsulation of C_{60} by [10]CPP and b) in silico optimized structure of [10]CPP $\supset C_{60}$ by DFT calculations at the M06-2X/6-31G* level of theory.

4.3. Host-Guest Chemistry

4.3.1. Selective Encapsulation of C₆₀ by [10]CPP

By analogy to the existence of layered carbon networks with curved surfaces, e.g., multiwalled CNTs,^[48] bucky onions,^[49] and, especially, fullerene peapods in which SWCNTs encapsulate fullerenes,^[4] the concave cavity of the CPPs should act as a host for π -conjugated molecules with a convex surface, such as fullerenes. Such a host–guest complex would be a suitable model for elucidating convex–concave π – π interactions.^[1d,50] Furthermore, the properties of CNTs are modulated by the encapsulation of fullerenes in fullerene peapods, and the preparation of CPP host–guest complexes encompassing fullerenes would provide good models to elucidate the peapod properties in the homogeneous phase. Although Kawase has reported the complexation of cycloparaphenyleneacetylenes with fullerenes,^[51] at the time of starting this work, there were no reports regarding the formation of host–guest complexes with CPPs so far.

¹H NMR and UV-vis spectroscopic studies on the hostguest chemistry between CPPs and C₆₀ revealed that C₆₀ was selectively encapsulated by [10]CPP, forming a 1 : 1 complex, [10]CPP \supset C₆₀ (Scheme 11a).^[20a] The size selectivity is worth emphasizing, in that only [10]CPP interacted with C₆₀ among the [8]–[12]CPPs, as clarified by ¹H NMR analysis by observing the downfield shift of the [10]CPP proton signal before and after C₆₀ addition (Figure 9a). The proton signals of the other CPPs did not change. The same downfield shift was observed when C₆₀ was added to a solution of isolated [10]CPP (Figure 9b).

The binding constant (K_a) of complex formation between C_{60} and [10]CPP was 2.79×10^6 L mol⁻¹ in toluene, as measured by fluorescence quenching experiments. The results revealed that [10]CPP and C_{60} are stabilized by about 38 kJ mol⁻¹ as a result of encapsulation; this value is about 100 times larger than that obtained for [6]cycloparaphenyleneacetylene $\supset C_{60}$, ^[1d,51a] which is the strongest host reported for C_{60} so far consisting of simple hydrocarbons until very recently (see below).

The structure of the complex optimized by DFT calculations at the M06-2X/6-31G* level of theory^[52] revealed that C_{60} sits snugly inside the cavity of [10]CPP (Scheme 11b). The interlayer distance between C_{60} and [10]CPP as calculated from the diameter of C_{60} and [10]CPP is 0.335 nm. The observed interlayer distance coincides with the interplanar van der Waals distance between graphite sheets,^[53] clearly indicating the importance of attractive van der Waals interactions for maximizing concave–convex π – π interactions. The structure of the complex was recently proven by single-crystal X-ray crystallographic analysis by Jasti and co-workers, and the X-ray structure is essentially identical to the calculated structure.^[8]

The dihedral angles between two adjacent PP units of $[10]CPP \supset C_{60}$ are 26–28°, which is significantly smaller than those of free [10]CPP (32–33°).^[14,33,34] However, since a singlet was observed in the ¹H NMR spectrum of $[10]CPP \supset C_{60}$ even at low temperatures (–80°C), the PP unit in the complex must be structurally flexible and be rapidly fluttering at this temperature, and the C_{60} molecule inside the [10]CPP cavity also freely rotates.

Very recently, Isobe and co-workers reported that a cyclic tetramer derivative of chrysene **13** also encapsulates C_{60} with an extremely high binding constant (log $K_a = 11.5$ in toluene).^[54] Since the binding constant of the complex was so strong, it can be considered as a bearing surface on the molecular scale; bearing molecule **13** holds the fullerene journal tightly to prevent its run-out motion, and the fullerene journal (or shaft) rolls anisotropically in the bearing despite the tight holding constraint.

4.3.2. Selective Encapsulation of C_{70} by [10] and [11]CPPs

SWCNT encapsulation of fullerenes with an anisotropic shape is of great interest because several geometrically distinct orientations are possible, unlike spheroidal C_{60} . C_{70} has an ellipsoidal shape with long (0.796 nm) and short (0.712 nm) axes, and has the highest aspect ratio (0.89) among fullerenes.^[55] On encapsulation by SWCNTs, this molecule adopts one of two different



Fig. 9. ¹H NMR spectra in CDCl₃ at room temperature of a) [8]–[12]CPPs i) before and ii) after C_{60} addition, and b) isolated [10]CPP i) before and ii) after C_{60} addition. Reprinted with permission from reference [20a]. Copyright 2011, John Wiley and Sons.



Fig. 10. Molecular structure of C70-CNT peapod with a) lying orientation and b) standing orientation.

orientations, namely "lying", where the long axis of C_{70} is parallel to the tube axis, and "standing", where it is perpendicular (Figure 10a and 10b, respectively).^[56] Okazaki and co-workers reported that the transition from lying to standing occurred at a tube diameter of 1.406 nm.^[57] However, the factor(s) controlling the orientation of C_{70} is (are) unclear, as the interaction between neighboring fullerenes is also proposed to play a significant role in determining the orientation.^[58]

In sharp contrast to the selective interaction between C_{60} and [10]CPP, both [10] and [11]CPPs formed a 1 : 1 complex with C_{70} , giving the resulting peapods as determined by ¹H NMR and UV-vis spectroscopy.^[20b] The binding constants of [10]CPP \supset C₇₀ and [11]CPP \supset C₇₀ in toluene were 8.4×10^4 L mol⁻¹ and 1.5×10^5 L mol⁻¹, respectively, at 25° C,^[59] meaning that complex formation was highly exergonic with ΔG values of -28 kJ mol⁻¹ and -30 kJ mol⁻¹ for [10] and [11]CPP, respectively. While these values are slightly lower than that of [10]CPP and C₆₀, this was one of the strongest host–guest interactions between C₇₀ and a simple hydrocarbon observed to date.

In silico structural optimization and single-crystal X-ray crystallographic analysis of the complexes revealed that C70 was found to exist in two distinct orientations inside the CPP cavity, namely lying and standing, depending on the specific size of the CPP (Figure 11). In [10]CPP⊃C₇₀, C₇₀ adopts the lying orientation inside the [10]CPP cavity, interacting with it at the equatorial region (Figure 11a). Note that X-ray crystal analysis was performed on the complex of [10]CPP and cyclopropyl-substituted C_{70} **28** (Figure 12). This mode of interaction is virtually identical to that observed between C₆₀ and [10]CPP. C₇₀ and [10]CPP were separated by 0.35 nm, supporting the importance of the attractive van der Waals interaction. These results are not surprising, as the short axis of C_{70} (0.712 nm) is almost identical to the diameter of C_{60} (0.710 nm). Since the diameter of "free" [10]CPP is 1.380 nm, the orientation of C_{70} in [10]CPP $\supset C_{70}$ is consistent with that observed in CNTs.^[57,60]

In contrast, C_{70} adopted the standing conformation in [11]CPP \supset C₇₀, interacting with [11]CPP along the long axis



Fig. 11. ORTEP drawings of a) $[10]CPP \supset 28$, b) $[10]CPP \supset 28$ (top view), c) $[11]CPP \supset C_{70}$, and d) $[11]CPP \supset C_{70}$ (top view) with 50% probability thermal ellipsoids. Solvent molecules and hydrogen atoms are omitted for clarity. O: red; C: gray. Reprinted with permission from reference [20b]. Copyright 2013, John Wiley and Sons.



Fig. 12. Structure of functionalized C₇₀ 28.

(Figure 11b). Since the diameter of free [11]CPP is 1.520 nm, the selectivity for the standing orientation is consistent with that observed for CNTs.^[57,60] The interaction between [11]CPP and C_{70} in its standing orientation involves the radial deformation of [11]CPP to an ellipsoidal shape. Interaction between C_{70} and [11]CPP is less ordered than that observed between [10]CPP and C_{70} , but the interfacial distances, defined as those between the centroid of a PP unit of [11]CPP and the nearest centroid of a hexagon or pentagon of C_{70} , came close to 0.35 nm (0.361–0.387 nm, except for in the helical region of the PP units) upon deformation. Therefore, this "induced-fit" maximizes the van der Waals interactions along the C_{70} long axis and the CPP. This is because CPPs are highly radially elastic molecules, and the deformation occurs readily with low energy loss.

It is noteworthy that the orientations of C_{70} units encapsulated within [11]CPP $\supset C_{70}$ were well fixed with no orientational disorder, while for [10]CPP \supset **28** half of the C_{70} units in the complex showed a directional disorder along the long axis of C_{70} . The radially elastic character of CPPs should contribute to the tight encapsulation, as orientational disorder has been commonly observed in the crystals of many fullerene inclusion complexes such as C_{60} complexes of rigid cyclic porphyrins.^[61]

The above results strongly suggest that the orientation of C_{70} in a C_{70} peapod is kinetically controlled by the interaction between C_{70} and the CNT depending on its size, even under the preparation conditions of fullerene peapods (~400°C under vacuum). The kinetically formed structure would be further stabilized by the interaction between neighboring C_{70} molecules in both the lying and standing orientations.

In the crystal packing, [10]CPP \supset 28 aligned along the *a* axis, as highlighted in blue in Figure 13a, and the other complexes (purple) filled the space. [11]CPP \supset C₇₀ aligned along the *b* axis (Figure 13b), and this highly ordered alignment generated a one-dimensional ordering of C₇₀ separated by the van der Waals distance. Therefore, this type of one-dimensional fullerene array opens up possibilities for the application of this crystal to anisotropic electronic devices such as charge-transport materials.^[62]

5. Conclusions and Future Perspectives

Several cyclic π -conjugated molecules, as exemplified by CPPs and a cage-like 3D molecule, were synthesized based on the platinum-mediated assembly of π -units to form closed-cage compounds, from which reductive elimination of platinum gave the target molecule. The assembly of π -units by this method mimics the self-assembly process for the formation of supramolecular ligand-metal complexes. Furthermore, despite the high strain energy of the target molecule, reductive elimination of platinum successfully took place with high efficiency. As there are numerous examples in the synthesis of supramolecular transition metal-ligand complexes with 3D cages and polyhedral structures through self-assembly of ligands and metals, the current assembly/reductive elimination strategy would provide a variety of new cyclic π -conjugated molecules with different structures and topologies, which are challenging to obtain by conventional synthetic methods.

Several size-dependent physical properties of CPPs, such as photophysical properties, redox properties, and host-guest chemistry, were also clarified. These results would be useful for the molecular-level understanding of CNT physical properties as well as fullerene peapods. Theoretical and electrochemical studies suggest that small CPPs and their derivatives should be excellent lead compounds for molecular electronics. Since the structural flexibilities and the availability of pure samples are potentially higher for CPPs and their derivatives than those of fullerenes and CNTs, CPPs, their derivatives, and 3D



Fig. 13. Three-dimensional array of complexes a) [10]CPP \supset **28** and b) [11]CPP \supset C₇₀. Solvent molecules and hydrogen atoms are omitted for clarity. Reprinted with permission from reference [20b]. Copyright 2013, John Wiley and Sons.

molecules offer unique structural and electronic diversities for organic materials used in molecular electronics.

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