



# The Supramolecular Chemistry of Cycloparaphenylenes and Their Analogs

Dapeng Lu<sup>1\*</sup>, Qiang Huang<sup>2</sup>, Shengda Wang<sup>2</sup>, Jinyi Wang<sup>2</sup>, Pingsen Huang<sup>2</sup> and Pingwu Du<sup>2\*</sup>

<sup>1</sup> School of Pharmacy, Anhui Medical University, Hefei, China, <sup>2</sup> Hefei National Laboratory for Physical Sciences at the Microscale, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, China

Cycloparaphenylenes (CPPs) and their analogs have recently attracted much attention due to their aesthetical structures and optoelectronic properties with radial  $\pi$ -conjugation systems. The past 10 years have witnessed a remarkable advancement in CPPs research, from synthetic methodology to optoelectronic investigations. In this present minireview, we highlight the supramolecular chemistry of CPPs and their analogs, mainly focusing on the size-selective encapsulation of fullerenes, endohedral metallofullerenes, and small molecules by these hoop-shaped macrocycles. We will also discuss the assembly of molecular bearings using some belt-persistent tubular cycloarylene molecules and fullerenes, photoinduced electron transfer properties in supramolecular systems containing carbon nanohoop hosts and fullerene guests, as well as the shape recognition properties for structure self-sorting by using dumbbell-shaped dimer of [60]fullerene ligand. Besides, the supramolecular complexes with guest molecules other than fullerenes, such as CPPs themselves, iodine, pyridinium cations, and bowl-shaped corannulene, are also discussed.

**Keywords:** supramolecular chemistry, fullerene guest, non-fullerene guest, carbon nanohoop, cycloparaphenylene

## INTRODUCTION

Supramolecular chemistry is the subject of the association of two or more chemical species held together by intermolecular forces, such as electrostatic interactions, hydrogen bonding, van der Waals forces, etc., which could lead to organized entities of higher complexity (Lehn, 1985, 1988). It is one of today's fastest growing disciplines, crossing a range of subjects from biological chemistry to materials science, and shows great potential in the fields of catalysis, drug delivery, biotherapy, electrochemical sensor, self-healing materials (Zhang and Wang, 2011; Yan et al., 2012; Dong et al., 2015; Yang et al., 2015; Zhang et al., 2017a; Zhou et al., 2017). As one of the most important aspect of supramolecular chemistry, the host-guest molecular recognition requires that the two species must complement each other both in geometry (size and shape) and binding sites (Lehn, 1985, 1988). Macrocyclic structures, in principle, meet the requirements as they usually contain the cavities, clefts, and pockets with appropriate size and shape that provide the framework for substrate species by multiple non-covalent interactions. The representative macrocyclic molecules during the development of supramolecular chemistry, such as crown ether, cyclodextrins, calixarenes, and cucurbiturils, have been the classical structures in this field (Yang et al., 2015; Zhou et al., 2017).

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### \*Correspondence:

Dapeng Lu  
ludapeng@ahmu.edu.cn  
Pingwu Du  
dupingwu@ustc.edu.cn

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Recently, the introduction of pillar[*n*]arenes (**Figure 1A**) as new types of macrocyclic hosts by Ogoshi et al. (2008), rapidly received significant attention for their prominent host-guest properties.

Meanwhile, another type of carbon-rich macrocyclic molecules with radially oriented  $\pi$  systems pointing inwards to the cavity have emerged as a new class of strained, non-planar aromatic structures, which were named as cycloparaphenylenes (CPPs) or carbon nano hoops because of their structural relationship with carbon nanotubes (CNTs) (Jasti et al., 2008; Jasti and Bertozzi, 2010). Despite their simple structures, however, the synthesis of CPPs was only achieved in 2008 from curved molecular precursors after intensive efforts (Jasti et al., 2008) Following this work, several other novel strategies for CPP synthesis were developed and a number of CPP-related carbon nanorings with various sizes and atomic compositions were prepared (Darzi et al., 2015; Segawa et al., 2016). More importantly, Itami et al. reported the successful synthesis of a carbon nanobelt, [12]carbon nanobelt ([12]CNB) comprising a closed loop of fully fused edge-sharing benzene rings in 2017 (Povie et al., 2017). Furthermore, development of this synthetic strategy to the preparation of [16]CNB and [24]CNB analogs were also reported by the same group (Povie et al., 2018). Using a new ligand system, the yield of the final belt-forming, nickel-mediated reaction for [12]CNB was improved from 1 to 7%, and [16]CNB and [24]CNB were obtained in 6 and 2% yield, respectively. These studies are important steps toward the bottom-up synthesis of other carbon nanobelt structures and CNTs. Another interesting and valuable work which should be mentioned is the thermally induced cycloreversion strategy for the synthesis of carbon nano hoops reported by Huang et al. (2016). They converted the anthracene photodimer synthon into anthracene-incorporated aromatic macrocycle through ring expansion reaction based on the cycloreversion of its dianthracene core. This work sheds light on the utility of the anthracene photodimerization-cycloreversion method for “bottom-up” carbon nano hoop synthesis. The past 10 years have witnessed a remarkable advancement in CPPs research, from synthetic methodology to optoelectronic investigations due to their size-dependent behavior and promising applications in materials (Segawa et al., 2012; Wu et al., 2018; Huang et al., 2019; Toyota and Tsurumaki, 2019; Xu and Delius, 2019).

In a recent work, Delius et al. overviewed the host-guest chemistry of carbon nano hoops, the preparation of mechanically interlocked architectures, and crystal engineering (Xu and Delius, 2019). In this present minireview, we only highlight the supramolecular chemistry of CPPs and their analogs, mainly focusing on the size-selective encapsulation of fullerenes, endohedral metallofullerenes, and small molecules by these hoop-shaped macrocycles. We will also discuss the assembly of molecular bearings using some belt-persistent tubular cycloarylene molecules and fullerenes, photoinduced electron transfer properties in supramolecular systems containing carbon nano hoop hosts and fullerene guests, as well as the shape recognition properties for structure self-sorting by using dumbbell-shaped dimer of [60]fullerene ligand. Besides, the supramolecular complexes with guest molecules other than

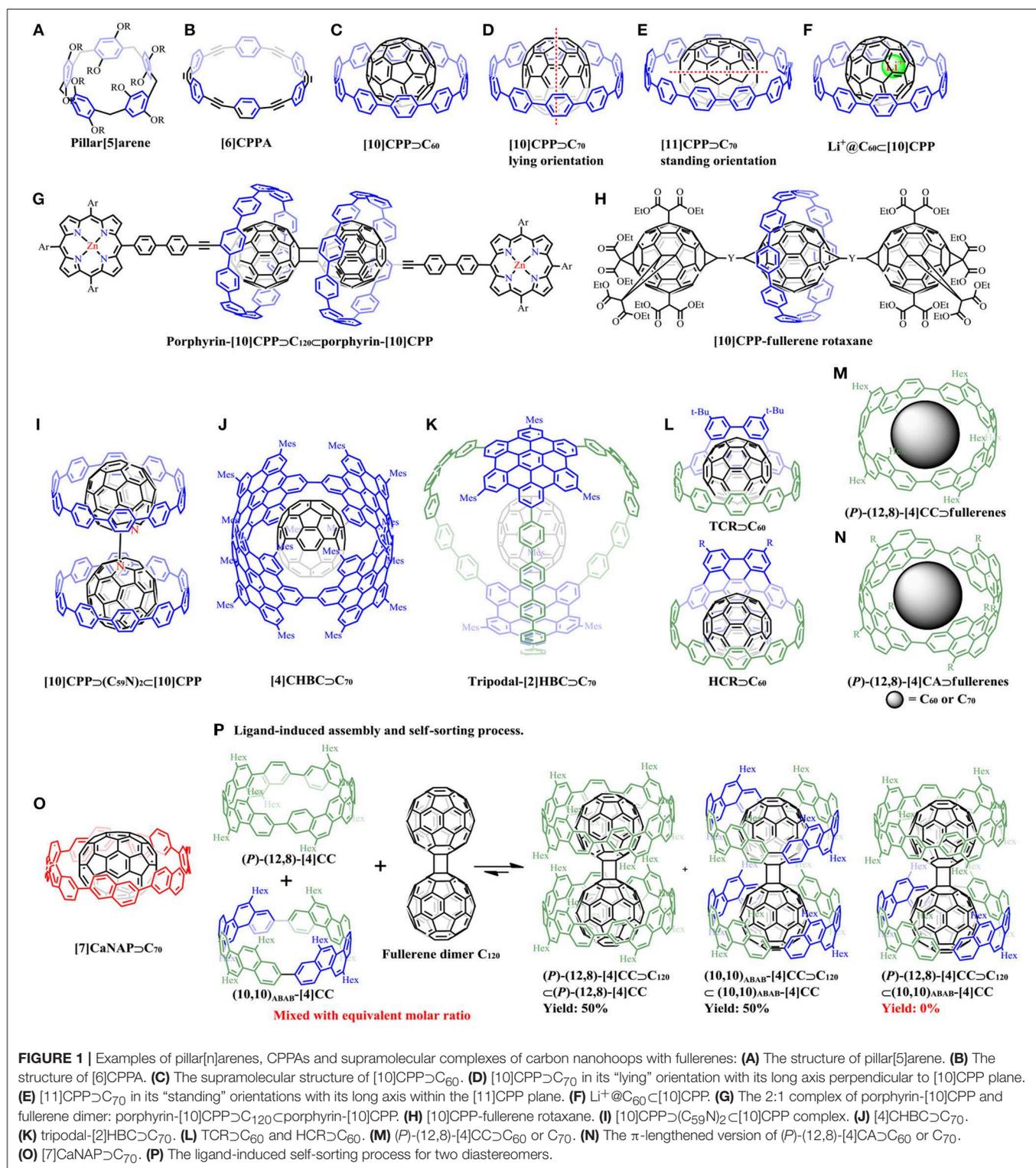
fullerenes, such as CPPs themselves, iodine, pyridinium cations, and bowl-shaped corannulene, are also discussed.

## SUPRAMOLECULAR COMPLEXES CONSISTING OF CPPs AND FULLERENES

The first series of macrocyclic hosts was the molecules with  $sp^2/sp$ -hybridized carbon atoms, cyclic paraphenyleneacetylenes (CPPAs) (**Figure 1B**), reported by Kawase et al. (1996). The complexation between CPPA congeners and fullerenes were extensively studied (Kawase et al., 2003a,b, 2007; Miki et al., 2013). Although CPPA derivatives tend to form tight complexes with  $C_{60}$ , their unstable nature hindered further experimental studies. In contrast, the solely  $sp^2$ -hybridized CPP derivatives without acetylene linkers are sufficiently stable, and could similarly encapsulate fullerene molecules.

The initial example of the host-guest complex of this type was reported by Iwamoto et al. (2011). The CPP receptor with 10 phenylene units ([10]CPP) has an ideal diameter (1.38 nm) to accommodate  $C_{60}$  (0.71 nm) (**Figure 1C**), showing a binding constant  $K_a$  of  $2.79 \times 10^6 M^{-1}$  in toluene determined by fluorescence quenching titration, which was two orders of magnitude higher than those obtained for [6]CPPA $\supset$  $C_{60}$  (Kawase et al., 2003a). The variable-temperature NMR (VT-NMR) spectroscopy experiments showed that the rapid exchange between free [10]CPP and [10]CPP $\supset$  $C_{60}$  took place at room temperature, and the energy barrier for the exchange was determined to be  $59 kJmol^{-1}$ . The crystal structure of [10]CPP $\supset$  $C_{60}$  obtained by Jasti' group revealed the presence of convex-concave  $\pi$ - $\pi$  interactions (Xia et al., 2012). It is noteworthy that  $C_{60}$  can be selectively encapsulated by [10]CPP among the mixture of [8]-[12]CPPs, indicating that the cavity sizes of other CPPs were not appropriate for constructing a strong complex with  $C_{60}$ . Interestingly, it was found that  $C_{70}$ , which has an ellipsoidal shape with long axis of 0.796 nm and short axis of 0.712 nm, could also be encapsulated by [10]CPP in its “lying” orientation with its long axis perpendicular to [10]CPP plane (**Figure 1D**), but with reduced association constant  $K_a$  ( $8.4 \times 10^4 M^{-1}$  in toluene) compared with [10]CPP $\supset$  $C_{60}$  (Iwamoto et al., 2013). Nevertheless,  $C_{70}$  was adopted the “standing” orientations to be accommodated in the cavity of [11]CPP with its long axis within the [11]CPP plane (**Figure 1E**). Besides, [11]CPP deformed into an ellipsoidal shape to maximize the van der Waals interactions with the long axis of  $C_{70}$ . All these results indicated the size- and orientation selectivity for the CPP $\supset$ fullerene systems. Furthermore, a deep exploration by analyzing geometry structures through theoretical calculations revealed that  $C_{70}$  selectively adopts lying, standing, and half-lying orientations when combined with [10]CPP, [11]CPP, and [12]CPP, respectively (Yuan et al., 2015).

In 2014, Shinohara et al. demonstrated the high binding abilities of [11]CPP toward  $C_{82}$ -based endohedral metallofullerenes, including  $Gd@C_{2v}-C_{82}$ ,  $Tm@C_{2v}-C_{82}$ , and  $Lu_2@C_{2v}-C_{82}$ , which provided a facile non-chromatographic strategy for  $Gd@C_{82}$  extraction and enrichment from crude fullerene mixtures (Nakanishi et al., 2014). Later, another



example of C<sub>82</sub>-based endohedral metallofullerene peapod, [11]CPP $\supset$ La@C<sub>82</sub> was reported (Iwamoto et al., 2014). The solid structure of the complex was determined by X-ray crystallographic analysis, which showed that the La atom was

located near the periphery of [11]CPP rather than the tube axis with the dipole moment of La@C<sub>82</sub> nearly perpendicular to the CPP axis. These evidence demonstrated the different orientations of La@C<sub>82</sub> in CPP and CNT peapods, which suggests that the

orientation of La@C<sub>82</sub> in CNT was mainly determined by interactions among the adjacent ones. More importantly, due to the strong electron accepting properties of La@C<sub>82</sub>, partial charge transfer (CT) from [11]CPP to La@C<sub>82</sub> in the ground state was firstly observed by electrochemical experiments combined with UV/Vis-near-infrared (NIR) titration studies and density functional theory (DFT) calculations, but no fully ionized complex was formed.

The CPP-based fully ionized complex, Li<sup>+</sup>@C<sub>60</sub>⊂[10]CPP, was synthesized and characterized by Ueno et al. (2015) (Figure 1F). The ionic crystal structure was confirmed by X-ray crystallographic analysis. Unlike the empty C<sub>60</sub>, the cationic Li<sup>+</sup>@C<sub>60</sub> core drastically increased the electron accepting ability which could induce strong charge transfer from the electron donors. Cyclic voltammetry experiments revealed that Li<sup>+</sup>@C<sub>60</sub> was harder to be reduced when accommodated by [10]CPP than Li<sup>+</sup>@C<sub>60</sub> itself, which could be ascribed to the higher electron density around the Li<sup>+</sup>@C<sub>60</sub> cage through CPP to Li<sup>+</sup>@C<sub>60</sub> charge transfer interaction. The strong charge transfer interaction also caused the positive charge of the lithium cation delocalized to the outer CPP ring. The broadened absorption bands at around 350 nm and in the NIR region was also related to this interaction. Besides, photoluminescence (PL) lifetime of Li<sup>+</sup>@C<sub>60</sub>⊂[10]CPP (2.5 ns) is shorter than that of [10]CPP (4.3 ns) and C<sub>60</sub>⊂[10]CPP (4.3 ns), suggesting that the charge transfer (CT) interaction may occur.

Recently, Delius et al. reported the synthesis of a porphyrin-[10]CPP conjugate, in which [10]CPP moiety served as a supramolecular junction for charge transfer between a zinc porphyrin electron donor and fullerene electron acceptor (Xu et al., 2018b). Efficient photoinduced electron transfer was observed with a lifetime of charge separation state up to 0.5 μs in the 2:1 complex between [10]CPP and the fullerene dimer (Figure 1G). The intramolecular energy transfer between [10]CPP and porphyrin was also observed. Later, the same group achieved the synthesis of two [2]rotaxanes consisting of one [10]CPP moiety binding to a central fullerene with bis-adduct binding site and another two fullerene hexakis-adduct stoppers using a concave-convex π-π template strategy (Figure 1H) (Xu et al., 2018a). [10]CPP served as an effective supramolecular directing group with the central fullerene as an efficient convex template, steering the reaction exclusively toward two *trans* regioisomers in the final step. The mechanically interlocked structures of [2]rotaxanes were analyzed by variable-temperature NMR (VT-NMR) and mass spectrometry. Transient absorption spectra revealed the interesting consequences of the mechanical bond on charge transfer processes. A later work conducted by Wegner et al. used a dumbbell-shaped dimeric azafullerene [(C<sub>59</sub>N)<sub>2</sub>] as the ligand to combine with two [10]CPP rings, giving [10]CPP⊃(C<sub>59</sub>N)<sub>2</sub>⊂[10]CPP complex (Figure 1I) (Rio et al., 2018). Two stage binding constants were determined to be K<sub>a1</sub> = 8.4 × 10<sup>6</sup> M<sup>-1</sup> and K<sub>a2</sub> = 3.0 × 10<sup>6</sup> M<sup>-1</sup>, respectively, with weak interactions between the two CPP rings. Photoinduced partial charge transfer was observed from [10]CPP to (C<sub>59</sub>N)<sub>2</sub> by differential pulsed voltammetry experiments.

## SUPRAMOLECULAR COMPLEXES CONSISTING OF π-EXTENDED CARBON NANOHOOPS AND FULLERENES

As the π-π interaction operates *via* the surface-to-surface contacts in supramolecular chemistry, it becomes important for large aromatic moieties with increasing π-surface areas. Based on the rapid development of the synthesis strategies, carbon nanostructures with embedded polycyclic aromatic hydrocarbon (PAH) structures, such as hexa-*peri*-hexabenzocoronene (HBC) (Quernheim et al., 2015; Lu et al., 2016; Huang et al., 2019), were subsequently prepared. These π-extended macrocycles usually show larger binding constants with guest molecules due to their larger contact area compared with simple CPP hosts.

The [4]cyclo-2,11-*para*-hexa-*peri*-hexabenzocoronene ([4]CHBC) synthesized in our laboratory was found to selectively incorporate C<sub>70</sub> with a binding constant K<sub>a</sub> of 1.07 × 10<sup>6</sup> M<sup>-1</sup> in toluene (Figure 1J), but no evidence of complexation with C<sub>60</sub> guest was observed, which could be due to the “standing” or “lying” orientations of C<sub>70</sub> in the cavity of the carbon nanoring (Lu et al., 2017). Similarly, another HBC-containing three-dimensional capsule-like carbon nanocage, tripodal-[2]HBC also exhibited the preference of affinity toward C<sub>70</sub> (K<sub>a</sub> = 1.03 × 10<sup>5</sup> M<sup>-1</sup> in toluene) rather than C<sub>60</sub>, which was demonstrated by MS, NMR, and photophysical experiments (Figure 1K) (Cui et al., 2018). More recently, our group achieved the synthesis of two novel π-extended crown-like molecules (TCR and HCR) with embedded curved nanographene units, HBC or TBP (tribenzo[*fj,ij,rst*]pentaphene) (Huang et al., 2019). These two species were found to show high binding affinity toward guest molecule C<sub>60</sub> with the association constants K<sub>a</sub> of 3.34 × 10<sup>6</sup> M<sup>-1</sup> for TCR⊃C<sub>60</sub>, and 2.33 × 10<sup>7</sup> M<sup>-1</sup> for HCR⊃C<sub>60</sub>, respectively (Figure 1L). The gradual increase in binding constants from [10]CPP⊃C<sub>60</sub> (K<sub>a</sub> = 2.79 × 10<sup>6</sup> M<sup>-1</sup>) (Iwamoto et al., 2011) to TCR⊃C<sub>60</sub>, then HCR⊃C<sub>60</sub>, should be ascribed to the increasing π-surfaces that could provide stronger π-π interactions between the hosts and C<sub>60</sub>. Besides, photocurrents were generated when using these molecular crowns or their supramolecular complexes on FTO electrodes under visible light irradiation. Time-resolved spectroscopic measurements suggested fast photoinduced electron transfer in the supramolecular heterojunctions.

The recently reported shape-persistent tubular carbon nanorings demonstrated the binding ability with fullerenes. Five structural isomers of [4]cyclo-2,8-chrysenylene ([4]CC) (Hitosugi et al., 2011), which were named as (*P*)-(12,8)-, (*P*)-(11,9)-, (10,10)<sub>AABB</sub>-, (10,10)<sub>ABAB</sub>-, and (+)-(16,0)-[4]CC, can form 1:1 complex with C<sub>60</sub> in solution (Isobe et al., 2013). The highest binding constant among similar complexes was recorded for (*P*)-(12,8)-[4]CC⊃C<sub>60</sub> (Figure 1M) in *o*-DCB with K<sub>a</sub> = 4.0 × 10<sup>9</sup> M<sup>-1</sup>, while isomers of (*P*)-(11,9)-, (10,10)<sub>AABB</sub>-, and (10,10)<sub>ABAB</sub>-[4]CC also showed the binding constant above 10<sup>9</sup> M<sup>-1</sup>. The lowest K<sub>a</sub> was recorded for (+)-(16,0)-[4]CC⊃C<sub>60</sub> (2.0 × 10<sup>4</sup> M<sup>-1</sup> in *o*-DCB), but was still higher than that for [10]CPP⊃C<sub>60</sub> (6.0 × 10<sup>3</sup> M<sup>-1</sup> in *o*-DCB) (Iwamoto et al., 2011). These results clearly show that the belt-persistence in tubular

structures also plays a crucial role in binding with fullerenes besides the cavity size. Therefore, a molecular rolling bearing with  $C_{60}$  in the [4]CC bearing was constructed as the bearing can hold the fullerene molecule tightly to prevent its run-out motion. The  $C_{60}$  molecule did not exchange and took rapid relative rolling motion on the NMR timescale within the bearing from the  $^1\text{H}$  NMR analysis of  $(P)$ -(12,8)-[4]CC $\supset$  $C_{60}$ . The crystal structures of this molecular bearing was further analyzed by X-ray diffraction, demonstrating the presence of smoothly curved surface that allows the dynamic motion of  $C_{60}$  even in the solid state (Sato et al., 2014). Theoretical studies by density functional theory (DFT) indicates that the calculated association energies were quite method-dependent, and the energy barriers for the rolling motions within the bearing were as low as 2–3 kcal mol $^{-1}$  with two distinct rolling motions (precession and spin) (Isobe et al., 2015).

Besides  $C_{60}$  guest, another twelve fullerenes, including  $C_{70}$ , nine exohedral functionalized fullerenes, and two endohedral fullerenes, were selected and assessed as rolling journals in the belt-persistent [4]CC bearing (Hitosugi et al., 2013). [4]CC tolerated the modified fullerenes but with reduced binding constant.  $C_{70}$  was found to be superior guest not only for the high binding constant ( $K_a = 5.0 \times 10^9 \text{ M}^{-1}$  in DCB), but also for its tolerance of introduction of bulky shaft without obvious decrease in binding constant. A lengthened version of  $(P)$ -(12,8)-[4]cyclo-2,8-anthanthreneylene ( $(P)$ -(12,8)-[4]CA) can also bind with  $C_{60}$  and  $C_{70}$  (Figure 1N) with enhanced association enthalpy as the increase of the C-C contact area compared with the shorter congener  $(P)$ -(12,8)-[4]CC (Matsuno et al., 2013, 2015).

The electronic properties of the molecular bearings were then systematically studied. The bearing systems can generate charge-separated species under light irradiation.  $(P)$ -(12,8)-[4]CC $\supset$  $C_{60}$  system exhibits a rapid back electron transfer to give triplet  $C_{60}$  journal after the formation of triplet charge-separated species via photoinduced electron-transfer (Hitosugi et al., 2014). The lengthened version of [4]CA $\supset$  $C_{60}$  could generate a triplet excited state at the outer bearing, whereas the endohedral fullerene  $\text{Li}^+@C_{60}$  enabled the back electron transfer processes without triplet excited species (Hitosugi et al., 2015).

Although there existed tight association between  $(P)$ -(12,8)-[4]CC and  $C_{60}$ , the solid-state dynamic rotations of  $C_{60}$  still enabled reorientation by a small energy barrier (+2 kcal mol $^{-1}$ ). The solid-state rotational motions reached a non-Brownian, inertial regime at 335 K (Matsuno et al., 2018b).

Unlike the relatively rigid conformation of the arylene panels in [4]CC, [7]cyclo-amphi-naphthylene ([7]CaNAP) was rather flexible with its panels rotate rapidly at ambient temperature (Sun et al., 2016). However, this rotation did not significantly affect its binding ability for  $C_{70}$  with the  $K_a$  in the range of  $10^7$ – $10^9 \text{ M}^{-1}$  (depending on the solvents) (Figure 1O) (Sun et al., 2019). More importantly, the structure of [7]CaNAP deformed during the rotation to track the orientation changes of the ellipsoidal  $C_{70}$ .

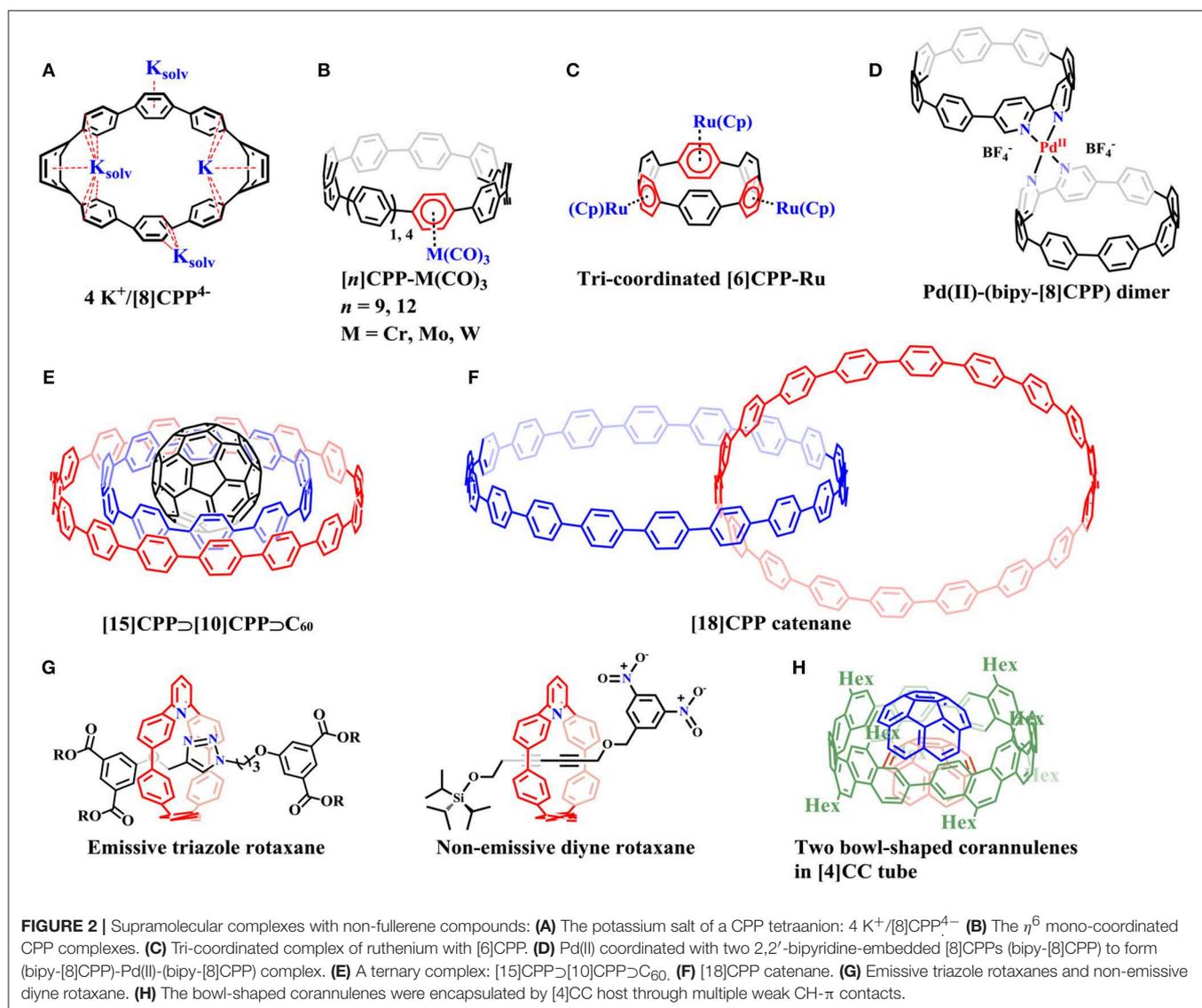
By using dumbbell-shaped  $C_{60}$  dimer ( $C_{120}$ ) as the ligand with two binding sites, two-wheeled composites can be assembled with the shape-persistent macrocycles as the receptors (Matsuno et al., 2016, 2017). The thermodynamics of the 2:1 complex

revealed the two-stage association constants, for example  $K_{a1}$  of  $7.3 \times 10^{11} \text{ M}^{-1}$  for the formation of the 1:1 complex  $[(P)$ -(12,8)-[4]CC $\supset$  $C_{120}$ ], and  $K_{a2}$  of  $9.7 \times 10^7 \text{ M}^{-1}$  for the 2:1 complex  $[(P)$ -(12,8)-[4]CC $\supset$  $C_{120}$  $\subset$  $(P)$ -(12,8)-[4]CC]. There was no self-assembly of the two [4]CC hosts without  $C_{120}$ . The ligand-induced self-sorting phenomena was observed from the [4]CC family $\supset$  $C_{120}$ . A moderate level of self-sorting was obtained when mixing a racemic mixture ([4]CC ( $(P)$ -(12,8)-[4]CC [ $(P)$ - $D_4$ ] and  $(M)$ -(12,8)-[4]CC [ $(M)$ - $D_4$ ]) and  $C_{120}$  with equivalent molar ratio: yielding 70% amount of the racemate complexes  $[(P)$ - $D_4$  $\supset$  $C_{120}$  $\subset$  $(P)$ - $D_4$  +  $(M)$ - $D_4$  $\supset$  $C_{120}$  $\subset$  $(M)$ - $D_4$ ], and 30% amount of the meso-form  $[(P)$ - $D_4$  $\supset$  $C_{120}$  $\subset$  $(M)$ - $D_4$ ]. A complete self-sorting was obtained when two diastereomers of [4]CC ( $(P)$ - $D_4$ ] and (10,10) $_{\text{ABAB}}$ -[4]CC [ $D_{2d}$ ]) were applied: yielding 50% amount of  $(P)$ - $D_4$  $\supset$  $C_{120}$  $\subset$  $(P)$ - $D_4$ , 50% amount of  $D_{2d}$  $\supset$  $C_{120}$  $\subset$  $D_{2d}$ , and no  $(P)$ - $D_4$  $\supset$  $C_{120}$  $\subset$  $D_{2d}$  was detected (Figure 1P). This shape recognition can be explained by the repulsive van der Waals interactions between aliphatic side chains caused by the H–H contacts at the interfaces of the receptors as revealed by the crystal structures.

## SUPRAMOLECULAR COMPLEXES WITH NON-FULLERENE COMPOUNDS

When two aromatic moieties stack in a face-to-face fashion, the  $\pi$ - $\pi$  interaction could hold the two species together, such as the case of CPP analogs with fullerenes. Besides, other non-covalent interactions, such as CH- $\pi$ , metal- $\pi$  interactions also play important roles in various supramolecular systems. The CH- $\pi$  interaction, which is a kind of atom-to-surface hydrogen bond and relatively weak, could also assemble host-guest complex. On the other hand, the metal- $\pi$  coordination usually could strongly stabilize the associated architecture.

In 2013, Petrukhina et al. reported the potassium salt of a CPP tetraanion ( $4 \text{ K}^+/[8]\text{CPP}^{4-}$ ) by direct reduction of [8]CPP with potassium metal (Figure 2A) (Zabula et al., 2013). The X-ray diffraction analysis revealed that [8]CPP $^{4-}$  functions as a multisite ligand with its *endo*- and *exo*- surfaces engaged in coordination with the potassium. Similarly, [6]CPP were also demonstrated to be reduced by alkali-metal to its mono- and di-anions, [6]CPP $^{1-}$  and [6]CPP $^{2-}$  (Spisak et al., 2018). Itami et al. synthesized  $\eta^6$  mono-coordinated CPP complexes  $[n]\text{CPP-M}(\text{CO})_3$  where  $n = 9, 12$  and  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$  (Figure 2B) (Kubota et al., 2015). The crystal structure of [9]CPP-Cr(CO) $_3$  showed that chromium coordinated on the convex surface of [9]CPP. Later, Yamago's group succeeded in the preparation of mono-, di-, and tri-coordinated complexes of ruthenium with  $[n]\text{CPP}$  ( $n = 5$  and 6) (Kayahara et al., 2016). Ru selectively coordinated to alternate phenylene units in multi-coordinated complexes (Figure 2C). Single-crystal analysis indicated that Ru also coordinated on the convex surface of CPPs. More recently, Jasti illustrated a general strategy for building up nanoHoops that could easily coordinate to transition metals (Van Raden et al., 2017). 2,2'-bipyridine-embedded [8]CPP (bipy-[8]CPP) synthesized in this work



can readily coordinate to  $\text{Pd}(\text{II})$  or  $\text{Ru}(\text{II})$  metal centers, forming (bipy-[8]CPP)- $\text{Pd}(\text{II})$ -(bipy-[8]CPP) (**Figure 2D**) or  $\text{Ru}(\text{II})$ -(bipy-[8]CPP) complexes, respectively.

Besides the role as supramolecular hosts, CPP molecules can also serve as guests to be included in larger nanoHoops with the “Russian doll” fashion. The strongest binding was predicted when the host and guest differed by five phenyl rings through theoretical calculations (Fomine et al., 2012; Bachrach and Zayat, 2016). Yamago et al. demonstrated these predictions by experimental studies:  $[n] \text{CPP}$ s ( $n = 5, 6, 7, 8, \text{ and } 10$ ) did selectively interact with  $[n+5] \text{CPP}$ s, forming  $[n+5] \text{CPP} \supset [n] \text{CPP}$  complexes (Hashimoto et al., 2017). A ternary complex,  $[15] \text{CPP} \supset [10] \text{CPP} \supset \text{C}_{60}$ , could also be assembled (**Figure 2E**).

By analyzing the ions in the gas phase of the complex mixture from CPP synthesis through matrix assisted laser desorption ionization (MALDI) together with ion-mobility

mass spectrometry (IMMS), Müllen’s group provided evidence for the existence of possible catenanes composed of CPPs, such as  $[12] \text{CPP} + [24] \text{CPP}$ ,  $2 \times [18] \text{CPP}$  (**Figure 2F**), or even a trefoil knot (Zhang et al., 2017b). Most recently, Itami et al. reported the synthesis of all-benzene catenanes and trefoil knot through silicon-based template method which adjoined two neighboring CPP fragments in a crossing pattern followed by removal of the silicon tether after macrocyclization (Segawa et al., 2019). Interestingly, the trefoil knot shows only a single proton resonance in  $^1\text{H}$ -NMR spectrum even at  $-95^\circ\text{C}$ , indicating its ultrafast motion on the NMR time scale. The  $[2]$ heterocatenane, in which  $[12] \text{CPP}$  and  $[9] \text{CPP}$  are mechanically interlocked shows energy transfer from  $[12] \text{CPP}$  to  $[9] \text{CPP}$  via the mechanical bond under light irradiation. Cong et al. reported the synthesis of a catenane consisting of two interlocked phenanthroline-containing nanoHoops by copper(I)-templated method (Fan et al., 2018). The solid state structure

shows a Möbius topology stabilized by non-covalent interactions. A 2,6-pyridyl embedded nano hoops were recently synthesized for the preparation of nano hoop-based rotaxanes through active metal template reactions (**Figure 2G**; Van Raden et al., 2019). The triazole-embedded [2]rotaxanes showed dramatic changes in fluorescence emission (turn-off) when Pd(II) salt was added, suggesting its possible applications in ion sensing. Inspired by this study, another non-emissive [2]rotaxane was devised and synthesized, which has a fluorescence-quenching 3,5-dinitrobenzyl stopper and a fluoride-cleavable triisopropylsilyl (TIPS) stopper. Upon the addition of tetra-*n*-butylammonium fluoride (TBAF), 123-fold emission was recovered as the nano hoop fluorophore was released, indicating that the nano hoop rotaxanes could effectively serve as turn-on fluorescence sensors.

Itami et al. described the assembly of iodine within [*n*]CPPs (*n* = 9, 10, and 12) (Ozaki et al., 2017). Upon electric stimuli, [10]CPP-I turned out to emit white light, caused by the formation of polyiodide chains inside the [10]CPP cavity through charge transfer between [10]CPP tubes and encapsulated iodine chains.

Gaeta reported the 1,4-dimethoxy modified [8]CPP which exhibits binding ability toward pyridinium cations (Della Sala et al., 2017). Density functional theory (DFT) calculations indicated that the CH... $\pi$  and N<sup>+</sup>... $\pi$ <sup>DMB</sup> (DMB = 1,4-dimethoxybenzene) interactions between the host and pyridinium guest played a crucial role in this supramolecular system. Another multi-(1,4-dimethoxy) modified [9]CPP synthesized by our group showed only weak supramolecular interactions for cationic molecules (Lu et al., 2018).

A novel type of host-guest complex assembled solely by CH- $\pi$  hydrogen bonds rather than  $\pi$ - $\pi$  interactions was devised by the Isobe group (Matsuno et al., 2018a). A bowl-shaped corannulene can be encapsulated by a [4]CC host through multiple weak CH- $\pi$  contacts to form a 1:1 complex in solution, driven by a large association enthalpy. The 1:2 host-guest combination was unveiled in the crystalline solid state (**Figure 2H**). Despite the multiple weak hydrogen bonds, the guest was still allowed dynamic rotational motions in the host. Solid state analysis revealed a single-axis rotation of the bowl in the tube.

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## SUMMARY AND OUTLOOK

In this featured article, we overviewed recent progress on supramolecular properties of CPPs and their analogs. Various types of new carbon nano hoops were prepared by transition metal-catalyzed coupling reactions. These macrocycles usually possess well-defined cavities with rigid conformation and fixed diameters, which makes them good supramolecular hosts for incorporating a wide range of compounds, such as spherical fullerenes through  $\pi$ - $\pi$ , metal- $\pi$ , and/or CH- $\pi$  interactions. These non-covalent interactions enabled efficient molecular recognitions and host-guest energy transfer. Although the synthesis of new carbon nano hoops and related supramolecular complexes has been growing very fast during the past decade, the applications of these carbon-rich architectures in some fields, such as, organic electronic devices, molecular sensing, and molecular machines, is still far from satisfaction. For further advancement, research efforts should be devoted to explore robust synthetic strategies which are essential for the diversification of carbon nano hoop family. Interdisciplinary studies with cooperative material sciences, analytical, biological, physical, and theoretical chemistry, will dramatically expand the understanding and application of the macrocycles and their supramolecular complexes. It is reasonable to expect that these carbon-rich structures will attract further research interests, and lead to the preparation of unique and unprecedented molecular tools and materials in the future.

## AUTHOR CONTRIBUTIONS

PD supervised the project. DL and PD mainly wrote the paper. QH, SW, JW, and PH co-wrote the paper. All authors discussed the results and commented on the manuscript.

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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