

2,2'-Bipyridyl-Embedded Cycloparaphenylenes as a General Strategy To Investigate Nanohoop-Based Coordination Complexes

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S Supporting Information

ABSTRACT: Because of their unique cyclic architectures, tunable electronic properties, and supramolecular chemistries, cycloparaphenylenes (CPPs) have the potential to act as a new class of ligands for coordination cages, metal–organic frameworks, and small-molecule transition-metal complexes. However, currently there is no general strategy to coordinate the cyclic framework to a variety of metal centers. We report here a general and scalable synthetic strategy to embed 2,2'-bipyridine units into the backbone of CPPs. We use this approach to synthesize a 2,2'-bipyridine-embedded [8]CPP, which we show can successfully coordinate to both Pd(II) and Ru(II) metal centers. The resulting coordination complexes, a Pd(II)–nanohoop dimer and a bis(bipyridyl)ruthenium(II)-functionalized nanohoop, show unique solid-state and photophysical properties. This work provides a proof of concept for a general strategy to use nanohoops and their derivatives as a new class of ligands.

The development of ligands with tunable electronic structures and unique three-dimensional molecular shapes has provided access to an abundance of metal coordination complexes with desirable properties for a wide range of applications. For example, the development of new redox-active ligands is a central driver in the fields of photocatalysis and photovoltaics.¹ In addition, the increase in functionalization of organic linker ligands² in metal–organic frameworks (MOFs) and coordination cages has enabled advanced functionality such as catalysis,^{3a,b} chemical sensing,^{3c} molecular recognition,^{3d,e} and energy transfer.^{3f} As many of the currently available ligands are centralized around a linear, flat aromatic framework,^{2b} the introduction of new cyclic ligand scaffolds—in particular those with radially oriented π systems—would provide new metal–ligand architectures that would offer unique features, thereby furthering the development and application of large metal–ligand assemblies as well as small-molecule transition-metal complexes.

The [n]cycloparaphenylenes (CPPs),^{4a} or nanohoops, are composed of n benzene rings linked at the para positions, resulting in a rigid, three-dimensional, fully sp^2 -hybridized cylindrical architecture with a radially oriented π system. The unique geometry of CPPs provides novel electronic properties such as narrowing HOMO–LUMO energy gaps and red-

shifting fluorescence with decreasing size—a trend exactly opposite to that of linear analogues.^{4b} In addition, the radially oriented π systems provide a hydrophobic, electron-rich cavity that acts as a strong host for electron-poor guests such as C_{60} .^{5a–d} These diameter-dependent optoelectronic properties, coupled with the molecular recognition capabilities, position CPPs and related cyclic derivatives^{6a–d} as a new class of inherently porous, cylindrical ligands with numerous potential applications. Using CPPs as ligands, however, is currently restricted to η -type coordination complexes^{7a,b} (Figure 1),

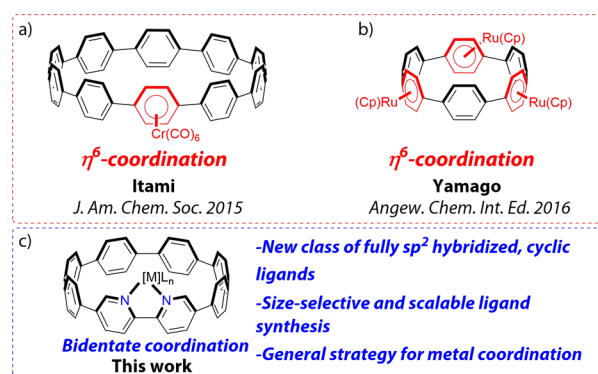


Figure 1. Current examples of metal–nanohoop coordination complexes.

which limits their use and potential as a general ligand class. An early report by the Itami group^{7c} suggested that embedding 2,2'-bipyridyl units into the nanohoop framework is possible, but the reported synthetic route was not amenable to CPPs of different diameters and the reported nanohoop was only accessed in small quantities. Herein we illustrate a general synthetic method to access 2,2'-bipyridyl-embedded nanohoops in a size-selective⁸ and scalable manner. By constructing a Pd(II) nanohoop dimer and a photosensitized Ru(II) nanohoop, we demonstrate that nanohoops can be used as ligands toward the construction of new cylindrical coordination cages as well as a novel photoactive transition-metal complexes with supramolecular capabilities.

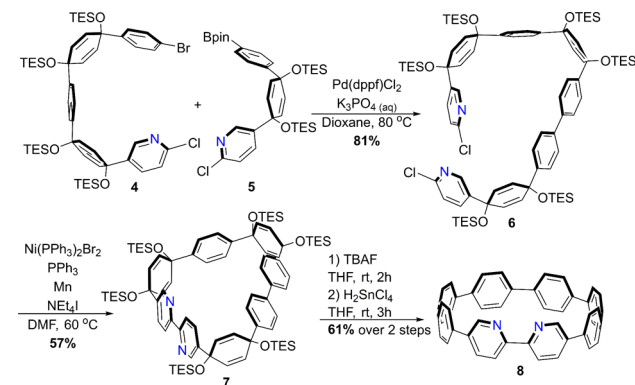
Our investigations began by developing synthetic methodology that would allow 2,2'-bipyridyl-embedded CPPs to be

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accessed in a size-selective and scalable manner. Previous work by our group^{4a} and others^{4d} has shown that CPPs and related derivatives are readily accessed by the reductive aromatization of macrocycles containing cyclohexadienes as “masked” aromatic rings (e.g., structure 7 in Scheme 1). These relatively

Scheme 1. Synthetic Route toward CPP Ligand 8



unstrained macrocycles can be prepared in a variety of sizes via aryl–aryl coupling reactions. We surmised that the most general synthetic strategy leading to the 2,2′-bipyridyl-embedded nano hoops would be one that formed the pyridine–pyridine linkage in the macrocyclization step. Because of the instability of 2-pyridylboranes,^{9a,b} we targeted reductive couplings of pyridyl halides as the key cyclization step.¹⁰ Yamago recently demonstrated that reductive homocoupling of aryl bromides can be used to prepare a precursor to [5]CPP.^{4c} In order to leverage previous methods relying on the orthogonal reactivity of aryl chlorides and bromides, we envisioned the reductive homocoupling of pyridyl chlorides as the key development for general access to the 2,2′-bipyridyl-embedded nano hoops. Guided by these thoughts as well as the work by Goldup^{10c} and Drew,^{10d} we prepared intermediate 6 with terminal pyridyl chloride units (Scheme 1) via Suzuki–Miyaura cross-coupling of bromide 4 and boronic ester 5 in good yield (see Supplementary Scheme 1 for the full synthetic route). Precursor 6 can be easily prepared on a multigram scale. After significant optimization of reductive nickel homocoupling conditions, we were then able to access macrocycle 7 in 57% yield. With macrocycle 7 in hand, we explored the reductive aromatization step and found that the mild H₂SnCl₄ strategy reported by Yamago^{4d} afforded the desired bipy-CPP ligand 8 in 61% yield over two steps. Noteworthy is the use of pseudodilution conditions for the macrocyclization step, which allows the ligand synthesis to be highly scalable (see the Supporting Information (SI) for full details). Additionally, the use of pyridyl chlorides over bromides allows for orthogonal lithium–halogen exchange and Suzuki–Miyaura coupling for rapid access to the macrocyclic precursor. Moreover, this strategy can be expanded to a variety of 2,2′-bipyridyl-embedded nano hoops with different diameters using strategies we have developed for cycloparaphenylene synthesis.^{4f}

As a first pass at exploring the coordination chemistry of these new ligands, we probed the feasibility of constructing a nanotube-inspired coordination cage from these systems. We began by first preparing intermediate 9 (Figure 2) via the reaction of PdCl₂ with bipy-CPP 8 in acetonitrile. Pd–CPP 9 was then combined with another equivalent of bipy-CPP 8 in the presence of 2 equiv of AgBF₄ for 2 h in dichloromethane,

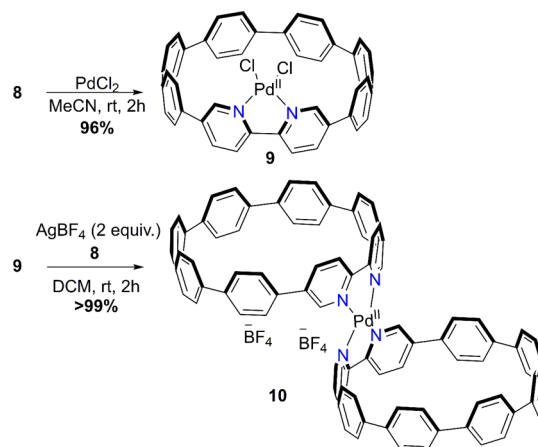


Figure 2. Synthetic route for nano hoop dimer 10.

providing nano hoop dimer 10 in quantitative yield. In the ¹H NMR spectrum of dimer 10 (see the SI), only three 3-pyridyl-centered protons were observed, suggesting high symmetry. However, this spectrum could result from a dimeric structure that possessed either of two geometries (trans or cis) about the Pd(II) metal center. In order to elucidate the exact geometry, dark-red crystals suitable for X-ray crystallography were obtained after slow vapor diffusion of pentane into a concentrated solution of 10 in acetone. Crystallographic analysis not only confirmed the formation of 10 but also provided direct solid-state evidence for a trans preference about the Pd(II) center. Bis(bipyridyl)palladium(II) complexes often show a distorted square-planar geometry because of steric repulsions between hydrogens of the coordinated bipyridine ligands.¹¹ Thus, the observed preference for a trans conformation about the Pd(II) center in dimer 10 can be explained on the basis that similar steric repulsions exist upon formation of complex 10.

We then investigated how the Pd(II) metal center impacted the nano hoop structure and solid-state packing. Detailed analysis of the crystal structure of 10 revealed that two different dimeric units are present, each of which shows subtle changes in their corresponding torsional (θ) and displacement angles (α°). In both dimers, the torsional angle between adjacent pyridyl rings, θ (Figure 3a), is approximately 6°, which

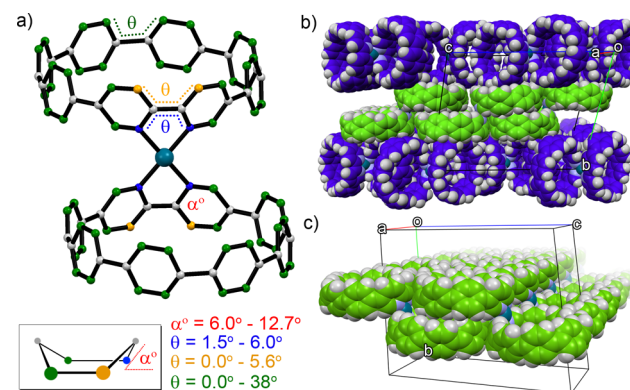


Figure 3. (a) Crystal structure of Pd dimer 10 showing torsional angles and pyridyl displacement angles. (b) Observed packing motif showing the multilayered structure. (c) View of the flat layer (see the SI for the herringbone layer). Counterions and solvent have been omitted for clarity.

is decreased significantly from that of the all-carbon nanohoops (average of approximately 31° for [8]CPP^{4b}). The torsional angles of the remaining aryl rings spanned from 0° up to nearly 38° . Additionally, the displacement angles of the pyridyl units, α° (Figure 3a), varied from 6.0° to 12.7° , similar to those in the parent all-carbon nanohoop [8]CPP.^{4b} Taken together, these data suggest that while ligation to a Pd(II) metal center does reduce the dihedral angle of the embedded bipyridyl unit, this does not strongly affect the remaining aryl rings. Interestingly, these two dimeric units contributed to an unusual multilayer packing motif (Figure 3b) in which each layer possesses a unique microstructure. In one case (Figure 3c), the dimeric units pack into flat, sheetlike arrangements. In the other case, the dimeric units arrange into a herringbone-type motif (Supplementary Figure 1), which is commonly observed in the parent all-carbon CPPs. While the reasoning for this packing arrangement is less clear, we anticipate that nanohoop ligands with different diameters will strongly affect both the packing motif and observed angle distortions. Moreover, through our synthetic methods, we can incorporate multiple pyridyl units such that the nanohoops can be extended into trimeric, oligomeric, or polymeric networks, which will enable new pathways toward novel porous materials.

In addition to the nanohoops' unique structural features, we were curious whether the tunable optoelectronic properties of the nanohoops could be leveraged in new coordination complexes as well. With this in mind, we found that refluxing bipy-CPP **8** with Ru(bipy)₂Cl₂ in ethanol (Figure 4) provided

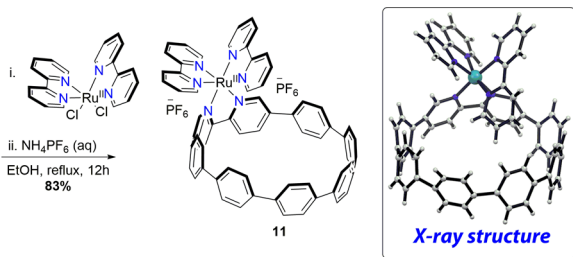


Figure 4. Synthetic route for Ru(II)-nanohoop complex **11**.

Ru(II)-nanohoop complex **11** in 83% yield as the racemate. Red platelike crystals suitable for X-ray crystallography were obtained by diffusion of diethyl ether into a dilute solution of **11** in acetone, and crystallographic analysis unambiguously confirmed both the structure of **11** and the racemic solid-state morphology (see the SI for full details). The electronic structures of **8** and **11** were then studied using UV-vis spectroscopy and compared with the parent system, [Ru(bipy)₃](PF₆)₂ (Figure 5). Bipy-CPP **8** has a λ_{max} of 345 nm ($\epsilon = 1.2 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$), which is similar to that of the parent all-carbon nanohoop [8]CPP ($\lambda_{\text{max}} = 340 \text{ nm}$, $\epsilon = 1.0 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$),^{4b} suggesting that the nitrogen atoms have little impact on the electronic structure—a common observation in other nitrogen-doped CPPs.^{4d,7c} On the other hand, the absorption spectrum of Ru(II)-nanohoop complex **11** showed a dramatic difference relative to those of **8** and [Ru(bipy)₃](PF₆)₂. The first absorption of complex **11** is centered at 290 nm and is due to bipyridine π to π^* transitions,¹² while the absorption at 357 nm originates from the nanohoop; both are broadened and red-shifted relative to those of **8** and [Ru(bipy)₃](PF₆)₂. The broad absorption from approximately

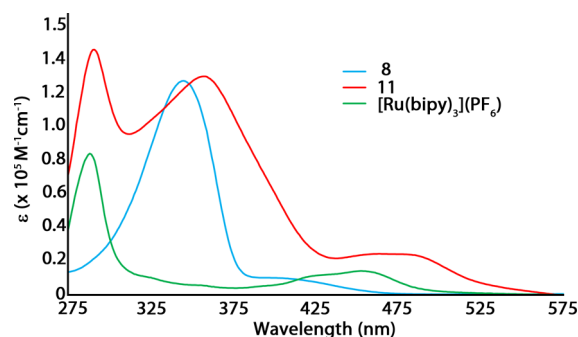


Figure 5. Absorption spectra of CPP **8**, Ru(II)-nanohoop complex **11**, and [Ru(bipy)₃](PF₆)₂ in dichloromethane.

425 to 575 nm is due to metal-to-ligand charge transfer (MLCT)—a hallmark of Ru(II)-polypyridyl complexes.¹²

In homoleptic [Ru(bipy)₃](PF₆)₂, irradiation with visible light creates an excited state that resides on one of three bipyridine ligands.¹² However, in the case of heteroleptic complex **11**, the destination of the charge is less obvious because of the presence of the nanohoop ligand. In order to further investigate the MLCT absorptions, we turned to density functional theory (DFT) and time-dependent DFT (TD-DFT). From TD-DFT studies, we found that five major transitions (Figure 6; see the SI for additional transitions and

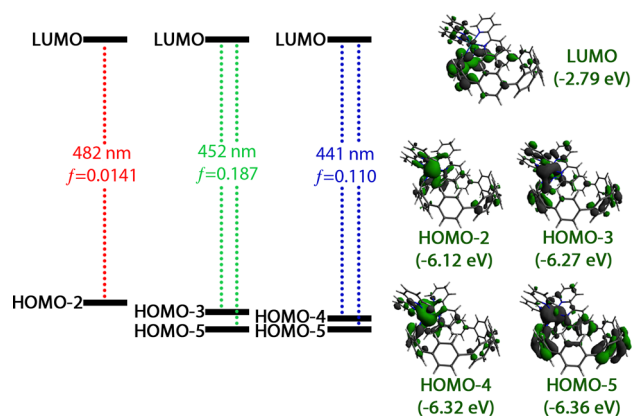


Figure 6. Major electronic transitions (TD-DFT) contributing to MLCT absorptions and representative frontier molecular orbitals for Ru(II)-nanohoop complex **11**, calculated at the B3LYP/6-31G(d,p) (C, H, N) and LANL2DZ (Ru) level of theory.

the calculated absorption spectrum of **11**) are responsible for the absorptions between 440 and 490 nm. In all cases, it was found that the filled molecular orbital was centralized around the Ru(II) metal center and the unfilled orbital was predominately localized on the nanohoop. This supports our expectations that the experimentally observed absorptions in the 430 to 500 nm range result from MLCT transitions. Additionally, this further suggests that there is a significant amount of electron transfer between the Ru(II) metal center and the nanohoop ligand, with apparently very minimal transfer to the bipyridine ligands. Taken together, these results indicate that the excited state of the Ru(II)-nanohoop complex is primarily localized on the nanohoop backbone. Given that the redox potential of nanohoops can be easily tuned,^{4c} we expect that this excited-state localization can be leveraged via supramolecular interactions to provide new functionality for catalysis and energy transfer with electron-deficient guests.

In conclusion, this work illustrates a general strategy for coordinating the nanohoop framework to common metal centers. We have shown that the ligand is readily accessible using straightforward methodology and can be obtained in sufficient quantity and good yield. The resulting coordination complexes, a homoleptic Pd(II) dimer and a Ru(II)–nanohoop complex, show excellent stability and unique solid-state and photophysical properties, suggesting that CPPs show promise as a new class of ligands. While this work centralized around a 2,2'-bipyridyl-embedded[8]CPP, we argue that the synthetic methodology is readily applicable to $[n]$ CPPs with different diameters, and work is currently underway to prepare both reduced- and expanded-diameter nanohoop ligands in order to explore new cylindrical metal–ligand assemblies with interesting supramolecular and solid-state properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.7b00359](https://doi.org/10.1021/jacs.7b00359).

Crystallographic data for **10** (CIF)

Crystallographic data for **11** (CIF)

Experimental procedures and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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