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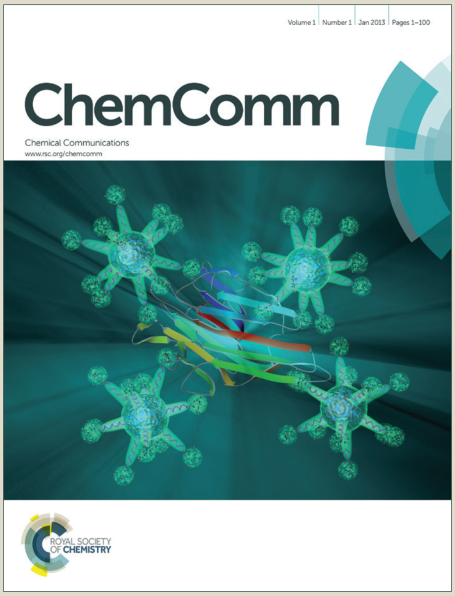

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# Molecular self-assembly of arene-Ru based interlocked catenane metalla-cages

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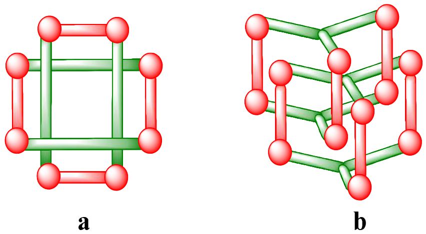
**Two interlocked trigonal prismatic metalla-cages are formed quantitatively through the self-assembly of π-electron rich arene-Ru acceptors with a new tridentate donor. Interestingly, non π-electron rich arene-Ru acceptors furnish simple trigonal prisms when they are combined with tridentate donor.**

Over the past two decades, the use of coordination-driven self-assembly in the design and synthesis of supramolecular coordination complexes has emerged as a powerful methodology to access a wide library of metallacycles and cages under relatively benign conditions with high efficiencies. The strategy of *directional bonding*, in which the edges, faces, and/or vertices of a target polygon or polyhedron are encoded into molecular precursors that are then combined in proper stoichiometries, has defined routes towards a suite of 2D and 3D supramolecules[1] ranging from small molecular boxes[2] to nanometer-sized Archimedean solids.[3] These supramolecular assemblies can be employed in molecular recognition and catalysis[4] and have been shown to act as templates for the synthesis of core-shell nanoparticles.[5] The inherent cyclic nature of edge-directed self-assembly, in which metallacycles and cages possess internal cavities, naturally introduces routes towards catenane and rotaxanes structures wherein discrete architectures can be fused or linked, motivating interest in using such supramolecular constructs as molecular machines.[6] Whereas 2D metallacycles have seen impressive use in the formation of catenane and rotaxanes species,[7] few examples of catenated coordination cages are known.[8]

In 1999, Fujita and co-workers reported the spontaneous self-assembly of ten components into two interlocked, three-stranded discrete coordination cages.[8a] Formation of the interlocked cages involved a reversible, metal-mediated process. A decade later, Hardie and co-workers described cobalt and zinc-based systems with a similar topologies.[9] Fukuda and co-workers reported an interlocked arrangement of two four-stranded palladium coordination cages.[10] Beer and colleagues prepared a interlocked system in which the crossing cycles consisted of covalent entities.[11] This assembly was templated by sulfate ions, which remained bound within the dimer after synthesis. The prevalent molecular phenomena behind these exemplary interlocked structures are metal-ligand coordination and H-bonding interactions.[12] Among these, there are few examples which invoke the importance of π-π interactions between subunits.[13] Mukherjee and co-workers reported a series of triply interlocked $Pd_{12}$ coordination prisms, but they get converted into non-interlocked $Pd_6$ prisms, through π–π stacking interaction, on addition of an aromatic guest.[14] Recently, we reported a self-assembled arene-Ru metalla-rectangle which encapsulated a second, identical rectangle, likely due to π-π interactions (Figure 1a).[15] The non-catenane interlocked, macromolecule-in-a-macromolecule motif was formed with multiple close π-π interactions between the tetracene-containing arene-Ru acceptors and the four π-electron-rich donors, as evidence by single crystal X-ray diffraction. Herein, we report the preparation of arene-Ru trigonal prisms that form either discrete $D_2A_3$ cages or interlocked $\{D_2A_3\}_2$ dimers with significant π-π interactions depending on the specific molecular clip used during self-assembly.



Non-Catenane$(M_2L_2)_2$ Interlocked Catenane $(M_3L_2)_2$ Interlocked

**Figure1.** Schematic representation **(a)** Non-catenane $(D_2A_3)_2$ Interloked **(b)** catenane $\{D_2A_3\}_2$ Interlocked structures by arene-Ru acceptors and N-donor ligands.

The formation of both singular and dimeric prisms follows a similar 2:3 acceptor to donor stoichiometry in which 1,3,5-tris(3-(pyridin-4-yl)-1H-pyrazol-1-yl)benzene (**D1**) is combined with one of four molecular clips [(*p*-cymene)RuCl (OO∩OO) RuCl(*p*-cymene)] (**A1**,OO∩OO = 5,8-dioxydo-1,4-naphthoquinonato (donq); **A2,** OO∩OO =5,11-dioxydo-6,12-tetracenquinonato (dotq); **A3,** OO∩OO =2,2'-bisbenzodimidazole]-1,1'-diide (bbid); **A4,** OO∩OO =4-carboxylato-

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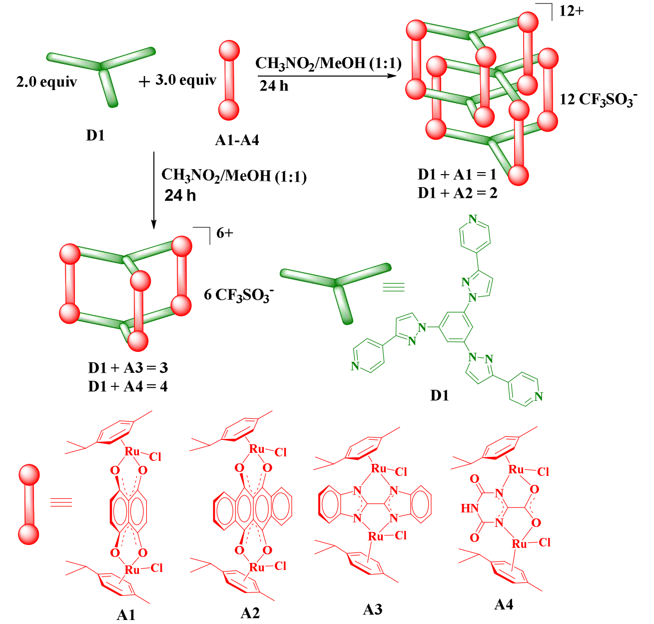
2,6-dioxo-2,6-dihydro-1H-1,3,5-triazin-3-ide, (cddt)). When **A1** or **A2** are used, interlocked cages, as shown in Scheme 1, are obtained and may represent a new paradigm for the formation of interlocked supramolecular species which form with π-π interactions as the impetus. Conversely, **A3** and **A4** ultimate furnish simple $D_2A_3$ trigonal prisms when combined with **D1**.

Ligand **D1** was synthesized in 50% yield by an Ullmann-type coupling with 1,3,5-tribromobenzene and 3-(4-pyridyl) pyrazole in the presence of CuI catalyst (Supporting Information). The dinuclear arene ruthenium complexes $[Ru_2\text{-}(arene)_2(OO\cap OO)Cl_2]$ (**A1-A4**); react in nitromethane-methanol (1:1) at room temperature in the presence of silver triflate as a halide scavenger with ligand **D1** in a 2:3 ration to give the trigonal prisms cations **1-4** (**1** = **D1** and **A1**; **2** = **D1** and **A2**; **3** = **D1** and **A3**; **4** = **D1** and **A4**) stabilized as triflate salts. The first indication of the interlocked nature of **1** and **2** were found in the $^1$H NMR spectra of their reaction mixtures. When assemblies were carried out in $CD_3NO_2$-$CD_3OD$ (1:1), the reaction mixtures could be directly subjected to $^1$H NMR analysis, exhibiting complex spectra after 24 h of stirring at room temperature.



**Scheme 1.** Synthesis of a Discrete $D_2A_3$ and $\{D_2A_3\}_2$ dimeric Supramolecules **1-4.**

The spectral complexity was initially interpreted as resulting from incomplete assembly, giving rise to a number of unique proton environments, however, elongating the reaction time to 3 days resulted in no noticeable difference in the spectra (Figure S4 and S5). In contrast, reaction mixtures forming **3** resulted in simple proton spectra that supported the formation of a symmetric, discrete prism. Notable upfield shifts are observed for the resonances corresponding to protons on **D1**, suggesting that ring current shielding offsets any loss of electron density associated with coordination and induction (Figure S6).[16] Although the aromatic proton signals were broadened and shifted upfield in the spectrum of **4** (Figure S7), the relatively simple spectrum is evidence for the formation of discrete prisms. Further proof for the structural assignments of **1-4** was obtained using electrospray ionization mass spectrometry (ESI-MS). The ESI-MS spectrum of interlocked metalla-cage **1** exhibited one charge state at m/z = 1793.87, corresponding to $[M\text{-}4OTf]^{4+}$. For interlocked metalla-cage **2**, charge states at m/z 1944.64 was assigned to $[M\text{-}4OTf]^{4+}$ (Figures 2). These charge states and isotopic spacings are unique to the $\{D_2A_3\}_2$ dimeric structure. While discrete $D_2A_3$ prisms would potentially show peaks at the same m/z values for the even charge states, the isotopic spacing would be different. Similarly, three charge states were observed for **3** at m/z = 1190.32 $[M\text{-}3OTf]^{3+}$, 855.18 $[M\text{-}4OTf]^{4+}$, and 654.67 $[M\text{-}5OTf]^{5+}$, and for cage **4** at m/z = 1113.18 $[M\text{-}3OTf]^{3+}$, 797.89 $[M\text{-}4OTf]^{4+}$, and 608.04 $[M\text{-}5OTf]^{5+}$ (Figures S8 and S9). These peaks were also isotopically resolved and in good agreement with the calculated theoretical distributions for single $D_2A_3$ structures. The $^1$HNMR coupled with the HR-ESI-MS data demonstrate that the $\{D_2A_3\}_2$ dimeric structure is present in the solution phase in the case of **1** and **2**.

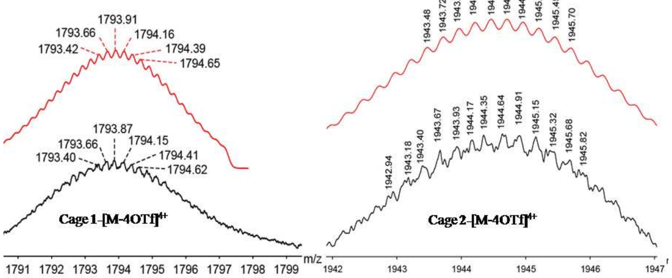


**Figure 2.** Theoretical (top) and experimental (bottom) ESI-MS results for interlocked cage **1** (left) and **2** (right**)**.

The interlocked nature of **2** was unambiguously determined by single-crystal X-ray analysis using synchrotron radiation (Figure 3). The X-ray crystal structure of **2** revealed that each Ru center of **A2** is coordinated by one pyridine unit of **D1** ligands to form the edge of the cage. Thus, three **A2** acceptors hold two **D1** donors in a cofacial arrangement to form the each individual $D_2A_3$ cage (Figure 3a).

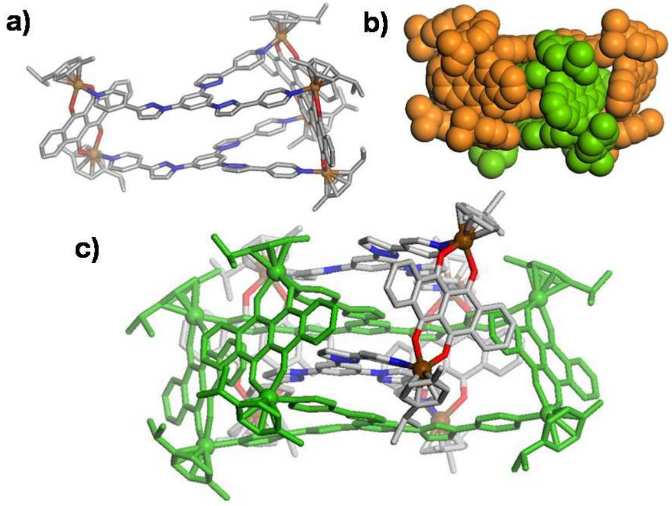


**Figure 3.** X-ray crystal structure of **2**: (a) a discrete cage (interlocked partner omitted for clarity); (b) a space-filling model. (c) the complete, interlocked cage. Hydrogen atoms, counter ions, and solvents of crystallization are omitted for clarity.

The twisting of one arm of each **D1** ligand renders each individual cage of **2** into distorted trigonal prisms (Figure S10). These distorted trigonal prisms are linked together, with the trigonal face of one prism occupying the internal cavity of its counterpart. The prisms are staggered with respect to one another to accommodate the molecular clip edges (Figure 3c). A noteworthy feature of the structure is the close contact between the **D1** ligands each cage, supporting the presence of intermolecular π-π interactions with distances of approximately

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3.4 Å (Figure 3b). The tetracene bridging ligands of the cages are bent outward with a distance of 8.40 Å between the intramolecular moieties. While the tetracene frame of the inner cage curls outward with a distance of 21.11 Å between moieties, potentially reducing the steric strain while maximizing the π-π interactions.

The electronic absorption spectra of **1-4**, along with those of their corresponding metal acceptors (**A1-A4)** and donor ligand (**D1**) were investigated in methanol (supporting information, Figure S11-S14).The absorption spectra exhibit bands at $\lambda_{abs}$ = 318 and 450 nm for **1** (Figure S11)**,** and $\lambda_{abs}$ = 273, 316, 567, and 614 nm for **2** (Figure S12)**,** $\lambda_{abs}$ = 320 nm for **3** (Figure S13)and $\lambda_{abs}$ = 318 nm for **4** (Figure S14). The high-energy bands observed in **1-4** were also present in the spectra of free ligand **D1**. As such, these bands are likely due to $\pi\rightarrow\pi^*$ transitions of the pyridyl donor which are preserved upon self-assembly, albeit with moderate red-shifts. The dinuclear arene-Ru acceptors exhibit high-energy absorption bands at 270–330 nm, as well as broad, low-energy absorption bands ranging from 480–600 nm. These bands are likely a combination of intra/intermolecular $\pi\rightarrow\pi^*$ transitions mixed with metal-to-ligand charge transfers. As with the pyridyl donor bands, these arene-Ru-based bands are also preserved upon self-assembly, giving rise to the strong absorptions observed in the spectra of **1-4**.[14,15b-d] The high-energy band of interlocked metalla-cage **1** and **2** are red-shifted with respect to that of donor **D1** by ~ 28 nm. Similar red-shifts are observed for bands in unlocked cage **3** and **4** that correspond to absorptions of **D1**.

## Conclusions

In conclusion, we have demonstrated for the first time two interlocked metalla-cages, **1** and **2**, which are formed quantitatively through the self-assembly of π-electron rich arene-Ru acceptors **A1** and **A2** with a tridentate1,3,5-tris(3-(pyridin-4-yl)-1H-pyrazol-1-yl)benzene donor, **D1**. The interlocked structure of **2** was confirmed by single crystal X-ray diffraction.The structure revealed that the interlocked prisms contain multiple close contacts of their aromatic fragments, consistent with significant π-π interactions occurring between the six tetracene-containing arene-Ru acceptors and wider size of the four π-electron-rich donors. These interlocked prisms are complemented by two examples of simple, discrete prisms formed using the same donor with alternative metal acceptors. As these cages lack the extensive intra molecular *π-π* stacking, no fused structures are observed. Future work will explore the inclusion of particular guest species such as any fluorescent molecules, enabling us to study confinement effects in these systems.

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## Notes and references

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