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Octapi Interactions: Self-Assembly of a Pd-Based [2]Catenane Driven by
Eightfold π InteractionsJinzheng Lu,[†] David R. Turner,[†] Lindsay P. Harding,[‡] Lindsay T. Byrne,[§] Murray V. Baker,[§] and
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The chemistry of topologically nontrivial supramolecules is emerging from being a chemical curiosity to being considered as a step toward synthesizing nanoscale machinery.¹ The synthesis of [2]catenanes has been approached from a number of directions, with perhaps the most prevalent method being the use of a templating species between the two macrocyclic rings.² An analogous approach using anionic species as the template also exists.³ Catenanes can also be formed without the use of an auxiliary species by using hydrogen-bonding interactions⁴ or reversible covalent bonds.⁵ While metal–ligand coordination and hydrogen bonding have dominated catenane formation, it has also been shown that π interactions can be used toward this end,⁶ as in recent examples of bistable, switchable systems.⁷ Although π interactions are not the strongest weapon in the supramolecular arsenal, when acting cooperatively they result in considerable attractive forces between the individual macrocyclic rings.⁸ Examples of [2]catenanes that utilize π interactions frequently contain interactions between only two aromatic groups, although there are a number of close-packed systems in which a stack of four aromatic moieties interact.⁹ A recent paper reports a rare example of a [3]catenane with an array of six aromatic groups.¹⁰

whose formation is driven by an unprecedented array (~ 2.5 nm in length) of face-to-face π interactions between eight aromatic groups. The formation of the catenane is dependent upon the length of the bridging ditopic ligand, which in turn affects the ability of the eight aromatic rings to all come within π -stacking distances of each other.

The ditopic ligands L^{Et} and L^{Pr} (Figure 1) contain two 4-(4-pyridyl)pyrazolyl arms that are connected by ethane and propane bridges, respectively. Similar ligands have previously been shown to form a variety of polymeric complexes when combined with “naked” metal ions.¹¹ However, when combined with [(dppp)Pd(OTf)₂], in which the metal is cis-protected, both ligands form M₂L₂ metallomacrocycles, with those containing the L^{Et} species becoming interlocked.

Single crystals of [(dppp)Pd(L^{Et})₂]₂·8BF₄ (**1**·8BF₄) and [(dppp)Pd(L^{Pr})₂·4OTf] (**2**·4OTf) (where **1** and **2** are the cationic M₂L₂ macrocycles) were obtained. Crystals of the catenane complex form in the space group *P*2₁/*n* with a complete catenane and eight associated tetrafluoroborate anions in the asymmetric unit. The most remarkable feature of the catenane is that it contains a continuous array of face-to-face π interactions along its longest dimension, with eight aromatic groups involved (Figure 2).

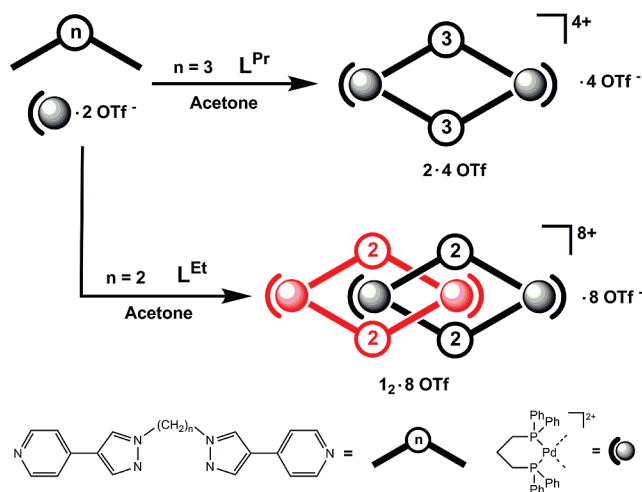


Figure 1. Cartoon representation of the formation of the π -stacked catenane, which is dependent on the length of the ditopic ligand ($n = 2$, L^{Et} ; $n = 3$, L^{Pr}).

Herein we report preliminary results detailing the synthesis and characterization of a [2]catenane consisting of Pd₂ macrocyclic rings

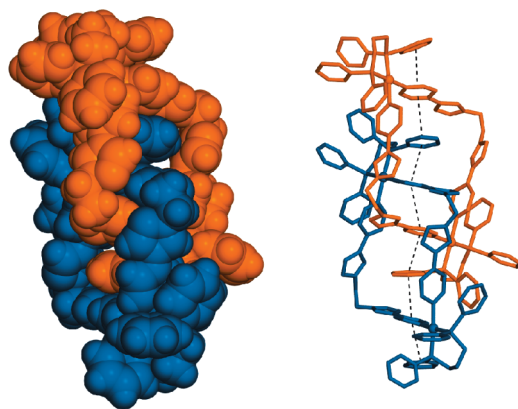


Figure 2. (a) Space-filling representation of the catenane **1**·8⁺. (b) Interactions between π rings that drive the formation of the interlocked species.

The π interactions in the catenane involve four pyridyl rings from the L^{Et} ligands and four phenyl rings from the dppp ligands. Each macrocycle acts as a host to two aromatic rings, a phenyl and a pyridyl, with the cavity size being ideal to fit these guests. The distance across each macrocycle is ~ 10.3 Å between ring centroids across the π interactions, allowing three face-to-face $\pi \cdots \pi$ interactions to occur within it. The distances between the ring

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centroids lie in the range 3.60–3.99 Å (see the Supporting Information). Within a single macrocycle, there are interactions between the exterior dppp ligands and the L^{Et} ligands, creating an interacting pair of π rings when both ligands are coordinated to Pd. It can be postulated that this initial pairing forms an intermediate species that acts as a template for one of the macrocyclic species. The extent to which the macrocycles overlap is quite remarkable, with the lengths of the individual macrocycles being 21.4 and 21.9 Å and that of the catenane being 27.3 Å.

The crystalline product containing the longer L^{Pr} ligand, $[(\text{dppp})\text{Pd}(\text{L}^{\text{Pr}})]_2 \cdot 4\text{OTf}$, does not contain a catenated complex, but instead there are two crystallographically unique M_2L_2 metallo-macrocycles (Figure 3). The squares loosely assemble, allowing four triflate counteranions to be hosted within a cavity. The 2^{4+} square complexes have interior distances that are significantly longer than those of the 1^{4+} macrocycles (~ 11.8 Å compared to 10.3 Å). This size increase means that the cavity can no longer act as a good host for the aforementioned pair of aromatic rings, and the formation of a catenated complex does not occur.

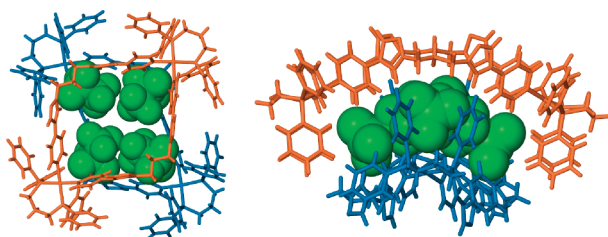


Figure 3. Crystals of $2 \cdot 4\text{OTf}$ show that the complex exists as noninterlocked M_2L_2 macrocycles (hydrogen atoms, lattice solvent, and “exterior” anions have been omitted for clarity).

^1H and ^{31}P NMR spectra of a 1:1 mixture of $[(\text{dppp})\text{Pd}(\text{OTf})_2]$ and L^{Et} reveal a mixture of products, analogous to the spectra of a redissolved crystalline sample of $1_2 \cdot 8\text{BF}_4$. While the ^1H NMR spectrum is complex, with many overlapping signals, the phosphorus spectrum shows that there are two major species (one significantly more abundant than the other) along with a number of other species producing much smaller signals.

Diffusion-ordered NMR (DOSY) spectra of the reaction mixture were collected and contrasted to those of the individual starting materials in order to ascertain the nature of the two major solution species. Of these two species, the major one was found to have a higher diffusion constant than the minor one (see the Supporting Information). The diffusion constants are related to the hydrodynamic radius (or Stokes radius) of the species¹² by the Stokes–Einstein equation. The major and minor species have Stokes radii of 12.1 and 13.6 Å, respectively, which are significantly larger than those calculated for the reagents. The difference in the radii is 12%, giving the minor species a volume that is 1.4 times greater than that of the major product. Measurements of a single 1^{4+} metallo-macrocyclic and the catenated complex 1_2^{8+} from the crystal structure agree well with the values obtained from the DOSY experiments, with lengths of 21.7 and 27.3 Å, respectively at their longest points. These values also highlight the remarkable degree of overlap between the two macrocyclic components of the catenane. The agreement between the crystallographically observed lengths and the calculated Stokes radii led us to conclude that the major species observed in solution is the single macrocycle 1^{4+} and the minor species is the catenane 1_2^{8+} . The remaining, very

minor signals are attributed to higher oligomers, as indicated by electrospray ionization mass spectrometry (ESI-MS) (see below). In sharp contrast to the solution behavior of the L^{Et} system, the ^1H and ^{31}P NMR spectra of the $[(\text{dppp})\text{Pd}(\text{OTf})_2]/\text{L}^{\text{Pr}}$ reaction mixture indicate that only one major species is present in solution and exhibit only a few other very minor peaks.

ESI-MS studies were also conducted on both the L^{Et} and L^{Pr} systems. In both cases, signals corresponding to the metallomacrocycles with varying numbers of counteranions were observed. The catenated complex 1_2^{8+} was also observed, with excellent agreement between the observed and calculated isotopic distribution patterns (see the Supporting Information). Minor signals corresponding to higher oligomeric products were also found, suggesting that the solution equilibrium behavior of these species is complicated.

In conclusion, we have demonstrated that an unprecedented 2.5 nm array of π interactions between eight aromatic rings drives the formation of a [2]catenane. Disruption of this array through the use of longer ligands results in the formation of only single, uncatenated rings.

Acknowledgment. We thank the Australian Research Council for funding and the Australian Synchrotron for beam time.

Supporting Information Available: CIFs and refinement details for $1_2 \cdot 8\text{BF}_4$ and $2 \cdot 4\text{OTf}$, NMR spectra, and additional diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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