Engineering Anisotropy in Pd_2L_4 Metal-Organic Cages

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Introduction

The study of metal-organic cages (MOCs) has grown exponentially over the last four decades. To promote efficient self-assembly the majority of ligands used are symmetrical and give rise to highly symmetrical architectures.

Unsymmetrical ligands[1] could be used to i) segregate functionality within a structure, and ii) develop more anisotropic cavities for shape-selective guest recognition.

Unsymmetrical ligands, however, can potentially result in mixtures of cage isomers. For Pd_2L_4 cages assembled from unsymmetrical ditopic ligands, for example, four potential isomers can be formed.

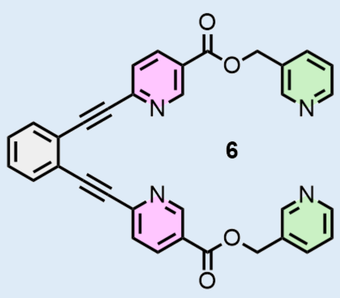
"All-up" (HHHH) | "Three-up-one-down" (HHHT) | *trans* (HTHT) | *cis* (HHTT)

Our group has been interested in the development of ligand design principles to control formation of specific cage isomers.

Pseudo-heterolepticity

As an extension of attempts to use steric and gometric constraints to control the self-assembly of unsymmetrical ligands, covalently tethering ligand fragments together via rigid linkers, thereby fixing their relative orientations, was explored.[3]

Ligand **6**, with two unsymmetrical dipyridyl fragments linked via a 1,2-diethynylbezene group, assembled into a Pd_2L_2 structure. The cavity generated within this assembly is akin to that of a HTHT-Pd_2L_4 cage isomer assembled from unsymmetrical ligands.



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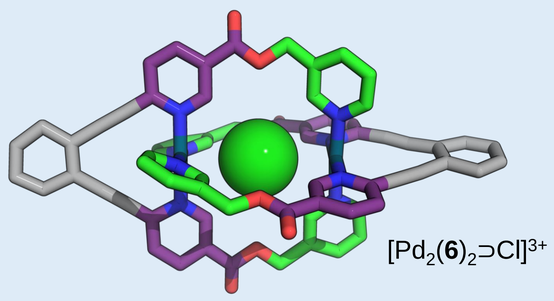
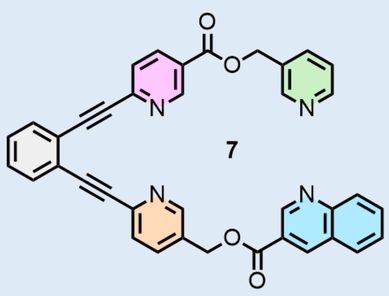


$[Pd_2(\mathbf{6})_2 \supset Cl]^{3+}$

Subsequently, ligand **7**, with two different, unsymmetrical, ditopic ligand fragments, was shown to assemble into a Pd_2L_2 cage. The cavity thus generated can be considered to be like that of a heteroleptic $Pd_2L_2L'_2$ cage assembled from two unsymmetrical ligands, with control over their relative arrangements.



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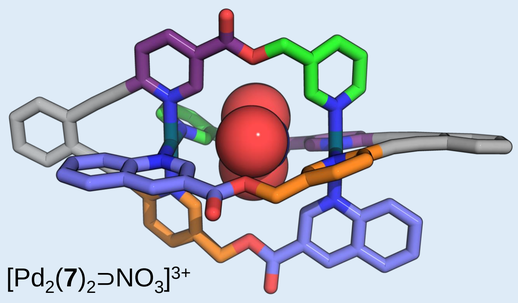
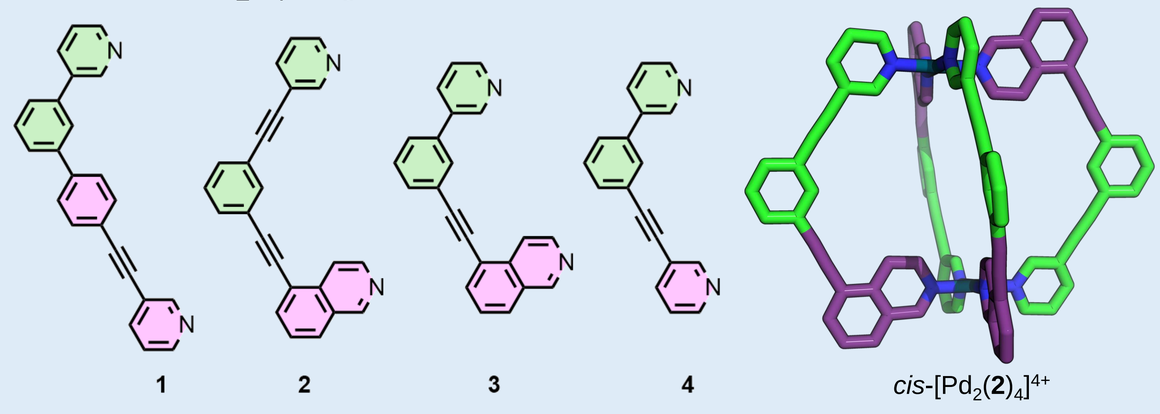


$[Pd_2(\mathbf{7})_2 \supset NO_3]^{3+}$

Geometric Constraints

By designing unsymmetrical ligands in which the coordination vectors of the donor groups are offset from each other, an anti-parallel arrangement of the ligands *trans* from each other across the Pd(II) ion should be favoured, targeting formation of the *cis* (HHTT) cage isomer.[2,3,4,5]

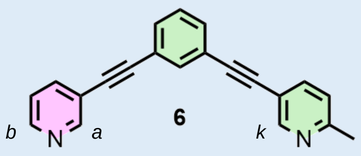
For ligands **1**, **2** and **3** this offset is sufficient for exclusive formation of the *cis*-Pd_2L_4 cage isomers to be observed by ^{1}H NMR. The relatively small geometric offset for ligand **4** led to assembly of a mixture of Pd_2L_4 cage isomers.[2,3]



1 **2** **3** **4** *cis*-$[Pd_2(\mathbf{2})_4]^{4+}$

Steric Constraints

It is also possible to use steric interactions around the coordinating units of ligands to control the formation of cage isomers. Interestingly, in CD_3CN ligand **5** assembles to give the *trans*-Pd_2L_4 cage isomer, whilst in d_6-DMSO a mixture of *cis* and *trans* isomers were obtained.[2]



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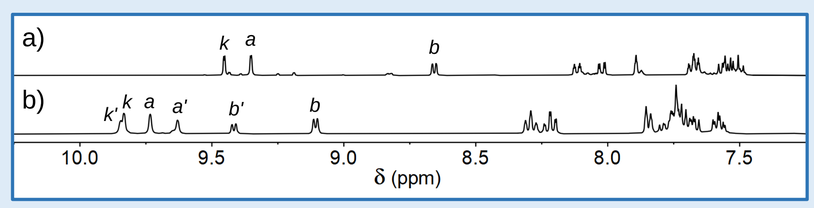
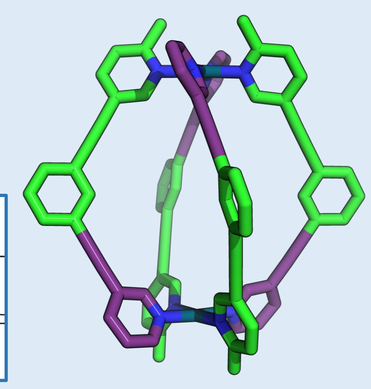
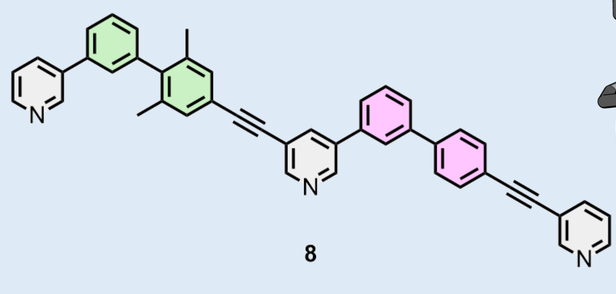


^{1}H NMR (400 MHz) of a) *trans*-$[Pd_2(\mathbf{6})_4]^{4+}$ in CD_3CN, and b) mixture of *trans*- and *cis*-$[Pd_2(\mathbf{6})_4]^{4+}$ in d_6-DMSO.



trans-$[Pd_2(\mathbf{5})_4]^{4+}$ (DFT structure)

Exploitation of design principles for geometrically constrained unsymmetrical ligands with tritopic scaffolds (e.g. **8**) allowed access to *cis*-Pd_3L_4 systems. Each of the cavities in these assembles are described by two different, unsymmetrical ligand fragments held in a specific relative orientation.



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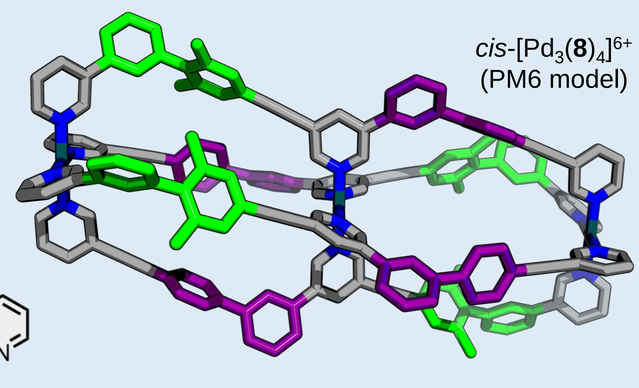

cis-$[Pd_3(\mathbf{8})_4]^{6+}$ (PM6 model)

With both of these design strategies, the term *pseudo-heteroleptic* is proposed to describe these systems. The cavities generated within the architectures are surrounded by two different ligand fragments, whilst the systems are formally assembled from a single ligand.

Conclusions

We have developed design principles for the controlled self-assembly of MOCs from unsymmetrical ligands. Through the use of steric or geometric constraints, or through covalent tethering of ligand fragments, cages with more anisotropic cavity spaces can be generated in a specific fashion. This paves the way for investigating the potential of shape-selective host-guest chemistry for more sophisticated applications of these abiotic hosts.

Acknowledgments

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[1] J. E. M. Lewis, J. D. Crowley *ChemPlusChem*, 2020, **85**, 815. [2] J. E. M. Lewis, A. Tarzia, A. J. P. White, K. E. Jelfs, *Chem. Sci.* 2020, **11**, 677. [3] J. E. M. Lewis, *Angew. Chem. Int. Ed.* 2022, **61**, e202212392. [4] J. E. M. Lewis, *Chem. Eur. J.* 2021, **27**, 4454. [5] A. Tarzia, J. E. M. Lewis, K. E. Jelfs, *Angew. Chem. Int. Ed.* 2021, **60**, 20879.