

Bending the Rules – Flexible and Dynamic Linkers for Metal-Organic Cages

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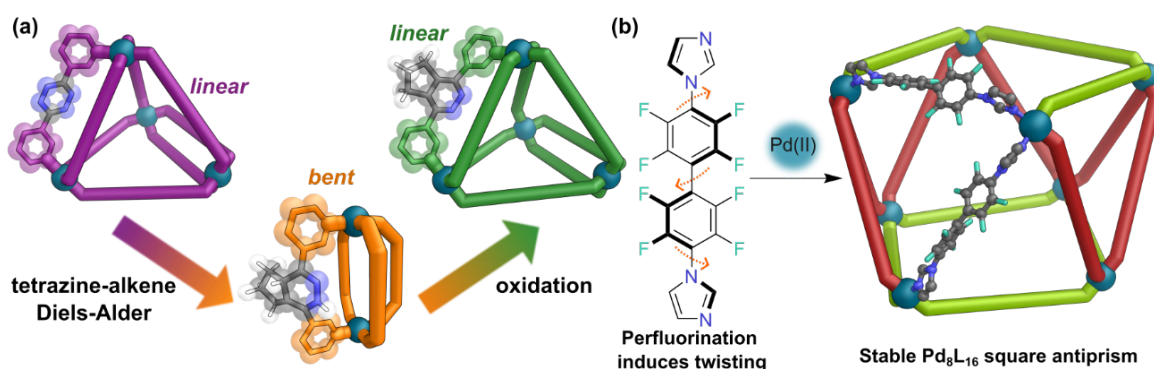
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Metal-organic cages (MOCs) provide discrete well-defined molecular cavities, accessible through the principles of modular self-assembly. By tailoring their size, geometry, and functionality, these MOCs offer powerful platforms for addressing challenges in areas such as catalysis, encapsulation of reactive species,¹ drug delivery, and chemical separation. The Pilgrim Group looks to address fundamental questions governing the self-assembly of MOCs in addition to strategies to control MOC functionality.

Though numerous examples have been reported, a dogma persists that ligands must be rigid and planar to avoid intractable mixtures of shapes. This talk will cover new strategies to introduce limited flexibility into the organic ligands, with novel approaches for controlling ligand twisting and bending. This has enabled us to induce structural transformations and construct previously unobtainable structures.

Most structural planning is performed assuming planarity and the angle between coordination vectors determined in a two-dimensional plane. We have observed profound differences in assemblies when switching from aryl to perfluoroaryl ligand scaffolds, due to the significant dihedral twist angles between perfluoroaryl rings. This allows unusual coordination vector angles in range 100-110°, giving access to the first thermodynamically stable Pd₈L₁₆ square antiprism² and Pd₉L₁₈ tricapped trigonal prisms.³ More recently we have demonstrated that twisting can both increase architecture size (up to Pd₁₂L₂₄) or decrease it, depending on the driving force. We have also been expanding the scope of coordination motifs, with a view to make structures more easily functionalised with groups of interest.

We have replaced rigid benzene motifs with 'click chemistry'-reactive tetrazine units.⁴ An inverse electron-demand Diels-Alder reaction can trigger a structural change from a Pd₄L₈ tetrahedron to a Pd₂L₄ lantern, driven by the new two sp³ centres imparting greater flexibility. Interestingly, these systems show integrative sorting of ligands, with both head-to-tail orientation and enantiomer selection, leading to a single isomer (from 39). We are looking to develop this into stimuli-responsive systems.



References

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