Metallic Cages and Cavitands Featuring Polar Interiors

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In this presentation, I will describe the synthesis of tetra-*α* isomers of aryl and super aryl-extended calix[4]pyrroles bearing four pyridyl substituents at their upper rims. I will show that only the tetra-pyridyl substituted super aryl-extended calix[4]pyrrole self-assemble into mono-metallic cages displaying two different polar binding sites by coordinating to one Pd(II) or Pt(II) metal center.[1] The assembled mono-metallic-cages are capable of reversibly including mono and ditopic polar guests in organic solvents. The characterization studies of the cages and its cage complexes will be detailed, both in solution and in the solid-state. The kinetic results for the guests' exchange suggesting the existence of a "french-doors" mechanism involving the four *meso*-phenyl substituents of the cage will be disclosed. The proposed mechanism serves to explain the dissimilar exchange dynamics experienced by included guests of the different size.[2] Recent findings on the self-assembly of analogous aqueous-soluble Pd(II)-cages, as well as closely related di-nuclear-metalo-bridged cavitands will be briefly commented.[3-4]

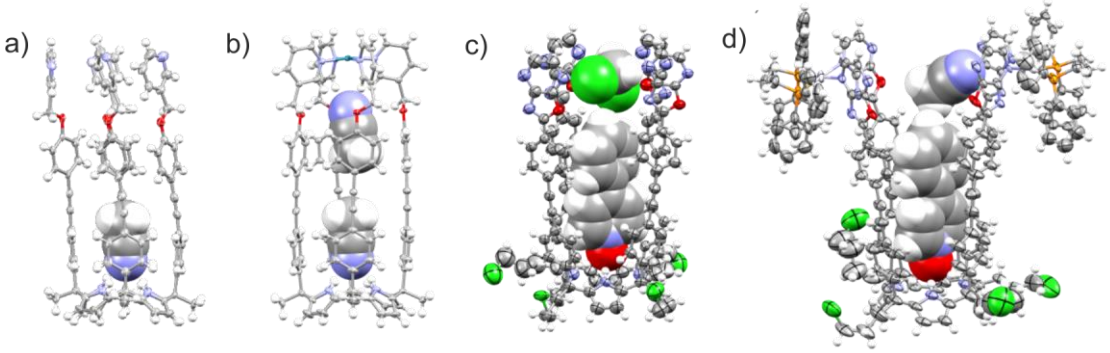

Figure 1. a) X-Ray structures of some inclusion complexes that will be discussed in this presentation: a) tetra-*α* tetra-pyridyl super aryl-extended calix[4]pyrrole ligand; b) corresponding self-assembled mono-nuclear Pd(II) cage; c) tetra-*α* tetra-pyrazinyl super aryl-extended calix[4]pyrrole ligand; d) resulting di-nuclear cavitand by coordination to two Pt(II)dppp metal corners. Receptors are shown in ORTEP views with thermal ellipsoids set at 50% probability for the non-hydrogen atoms. Hydrogen atoms are depicted as fixed-size spheres of 0.3 Å radius. The included guests are shown as CPK models. For clarity, triflate anions and non-included solvent molecules are omitted.

References

[1] L. Escobar, D. Villarón, E. C. Escudero-Adán and P. Ballester, *Chem. Commun.*, **2019**, *55*, 604-607.
[2] L. Escobar, E. C. Escudero-Adán and P. Ballester, *Angew. Chem., Int. Ed.*, **2019**, *58*, 16105-16109.
[3] Q. Sun, L. Escobar, J. de Jong and P. Ballester, *Chem. Sci.*, **2021**, *12*, 13469-13476.
[4] Q. Sun, L. Escobar, P. Ballester, *Angew. Chem., Int. Ed.* **2022**, *n/a*, 10.1002/anie.202202140.