

Probing Possible Non-Covalent Interactions on a Hexacationic Ag(I)-Pillarplex-Dodecyldiammonium Pseudo-Rotaxane as Terephthalate Salt

Alexandra A. Heidecker¹, Alexander Pöthig¹

¹Supramolecular Organometallics – Chair of Inorganic and Metal-Organic Chemistry, Technical University of Munich, alexandra.heidecker@tum.de, Germany

The tubular pillarplex is a supramolecular organometallic complex (SOC)[1] built up by eight metal-ions ($M = \text{Ag}, \text{Au}$) and two macrocyclic NHC ligands (L^{Me}). [2] Besides tunable solubility via anion-exchange and intrinsic luminescence of Au-congeners, the shape-selective encapsulation of linear guests leads to the formation of so-called pseudo-rotaxanes. As the structural self-assembly is predicted to be governed by non-covalent interactions between the pillarplex cation and its surrounding [3], a deep experimental understanding of these interactions and their influence is desirable. Besides charge-assisted interactions between cation and counter-anions, the encapsulation of a guest or the presence of solvent molecules introduce parameters potentially altering the self-assembly. To study this behavior, the pillarplex cation is conceptually divided into different regions: (I) cavity, (II) aromatic rings, (III) metal ions and (IV) rim, where non-covalent interactions can be expected (Fig. 1A).

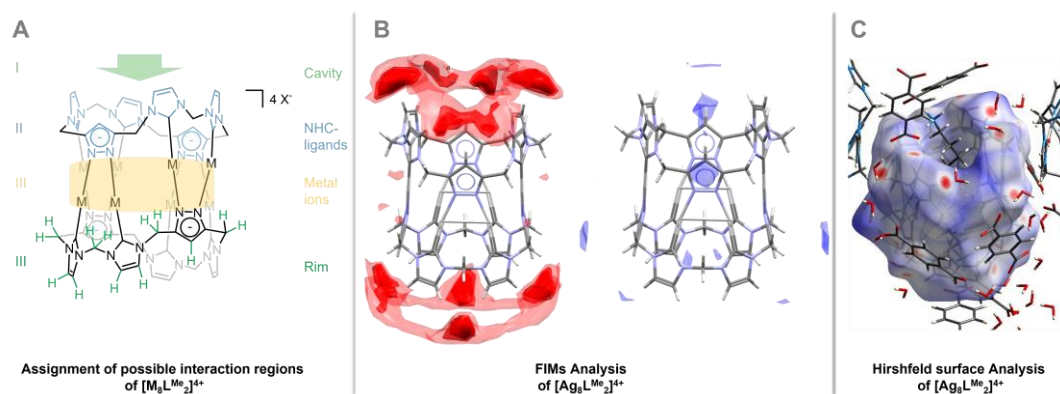


Figure 1: A: Partition of pillarplex into potential interaction sites; B: Full Interaction Maps (FIMs) Analysis of $[\text{Ag}_8\text{L}^{\text{Me}_2}]^{4+}$ towards acceptor carbonyl oxygen and donor uncharged NH; C: Hirshfeld surface Analysis of $[\text{Ag}_8\text{L}^{\text{Me}_2}]^{4+}$.

Herein, we introduce a hexacationic pseudo-rotaxane containing $[\text{Ag}_8\text{L}^{\text{Me}_2}]^{4+}$ as ring compound, 1,12-diaminododecane as linear guest and terephthalate anions, as an exemplary system to probe all of the aforementioned interactions. While predictions of possible interactions using full interaction maps (FIMs)[4] can only be made for the organic regions (II, III) (Fig. 1B), Hirshfeld surface analysis (Fig. 1C) was carried out with the program CrystalExplorer[5] and all possible non-covalent interactions are indeed observed experimentally in the solid state. The interactions are discussed in detail and are quantified towards their different contributions (e.g., hydrogen bonding vs. metal coordination etc.).

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