

## Rim-functionalized Pillarplexes: Shape-Adaptive Metallocavitands via Modification of Macrocyclic NHC Ligands

Shengyang Guan<sup>1</sup>, Thomas Pickl<sup>1</sup>, Christian Jandl<sup>1</sup>, Leon Schuchmann<sup>1</sup>, Xiaoyu Zhou<sup>1</sup>, Philipp J. Altmann<sup>1</sup> and Alexander Pöthig<sup>1</sup>

<sup>1</sup> Catalysis Research Center & Department of Chemistry, Chair of Inorganic and Metal-Organic Chemistry, Technische Universität München, Ernst-Otto-Fischer Str. 1, D-85748 Garching b. München, Germany, alexander.poethig@tum.de

A new class of metallocavitands [1] is introduced: Triazolate-based pillarplexes [2], supramolecular organometallic complexes (SOCs) [3] featuring a shape-adaptive tubular pore. Following a macrocycle-templated synthesis strategy (Figure 1), a hybrid imidazolium/triazole cyclophane of defined ring size was used as ligand precursor, serving also as a supramolecular element, as recently defined by Schmidt and Würthner [4], in the subsequent SOC self-assembly. The new pillarplexes in part behave similar to previously reported pyrazolate-based congeners [5], e.g., regarding luminescence or host-guest properties. In contrast, crystallographic analysis revealed the above-mentioned, unprecedented shape adaptive behaviour for the Au(I) complex in the solid-state. The latter is caused by the additional nitrogen atoms being present in the rim, lowering the steric demand in the rim of the cavitant. Additionally, complementary hydrogen bonding between the cationic complexes is observed in the crystal structure, proving that the rim modification not only modulates the flexibility of the cavitant but is also a tool to introduce further functionality into the SOC.

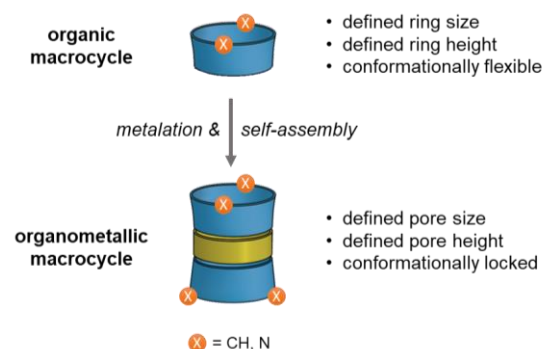


Fig 1 Macrocyclic templation strategy of pillarplexes.

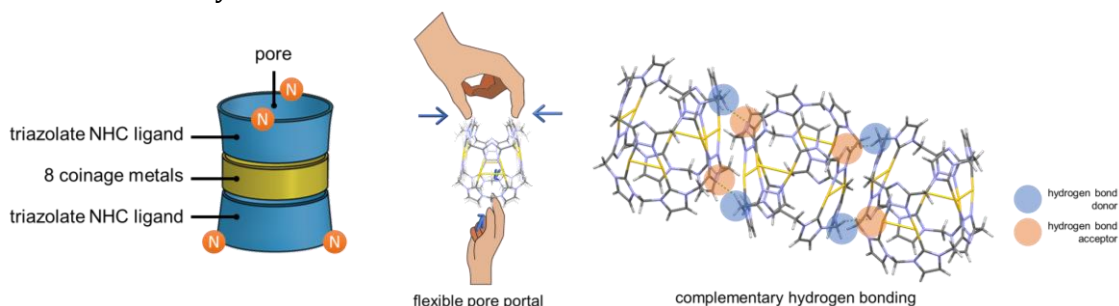


Fig 2 Schematic illustration of: Left – constitution of triazolate pillarplexes. Middle – shape adaptivity of the cavitant portal. Right – complementary hydrogen bonding leading to self-assembly in the solid-state.

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