

2nd Generation Pillarplexes – Shape-Adaptive and Reactive Supramolecular Organometallic Complexes

Thomas Pickl and Alexander Pöthig*

Technical University of Munich, Catalysis Research Center,
Ernst-Otto-Fischer Str. 1, Garching, Germany.
(e-mail: thomas.pickl@tum.de)

Pillarplexes^[1] are supramolecular organometallic complexes (SOCs)^[2] self-assembled by two macrocyclic NHC ligands and eight coinage metal ions (Ag^I and Au^I, cf. Figure 1). They possess a shape-persistent tubular pore and can act as metallocavitands with remarkable properties, such as intrinsic photoluminescence, tunable solubility *via* anion exchange, and shape-selective guest insertion of linear molecules. These complexes can also be applied as building blocks in mechanically interlocked rotaxanes^[2] and show promising properties in a biological context,^[3] as well as in crystal engineering.^[4]

We now have extended the scope of the first generation of pillarplexes in two ways:

(1) We chemically modified the rim of the pillarplex by altering the ligand backbone (Figure 1, left), introducing a higher flexibility of the metallocavitand.^[5] In detail, we were able to observe a shape-adaptive behavior of the pillarplex in the solid state, mainly driven by hydrogen bonding. The modified rim of the pillarplexes induces less steric repulsion, resulting in a lower energy penalty upon compression as rationalized by DFT calculations.

(2) We successfully synthesized and fully characterized Cu^I pillarplexes (Figure 1, right). Hereby, the overall structure of the pillarplex is preserved, while the lighter coinage metal ions are envisioned to introduce intrinsic reactivity to the supramolecular organometallic complex.

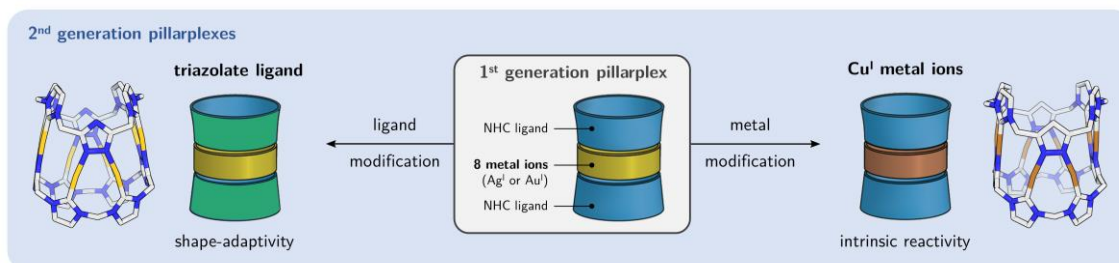


Figure 1. Overview of 2nd generation pillarplexes. Left: Rim-modification of pillarplex ligands leads to shape adaptivity. Middle: Schematic representation of a 1st generation pillarplex. Right: Introduction of Cu^I metal ions as potentially reactive sites within pillarplexes.

References

- [1] P. J. Altmann, A. Pöthig*, *J. Am. Chem. Soc.* **2016**, *138*, 13171.
- [2] P. J. Altmann, A. Pöthig*, *Angew. Chem., Int. Ed.* **2017** *129*, 15939.
- [3] A. Pöthig*, S. Ahmed, H. C. Winther-Larsen, S. Guan, P. J. Altmann, J. Kudermann, A. M. Santos Andresen, T. Gjøen, O. A. Høgmoe Åstrand*, *Front. Chem.* **2018**, *6*, 584.
- [4] A. A. Heidecker, M. Bohn, A. Pöthig*, *Z. Kristallogr. Cryst. Mater.* **2022**, *237*, 167.
- [5] T. Pickl, S. Guan, C. Jandl, L. Schuchmann, X.-Y. Zhou, P. J. Altmann, A. Pöthig*, *Org. Chem. Front.* **2021**, *8*, 4061.