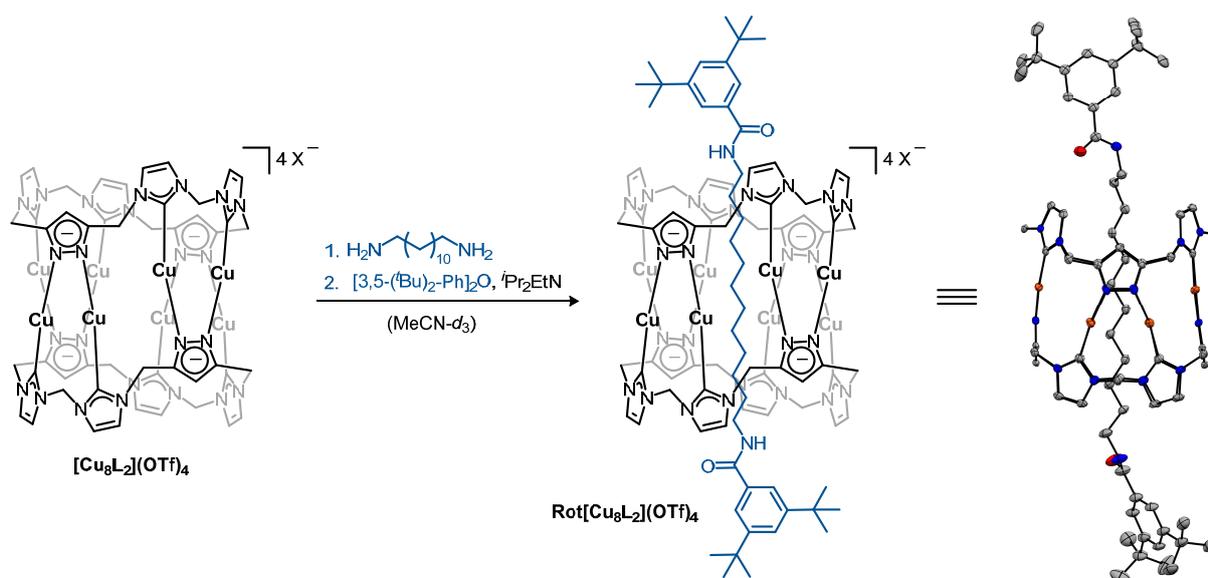


Copper(I)-Based Pillarplexes: Platforms for Supramolecular Assemblies with Intrinsic Reactivity

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Pillarplexes are supramolecular organometallic complexes with a tubular pore and a high affinity for the incorporation of linear alkanes [1]. The cavitands consist of two macrocyclic ligands (**L**) linearly coordinated by eight group 11 metal ions (Ag^{I} or Au^{I}). Host-guest assemblies derived from the insertion of linear diamines into the pore can be post-synthetically modified. The attachment of bulky stopper groups by amide formation leads to mechanically interlocked rotaxanes [2]. To date, no such organometallic host with intrinsic reactivity has been accessed yet. In analogy to the reported pillarplexes, we investigated the formation of a Cu^{I} pillarplex which is also envisioned to share the rich reactivity of Cu^{I} along with the host-guest insertion chemistry of the pillarplex platform. In this contribution, we report on the synthesis of the title compounds, $[\text{Cu}_8\text{L}_2](\text{X})_4$ ($\text{X} = \text{OTf}, \text{PF}_6$), which could be isolated in excellent yield by the treatment of the macrocyclic proligand $\text{H}_6\text{L}(\text{X})_4$ with Cu_2O [3]. The triflate and hexafluorophosphate pillarplexes show the same ^1H NMR signal pattern as their heavier congeners and first insertion studies with 1,12-diaminododecane as a guest demonstrate the ability to incorporate linear molecules into the shape-persistent pore of the complexes. Treatment of the diaminoalkane-pillarplex assembly with bulky 3,5-di-*tert*-butylbenzoic anhydride led to the formation of a mechanically interlocked molecule, **Rot** $[\text{Cu}_8\text{L}_2](\text{X})_4$. The structure of the [2]rotaxane was elucidated by SC-XRD (space group $P2_1/c$) and is discussed in this contribution along with its packing. Further studies on the organometallic host component aim to identify prospective chemical reactions making use of the redox chemistry of copper to enable shape-selective chemical transformations, potentially in a catalytic manner.



[1] P. J. Altmann and A. Pöthig, *J. Am. Chem. Soc.*, **2016**, 138, 13171–13174.

[2] P. J. Altmann and A. Pöthig, *Angew. Chem. Int. Ed.*, **2017**, 56, 15733–15736.

[3] A. A. Danopoulos, T. Simler and P. Braunstein, *Chem. Rev.*, **2019**, 119, 3730–3961.

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