Exploring Endohedral and Exohedral Weak Interactions of Pillarplex-Based Nanotubes

A. Pöthig

Technical University of Munich, School of Natural Science, Department of Chemistry | Catalysis Research Center

alexander.poethig@tum.de

Pillarplexes represent a distinct class of porous organometallic nanotubes [1], able to encapsulate linear molecules in their hydrophobic pore [2]. They can also be used as functional ring components in rotaxanes. Structurally, they are characterized by their extended aromatic surfaces, centrally coordinated metal ions, and C-H acidic rims, enabling a manyfold of weak intermolecular interactions [3] including recognition of non-canonical DNA structures [4].

Recent SC-XRD studies have demonstrated the possibility of metal coordination within pillarplex cavities. Endohedral interactions facilitate substrate insertion, with Cu–O binding motifs stabilizing sterically mismatched guests, exemplified by the coordination of tetrahydrofuran (THF) [5]. Beyond coordination chemistry, mechanically interlocked pillarplex [2]rotaxanes showcase how noncovalent interactions—particularly CH-π interactions and hydrogen bonding— can actively enhance functional group reactivity [6]. Instead of sterically hindering reactions, the macrocyclic framework preorganizes reactive sites, drastically accelerating Fmoc* deprotection. These findings challenge the conventional view of mechanical bonds as steric barriers, demonstrating their ability to fine-tune molecular reactivity through spatial control.

By integrating crystallographic insights with complementary spectroscopic and computational studies, this contribution will highlight endohedral metal coordination and exohedral noncovalent interactions in pillarplex-based nanotubes, offering new perspectives for catalysis, molecular machines, and supramolecular design.

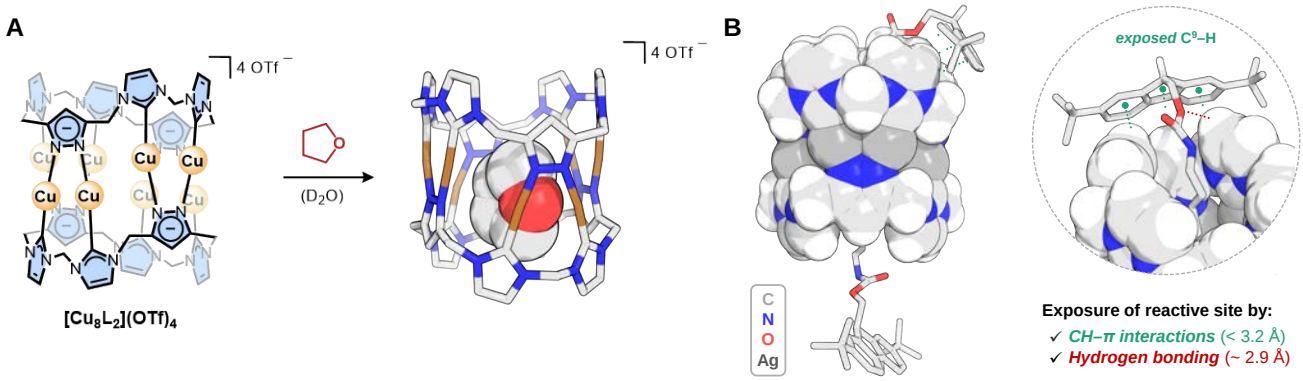

Figure 1. A: Guest inclusion and endohedral coordination of THF into a Cu^{I} pillarplex [5]. B: Perspective views of a Ag^{I}-pillarplex rotaxane, highlighting exohedral CH–π interactions (green) and hydrogen bonds (red) between Fmoc* and the pillarplex rim.

[1] Altmann, P. J., Pöthig, A. (2016). *J. Am. Chem. Soc.*, **138**, 13171.

[2] Altmann, P. J., Pöthig, A. (2017). *Angew. Chem. Int. Ed.*, **56**, 15733.

[3] Heidecker A. A., Bohn, M., Pöthig, A. (2021). *Z. Kristallogr. - Cryst. Mater.*, **237**, 167.

[4] Craig, J. S., Pöthig, A., Hannon, M. J. et al. (2023). *J. Am. Chem. Soc.*, **145**, 13570.

[5] Pickl, T., Halter, D., Pöthig, A. et al. (2025). *Chem. Eur. J.*, e202500775. https://doi.org/10.1002/chem.202500775

[6] Pickl, T., Stark, C., Briganti, D., Curcio, M., Pöthig, A. (2025). *Submitted*