Design of Pillarplex–Rotaxanes based on Functionalized Fmoc Stoppers

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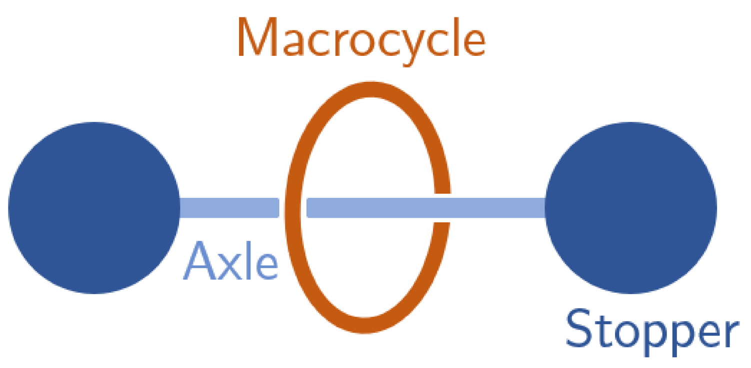
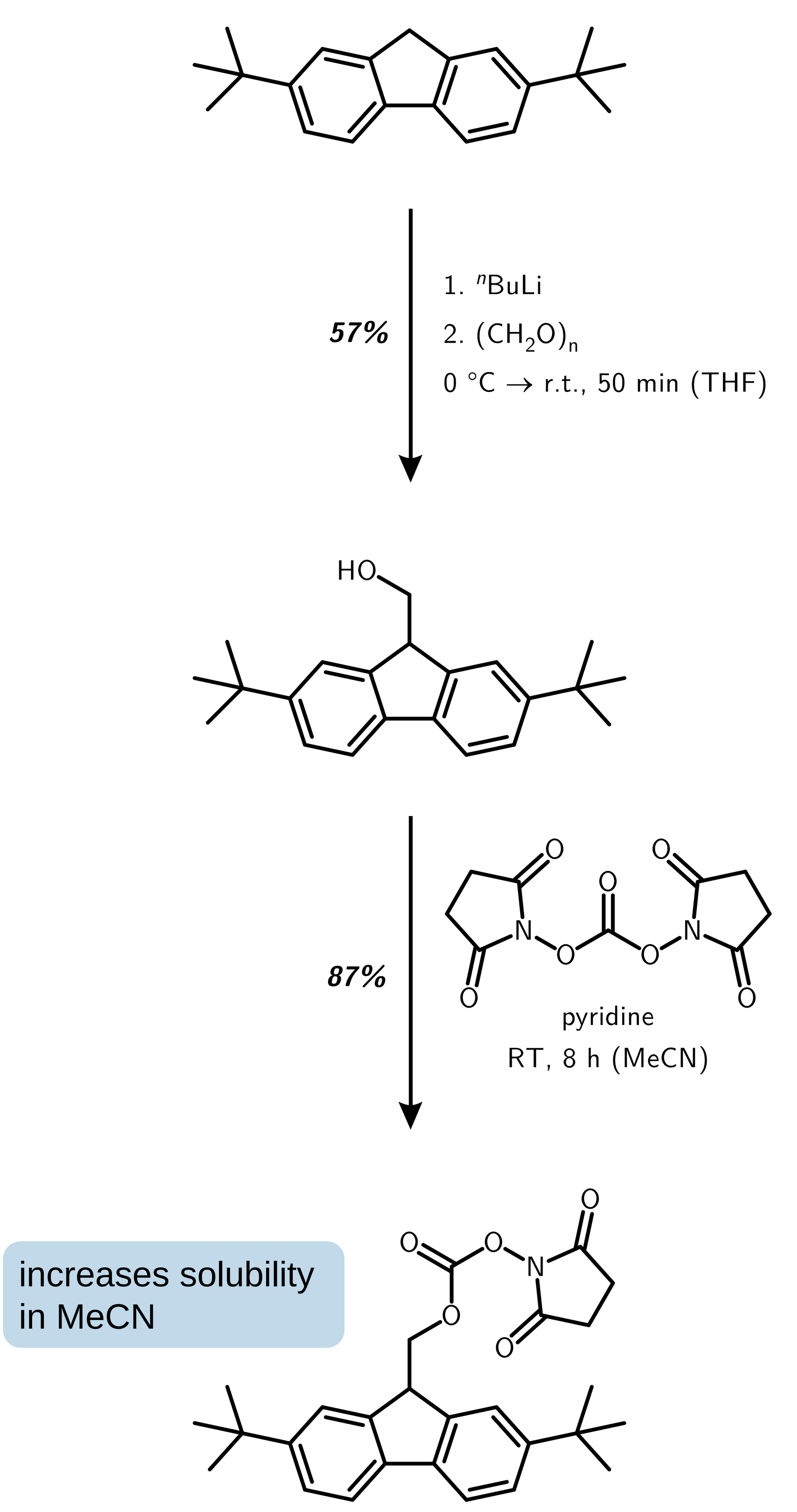
Introduction

Mechanically interlocked molecules (MIMs) are molecular assemblies in which two or more components are connected via a mechanical bond instead of covalent or coordinative bonds. One famous example of MIMs are rotaxanes. Usually, rotaxanes are based on organic ring components. Pöthig and co-workers presented a rotaxane based on metallocavitand "pillarplexes".[1, 2] While the isolation of Au(I)- and Ag(I)-based pillarplexes proved to be straightforward, a Cu(I) congener has not been reported so far. However, preliminary studies indicated that the respective Cu(I) pillarplex–rotaxane can be synthesized and purified. This might be a starting point for the isolation of the Cu(I) pillarplex. Such an approach requires a rotaxane with reversibly bound stoppers and good solubility in polar aprotic solvents, as these are the only media were the pillarplex is soluble.

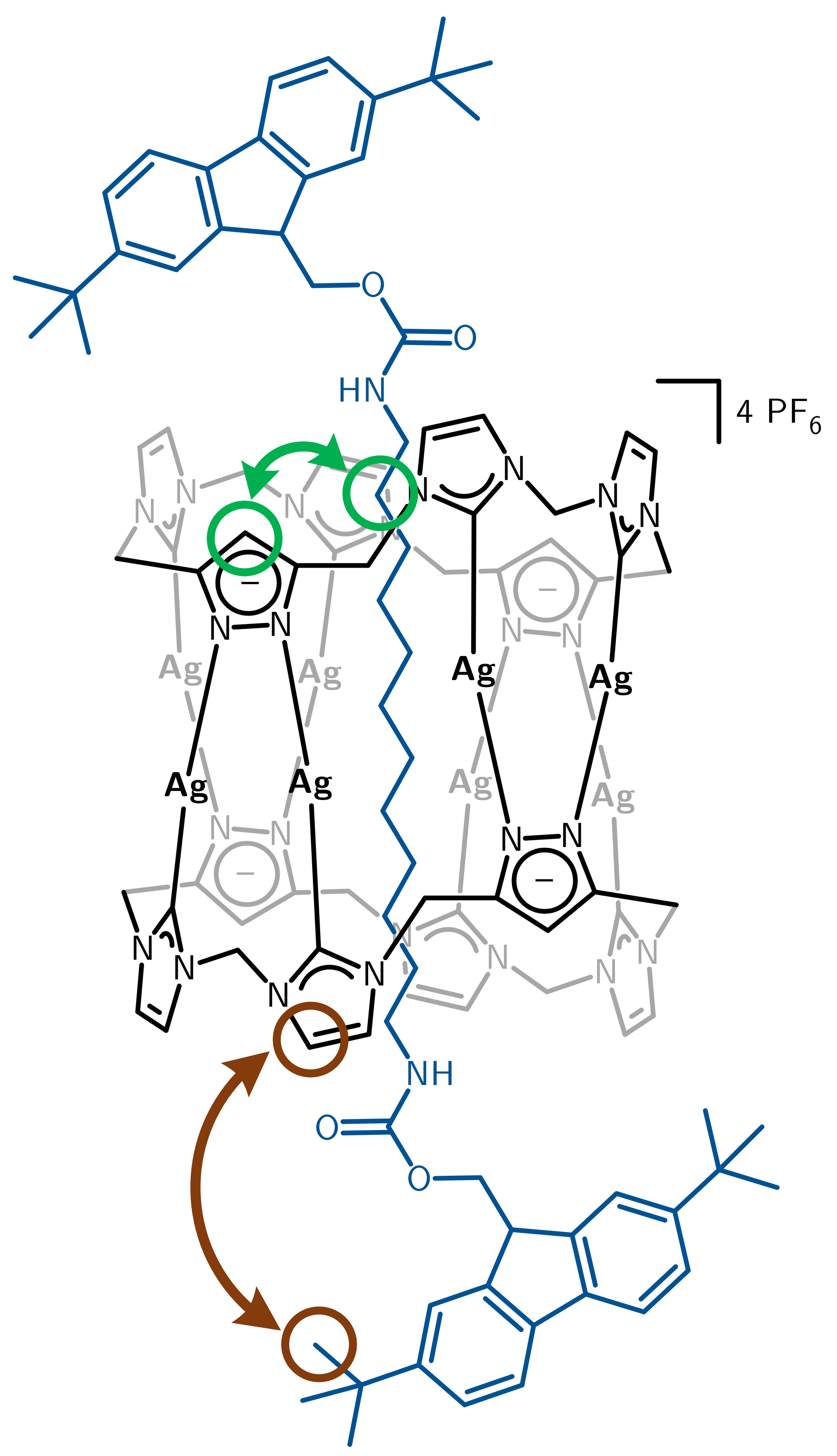
Rotaxanes



Stopper Synthesis

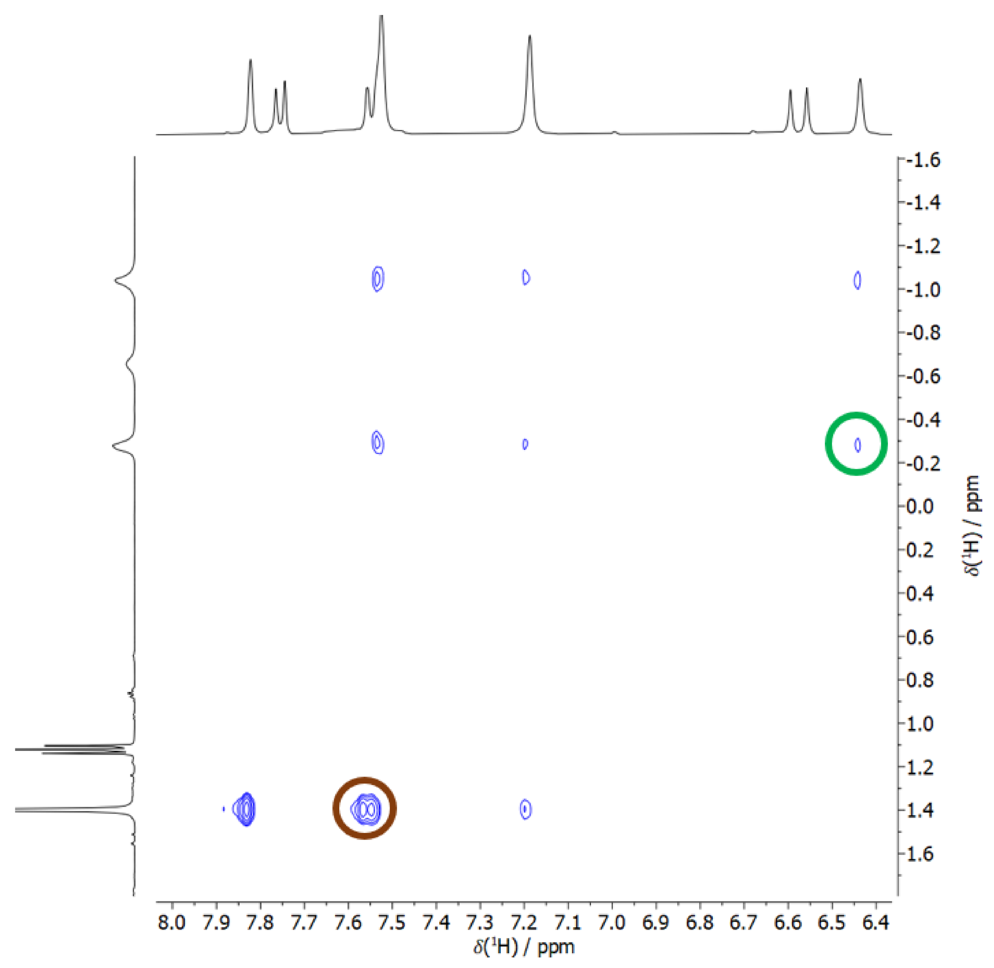


2,7-(^{t}Bu)$_2$-Fmoc-OSu

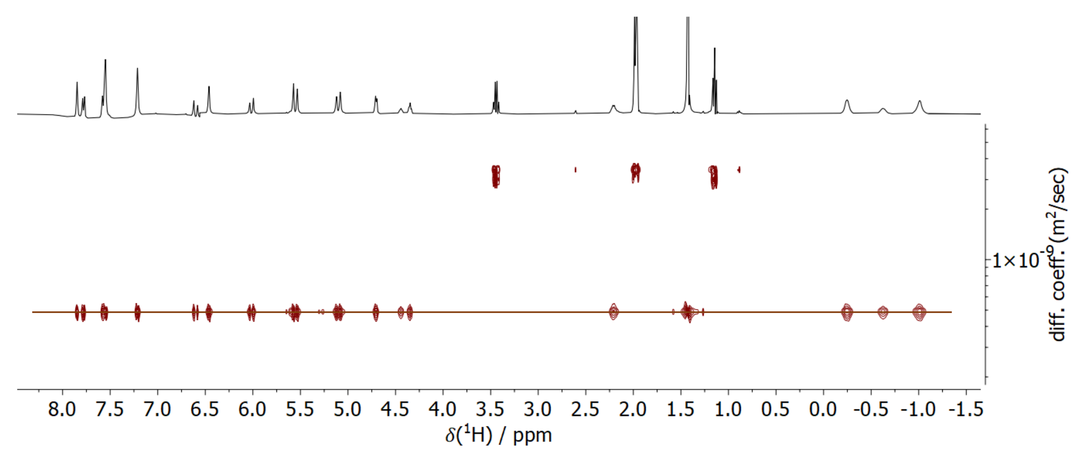


[Ag_8L_2][^{t}Bu_2-Fmoc-Rot](PF_6)$_4$
pillarplex–rotaxane

^{1}H,^{1}H NOESY spectrum shows selected through-space correlations between pillarplex and axle with stoppers

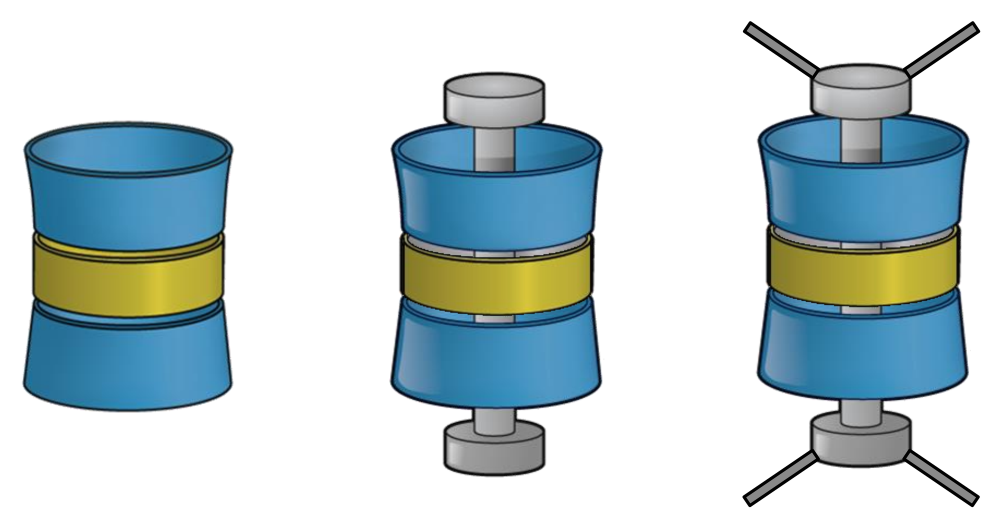


^{1}H DOSY shows only one species in solution



Solvodynamic radius and molecular weight can be estimated from the diffusion coefficient

Compound	D / (10^{10} m²/s)	r / Å	M_W / (g/mol)	ΔM_W / %
Pillarplex[2] (1)	5.90	10.4	2283	6
Fmoc-Rot[3] (2)	5.17	11.8	3301	8
^{t}Bu$_2$-Fmoc-Rot (3)	4.81	12.7	3642	4



1 **2** **3**

Conclusion

An Fmoc-based pillarplex–rotaxane with improved solubility in polar solvents, such as acetonitrile, was achieved. This enables follow-up reactions as well as in-depth structural investigation by SC-XRD. In this context, 2,7-di-*tert*-butylfluorene was successfully functionalized to yield **2,7-(^{t}Bu)$_2$-Fmoc-OSu** *via* an unprecedented reaction pathway involving less toxic and environmentally harmful chemicals than reported literature procedures. It was proven experimentally, that **2,7-(^{t}Bu)$_2$Fmoc-OSu** can be used as stopper group for rotaxane assembly by forming carbamate bonds with the inserted diamino axle. As anticipated, the final rotaxane showed high solubility in acetonitrile. With this reversible and soluble Ag(I) rotaxane in hand, the transmetalation to a Cu(I) rotaxane and subsequent isolation of the Cu(I) pillarplex might be possible.

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[1] Altmann, P. J.; Pöthig, A., *J. Am. Chem. Soc.* **2016**, *138*, 13171-13174.
[2] Altmann, P. J.; Pöthig, A., Angew. Chem. Int. Ed. 2017, 56, 15733-15736.
[3] Pickl, T., Master's Thesis, Technical University of Munich, 2020.