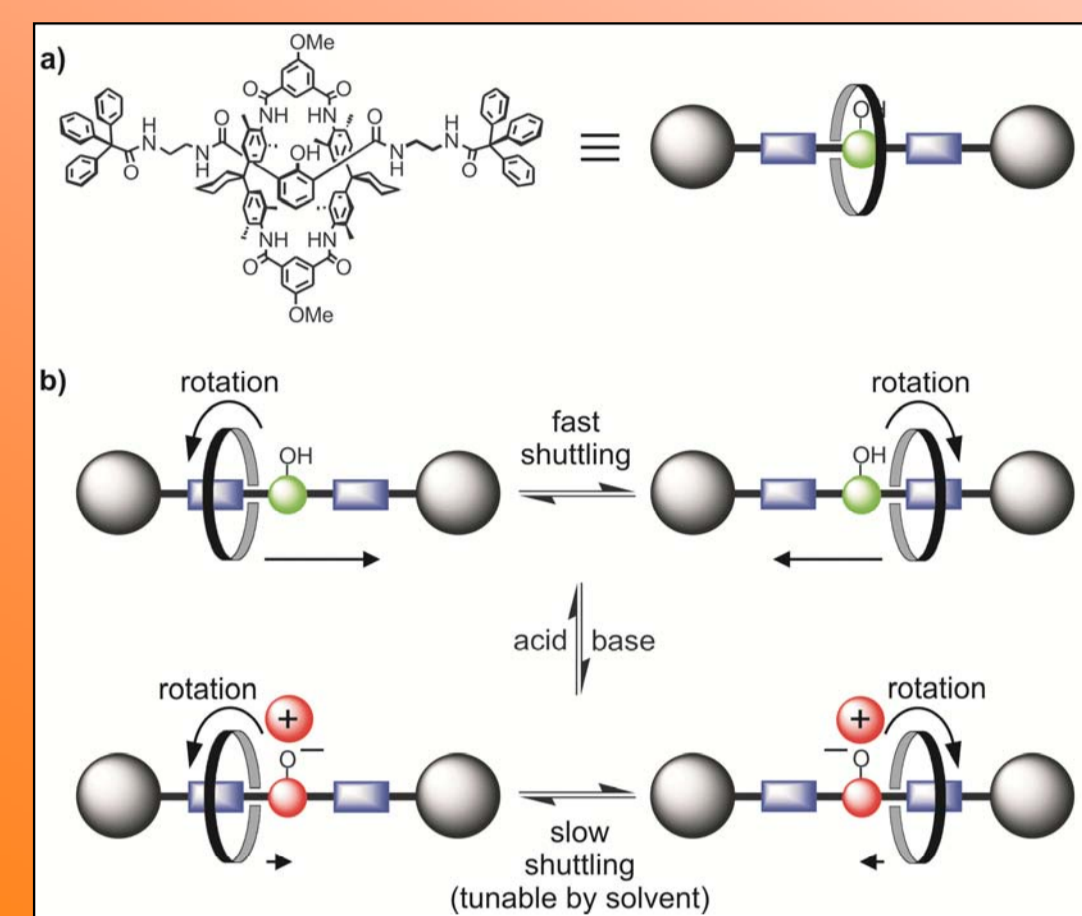


I. Introduction

Mechanically bound molecules such as rotaxanes belong to the best understood systems in the field of supramolecular chemistry so far. Nevertheless, the research interest increases more and more, especially in systems such as molecular switches or shuttles. One of these molecules of interest is the rotaxane shown below (a).^[1] The shuttling speed of the wheel along the axle can be switched between a fast and a slow motion by the addition of acid or base (b) causing protonation and deprotonation of the hydroxyl-group located at the central phenyl ring. The reduction of the shuttling speed can be controlled by the solvent or the size of the counter cation, which forms a strong ion pair with the phenolate. In the present project, we try to immobilize this and other switchable rotaxanes on a surface using the Layer-by-Layer self-assembly approach.

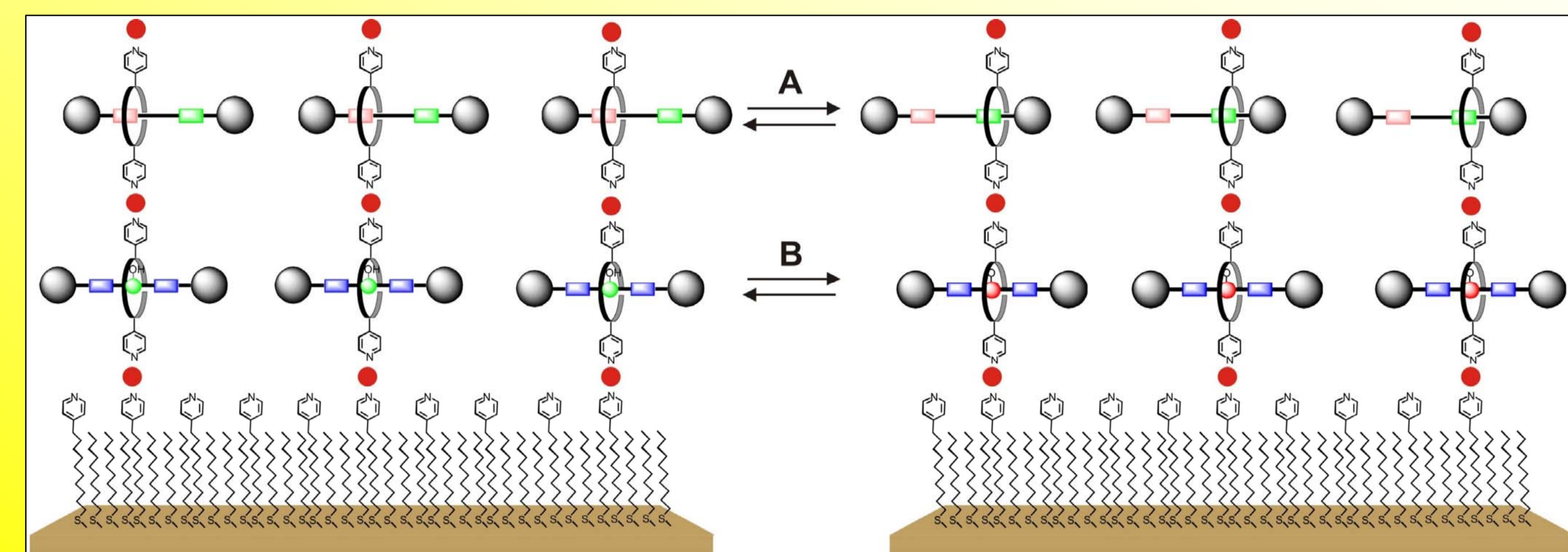


Layer-by-Layer self-assembly (LbL-SA) is a relatively new technique for the controlled deposition of organic multilayers on surfaces. The conventional LbL-SA approach works simply through the alternating deposition of building blocks with complementary properties, e.g. hydrogen bond donor/acceptor and electrostatic interactions. Our approach uses the deposition of a metal ion, followed by an organic ligand, which can again coordinate another metal ion. This procedure can result in very complex metal-organic frameworks, as shown in the box on the right. This method gives the opportunity to create highly ordered arrays with a specific programmable sequence of complex molecular architectures.

[1] P. Ghosh, G. Federwisch, M. Kogej, C. A. Schalley, D. Haase, W. Saak, A. Lützen, R. Gschwind *Org. Biomol. Chem.* **2005**, *3*, 2691.

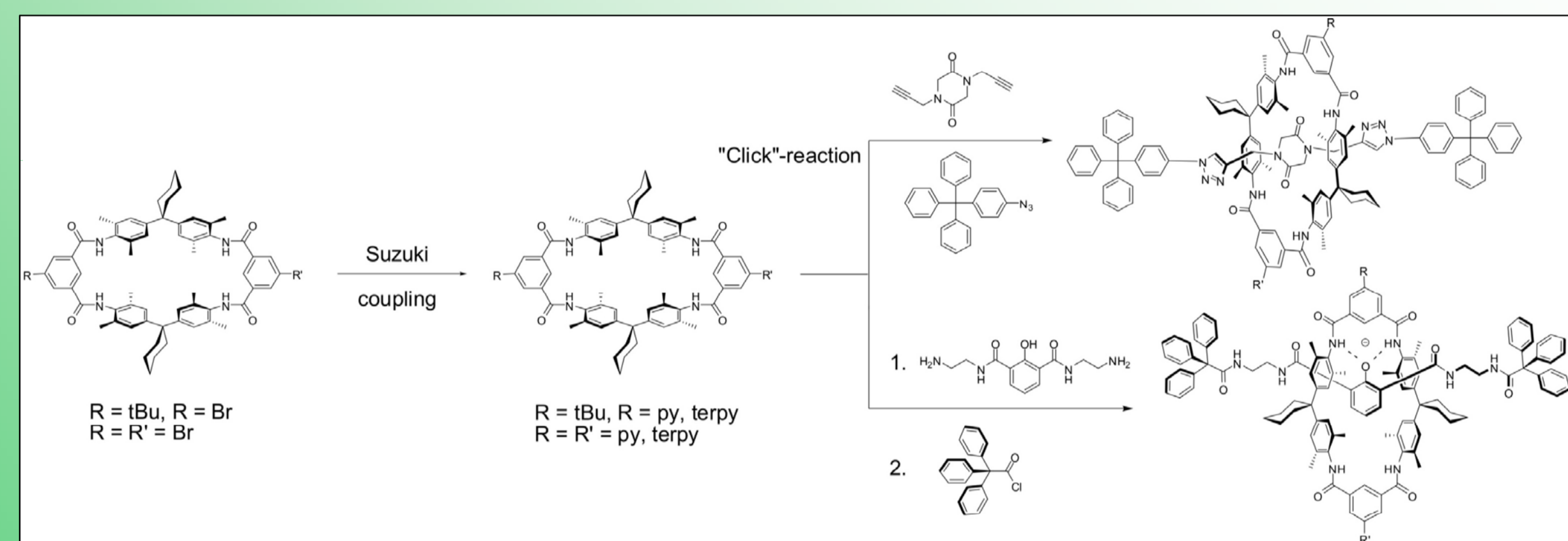
II. The Project

The goal of this project is the combination of mechanically bound molecules with the Layer-by-Layer self-assembly approach to create highly ordered metal-organic frameworks including switchable rotaxanes as shown below. This architecture provides interesting properties, for example the concerted movement of an axle through a wheel by controlled switching of the rotaxane (process A) or the variation of the shuttling speed of the axle (process B). These processes, however, are known to occur in solution. But only in highly ordered arrays on solid substrates there can be a concerted direction in the movement, which is absolutely essential for the fabrication of molecular machines.

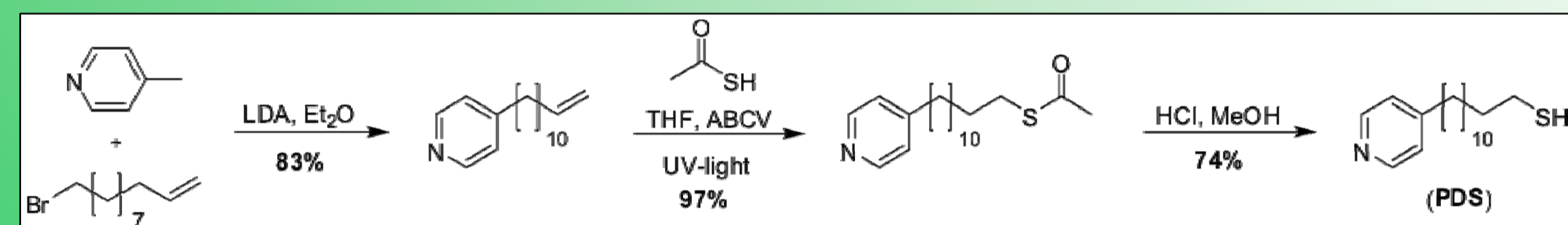


III. Synthesis

Synthesis and functionalization through Suzuki coupling of the macrocycle used in this study is published elsewhere.^[2] The [2]-rotaxanes with the glycine anhydride station were synthesized through 1,3-dipolar cycloadditions between an azide and an ethynyl-moiety ("click"-reaction), forming the axle.^[3] The amide-type [2]-rotaxane were synthesized using an anion template effect, developed by Schalley et al.^[4]

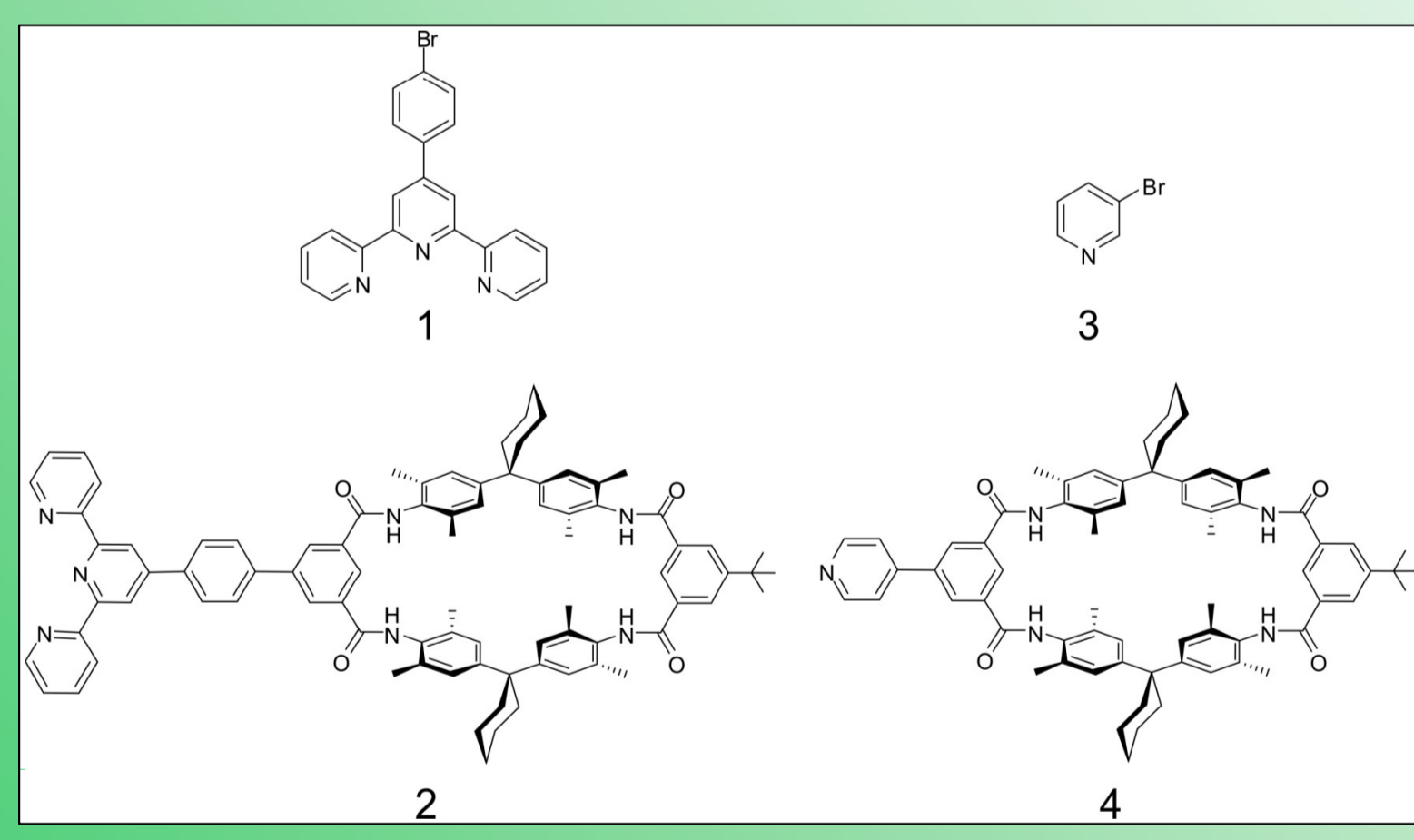


The synthesis of the pyridine terminated thiol (PDS) proceeds via S_N2 -reaction at 11-bromoundecene followed by the radical addition of thioacetic acid to the terminal double bond, through "thiol-ene click" chemistry. Deprotection of the thioacetate gives the thiol (PDS) in good yields.



The molecules shown on the right were synthesized according to literature known procedures.^[2] Their purpose is to improve the deposition procedure for the coordination of the organic ligands to the metal ions, without wasting too much of the precious rotaxanes.

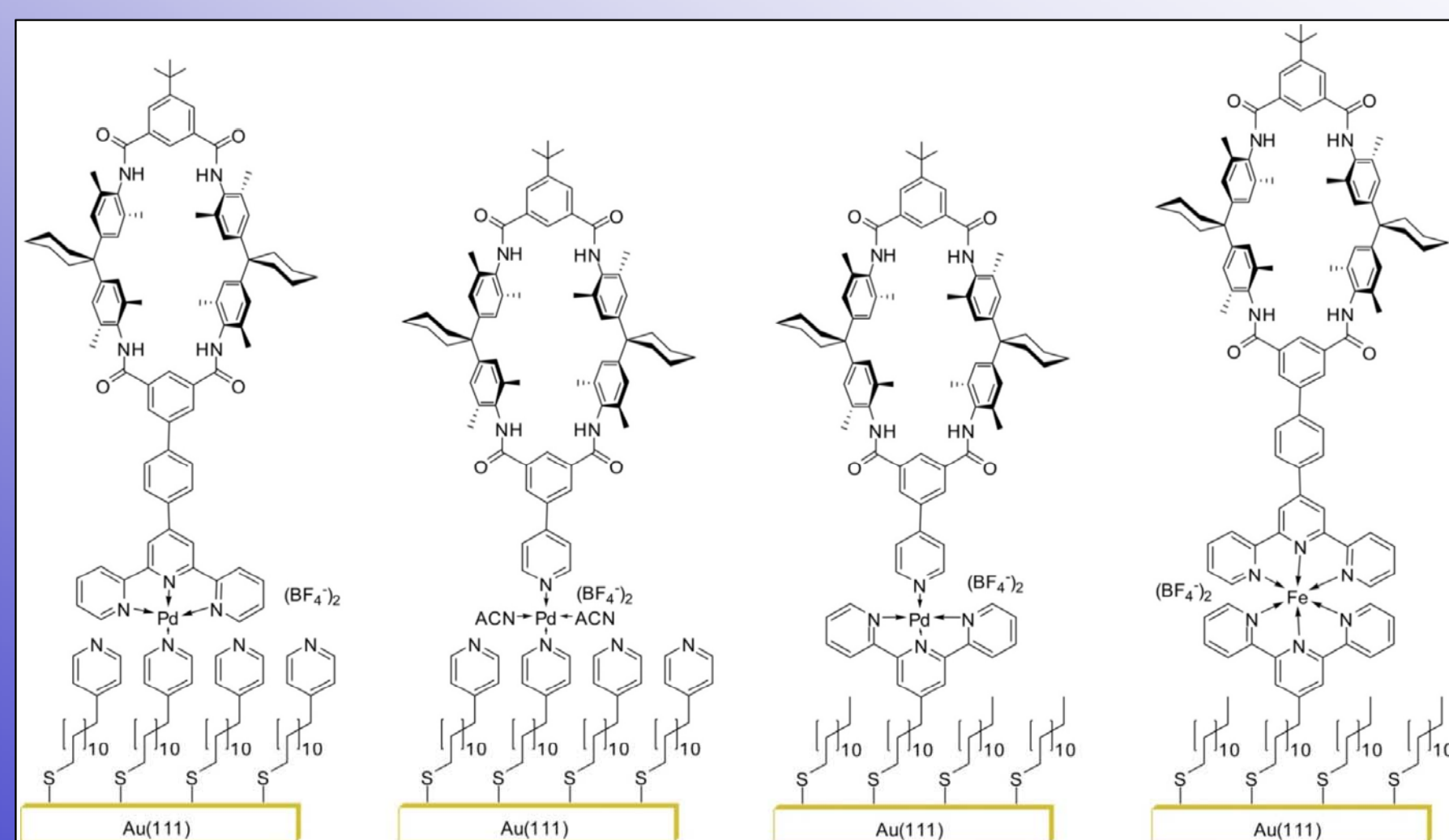
[2] B. Baytekin, S.S. Zhu, B. Brusilowski, J. Illgen, J. Ranta, J. Huuskonen, K. Rissanen, L. Kaufmann, C.A. Schalley *Chem. Eur. J.* **2008**, *14*, 10012.
 [3] E. Dzyuba, unpublished results.
 [4] P. Ghosh, O. Mermagen, C. A. Schalley *Chem. Commun.* **2002**, 2628.



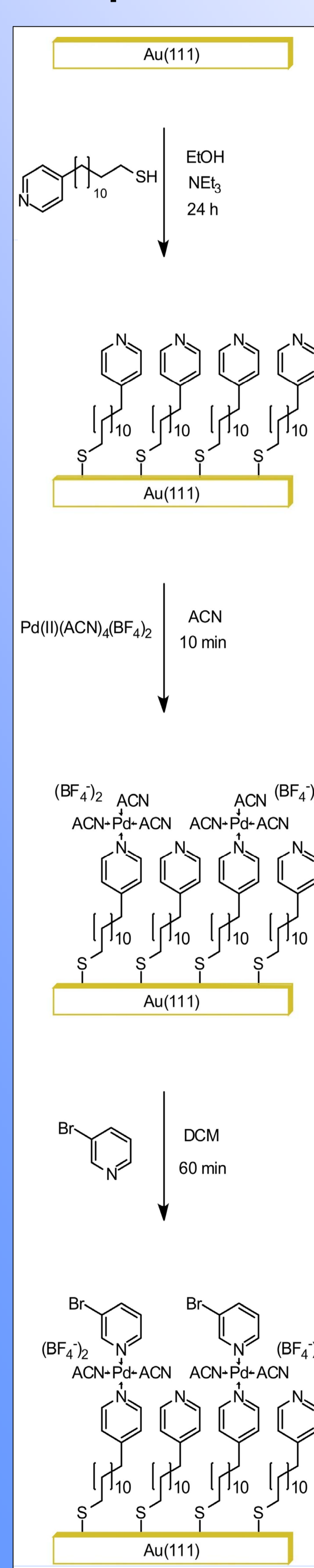
V. Conclusion and Outlook

The Synchrotron-XPS, AFM-pictures and ToF-SIMS measurements clearly show, that deposition of the SAM and the coordination of the Pd(II) were successful. In addition to that, the detection of the bromine signal after deposition of **3** indicates the ligand coordination procedure to be applicable as well. The next step to realize the project, is the deposition of the macrocycles **2** and **4** followed by a full characterization of the resulting layer, shown below on the left.

The formation of more stable complexes on the surface, requires the deposition of a terpyridine terminated SAM. Therefore it might be necessary to follow a mixed monolayer approach, due to the steric hindrance of the terpyridine units.



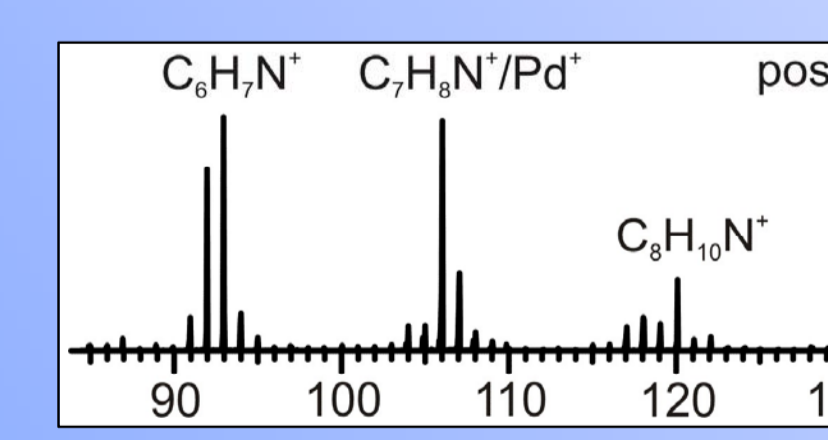
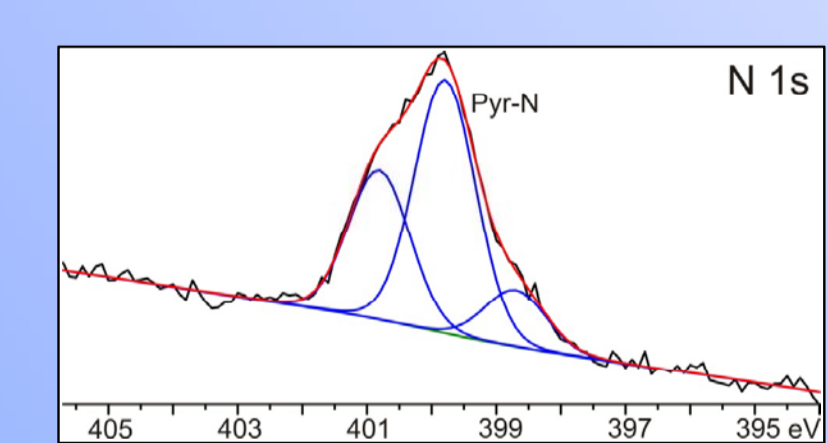
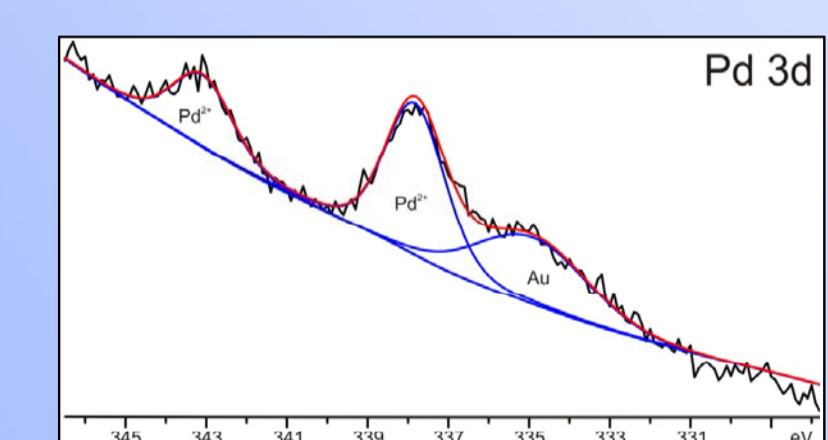
IV. Supramolecular Chemistry on Gold-Surfaces



Characterization of the self assembled monolayer (SAM) was performed by Synchrotron-XPS, AFM and ToF-SIMS measurements.

The high-resolution XP-spectrum of the N 1s region shows only one nitrogen species, which is expected for a pyridine terminated SAM. The S 2p region is also typical for a monolayer of organic thiols on Gold. The splitting of the S 2p-signal is due to the different binding states of the sulfur in the SAM, detectable only by high resolution Synchrotron-XPS.

The AFM-pictures reveal the SAM to be homogeneous and free from large aggregates. The positive mode ToF-SIMS measurement clearly shows the molecular ion of PDS (m/z 278) and the typical fragmentation pattern for alkyl chains.



The coordination of the Pd(II) to the pyridine moiety on top of the SAM was again detected by Synchrotron-XPS and ToF-SIMS measurements. The Pd 3d region shows two signals at 343.9 eV and 338.6 eV, which are characteristic for Pd(II). The new nitrogen species observed in the N 1s region gives strong evidence for the coordination to the pyridine.

The pos. ToF-SIMS shows only a small signal for Pd, but again very high intensities for PDS. In the neg. ToF-SIMS, we were able to detect the counterion (BF_4^-), which clearly indicates the presence of Pd(II) on the surface.

For the coordination of the first ligand layer, several test molecules were synthesized and deposited on the Pd(II) functionalized SAM. The test molecules (**1** – **4**) are shown on the left. So far, it was not possible to perform ToF-SIMS measurements of the first ligand layer. Therefore, the analytical data of the deposited test molecules is limited to Synchrotron-XP-spectra yet. The test molecules **1** and **3** could be easily detected by the presence of the characteristic doublet at approx. 69 eV in the high resolution Synchrotron-XP-spectra of the Br 3d-region as shown on the right (Deposition of **3**).

Detection of the coordination of the macrocycles **2** and **4** only with Synchrotron-XPS, revealed to be very difficult. The possible detection of the Amide-nitrogen species in the N 1s region turned out to be not applicable, because of the overlap between the amide and the pyridine signals.

