Functionalized Macrocycles and Rotaxanes : A Toolbox for Supramolecular Assemblies

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The Idea of Having a Toolbox

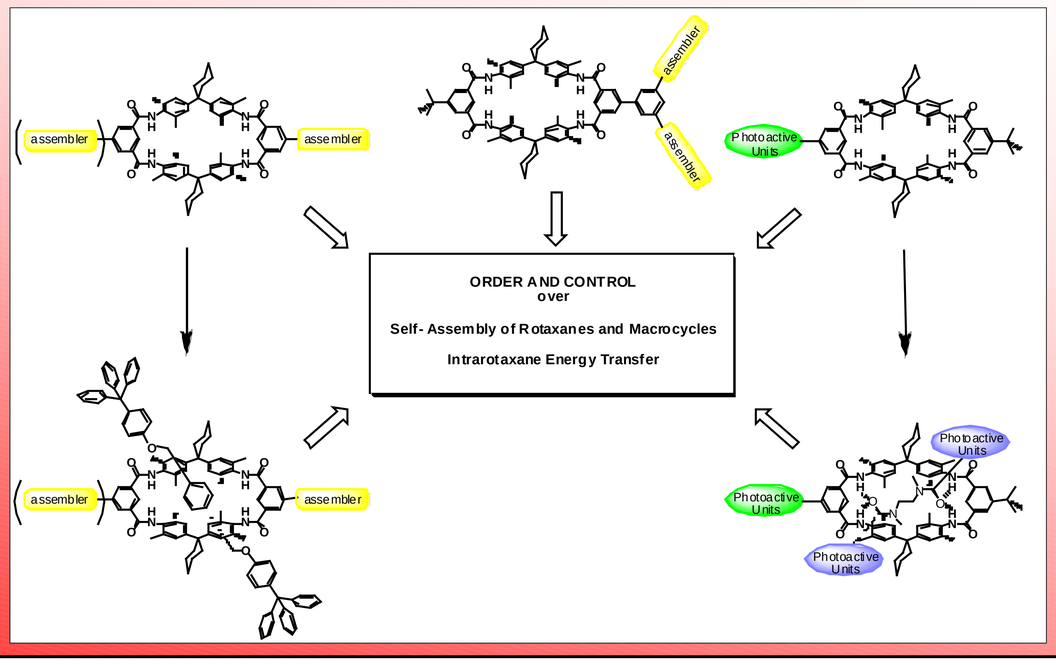
Complex architectures such as the ones existing in nature are composed of small building blocks interacting with each other dynamically and self-assembling reversibly.

The design of the right building blocks is of vital importance to obtain the correct architecture and finally to achieve the desired function in high efficiency.

A larger variety of building blocks for such architectures

- **increases the possibility of formation of different architectures**
- **is a chance to build complicated systems which self-assemble to the desired architectures**
- **performs the expected function in high efficiency**
- **self-sort and self-heal**

The idea of an easily accesible toolbox consisting of differently functionalized macrocycles and rotaxanes for building complex architectures is reported here.



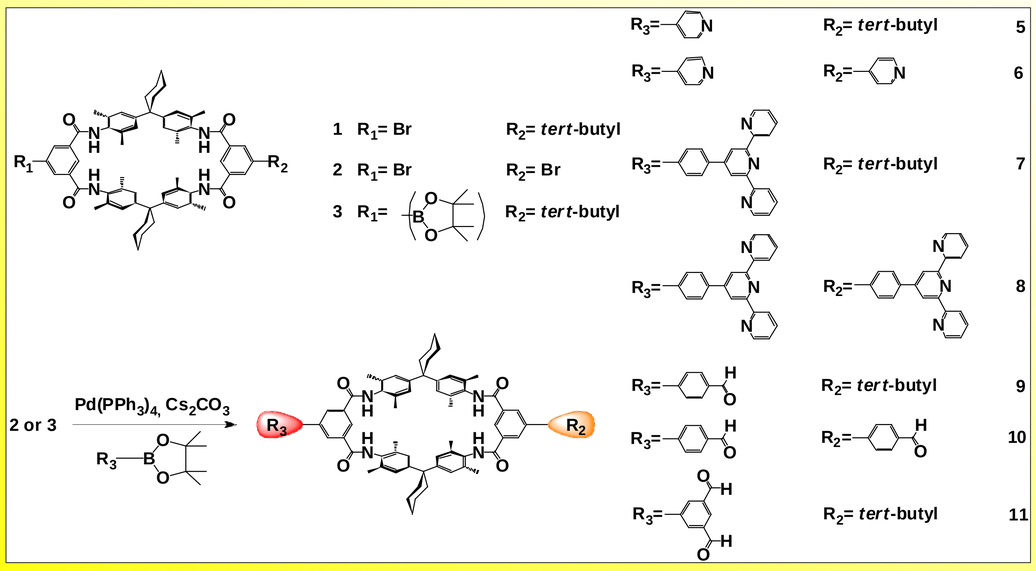
Picking up the Right Building Blocks

The building blocks to be synthesized were chosen to fit the future needs and purposes of

- **Metal-directed self-assembly of macrocycles and rotaxanes**
- **Self-assembly of macroccycles and rotacxanes via imines**
- **Multivalency studies**
- **Intrarotaxane energy transfer**

and combination of these.

Syntheses of Precursors and the Route to Functionalized Macrocycles



The macrocycle body used in the study is the previously known [1] wheel which had been used in the amide and anion template syntheses of rotaxanes. [2]

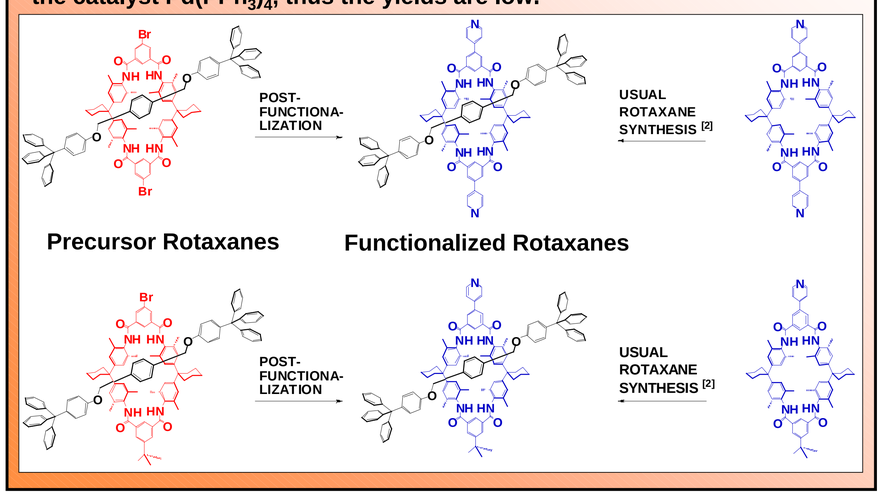
Functionalizing the macrocycles at the 5-position of the iso-phthaloyl units through *Suzuki Coupling* has the advantages of

1. **Retention of the cavity's size and shape; unchanged hydrogen bonding sites in the cavity (vital for the rotaxane synthesis)**
2. **Straightforward access to a variety of macrocycles and rotaxanes from the same precursors**
3. **High yields in obtaining the functionalized macrocycles and rotaxanes**

Functionalized Rotaxanes and Post-Threading Functionalization

It is possible with this approach to obtain precursor rotaxanes and functionalize them with various groups once they are formed.

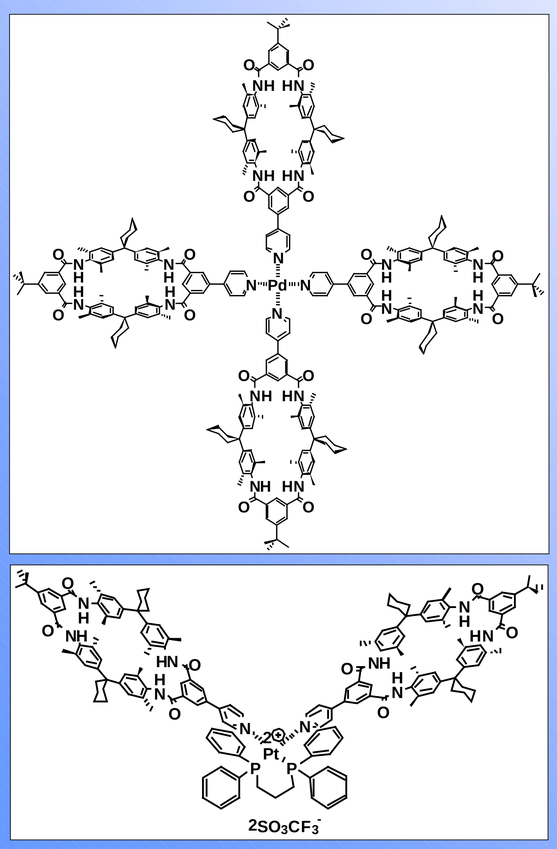
The yield of the functionalized rotaxane depends on the stability of the axle in Suzuki reaction; with the phenyl ether axles dethreading is promoted by the catalyst $Pd(PPh_3)_4$, thus the yields are low.

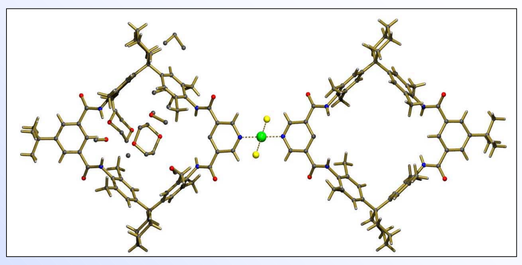


Metal Directed Self-Assembly of Macrocycles

Ligand-decorated macrocycles can be used to have metal complexes with different geometries of the wheels around the metal centers.

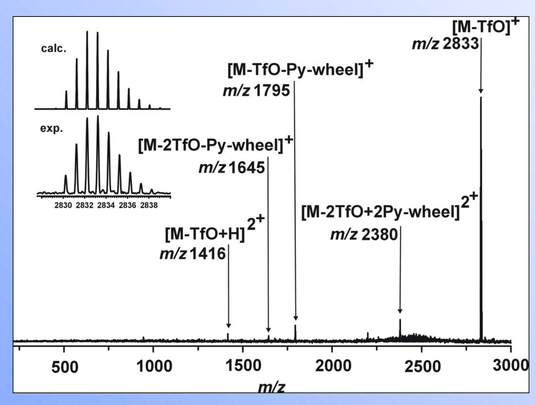
These further can be used
- **in the controlled self-assembly of macrocycles and rotaxanes**
- **as multivalent hosts for multivalent guests.**



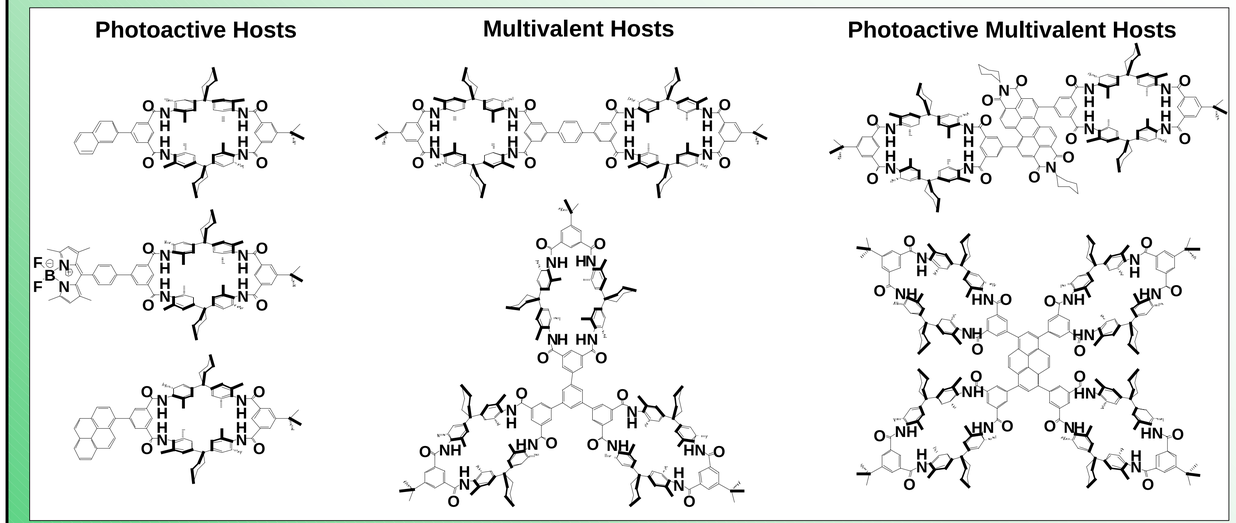


X-ray crystal structure of the trans-$PdCl_2$ complex of a model compound indicates a proper orien-tation of wheels. As a whole, the complex is an ideal divalent host with the all-in conformation of the amide hydrogens that can be used as a template for multivalent guests.

ESI-MS and NMR studies show the divalent cis-Pt complex and tetravalent Pd complexes to form almost quantitatively. These complexes can be used in multivalency studies with appropriate multivalent axles.



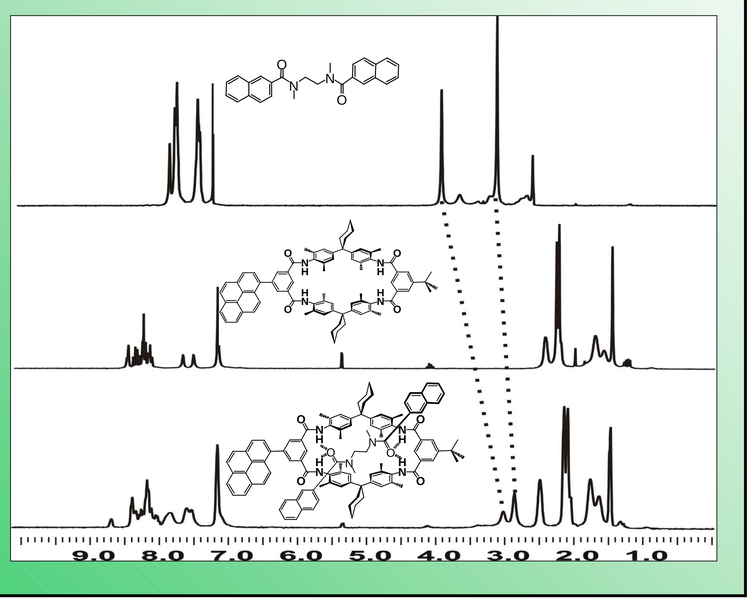
Photoactive Units and Multivalent Hosts



Functionalization of the macrocycles and rotaxanes with photoactive groups

- **provides the chance to determine binding constants of the host complexation from spectroscopic measurements**
- **to study the intrarotaxane energy transfer**
- **to operate future molecular machines built from these rotaxanes by light.**

Upon mixing a pyrene-functionalized macrocycle and the naphthalene axle, the expected pseudorotaxane forms. The ^1H NMR spectrum indicates complex formation by the high-field shift of the axle methyl and methylene protons.



[1] Goerts, Y., Muscat, D., Müllen, K. *Macromol. Chem. Phys*. 1995, 196, 3425-3435.
[2] Hübner, G. M., Gläser, J., Seel, C., Vögtle, F. *Angew. Chem*. 1999, 111, 395- 398. Angew. Chem Int. Ed. 1999, 38, 383-386.

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