

Towards Complex Threaded Molecular Architectures – Functionalized Macrocycles and Rotaxanes Serving As A Toolbox

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The Idea of Having a Toolbox

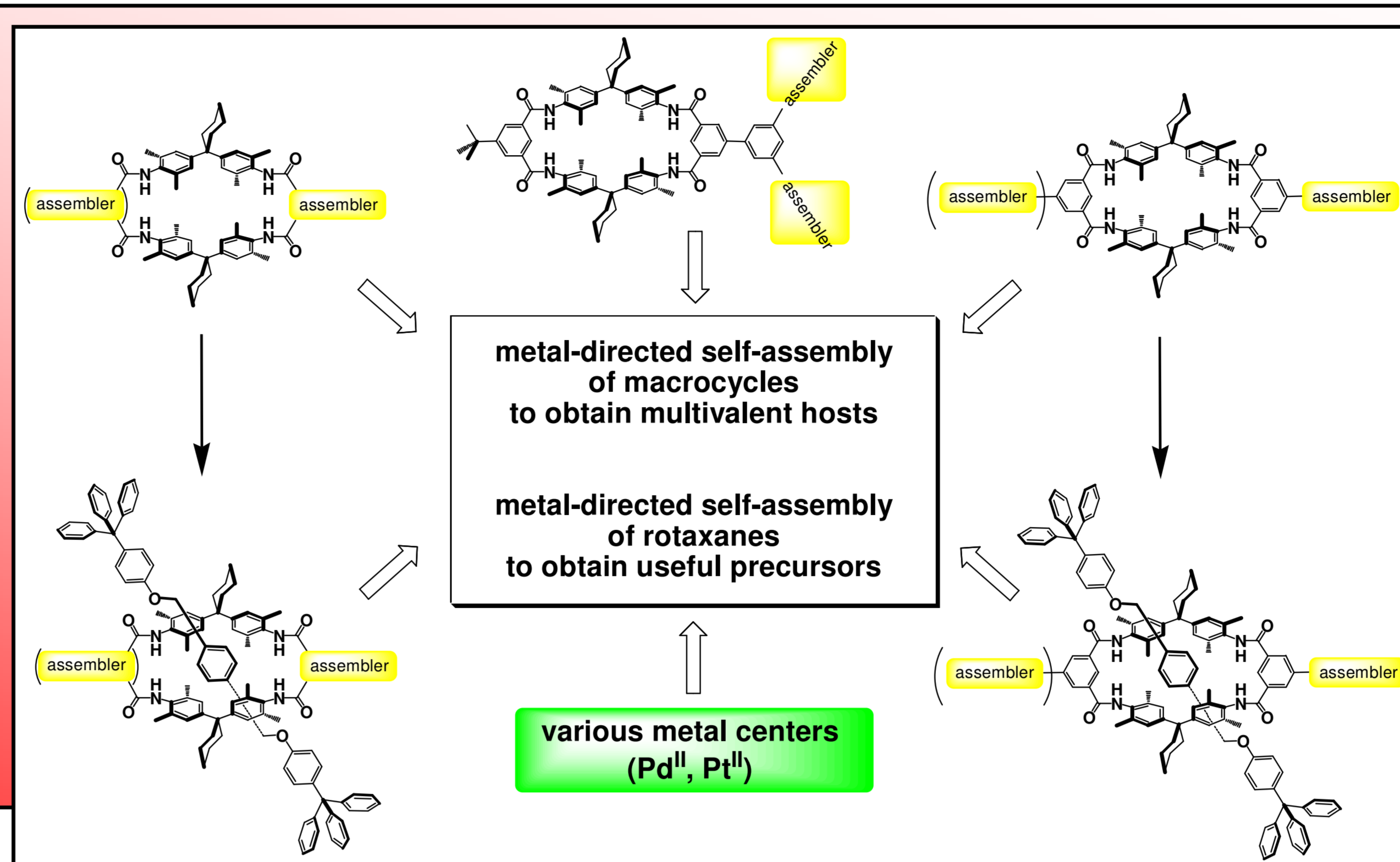
Complex architectures such as the ones existing in nature are composed of small building blocks interacting with each other dynamically and self-assembling reversibly.

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 accessible toolbox consisting of differently functionalized macrocycles and rotaxanes for building complex architectures is reported here.

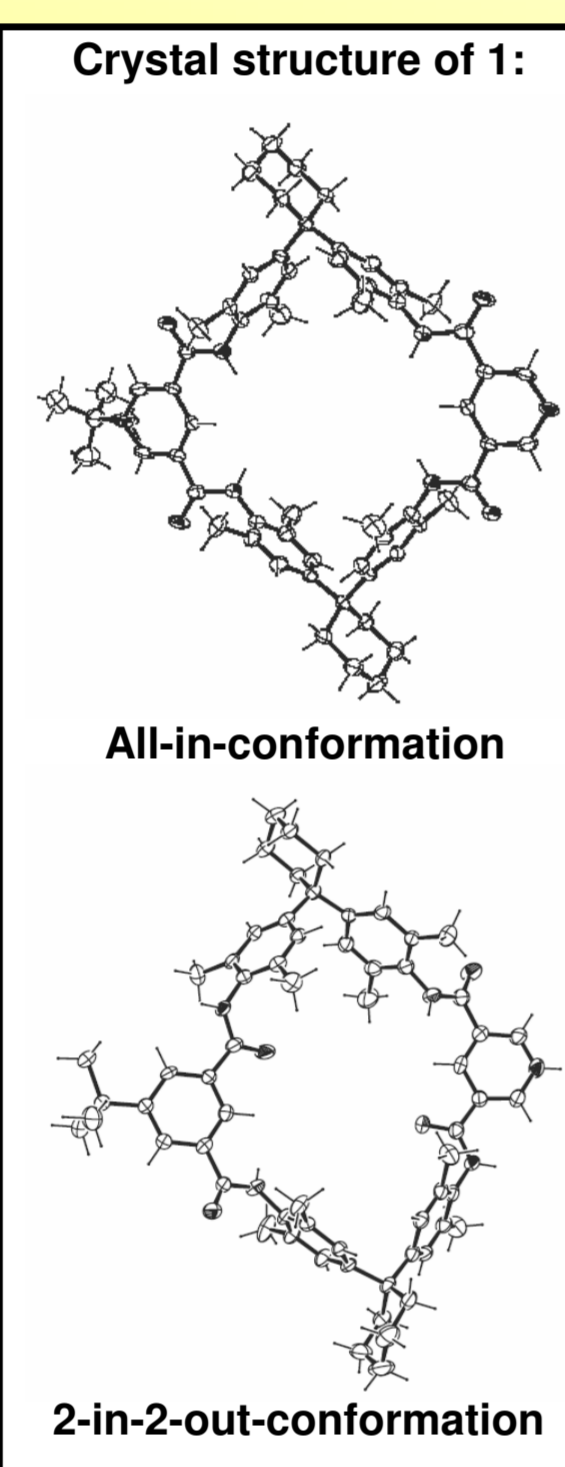
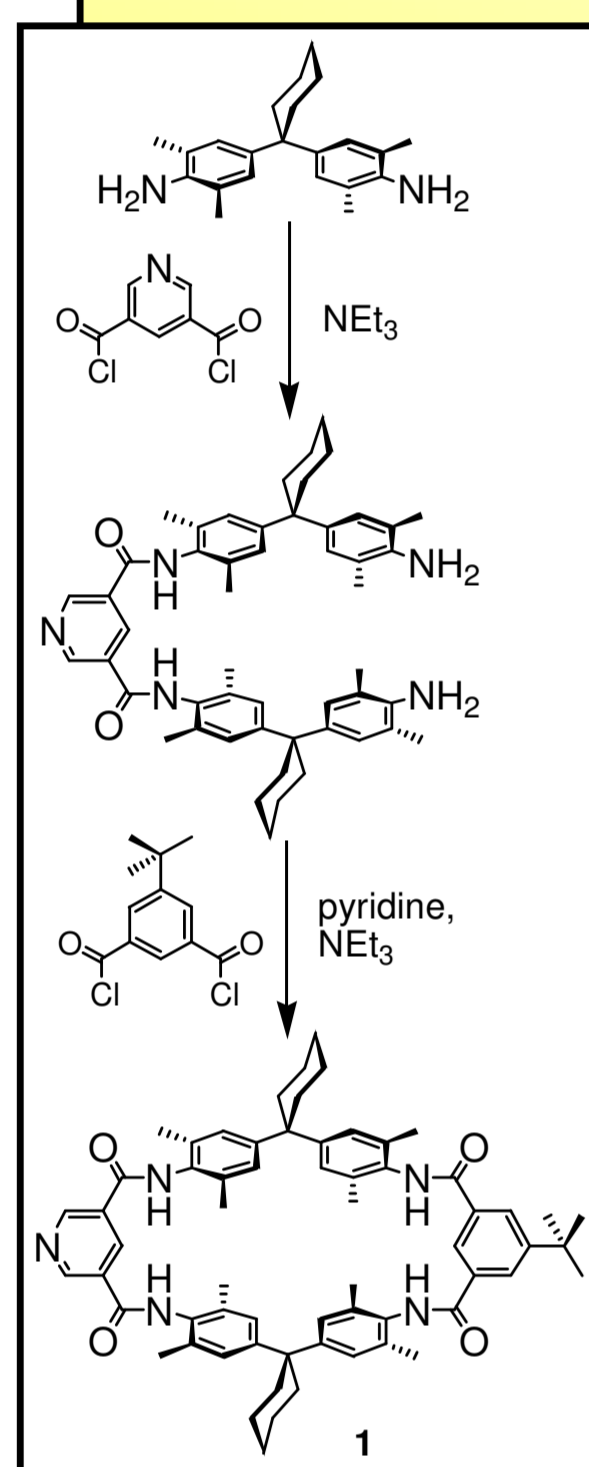


Investigation of multivalency effects

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

- Metal-directed self-assembly of macrocycles and rotaxanes to obtain multivalent hosts and precursors
- Multivalency studies (Multivalency = host-guest interactions existing simultaneously between two or more binding sites): Gaining a deeper understanding of the multivalency concept and exploring its utilizability in supramolecular chemistry

Syntheses of Precursors and the Route to Functionalized Macrocycles

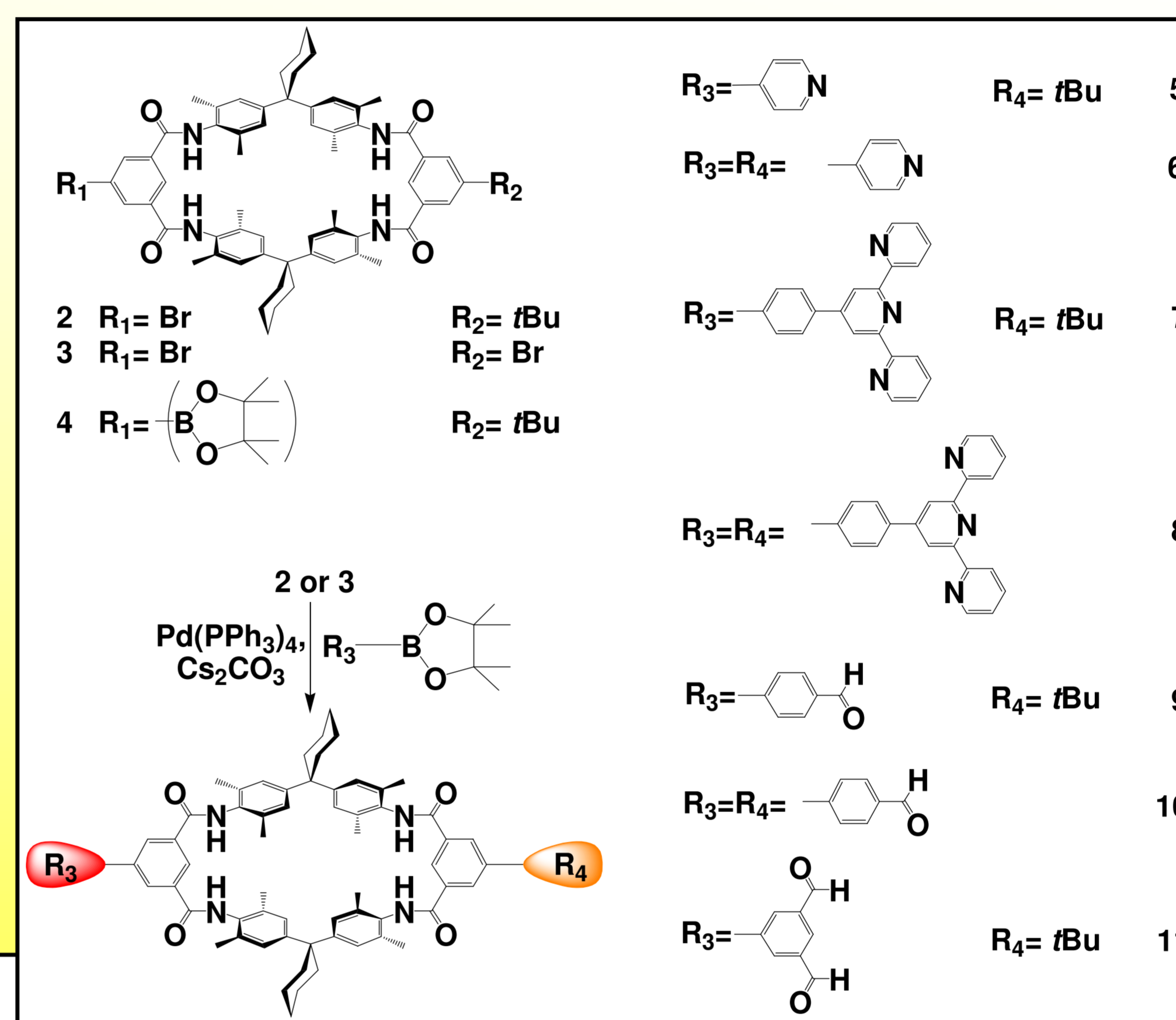


The macrocycle body used in the study is the previously known ^[1] tetralactam macrocycle which had been used in the amide and anion template syntheses of rotaxanes. ^[2] Two different routes to functionalized macrocycle are feasible:

a) Incorporating the ligand functionality into the macrocycle body (1, see left)

b) Functionalizing the macrocycles at the external 5-position of the isophthaloyl units through *Suzuki Coupling* (5–11, see right)

Macrocycles obtained through route a) such as 1 are more rigid in terms of ligand-macrocycle-connection. The crystal structure show that the molecule exist in two different conformations: 50% are all-in (all amide protons pointing into the cavity) and 50% are 2-in-2-out.



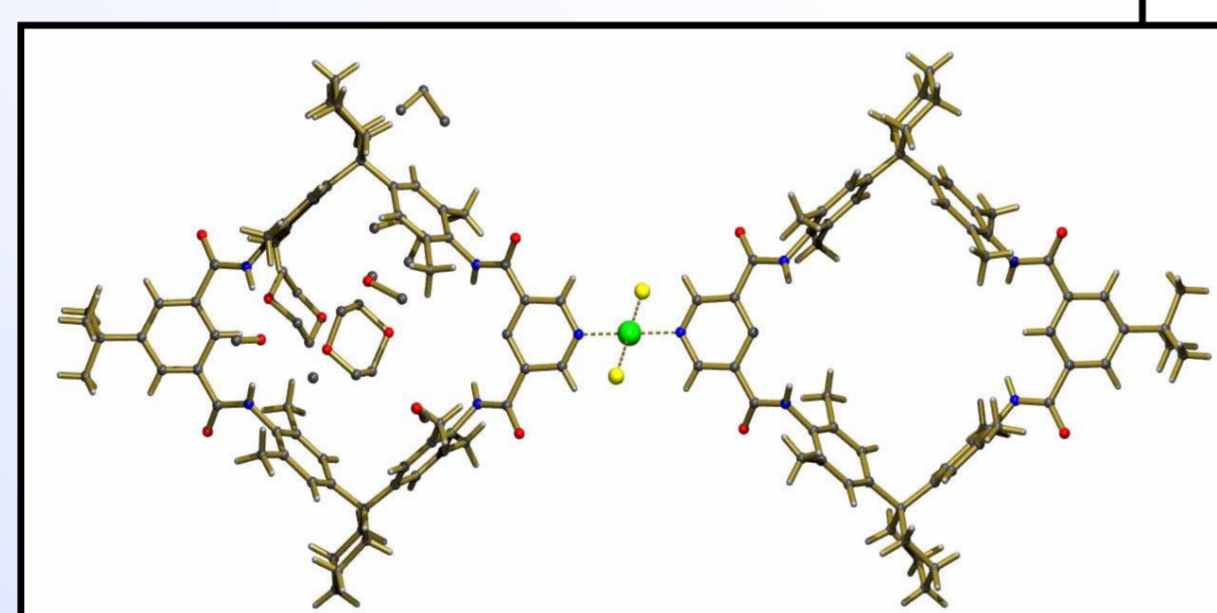
Route b) has the following advantages:

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

Metal Directed Self-Assembly of Macrocycles

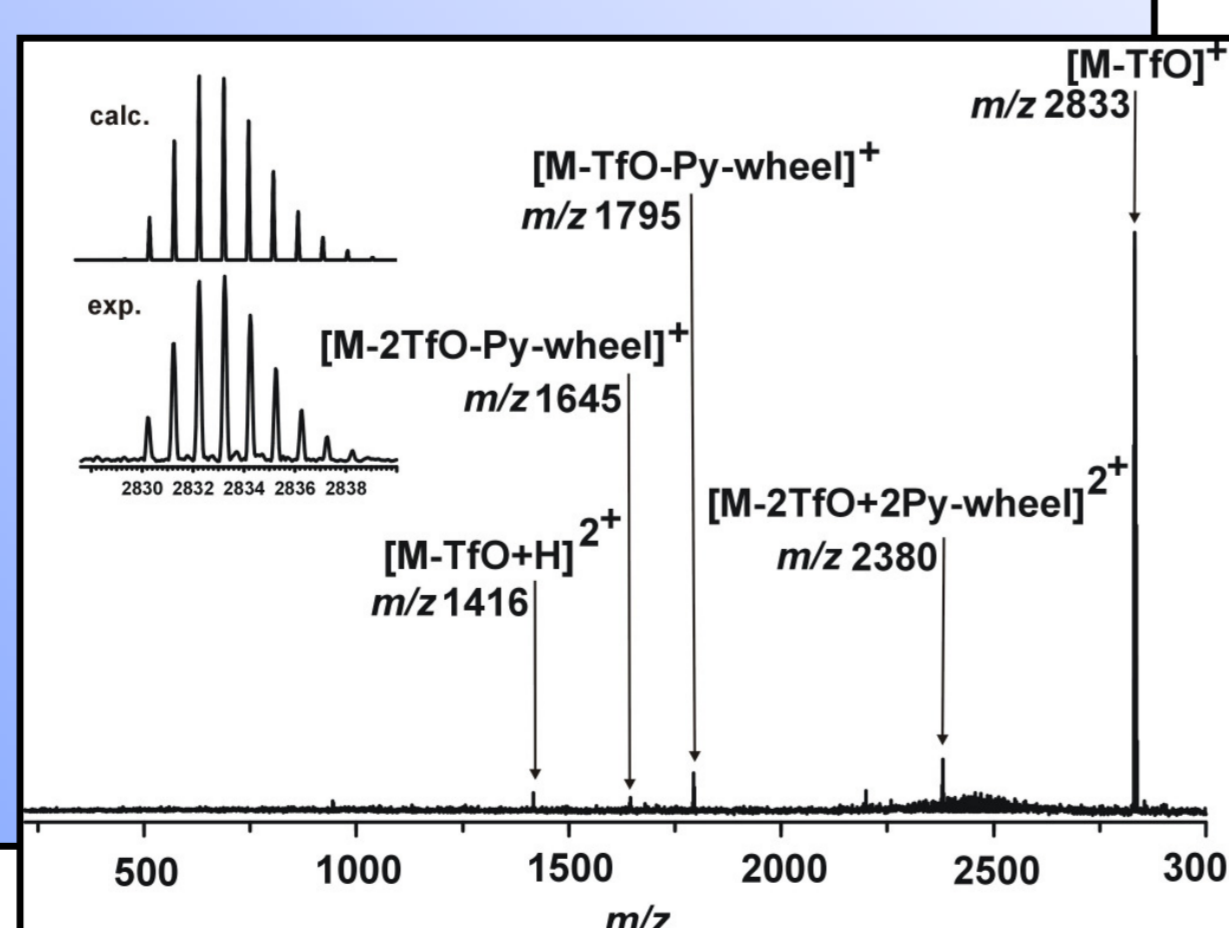
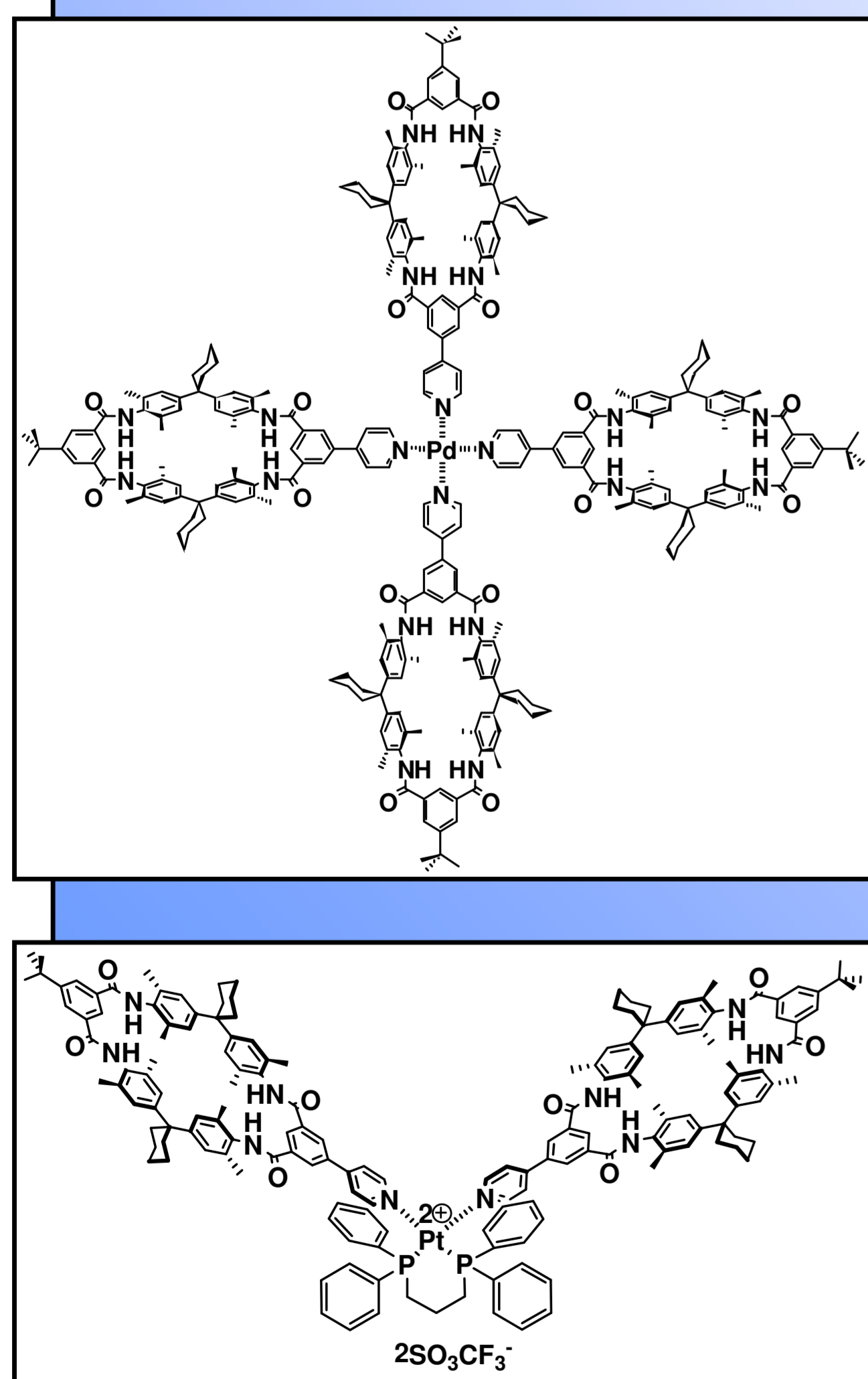
Ligand-decorated macrocycles can be used to obtain metal complexes with different geometries of the macrocycles around metal centers.

- in the controlled self-assembly of macrocycles and rotaxanes
- as multivalent hosts for multivalent guests.

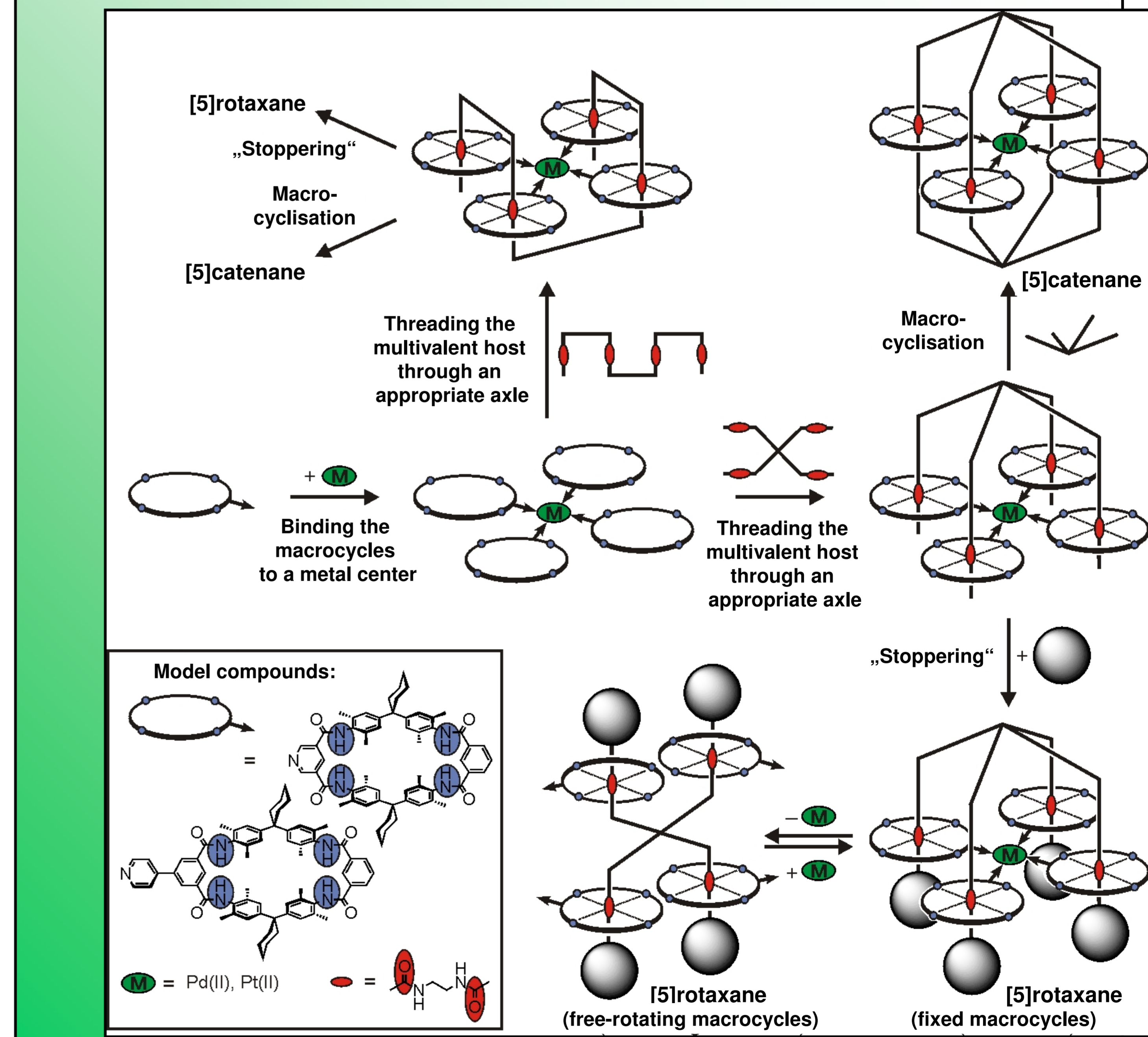


X-ray crystal structure of the trans-PdCl₂ complex of macrocycle 1 indicates a proper orientation of macrocycles. As a whole, the complex is an ideal divalent host with the all-in conformation of the amide hydrogens that can be used as a template for multivalent guests.

ESI-FTICR-MS and NMR studies show that the divalent *cis*-Pt complex and tetravalent Pd complex of macrocycle 5 are formed almost quantitatively. These complexes can be used in multivalency studies with appropriate multivalent axes.



Further Route to Complex Threaded Architectures



[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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