DOCTORAL THESIS

Utilization of Dynamic Interlocking Rotaxanes for Isomer Synthesis, Metal Ion Sensing and Potential Catalysis

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ABSTRACT

The synthesis of mechanically interlocked molecules (MIMs), such as rotaxanes and catenanes has drawn interest due to their special topologies. MIMs have been applied recently in various area such as catalysis and sensing. In this thesis, a new synthetic approach for co-conformational rotaxane isomer was developed and discussed. Related rotaxanes were applied for metal ion sensing and potential catalysis. A general introduction on the mechanically interlocked molecules with selected applications is presented in Chapter 1.

In Chapter 2, π-π interaction, stopper-stabilized dynamic interlocking was used as a new strategy for isomeric rotaxane synthesis. With π-electron rich components, e.g., phenanthroline and anthracene, novel [2]rotaxanes have been synthesized by dynamic imine clipping reaction. Their X-ray crystal structures indicate the π-π interaction between the anthracene moiety on axle with the macrocycle of the rotaxanes. Also, the length of glycol chains affects the extra π-π interaction between the phenyl groups and the dimethoxy phenyl groups on the thread. Dynamic combinatorial library has shown at best of 84% distribution of anthracene-threaded phenanthroline-based rotaxane, coinciding to the crystallography that the additional π-π interaction could increase the thermodynamic stability and selectivity of the rotaxanes. Moreover, two isomerically pure bistable [2]rotaxanes, **2-16**-2H·2PF_6 and **2-19**-2H·2PF_6, were synthesized and

separated to demonstrate the scope of using π-π interaction for synthesizing co-conformational rotaxane isomer, while the X-ray crystal structure of **2-16-**$2H\cdot2PF_6$ also shows the presence of π-π interactions.

In Chapter 3, fluorescent [2]rotaxanes were synthesized for metal ion sensing. The fluorescence of [2]rotaxanes **RA**-$H\cdot PF_6$, **RB**-$H\cdot PF_6$, **RRA** and **RRB** were quenched because there was a photoelectron transfer between the diimine/diamine and the anthracene components. The dynamic covalent bond of [2]rotaxane **RA**-$H\cdot PF_6$ can be hydrolyzed by trivalent metal ions in MeCN/H_2O solution (99:1, *v*/*v*), giving fluorescence after the breakdown of the interlocked structures at λ_{max} 424 nm. **RA**-$H\cdot PF_6$, **RB**-$H\cdot PF_6$ were reduced to obtain kinetically stable rotaxanes **RRA** and **RRB**, respectively. Mechanically interlocked structure was observed in the solid-state crystal structure of **RRA**. In water-compatible (50 vol %) solution, **RRA** and **RRB** are selective to Au^{3+} binding among the 28 metal ions. The Au^{3+} detection works at a range of pH 4 – 10. 50-Fold and 1.2-fold fluorescence turn-on of **RRA** and **RRB** can be achieved after addition of Au^{3+}, respectively. Also, linearly increase of fluorescence intensity of **RRA** and **RRB** to the concentration of Au^{3+} are observed till the excess of Au^{3+}. In addition, no significant metal interference on Au^{3+} detection is observed for both reduced rotaxane. To demonstrate the potential bio-application of rotaxane, **RRB** was used to image Au^{3+} in the HeLa cells. Results showed mechanically interlocked

molecules can be used for metal ion detection in water-compatible media and biological system.

In Chapter 4, by continuing the study on metal ion recognition, **RRA** has been applied for Au ion catalyzed aldehyde-alkyne-amine reaction (A^3 coupling reaction). Further experiments on the fluorescence response of **RRA** towards Au ions and complexes in solution indicated that **RRA** also partly recognizes Au^+ in selected organic and water-compatible solution. **RRA** has been employed as ligand to assist the A^3 coupling of benzaldehyde, phenylacetylene and morpholine. Primary results showed **RRA** can be used for the potential catalysis.

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