

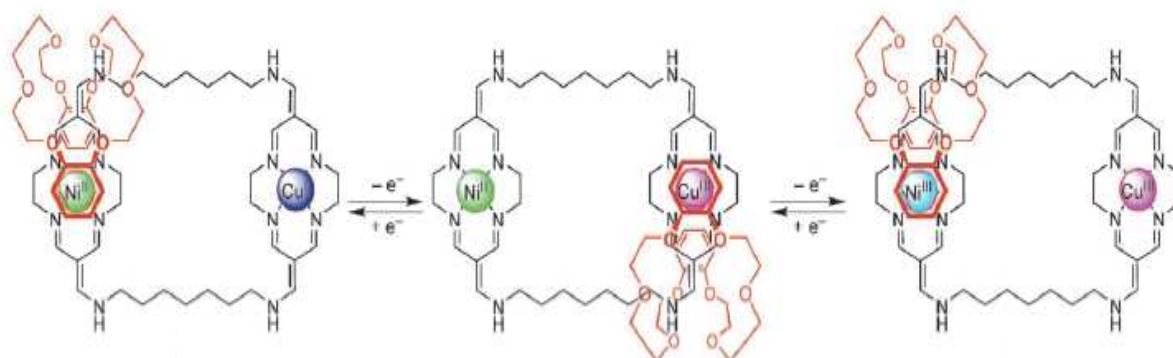
# Macrocyclic Metal Complexes as Building Blocks for Construction of Molecular Devices

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Tetraaza macrocycles, such as cyclam as well as its unsaturated analogues form stable complexes with transition metal ions, and frequently stabilize their unusual oxidation states. On the other hand tetraimine macrocyclic complexes are able to interact, depending of the coordinated metal oxidation state, as either  $\pi$ -donors or  $\pi$ -acceptors with another  $\pi$ -electron systems.

We have developed synthetic strategies allowing the production of macrocyclic derivatives incorporating two or more [14]cyclidene unites coordinating transition metal ions.<sup>1</sup> Such bismacrocylic molecules form rectangular box-like cations enclosing an empty space inside. It appears that, in the case of sufficiently large intramolecular voids, for example, with aliphatic linkers that are seven carbon atoms long, they can host some small guest molecules such as water or  $\pi$ -electron-donating compounds. When the cyclization reaction was carried out in the presence of an appropriate macrocyclic  $\pi$ -donor guest (eg. dibenzo-24-crown-8) a new type of [2]catenanes exhibiting potential-driven intramolecular motion were formed. The interlocked crown ether unit adopts the *cis* conformation in such a manner that one of its aromatic rings sits parallel to and between the two metal-coordinating macrocyclic rings of a biscyclidene complex. Since both of the coordinated metal ions were identical, the translocation of the crown ether moiety from one site to the other produces the same catenane arrangement. However, intertwining of the dibenzo-24-crown-8 with a heterodinuclear bismacrocylic complex (Cu, Ni) lead to two possible arrangements,<sup>2</sup> where the  $\pi$ -electron-rich benzene rings are located in the vicinity of either the copper or the nickel-complexing macrocycle, depending on the oxidation state of the coordinated ions (Scheme 1). Electrochemically switched relocations reflect a shuttle like behavior triggered by application of an appropriate potential. The phenomenon of controlled reversible intramolecular motion can potentially be applied in molecular devices.



**Scheme 1**

1. B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak, *J. Am. Chem. Soc.* 2001, **123**, 9356 – 9366.

2. B. Korybut-Daszkiewicz, A. Więckowska, R. Bilewicz, S. Domagała, K. Woźniak, *Angew. Chem. Int. Ed.* 2004, **43**, 1668 – 1672.