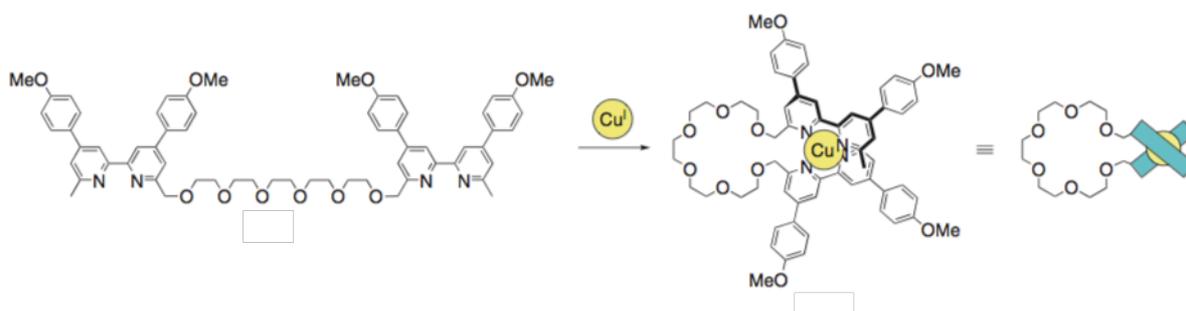


Regulation of molecular recognition through the formation of pseudomacrocycles

• Formation of a pseudo-crown ether bearing a tetrahedral-Cu(II) complex unit.

A podand with two 2,2'-bipyridyl groups on both ends of a linear polyether was designed and synthesized. Cu(I) ion, which forms 1:2 complex with bipyridine to give a tetrahedral complex, was reacted with the ligand to yield a pseudo-crown ether quantitatively via intramolecular cyclization. This molecule acts as a host to recognize alkaline metal ions. Notably, its selectivity toward K^+ ion was increased as a result of complexation with Cu(I).

(*Tetrahedron Lett.* **1987**, 28, 6211-6214; *Inorg. Chem.* **1993**, 32, 1407-1416.)



• Formation of a pseudo-cryptand bearing an octahedral Fe(II) complex unit.

A tripodand with 2,2'-bipyridyl groups on each end of three polyether chains was designed and synthesized. Fe(II) ion, which forms 1:3 complex with bipyridine to give an octahedral complex, was reacted with the ligand to yield a bicyclic pseudo-cryptand quantitatively via intramolecular complexation. It has the shape of a beautiful triple-stranded helicate, within which there is an internal cavity surrounded by three polyether chains. After careful investigations, it was found that the pseudo-cryptand selectively recognizes Cs^+ ion, an alkaline ion with large size, while it did not bind Na^+ . The result was in clear contrast to that of the precursor (tripodand) which strongly interacts with Na^+ . In summary, this system switches the recognition ability towards Na^+ and Cs^+ by allosteric effects, which was the result of significant structural change upon the addition of Fe(II).

(*J. Am. Chem. Soc.* **2003**, 125, 28–29; *Tetrahedron Lett.* **2006**, 47, 3541–3544.)

