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Multimetal supramolecular systems for cooperative regulation of unique structures and functions

Cooperative regulation is one of the most effective ways to finely change molecular functions in biological as well as artificial supramolecular systems by utilizing information at molecular level. The cooperative and synergistic chemical events should decrease the reaction steps for chemical conversion to a product and to create novel functions that cannot be achieved by a non-cooperative single molecular system. Thus, these regulation mechanisms would strongly contribute to green and sustainable chemistry because of reducing the laborious processes. Hence we have studied functional supramolecules responding to external stimuli as a cooperative system. Here we introduce our concept on the organic-inorganic hybrid supramolecular systems with high cooperativity on structural and functional modulations. In particular, multimetal systems on the basis of ligands containing C=N functionality are discussed.

We have designed and synthesized linear and macrocyclic Schiff base and their related compounds containing 1,2-bis(salicylideneaminoxy)ethane (salamo) units, etc. to construct metallo-supramolecular systems for cooperative functions. These ligands can be converted to multimetal complexes in high yield and to show unique functions. For example, the acyclic bis-salamo ligands exhibited very cooperative complexation ability to Zn(II) to give homotrimeric Zn complexes, which can be quantitatively converted to heterotrimeric $Zn_2 \cdot M$ ($M=La, Ca, \text{etc.}$) complexes. The calcium selectivity of the transmetalation among alkali and alkaline metal ions is extremely high. In addition, di- and tri-salamo ligands react with different metal ions to give the helical heteromulti-nuclear complexes in high yields. When a chiral auxiliary is incorporated into a salamo-saleno hybrid ligand, one of the helical multi-metal complexes is formed predominantly over the other complex with opposite helicity. Another hybrid ligand containing two crown ether moieties also reacts with metal ions to give the helical multimetal complex. The helical sense can be well controlled by changing length of diammonium guests (molecular leverage concept). A linear trisalamo ligand bearing a chiral auxiliary at the termini was designed and synthesized for multisequential and multimode helicity inversion. The helicity of this multimetal system can be regulated by the stepwise addition of metal ions. To the best of our knowledge, this is the first example of multistep regulation of molecular helicity by external stimulus. More examples of saloph and salamo-metallo-supramolecular systems will be discussed.

Biography

Tatsuya Nabeshima received his B.S. (1979) from The University of Tokyo, M.S. (1981) from University of Tsukuba, and Ph. D. degrees (1985) from Kyoto University. In 1985, he joined Stanford University as a postdoctoral fellow. He was promoted to Assistant Professor of University of Tsukuba in 1987. He became an associate professor in 1995, Professor in 1999, and the director of TIMS (a research center in Univ. of Tsukuba, 2010-2013). He has received The Chemical Society of Japan Award for Creative Work in 2008.

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