Numerical Study for Kinetic Control of Coordination Self-Assembly: M_4L_4 Square Complex as an Example

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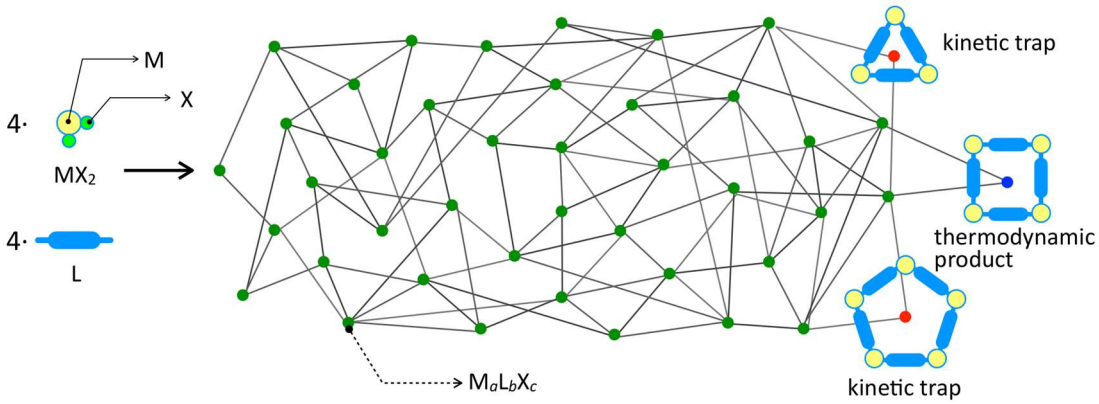
Molecular self-assembly is one of the fascinating phenomena, in which constituent atoms and molecules spontaneously assemble into the products having specific geometries depending on the types and strengths of the available chemical interactions. In most of such processes, the final products distribute in the well-known Boltzmann's manner, and so the reaction pathways of molecular self-assembly have tended to be neglected. However, if the molecular self-assembly can be carried out under kinetic control, digging into the details of reaction pathways makes us understand how to control molecular self-assembly with varying the reaction conditions and suitable design of the building blocks.

In this work, as a prototype system for numerically studying such a possibility to the kinetic chemical reaction control, we adopted the coordination self-assembly of a M_4L_4 square complex composed of transition metal complexes MX_2 (M and X represent the metal ion and the leaving ligand, respectively) and a ditopic ligand L. A chemical reaction network was constructed by considering all elementary reactions among 35 possible species including chain-like oligomers $M_aL_bX_c$ (a = 1–10) and macrocycles M_aL_a (a = 3–5). Simulations of the self-assembly were conducted under various kinetic parameter sets and reaction conditions such as the way of mixing of the components (MX_2 and L), which led to a general principle that enables us to produce most stable assembly (M_4L_4) in higher yield by choosing a proper self-assembly pathway. This idea was experimentally confirmed for Pd_nL_{2n} coordination self-assembly systems.



Schematic representation of the self-assembly of a M_4L_4 square in a chemical reaction network.