Kinetically Controlled Coordination Self-assembly: Approaches to Pathway Selection

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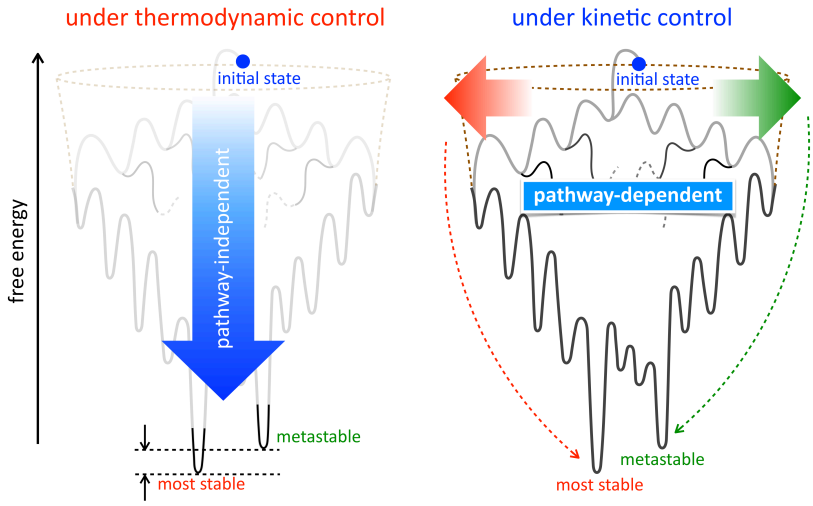
In most cases, molecular self-assembly proceeds under thermodynamic control to reach equilibrium, which makes a great advantage in that wrong connection between the building blocks can be corrected so that the thermodynamically most stable assembly is dominantly produced. Considering that in such a molecular self-assembly the products should Boltzmann distribute, we notice that there are limitations in thermodynamically controlled molecular self-assembly. The first is that the most stable assemblies cannot be produced more than the Boltzmann distribution though they are always the major product under thermodynamic control. The second is that as is often the case with multicomponent self-assembly where various assemblies with similar thermodynamic stability tend to be produced, a single assembly cannot be selected under thermodynamic control. Furthermore, the selective production of a metastable assembly is impossible. These difficulties arise from the fact that equilibrium reactions obey the thermodynamic law. In contrast, if the self-assembly is controlled by kinetics, we have a chance to produce desired assemblies in higher yield and selectivity than those under thermodynamic control.



Here, we present two approaches to pathway selection which enable us to produce thermodynamically stable assemblies and metastable ones beyond the Boltzmann distribution. These are based on the idea that even though the elementary reactions in molecular self-assembly are reversible, we can make a situation where self-assembly proceeds under kinetic control: global irreversibility with local reversibility (GILOR) on the energy landscape. We will discuss these approaches applied to Pd(II) coordination self-assembly systems as a proof-of-principle.