Hybridization of reversibility and irreversibility in a reaction network: Numerical analysis of catalytically promoted molecular self-assembly

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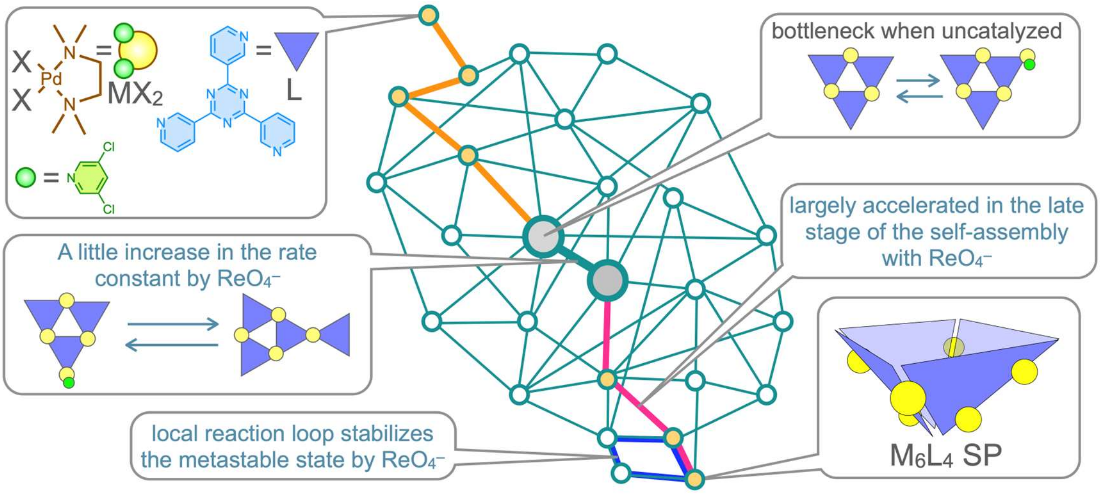
In the self-assembly of a M_6L_4 square-based pyramid (SP) complex, the yield of the target product was found to significantly increase when ReO_4^- is present as a catalyst. For this experimental fact, we performed numerical simulations and analysis based on the numerical method we have developed,[1] with a mathematical model in which a chemical reaction network is composed of reversible elementary reactions.

Main reaction pathways were found to be similar without and with the catalyst. In the absence of catalyst, triangular species (M_3L_3 and M_4L_3X) were trapped, and their conversions afterward were prevented. ReO_4^- indirectly promoted the subsequent elementary reactions by largely accelerating the later steps in the self-assembly, though the direct increase in the rate constant was small for the most difficult reaction step to reach M_6L_4 SP. This unequal acceleration is due to the fact that the acceleration trend depends on the coordination ability of L. The metastable state biased to M_6L_4 SP was maintained by reaction loops involving SP.[2] An appropriate co-creation of global irreversibility and local reversibility promoted by the catalytic action of the anion was found to lead to an increase in the product yield and acceleration of the global self-assembly reaction.



1) For example, S. Takahashi, T. Abe, H. Sato, S. Hiraoka, *Chem* **2023**, *9*, 2971–2982. 2) S. Takahashi, T. Abe, H. Sato, S. Hiraoka, submitted.