

Construction of Kinetically Controlled Dynamic Host-Guest Systems

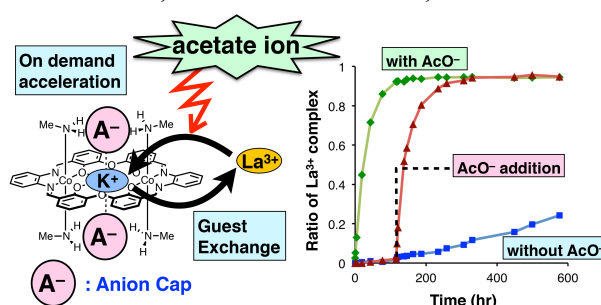
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Keywords: Supramolecular Chemistry, Metal Coordination, Kinetic Control, Host-Guest Chemistry, Self-Assembly

The recent advances in supramolecular chemistry, which deals with noncovalent interactions between molecules, have allowed numerous studies of molecular recognition behaviors and self-assembly processes. While they are generally thermodynamically controlled events, kinetic control of such processes is essential for the development of new supramolecular functional systems. In this study, we created new responsive systems whose functions can be kinetically controlled^{1-6,9} and synthesized a new class of kinetically-stable self-assembled metal complexes.⁷⁻⁸

1. Development of Kinetically Controlled On-Demand Molecular Recognition System

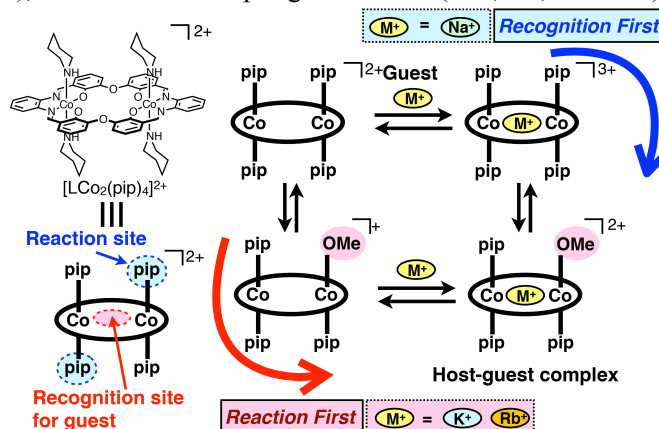
The control of kinetic parameters such as guest inclusion/exchange rate is important for the development of new host-guest system in which a desired function is driven by guest recognition. However, the strategies for the precise control of these kinetic processes have rarely been reported. Here we succeeded in on-demand acceleration of guest exchange rates of a cationic cobalt(III) dinuclear macrocyclic metallohost by the replacement of the counteranions. The newly synthesized cationic cobalt(III) macrocyclic metallohost, [LCo₂(CH₃NH₂)₄](OTf)₂ encapsulated alkali metal, alkaline-earth metal, and lanthanide cations in such a way that the counteranions capped the cavity openings. The guest inclusion rates highly depended on the guest cations or anion caps. We also found that the replacement of the triflate anions by acetate anions drastically accelerated the guest exchange rates.



2. Unveiling the Molecular Recognition Mechanism of Multinuclear Metallohosts

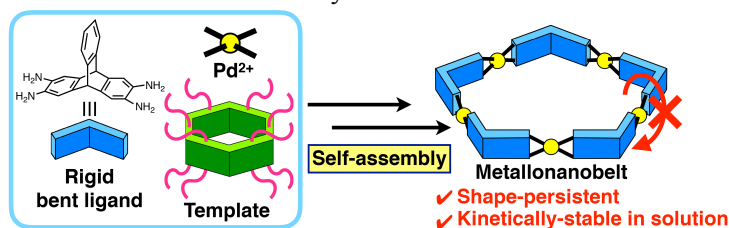
Molecular recognition processes coupled to conformational changes in biomolecules are generally classified into two types of mechanisms, “induced fit” and “conformational selection”. Even for artificial host-guest system, host-guest binding sometimes triggers the subsequent chemical reactions of the host framework. Although it is sometimes difficult to differentiate the mechanisms from the alternative one in which the guest binding occurs after the reaction, it is important to distinguish the two mechanisms when we develop new molecules based on time-dependent functions. Here we investigate the molecular

recognition mechanism of a new macrocyclic dinuclear cobalt(III) metallohost, $[\text{LCo}_2(\text{pip})_4](\text{OTf})_2$ (pip = piperidine), which can take up a guest cation (Na^+ , K^+ , and Rb^+) into its cavity causing concomitant exchange of the axial piperidine. Detailed kinetic analysis revealed that the recognition pathway can be switched by changing the guest cations. Control of molecular recognition behaviors by ligand exchange on cobalt(III) ions will be also presented.



3. Construction of Kinetically Stable Metallonanobelt Prepared by Template-Directed Self-Assembly Process

Shape-persistent belt-shaped macrocyclic compounds, which have no rotatable single bond, have attracted much interest due to their unique structural and electronic features. However, there are only a limited number of such macrocyclic complexes. Here we constructed new sufficiently inert shape-persistent molecular belt, prepared by reversible metal-assisted self-assembly processes. The shape-persistent belt-shaped metallomacrocyclic, metallonanobelt, was synthesized by the self-assembly of a triptycene-based rigid bent ligand **L** and square planar Pd^{2+} . Particularly, the pentamer metallonanobelt was selectively formed by the complexation of **L** with Pd^{2+} in the presence of pillar[6]arene derivative **P6** having triethylene glycol chains as a template. The guest free pentamer was also successfully isolated and it was found to be remarkably stable towards size-conversion in solution. We also succeeded in the functionalization of metallonanobelt using quinoxaline formation.



- 1) Y. Sakata, C. Murata, S. Akine, *Nature Commun.* **2017**, 8, 16005.
- 2) Y. Sakata, M. Tamiya, M. Okada, S. Akine, *J. Am. Chem. Soc.* **2019**, 141, 15597-15604.
- 3) Y. Sakata, M. Okada, M. Tamiya, S. Akine, *Chem. Eur. J.* **2020**, 26, 7595-7601.
- 4) Y. Sakata, M. Okada, S. Akine, *Chem. Eur. J.* *in press*.
- 5) Y. Sakata, S. Chiba, M. Miyashita, T. Nabeshima, S. Akine, *Chem. Eur. J.* **2019**, 25, 2962-2966.
- 6) Y. Sakata, S. Kobayashi, S. Akine, *Chem. Commun.* **2017**, 53, 6363-6366.
- 7) Y. Sakata, R. Yamamoto, D. Saito, Y. Tamura, K. Maruyama, T. Ogoshi, S. Akine, *Inorg. Chem.* **2018**, 57, 15500-15506.
- 8) Y. Sakata, Y. Furukawa, S. Akine, *Tetrahedron Lett.* **2019**, 60, 2049-2053.
- 9) Y. Sakata, T. Ogura, S. Akine, *Chem. Commun.* **2020**, 56, 8735-8738.
- 10) For a review on kinetic control of host-guest binding, see: S. Akine, Y. Sakata, *Chem. Lett.* **2020**, 49, 428-441.