

Metal-containing host molecules that can close their apertures

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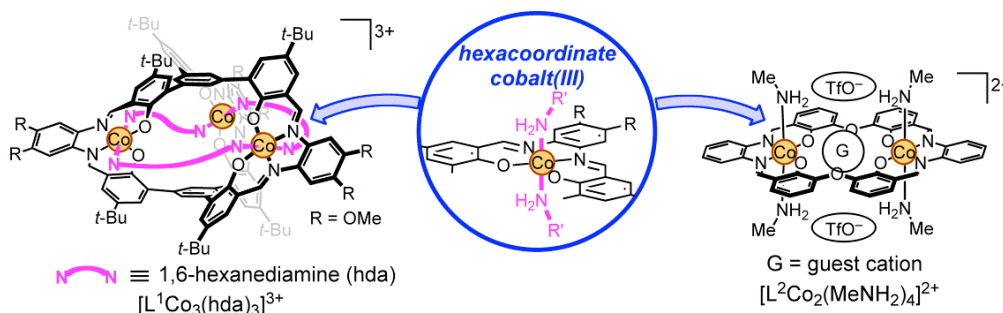
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- DATE & TIME: April 25th (WED) 11:00 AM
- PLACE: Research Bldg. 1, #112, POSTECH
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Macrocyclic compounds and molecular cages are known to act as a good host molecule. Usual host molecules easily and quickly take up a guest species in the cavity, but some molecular cages can permanently confine the guest species in the cavity. This confinement effect depends on the guest size compared with the cage portal can enter and exit the cavity. If we introduce a cap function into the host compounds, we can switch the guest confinement effect; the guest is confined in the cavity when the cap is closed, while the guest freely enters and exits when the cap is open. In order to achieve this open/close function, we designed two new molecular scaffolds based on oligo(salen)-metal structures.^[1] In this lecture, guest recognition control behavior of the macrocyclic and cage-like oligo(salen) structures will be presented.

1. Cage-like metallocryptand that can close the aperture.^[2] A tricobalt(III) metallocryptand $[L^1Co_3(hda)_3](OTf)_3$, which has 1,6-hexanediamine (hda) ligands at the apertures of the molecular cage, was synthesized. This complex selectively recognized Cs^+ , but it took more than 50 h for the complete conversion to the Cs^+ complex. The uptake rate was more than 2000 times slower than that of the open cage analogue. The closed-cage structure with diamine ligands efficiently slowed down the guest uptake.

2. Anion-capped macrocyclic metallohost.^[3] A macrocyclic dicobalt(III) metallohost $[L^2Co_2(MeNH_2)_4](OTf)_2$ recognized various cations (Na^+ , K^+ , Rb^+ , Ca^{2+} , La^{3+}) to give the inclusion complexes, in which the binding site was capped with two triflate anions. The guest uptake became significantly slow due to the capping effect so that we could obtain kinetically trapped state where a disfavored guest was taken up prior to a favored guest. Based on the fact that the capping effect depends on the type of anions, we achieved an on-demand guest exchange triggered by replacing the anion caps starting from the kinetically trapped state.



References:

- [1] S. Akine, *J. Inclusion Phenom.*, **2012**, 72, 25; S. Akine and T. Nabeshima, *Dalton Trans.*, **2009**, 10395.
- [2] S. Akine, M. Miyashita, T. Nabeshima, *J. Am. Chem. Soc.*, **2017**, 139, 4631.
- [3] Y. Sakata, C. Murata, S. Akine, *Nat. Commun.*, **2017**, 8, 16005.