

# Coordination Chemistry Strategy for Dynamic Structural Switching in Helical Metal Complexes



**Hiroyuki MIYAKE**

Department of Chemistry, Graduate School of Science, Osaka City University, Osaka, Japan

Dynamic structural switching in response to a combination of several external stimuli is essential phenomenon for developing sophisticated artificial molecular devices in supramolecular level, which is promising approach to switch on subsequent functional events. Since metal complexes can create a variety of supramolecular structures depending on the nature of metal center and ligand properties employed, they have distinct advantages in the formation of several dynamic helicates.<sup>1</sup>

I and my colleagues have designed chiral ligands that afford exquisite single-stranded helices upon metal complexation, where the chiral information is transferred to the metal center from the asymmetric carbon center of the ligand to induce one-handed helicity. In case of Co(II) complexes, the sign of circular dichroism (CD) signal around 550 nm reflects the helical sense of the complexes.<sup>2</sup> Since the time scale of the dynamic chirality transfer process can be controlled by the lability of the metal center, such "time-programmable helicates" can be designed to work as elegant and sophisticated helicity switches and memories.

We applied the dynamic coordination chemistry to an elastic structure switching and helicity inversion of the chiral Co(II) complex, in which achiral acid, base and NO<sup>3-</sup> anion work as external stimuli.<sup>4</sup> We further demonstrated that the cobalt center works as a redox responsive center to switch the dynamic situation of the complex.<sup>5</sup> The formed inert Co(III) complex having contracted- $\Lambda$  structure was easily reduced to the labile Co(II) complex having contracted- $\Lambda$ , extended- $\Lambda$  or extended- $\Delta$  structures depending on a combination of external stimuli.

Since the metal helicates have characteristic dynamic properties as a function of asymmetric coordination chemistry, they function as chirality switches and chirality memory in a fundamentally different fashion from organic foldamers and helical polymers.

## References

1. H. Miyake and H. Tsukube, *Chem. Soc. Rev.*, **2012**, 41, 6977.
2. H. Miyake, K. Yoshida, H. Sugimoto, H. Tsukube, *J. Am. Chem. Soc.*, **2004**, 126, 6524.
3. H. Miyake, H. Kamon, I. Miyahara, H. Sugimoto, H. Tsukube, *J. Am. Chem. Soc.*, **2008**, 130, 792.
4. H. Miyake, M. Hikita, M. Itazaki, H. Nakazawa, H. Sugimoto, H. Tsukube, *Chem. Eur. J.*, **2008**, 14, 5393.
5. J. Gregoliński, M. Hikita, T. Sakamoto, H. Sugimoto, H. Tsukube, H. Miyake, *Inorg. Chem.*, **2016**, 55, 633-643.