# Dynamic Triple-helical Metallocryptand: Time-Programmable Helicity Inversion Triggered by Alkali Metal Ions

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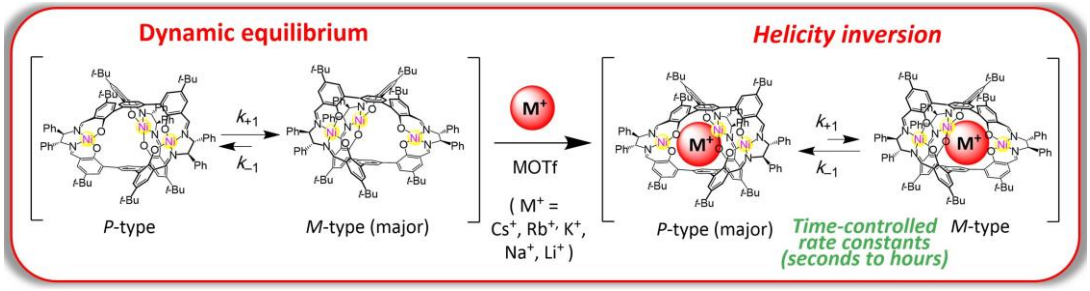
'Helicity inversion' is one of the most sophisticated processes in biological and artificial systems.[1] Biological DNA and proteins often alter their helix sense in response to particular external stimuli and switch biologically important events in controlled time scale. Dynamic helical molecules, which are capable of undergoing reversible helicity inversion, are useful as a basic framework for chiral switching systems. There have been several examples of dynamic helical molecules whose helix inversion rates can be tuned by changing solvent polarity, constituent metal ions of helicates, etc.[1-3] However, in order to efficiently control the helix inversion rate, combination of such a dynamic helix inversion with host-guest complexation would be effective.

A novel chiral tris(salen)-type trinickel(ll) cryptand was designed and synthesized. This complex was characterized by various spectroscopic techniques such as $^1$H NMR, ESl-MS, UV-vis, CD spectroscopy, and X-ray crystallography, as well as the theoretical calculations. The nickel(ll) cryptand underwent a dynamic interconversion between the *P* and *M* isomers in solution, preferring M-isomer, with a half-life of $t_{1/2}$ = 5.0 min. Guest encapsulation studies on a series of alkali metal ions were performed with this metallocryptand. The present metallocryptand offers time-tunable helicity inversion on the time scales from seconds to hours ($t_{1/2}$ = 12 sec for $K^+$ complex; $t_{1/2}$ = 1.05 h for $Cs^+$ complex).




**Scheme 1.** Dynamic Triple-helical Metallocryptand for recognition of alkali metal ions and helicity inversion.

1) H. Miyake, H. Tsukube, *Chem. Soc. Rev.*, **2012**, *41*, 6977-6991. 2) S. Akine, M. Miyashita, S. Piao, T. Nabeshima, *Inorg. Chem. Front.*, **2014**, *1*, 53-57. 3) S. Akine, M. Miyashita, T. Nabeshima, *Inorg. Chem.*, **2021**, *60*, 12961-12971.