Selective encapsulation of alkali metal ions in a chiral trinickel(II) metallocryptand and its regulation of helicity inversion

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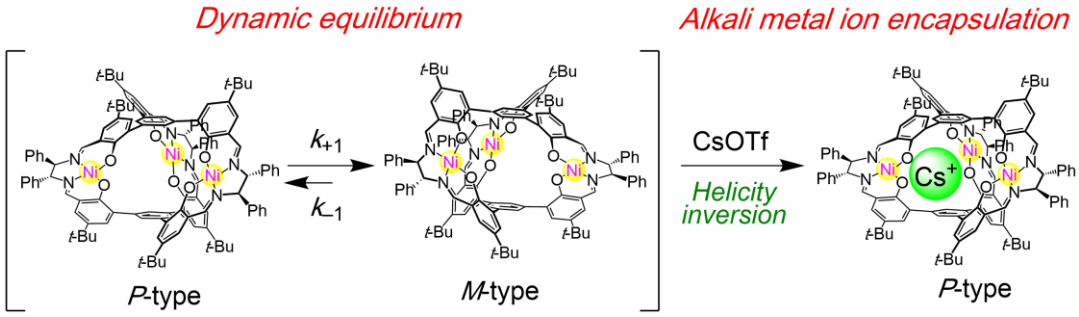
Dynamic helical molecules, which are capable of undergoing reversible helicity inversion, are useful as a basic framework for chiral switching systems.[1] There have been several examples of dynamic helical molecules whose helix inversion rates can be tuned by changing solvent polarity, constituent metal ions of helicates, etc.[2,3] However, in order to efficiently control the helix inversion rate, combination of such a dynamic helix inversion with host-guest complexation would be effective.

We have synthesized a novel tris(salen)-type trinickel(II) metallocryptand having six chiral carbon centers (Scheme 1). This complex was characterized by various spectroscopic techniques such as ^{1}H NMR, ESI-MS, UV-vis, CD spectroscopy, X-ray crystallography, etc. The nickel(II) metallocryptand underwent a dynamic conversion between the *P* and *M* isomers in solution, preferring one isomer in a ratio of up to 10:90. In contrast, the single crystals showed the presence of both *P* and *M* isomers exactly in a 1:1 ratio in the unit cell. Guest encapsulation studies on a series of alkali metal ions were performed with this metallocryptand. Whereas it showed first negative Cotton effect (tentatively assigned to the *M*-type helicity) in the absence of guests, the complexation with CsOTf caused the CD signal inversion (*P*-type helicity major). We will present such helicity inversion and helicity control behaviour associating with the encapsulation of a series of alkali metal ions.



Scheme 1. Helical metallocryptand for recognition of alkali metal ions and helicity inversion.

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