Regioselective deprotonation of twisted trinuclear macrocycles to control the rate of helicity inversion

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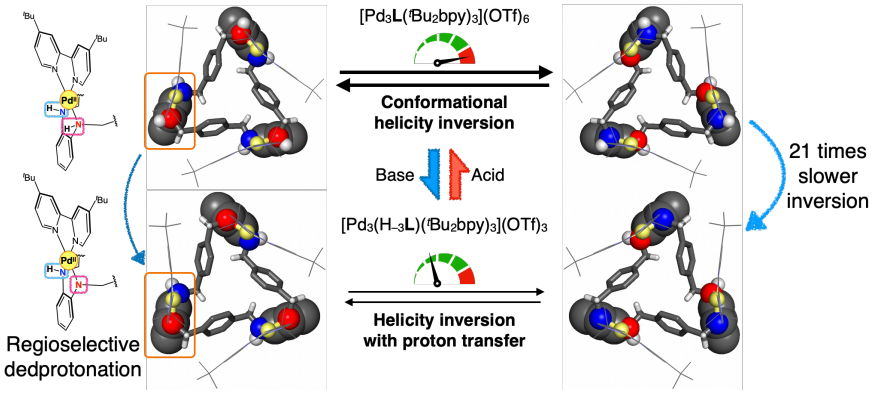
Molecular motions including translation and rotation are controlled by various external stimuli, such as acid and base, to achieve molecular machines that work reversibly. For example, Stoddart and his co-workers demonstrated reversible translation motion of a molecular shuttle controlled by electrostatic repulsion upon addition of acid and base.[1] In this study, we aimed to control the inversion rate of a helically twisted trinuclear Pd^{II} complex, $[Pd_3\mathbf{L}(^t Bu_2bpy)_3](OTf)_6$, by regioselective deprotonation. Indeed, the inversion rate of the deprotonated $[Pd_3(H_{-3}\mathbf{L})(^t Bu_2bpy)_3](OTf)_3$ was significantly slowed down. Reversible conversion between the original and deprotonated Pd^{II} complexes by acid and base was also confirmed.

A trinuclear Pd^{II} complex, $[Pd_3\mathbf{L}(^t Bu_2bpy)_3](OTf)_6$, was synthesized by the reaction of a macrocyclic ligand **L** with a Pd^{II} salt. Single-crystal XRD and ^{1}H NMR analyses revealed that the macrocyclic framework of the Pd^{II} complex was helically twisted by intramolecular C-H···π interactions. This Pd^{II} complex exhibited helicity inversion between (*P*)- and (*M*)-helicity, with an estimated inversion rate of 3.31 s^{-1} at 300 K in acetone-d_6 by EXSY NMR analysis. The Pd^{II} complex was then reacted with 26 equiv. of Na_2CO_3 and ^{1}H NMR analysis revealed that only three of the six amine protons of **L** were site-selectively deprotonated to $[Pd_3(H_{-3}\mathbf{L})(^t Bu_2bpy)_3](OTf)_3$. Furthermore, the effect of regioselective deprotonation on the helicity inversion rate was investigated using EXSY NMR, and the inversion rate of $[Pd_3(H_{-3}\mathbf{L})(^t Bu_2bpy)_3](OTf)_3$ was 0.155 s^{-1} at 300 K in acetone-d_6, which is 21 times slower than that of $[Pd_3\mathbf{L}(^t Bu_2bpy)_3](OTf)_6$ due to the intramolecular proton transfer. This presentation will explain the mechanism of helicity inversion.



[1] R. A. Bissell, E. Córdova, A. E. Kaifer, and J. F. Stoddart, *Nature* **1994**, *369*, 133-137.

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