

Control of inversion motion by *in/out*-isomerization of helically twisted Pd₃-macrocycles

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Isomerization is one of the most important factors in controlling molecular motions such as rotation and gearing. Photo-induced *cis/trans*-isomerization has been used in many molecular machines, but control of molecular motions based on other isomerization reactions is still challenging. Previously, our group reported an inversion motion between (*P*)- and (*M*)-enantiomers of a helically twisted Pd₃-macrocycle, [Pd₃LCI₆], but precise control of the inversion motion has not been achieved.^[1] In this study, we found that helically twisted Pd₃-macrocycles, [Pd₃L('Bu₂bpy)₃](OTf)₆, form two markedly different structural isomers, *in*- and *out*-isomers, and that each isomer is in equilibrium as a racemic mixture of the (*P*)- and (*M*)-forms. The inversion kinetics of these two sets of enantiomers were remarkably different, indicating the possibility that they could be involved in an excellent molecular switching system *via* the “inside-out” isomerization.

The *in*- and *out*-isomers of the Pd₃-macrocycles were selectively synthesized under different conditions and their structures were determined by single-crystal XRD and ¹H NMR analyses. The *out*-isomer showed conformational inversion between the *out*-(*P*)- and (*M*)-enantiomers, and the inversion rate was evaluated to be $3.23 \pm 0.06 \text{ s}^{-1}$ at 300 K in acetone-*d*₆ by EXSY analysis. In stark contrast, the inversion between the *in*-(*P*)- and (*M*)-isomers was not observed in 4 days ($< 10^{-6} \text{ s}^{-1}$) because it requires configurational changes of all amine nitrogen atoms.

In addition, we found that the very slow reversing *in*-isomer slowly isomerizes into the fast reversing *out*-isomer, and the rate of this *in*-to-*out* isomerization was estimated by time course NMR analysis. We will also discuss how this entire system can be controlled by external stimuli.

[1] R. Kubota, S. Tashiro, M. Shionoya, *Chem. Sci.* **2016**, 7, 2217–2221.

