

論文の内容の要旨

Control of Molecular Rotational Motions toward the Construction of Highly Functionalized Molecular Machines

(高度に機能化された分子機械の構築に向けた分子回転運動の制御)

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1. Introduction

Rotary motion transmission, especially by gear coupling, is indispensable to the construction of macroscopic machines, which can be used for adjustment of the direction and torque of the rotation as well as of integration or division of the power. Synthetic molecules with a similar structure would show promise as an important element of highly sophisticated molecular machines.

Several examples have been previously reported on motion transmission based on the mechanical meshing of gear-shaped molecules. However, most of them are two-gear systems and there is no report that demonstrates mechanical transmission through more than three engaging gears, because, with an increase in the number of gears, it becomes more difficult to design, synthesize, and analyze the motion of gear systems.

In this study, I have constructed a circularly arranged sextuple triptycene gearing system, and characterized the molecular structures and motion behaviors by NMR spectroscopy and single-crystal XRD analysis, in which triptycene with a rigid and highly symmetrical three-bladed structure served as a rotatable gear. The efficiency of the motion transmission through gear meshing and the effect of site-selective metal binding to one of the gears on the motion behaviors have been quantitatively evaluated by variable temperature-¹H NMR spectroscopy.

2-1. Construction of a sextuple triptycene gearing system

A gear molecule **1**, in which six triptycenes are circularly attached to a central benzene ring through an ethynyl linker, was designed and synthesized (Figure 1). The key reaction to construct such a crowded structure was a trimerization reaction of bis-substituted alkynes to generate a hexakis-substituted benzene in the final step.

Its tightly interlocked structure was determined both in solution and in the solid state by NMR spectroscopy and single-crystal X-ray analysis, respectively. Rotational speeds of the triptycene gears in solution were evaluated by variable-temperature NMR spectroscopy. The activation enthalpy and entropy were estimated to be $+12.4 \text{ kcal}\cdot\text{mol}^{-1}$ and $+3.17 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively, as determined by the Eyring plots.

2-2. Metal-mediated control of the gearing system

In the light of the fact that triptycene forms an arene complex with a cationic RuCp^* (Cp^* = pentamethylcyclopentadienyl) complex, it was assumed that, if a RuCp^* group forms an arene complex with one triptycene phenylene ring of **1**, the bulky RuCp^* complex would significantly restrict the motion of the whole gear system.

By mixing the gear molecule **1** with $[\text{RuCp}^*(\text{NCMe})_3]\text{PF}_6$ at room temperature, a 1:1 complex $[\mathbf{1}\cdot\text{RuCp}^*]\text{PF}_6$ was obtained in 55% yield (Figure 2). The complex was well characterized by a wide variety of NMR measurements, ESI-MS spectrometry, and elemental analysis. The signals in the aromatic region of the NMR spectrum became more complicated after complexation, indicating that the RuCp^* complex was attached not to the central benzene ring but to one of the surrounding triptycene phenylene rings. At 320 K, the RuCp^* -bound triptycene showed distinctive signals, and the other five triptycenes

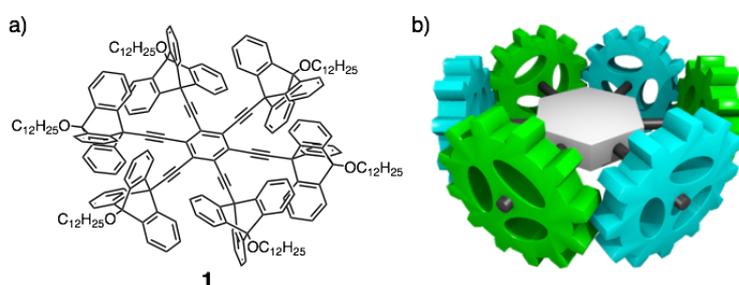


Figure 1. a) Chemical structure of the gear molecule **1**. b) Schematic representation of the gear molecule **1**.

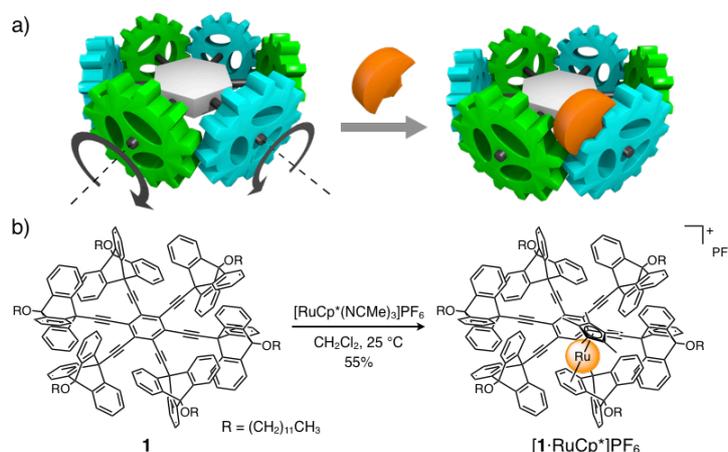


Figure 2. a) Schematic representation of the effect of a bulky “stopper” on the gear system. b) Synthetic scheme of complexation between $[\text{RuCp}^*(\text{NCMe})_3]\text{PF}_6$ and **1**.

showed coalescence for each triptycene moiety. This indicates that the other five triptycenes can rotate at this temperature regardless of the presence of the bound RuCp*. If all the rotational motions are completely restricted in the whole molecule, all the eighteen benzene rings should provide distinctive signals, because this metal complex is chiral and therefore all the six triptycenes are chemically inequivalent.

The dynamic behaviors of [1·RuCp*]PF₆ were investigated by VT-NMR spectroscopy in detail. The rotation rate of the RuCp*-bound triptycene was assumed to be zero ($k'_1 = 0$, table in Figure 3) in the range of measured temperatures based on the result of ¹³C NMR measurement. For the other five triptycenes, a part of signals in the aromatic region of the spectrum was simulated, and the rate constant k' of each triptycene was estimated as shown in the table of Figure 3. With increasing distance from the Ru center (from k'_2 to k'_6), the values increase. This result suggests that the gears are not completely meshed with each other but a "gear slippage" takes place to some extent.

Notably, the rotational speed calculated from k'_4 , that for unadjacent triptycene to the Ru-attached position, is smaller than that of a metal-free gearing system **1**. This indicates that, although it is incomplete due to the gear slippage, the rotational motion is definitely transmitted through the gearing process.

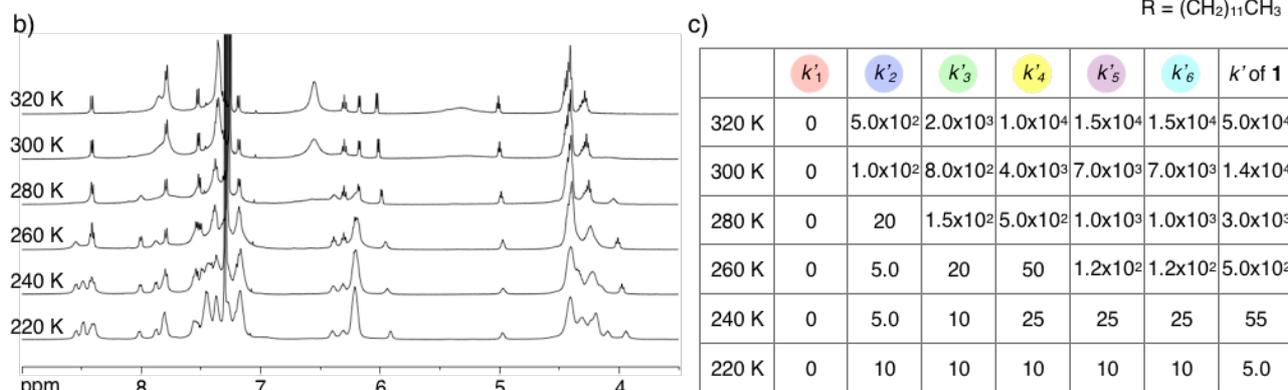


Figure 3. a) Structure of [1·RuCp*]PF₆. b) VT-¹H NMR spectra of [1·RuCp*]PF₆ (CDCl₃, 500 MHz). c) Table of the estimated rate constants (k') for the rotational motion of triptycenes at each temperature.

3. Conclusion

In this study, I have established the synthesis of the circularly arranged sextuple triptycene gearing system, and evaluated its rotational motion with or without a metal-based inhibitor. Addition of a RuCp* complex has a significant influence on the whole motion of the gearing system. The result also suggests that considerable gear slippage motions occurred in spite of the tightly meshed structure. By tuning the structure, transmission efficiency would be improved. Combination with a molecular motor would provide highly functionalized molecular systems for constructing hybrid molecular machines.