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Rotational Control of a Dirhodium-Centered Supramolecular Four-Gear System by Ligand Exchange

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Supporting Information Placeholder

ABSTRACT: Self-assembled molecular machines have great potential to enable non-covalent regulation of a coupled motion of the building blocks. Herein we report the synthesis and the rotational control of a lantern-type dirhodium complex with circularly-arranged four 2,3,6,7,14,15-hexamethyltriptycene carboxylates as gears and two axial ligands as the rate control elements. The rotating rates in solution were markedly affected by the coordination ability and the bulkiness of axial ligands. Notably, the rate changes were closely correlated with the changes in the electronic states of the dirhodium center. Such ligand exchange-based control of rotational motions with color changes would advance stimulus-responsive metallo-molecular multi-rotors.

Biological molecular machines, such as ATP synthase and motor proteins, are fascinating molecular systems in which the rate and direction of the motions are highly controlled in a synergistic manner to integrate functions of motor, actuator, converter, and transmitter.[1] Inspired by their sophisticated structure and mechanism, a variety of excellent examples of synthetic molecular machines have been reported as miniature versions of macroscopic devices from 1980's.[2,3] So far, several types of functional molecular machines such as unidirectional motion,[4] on/off switching by external stimuli,[5] transmission of energy through coupled motions,[6] and others are known. In synthetic molecular machines, self-assembled molecular machines have great potential to enable non-covalent regulation of a coupled motion of the building blocks.[7]

Since Iwamura[8] and Mislow[9] independently reported the first molecular gearing systems, triptycene has been often used as a three-bladed gear, whereas pentiptycene,[10] porphyrin,[11] and tetraphenylcyclobutadiene[10] have been used as four-bladed gears. Most of them are two gear-meshed molecules, and only a limited number of examples have been reported for linearly-meshed three gear systems.[11,13–16] Gear meshing in a two or three gear system can be controlled by fluoride ion[17] or by acid/base,[11,16] and, to the best of our knowledge, there is no example for the rate control of multiple gearing systems. Moreover, visualization of chemical phenomena can provide a new insight into molecular dynamics and chemical reactions.[18] Although methods with optical microscopy enable us to obtain some images of molecular motions,[19] the connection with a sub-micrometer-sized probe that is several hundreds times as large as the molecular machine possibly varies the original kinetics and dynamics.[20] Alternatively, the correlation between motions and color changes of molecular machines is useful as a non-invasive estimation method as well as light-sensitive molecules.

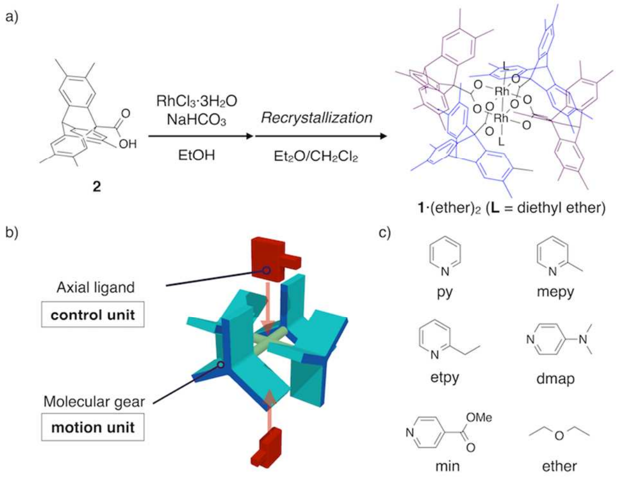

Figure 1. (a) Synthesis and chemical structures of dirhodium-centered circular four-gear complexes **1**·$\mathbf{L}_2$. (b) Schematic representation of rotational control of the molecular motions by the axial ligand exchange. (c) Axial ligands used in this study.

Herein we report the synthesis and rotational control of a lantern-type dirhodium complex with circularly-arranged four 2,3,6,7,14,15-hexamethyltriptycene carboxylates as meshed gears and two axial ligands as the rate control elements (Figure 1). The rotational rates in solution were markedly affected by the coordination ability and the bulkiness of axial ligands, diethyl ether and pyridine derivatives (Figure 1b). Moreover, UV-vis absorption of solutions containing a different axial ligand was significantly affected by the type of the axial ligands. Although a few examples of lantern-type complexes that look like molecular gears have been reported,[21–23] their dynamic behaviors have not been investigated.

Tetrakis(2,3,6,7,14,15-hexamethyltriptycene carboxylato)dirhodium·(ether)$_2$ complex, **1**·(ether)$_2$, was prepared by refluxing a mixture of 2,3,6,7,14,15-hexamethyltriptycene carboxylic acid (**2**), $RhCl_3 \cdot 3H_2O$, and $NaHCO_3$ in ethanol (Figure 1a). After purification by column chromatography and recrystallization from CH_2Cl_2/diethyl ether, diethyl ether adduct, **1**·(ether)$_2$, was obtained as green crystals in 48% yield. The two axial diethyl ether ligands could be replaced by several types of pyridines to form **1**·**L**$_2$ [**L** = py (pyridine), mepy (2-methylpyridine), etpy (2-ethylpyridine), dmap (*N*,*N*-dimethyl-4-aminopyridine), min (methyl isonicotinate)] by adding two equiv. of each pyridine derivative in CH_2Cl_2 (see the Supporting Information).

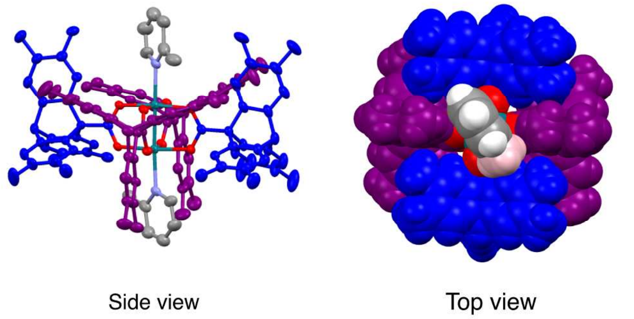

Figure 2. ORTEP drawing with 50% probability (side view) and space filling model (top view) for **1**·(mepy)$_2$. Diagonal triptycenes are displayed in the same color. Hydrogen atoms are omitted for clarity in the ORTEP drawing. Methyl groups of the mepy ligands are highlighted in pink in the space-filling model.

Crystal structures of all the six complexes were determined by single-crystal X-ray analyses. As shown in the structure of **1**·(mepy)$_2$ (Figure 2), the dirhodium core of the lantern-type complex has circularly-arranged four carboxylate gears meshing with each other. The two axial ligands bind to the dirhodium center along the Rh–Rh bond axis.

The structural parameters around the axial ligands are summarized in Table 1. The Rh–Rh distances for pyridine ligands were approximately 2.40 Å, and the Rh–**L** distances were roughly in the range from 2.20 to 2.30 Å regardless of the type of coordination atoms and substituents of the pyridine ligands. On the other hand, the bending angles of the axial pyridine ligands from the Rh–Rh bond axis (Rh-Rh-**L**) took on a wide range of values. Notably, the steric effects of the substituents (H-, CH_3-, and C_2H_5-) at the 2-positions of the pyridine ligands were significant as shown in the increasing values, 3.50°, 13.6°, and 15.0° for **1**·(py)$_2$, **1**·(mepy)$_2$, and **1**·(etpy)$_2$, respectively (Table 1) (see the Supporting information).

Table 1. Structural parameters

L	Rh-Rh (Å)	Rh-**L** (Å)	Rh-Rh-**L** (°)
py	2.40	2.25	3.50
mepy	2.41	2.28	13.6
etpy	2.41	2.30	15.0
damp	2.41	2.22	16.2
min	2.40	2.23	6.30
ether	2.37	2.31	2.67

In NMR spectra of **1**·**L**$_2$ in $CDCl_3$ at 300 K, the signals of methyl groups at the 2,7,14-positions of triptycenes of each complex were shifted upfield compared with those of carboxylic acid **2**. This result strongly indicates that all the four triptycenes in the circularly-arranged structure around the central dirhodium axis mesh with each other in solution.

The temperature effects on the motional behaviors of the meshed triptycene parts were then examined by variable-temperature NMR (VT-NMR) spectroscopy. For instance, in the NMR spectrum of 2-methylpyridine adduct **1**·(mepy)$_2$, all the signals for the blades of the triptycene parts became broadened and then split at 250 K. This result suggests that a zigzag conformation of the triptycene parts is stable in the light of the fact that the signals of the blade were split in an upfield (orange)-to-downfield (blue) ratio of 2:1 (Figure 3). For reference, another possible tongue-in groove conformation would show an upfield-to-downfield ratio of 1:2 due to the shielding effect of two benzene rings on a benzene ring of the neighboring triptycene. Similar splitting patterns were also observed in the spectra of a 2-ethylpyridine adduct **1**·(etpy)$_2$ and **1**·(ether)$_2$. In contrast, the spectra of a pyridine adduct **1**·(py)$_2$, an *N*,*N*-dimethyl-4-aminopyridine adduct **1**·(dmap)$_2$ and a methyl isonicotinate adduct **1**·(min)$_2$ showed no splitting behaviors even at 220 K (see the Supporting Information).

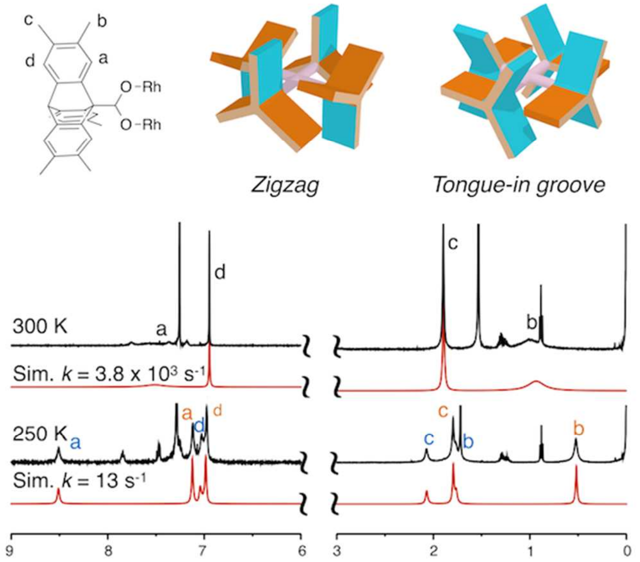

Figure 3 Dynamic ^{1}H NMR line-shape simulations (Sim) to determine the rate constants (k) of a 60° rotation process for **1**·(mepy)$_2$ using the iNMR software (ver. 5.3.3).

The rotational rates of these complexes at a given temperature were determined by dynamic NMR experiments. The activation energy parameters were determined from the temperature dependence of the changes in the signals for **1**·(mepy)$_2$, **1**·(etpy)$_2$, and **1**·(ether)$_2$ (Table 2). The rotational rate (k) of each complex was determined for a 60° flipping between orange and blue blades in a zigzag conformation. The rotational rates and activation parameters for **1**·(py)$_2$, **1**·(dmap)$_2$, and **1**·(min)$_2$ could not be determined because no splitting took place at low temperatures due to their faster motion compared with the NMR timescale. As for these three complexes, the activation energy barrier ($\Delta G^‡$) can be roughly estimated lower than 12 kcal mol^{-1} from the chemical shift gap $\Delta\nu > 0.1$ ppm and the coalescence temperature $T_c < 220$ K according to the following equation,[24] where T_c is the coalescence temperature:

$$\Delta G^‡ = 4.55 \times 10^{-3} \times T_c\{9.97 + \log T_c - \log(500 \times \Delta \nu))$$

It is apparent that the rotational rates of the pyridine adducts are influenced by the substituents at the 2-positions of the pyridines, as compared between **1**·(py)$_2$, **1**·(mepy)$_2$, and **1**·(etpy)$_2$ (Table 2). This suggests the possibility of ligand exchange-based rate control of molecular motions. At 220 K, further splitting was observed in the spectra of **1**·(mepy)$_2$ and **1**·(etpy)$_2$ presumably due to the slowed-down rotation of unsymmetrical axial ligands (see the Supporting Information).

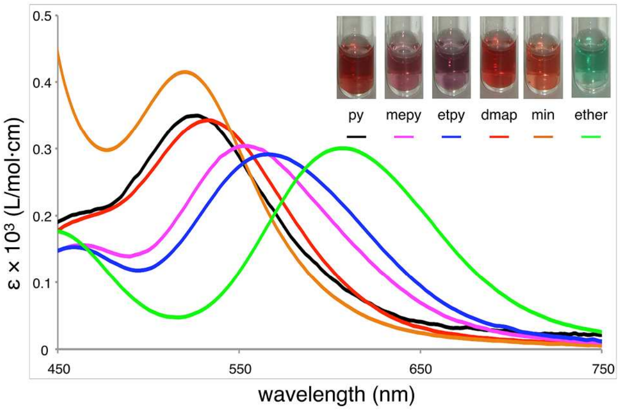

Figure 4 (a) Visible absorption spectra of molecular gear complexes (0.6 mM for py, 1 mM for others in CHCl$_3$, 293 K) and the pictures of solutions containing molecular gear complexes in CHCl$_3$.

Table 2. Absorption maximum and activation energy parameters of 1·L$_2$

L	λ_{max} (nm)	$\Delta H^‡$ (kcal mol^{-1})	k @260 K (s^{-1})
py	527	n.a.	n.a.
mepy	554	14.5 ± 1.2	5.5×10^2
etpy	566	18.0 ± 0.5	15
damp	534	n.a.	n.a.
min	520	n.a.	n.a.
ether	608	11.4 ± 0.2	1.0×10^3

n.a. = not available

UV-visible spectra of the complexes in CHCl$_3$ are shown in Figure 4 and Table 2 to compare the effects of the axial ligands on their electronic states. The effects of the type of carboxylates bridging Rh-Rh on the electronic states have been well studies.[25] It is well known that there are two peaks around 500~600 nm (band I) and 450 nm (band II) in the visible region, which can be assigned to the allowed transitions, $\pi^* \rightarrow \sigma^*$ and $\pi^* \rightarrow$ Rh–O σ^*, respectively.[25] Indeed, band I was markedly affected by the type of the axial ligands as shown in Figure 4, while band II around 450 nm remained almost unchanged (see the Supporting Information). In comparison between the axial pyridine ligands with a substituent at the 2-position, **1**·(py)$_2$, **1**·(mepy)$_2$, and **1**·(etpy)$_2$, bulkier axial ligands showed absorption at a longer wavelength in the order of **1**·(py)$_2$ (527 nm) < **1**·(mepy)$_2$ (554 nm) < **1**·(etpy)$_2$ (566 nm). On the other hand, only small electronic effects were observed with **1**·(dmap)$_2$ (red-shift by 7 nm) and **1**·(min)$_2$ (blue-shift by 7 nm), which has an electron donating dimethylamino group and an electron withdrawing methoxycarbonyl group, respectively, at the 4-position. It should be noticed that the band I for **1**·(ether)$_2$ appeared in the longest wavelength side (608 nm). This result indicates that the type of coordinating atoms is a more effective factor affecting the electronic states of the complexes.

In conclusion, we have constructed a dirhodium-centered circular four-gear system, in which the gears have a circularly meshed structure both in solution and in the crystal state. Dynamic NMR analysis revealed that the exchangeable axial ligands can remarkably affect the rotational behaviors of the molecular gear system mainly due to the steric effects of the substituents and the type of the coordination atoms of the axial ligands as shown by NMR spectroscopy and visible absorption study. These findings would provide a useful design guide for stimulus-responsive metallo-molecular rotors that realize ligand exchange-based rotational motions in a self-assembled system.

ASSOCIATED CONTENT

Experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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No competing financial interests have been declared.

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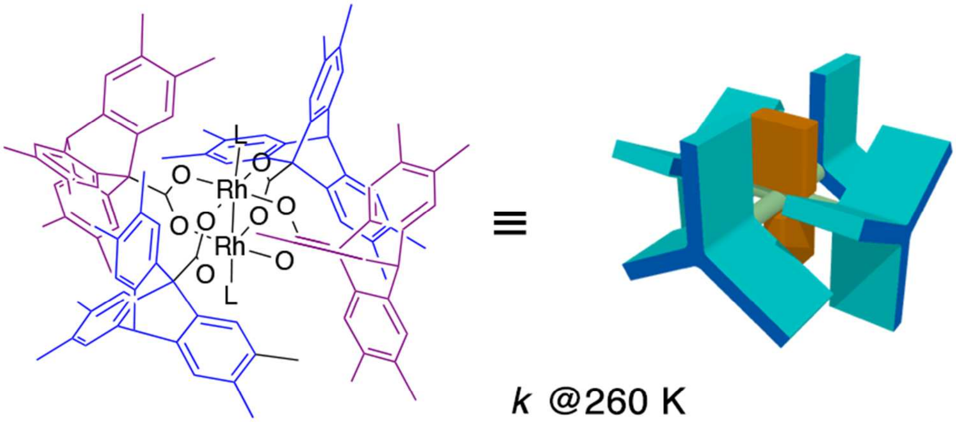


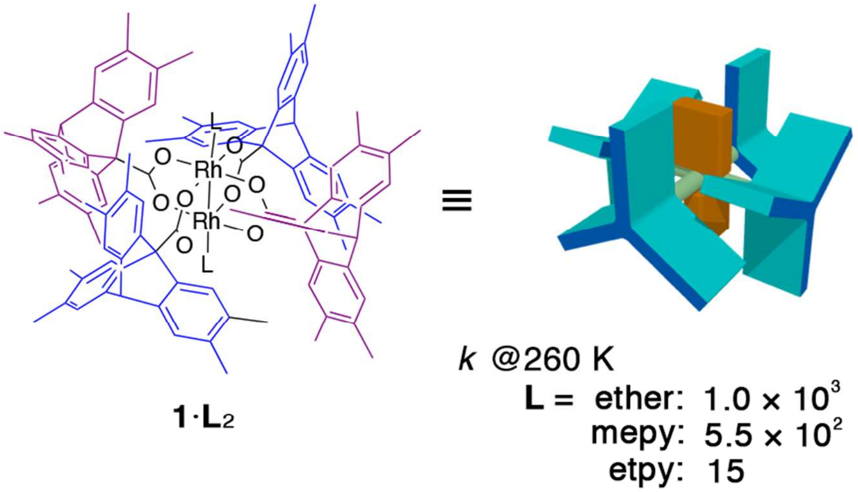
1·**L**$_2$

k @260 K

L = ether: 1.0×10^3

mepy: 5.5×10^2

etpy: 15



Synthesis of a lantern-type dirhodium complex with circularly-arranged four 2,3,6,7,14,15-hexamethyltriptycene carbox- ylates as gears and two axial ligands as velocity control elements are reported. The rotating velocities in solution were mark- edly-affected by the donating properties of coordinating atoms and the bulkiness of axial ligands. Notably, the velocity changes were accompanied by the color changes of each solution.
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