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A Bevel-Gear-Shaped Rotor Bearing a Double-Decker Porphyrin Complex

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The combination of molecular interactions and transmitted dynamics generates function in biological systems. In the natural rotary motor adenosine triphosphatase (ATPase), the F_O and F_1 motors exhibit distinct rotational activities through mutual mechanical and chemical interactions.[1–3] The meshing of molecule-based rotors is necessary when assembling them into complex machinery systems that resemble those found in natural and mechanical devices. In the 1980s, tripticene-based molecular gears, the blades of which mesh together, were reported independently by Iwamura and Mislow.[4] Since their pioneering work, the transmission of the activities of molecular rotors has attracted much attention.[5–8] One of the synthetic molecular rotors, metal bis(porphyrinate)s double-decker complexes (DD), can serve as a rotating module in which two porphyrin rings rotate around the sandwiched metal ion as their rotational axis.[9] We have previously reported that the rotational activity of the porphyrin rotor in a lanthanum(III) bis(porphyrinate)s double-decker (LaDD) is switchable by using chemical stimulation.[9e] It occurred to us that when a molecular rotor is introduced at the peripheral position of a LaDD rotor such that they mesh each other, the rotational activity of the introduced rotor would be changed as a result of the switching of the rotational rate of LaDD. This concept that utilises LaDD as a component for molecular gears would be conducive to the creation of molecular-based machines,[10] which are capable of altering the rotational information among rotors in response to external stimulation.

Herein, we demonstrate the interlocking of two distinct porphyrin-based molecular rotors into a bevel-gear-shaped structure[4a–h,5a,e,11] (**1** in Figure 1 a), which features LaDD and a porphyrinatorhodium(III)-based rotor; the former has the switchable rotational activity and the latter has a higher rotational activity than that of LaDD. By using ^{1}H NMR spectroscopy, we found that mechanical interactions between the teeth of the two molecular rotors enabled them to mesh and rotate with almost identical activation energies. In addition, switching the rotational activities of LaDD induced a change in the cooperative rotational motions of the two rotors.

Scheme 1 a illustrates our design for a bevel-gear-shaped rotor that is bound to two rotors that possess different rotational activities. One is a double-decker metal bis(porphyrinate)-based rotor that is driven by heat fluctuation (Scheme 1 a and Figure 1 a; top, red).[9] The rotational rate of LaDDs are almost on the same time scale as that of NMR spectroscopy. The slow rotational frequency of LaDD enabled us to evaluate the rotational properties of the top rotor by using variable-temperature (VT) ^{1}H NMR spectroscopic techniques. The aryl groups at the *meso* positions determine the step angle of 90° in LaDD (Scheme 1 b). The other rotor (Scheme 1 a and Figure 1 a; side, blue) possesses a pyridine$-$Rh^{III} coordination bond[12] as its rotation axis. In the absence of the top porphyrin unit, the side rotor rotates too rapidly to evaluate the rotational rate. A porphyrin ligand presenting a pyridine substituent (Scheme 1 a and Figure 1 a; core, black) is shared by the top and side rotors, and consequently the two rotors are mounted on rotational axes that are aligned at an angle of almost 90°. In the bevel-gear-shaped molecular rotor **1**, four protruding aryl substituents at the *meso* positions in each porphyrin-based rotor (top

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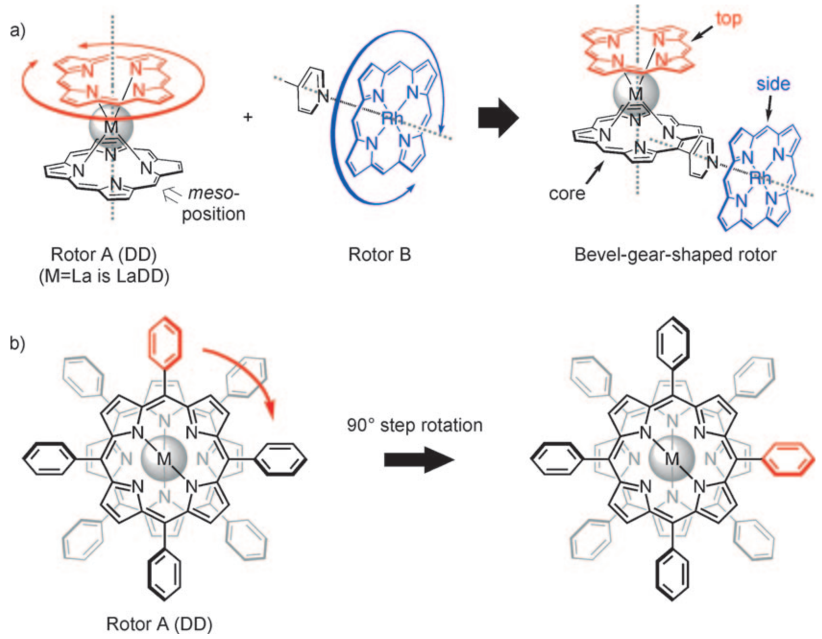

Scheme 1. a) Design scheme of a bevel-gear-shaped rotor comprising two rotors (top and side). These rotors are aligned almost orthogonally and connected through a core (see Figure S9 in the Supporting Information), b) Each porphyrin ligand in the metal bis(porphyrinate)-based rotor (DD) undergoes a stepping rotation of 90° because of the phenyl groups in the *meso* positions.

and side) produce a stepping rotation of the side rotor meshing mutually with the top rotor. Thereby, we expect to transmit the rotational frequency of the top rotor to the side rotor and turn down the rotational frequency of the side rotor. The top and side rotors are unsymmetrical because of the presence of the side and top porphyrin units, respectively; this situation allows the rotational behaviour of each rotor to be evaluated by using ^{1}H NMR spectroscopy (Figure 1 b).

Firstly, we confirmed that a pyridine–Rh^{III} coordination bond in **1** can be regarded as its rotation axis from the fact that in the temperature range 193–353 K complexation–uncomplexation dynamics between the pyridine and the porphyrinato Rh^{III} in [D$_2$]dichloromethane (193–298 K) and [D$_4$]tetrachloroethane (353 K) was not observed from VT ^{1}H NMR spectroscopy.[14]

Given the molecular structure of **1**, the *tert*-butyl protons of the top unit or the β-pyrrole protons of the side unit exchange from area (i) to area (ii) upon a 180° rotation of the top or side units, respectively (Figure 1 b). When the exchange rate is comparable with the time scale of ^{1}H NMR spectroscopy at a certain temperature, the rotary motions of the top and side units can be monitored readily by using the coalescence properties of the signals of each pertinent set of protons, that is, the *tert*-butyl and β-pyrrole protons, respectively. We evaluated the rotary motions of the top and side rotors in **1** through VT ^{1}H NMR spectroscopy over the temperature range 253–298 K. At 253 K, in addition to two sharp singlets at 1.44 and 1.53 ppm, which could be assigned to the *tert*-butyl protons of the top unit, the β-pyrrole protons of the side unit appeared at 9.08 and 9.25 ppm. The rotational rate of the side rotor in **1** was sufficiently slow to be detected on the ^{1}H NMR spectroscopic time scale. Upon increasing the temperature, the signals of the *tert*-butyl protons in the top unit and the β-pyrrole protons in the side unit gradually and simultaneously broadened, eventually coalescing into single peaks at 298 K (see Figure 2). From the similar tendencies in the coalescence properties of the top and side rotors in **1**, we deduced their mutual meshing. To examine the rotary motion in detail, we calculated the rotational rates of the top and side rotors by means of a nonlinear least-squares method[15] at each temperature. The simulated spectra of the signals of the *tert*-butyl protons of the top unit and the β-pyrrole protons of the side unit were coincident with those observed experimentally (see Figure S7 in the Supporting information); the calculated rotation rates of the 180° steps are shown in Figure 2. From plots of log$k$ (rate constants of rotation: k_{top} and k_{side}) versus T^{-1} (Arrhenius plot; correlation coefficient (R): >0.99), we calculated the activation energies (E_a) for the rotations of the top and side rotors to be 30.1 and 30.7 kJ mol^{-1}, respectively (see Figure S8 in the Supporting Information). Moreover, we calculated the following thermodynamic parameters for the rotors at 273 K: $\Delta G^{\ddagger}=60.5\,\mathrm{kJ\,mol^{-1}}$, $\Delta H^{\ddagger}=27.8\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}=-120\,\mathrm{J\,K^{-1}mol^{-1}}$ for the top rotor; $\Delta G^{\ddagger}=57.4\,\mathrm{kJ\,mol^{-1}}$, $\Delta H^{\ddagger}=28.4\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}=-106\,\mathrm{J\,K^{-1}mol^{-1}}$ for the side rotor (a summary of the thermodynamic and kinetic parameters of the top and side rotors in **1** is given in Table 1). These similar activation energies and thermodynamic parameters indicate that the rotary motions of the side unit were slowed through mutual mechanical interactions; in other words, meshing occurred among the protruding substituents. Although the rates of rotation of the side rotor decreased accordingly, they remained almost four times larger than those of the top rotor. We have deduced that the two rotors are meshed in such a manner that the protruding tooth of the side unit slipped through two adjoining teeth of the top unit (see Figure S9 in the Supporting Information).

An intrinsic feature of LaDD is that its rotational activity can be altered. In LaDD, seven of the eight pyrrole nitrogen atoms in the two porphyrin units are coordinated to the La^{III} atom and one nitrogen atom remains uncoordinated.[16] Addition of base to LaDD induces dissociation of the unco-

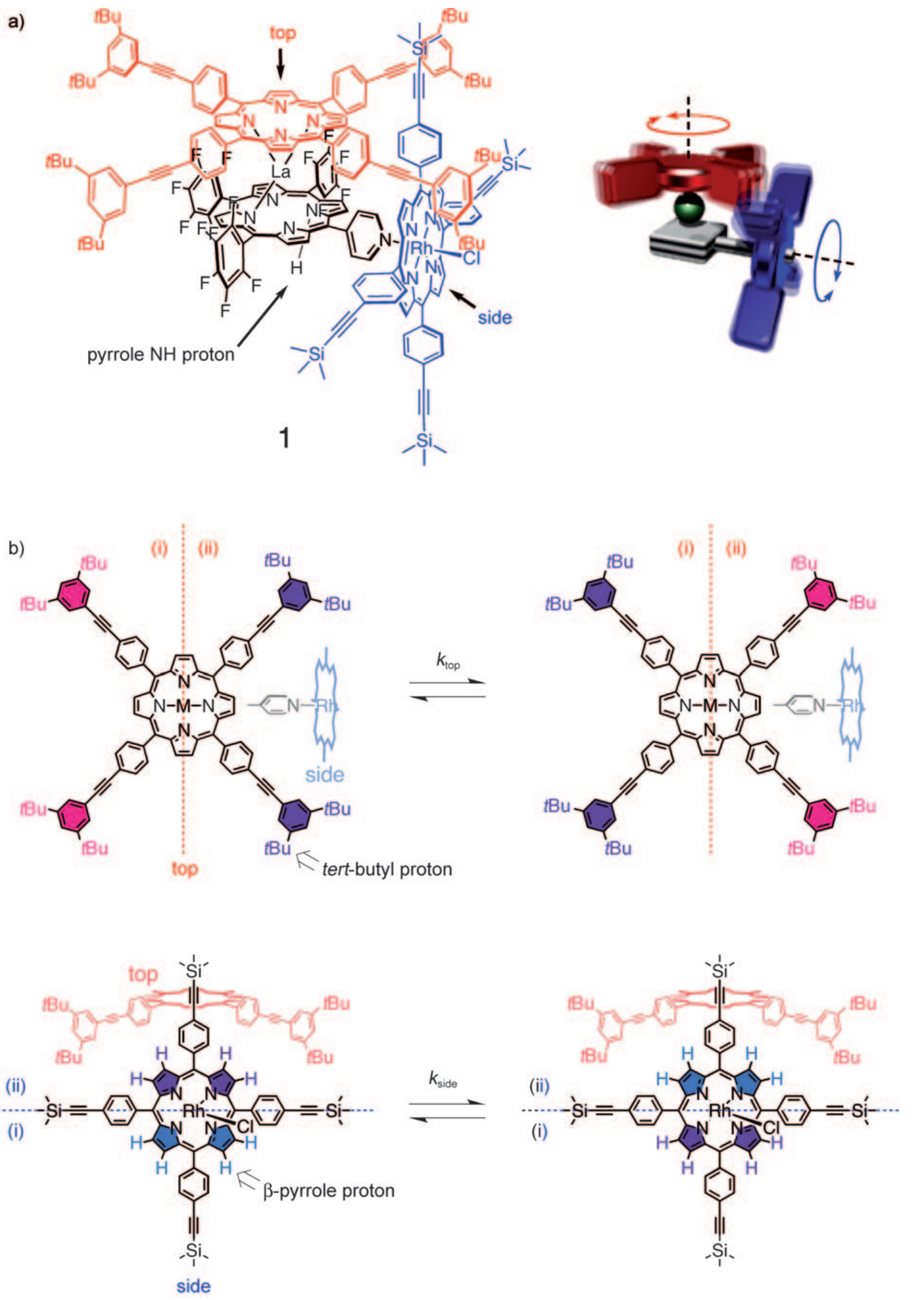

Figure 1. a) Molecular structure of compound **1**. In **1**, one pyrrole NH proton remains in the porphyrin ligand at the core, as depicted, because of the presence of the three electron-withdrawing pentafluorophenyl moieties (see Figure S6 in the Supporting Information);[13] b) From the view of porphyrin planes of the top and side units, the protons in area (i) experience a different magnetic field from those in (ii), owing to the unsymmetrical circumstances when their rotations are slower than the NMR spectroscopic time scale; the remarkable protons, the *tert*-butyl protons of the top unit and the β-pyrrole protons of the side unit in **1**, exchange through rotation of 180° in each rotor. If their rotations are faster than the NMR spectroscopic time scale, the protons in areas (i) and (ii) will be observed as single peaks.

ordinated pyrrole NH proton (to form an N$^-$ group); upon deprotonation, the value of λ_{max} of the Soret band of LaDD shifts to shorter wavelength with a hyperchromic effect, and the coalescence temperature (T_c) of the porphyrin rotation in LaDD increases (i.e., the rotational oscillation frequency decreases).[9e] This change in T_c is attributed to stronger π–π interactions between the porphyrin planes of LaDD after deprotonation. Such treatment can, therefore, be regarded as a switch in the rotational activity of one of the rotors (i.e., the top rotor), and furthermore makes ^{1}H NMR spectra of **1** simpler because of the appearance of higher symmetrical porphyrin ligand. Indeed, addition of triethylamine (TEA) to **1** in dichloromethane induced a shift of the absorption maximum (415.0 nm) of the Soret band of the LaDD moiety to shorter wavelength (413.0 nm) with a hyperchromic effect (see Figure S10 in the Supporting Information). When we added an excess of TEA (25 equivalents per molecule of **1**) to dissociate the pyrrole NH proton, the two signals for the β-pyrrole protons in the side unit became a single resonance at 9.17 ppm, even at 243 K (Figure 3a). We simultaneously confirmed that no ligand exchange of the pyridine–Rh^{III} coordination bond in side rotor to TEA–Rh^{III} bond occurs in the presence of 25 equivalents of TEA by the results from using control compounds (also see Figure S5 in the Supporting Information). Meanwhile, the two signals attributable to the *tert*-butyl protons of the top unit appeared at 1.44 and 1.51 ppm at 243 K, even after the addition of TEA, and remained there without coalescence upon increasing the temperature up to 313 K. These results suggest that the rotational rate constant k_{top} was less than 5 s^{-1} at 313 K and that k_{side} was greater than 5000 s^{-1}, even at 243 K; therefore, the addition of TEA altered the cooperative mechanical interactions of the top and side rotors. The side rotor in **1** slipped out of gear, most likely because of the changes in the conformations of the LaDD unit.[17] Interestingly, neutralisation of TEA through the addition of trifluoroacetic acid (TFA) reinstated the mechanical interaction between the top and side rotors in **1**; again, we observed simultaneous coales-

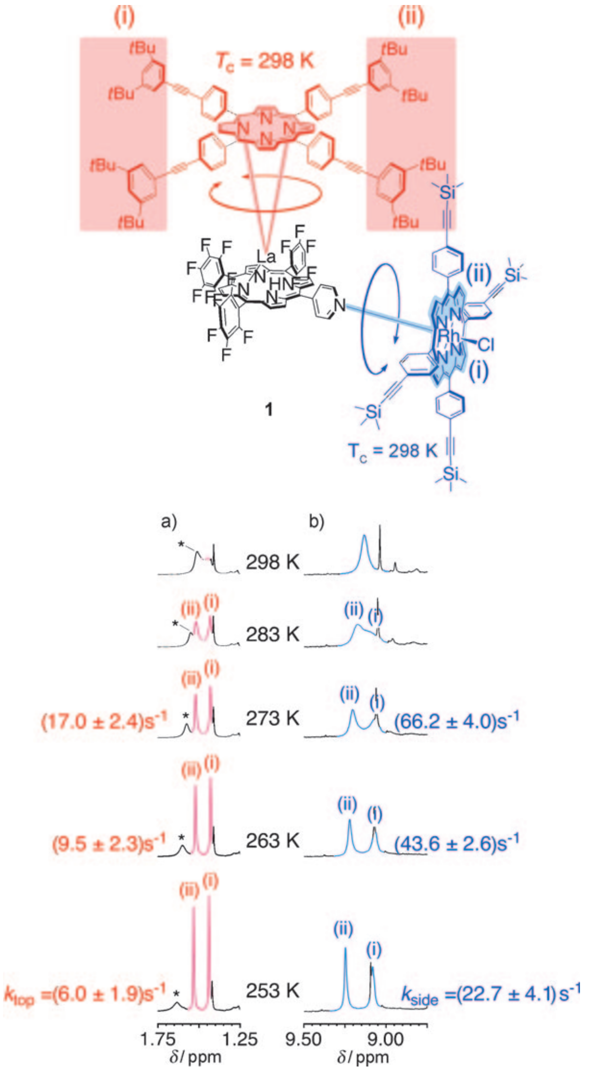

Figure 2. Partial VT ^{1}H NMR spectra of **1** in [D$_2$]dichloromethane ([**1**]=1.0×10^{-3} mol dm^{-3}). The observed spectra display the signals of the *tert*-butyl protons of the top unit (a) and β-pyrrole protons of the side unit (b). The calculated rotational rates of the 180° steps are presented along with the spectra. The asterisk (*) denotes the signal for water in [D$_2$]dichloromethane. The descriptors (i) and (ii) denote protons in the areas defined in Figure 1 b.

Table 1. Thermodynamic and kinetic parameters of the top and side rotors in **1**.

Rotor	k [s^{-1}]	E_a [kJ mol^{-1}]	ΔG^{+} [kJ mol^{-1}]	ΔH^{+} [kJ mol^{-1}]	ΔS^{+} [J K^{-1} mol^{-1}]	k (with TEA) [s^{-1}]
top	17.0	30.1	60.5	27.8	−120	< 5
side	66.2	30.7	57.4	28.4	−106	5000 <

cence properties at 298 K (see Figure S13 in the Supporting Information).

To demonstrate further extension of the DD-based rotor system, we synthesised a supramolecular rotor **2** in which LaDD is bound by two side rotors at the distal *meso* positions through coordination bonds (Figure 4). We evaluated the transmission of the rotational activity from one top to two side rotors in **2** by using ^{1}H NMR spectroscopy over the temperature range 233–298 K. Indeed, VT ^{1}H NMR spectroscopic studies revealed that the β-pyrrole protons of the top and the side units in **2** gradually and simultaneously broadened, eventually coalescing into single peaks at 298 K (Figure S14 a in the Supporting Information). The top rotor was also able to decelerate the rotation of two side rotors and their cooperative rotational motion was switchable in a similar manner to **1** (Figure S14 b in the Supporting Information).[18]

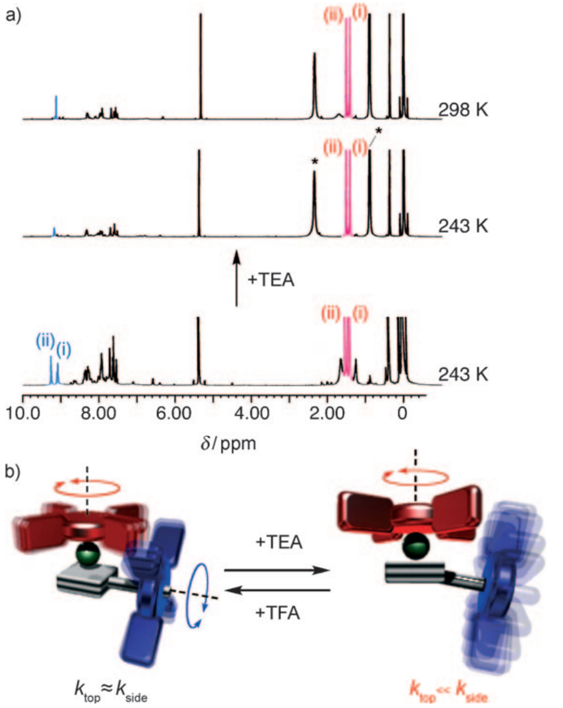

Figure 3. a) VT ^{1}H NMR (600 MHz) spectra of **1** (1.0×10^{-3} mol dm^{-3}) at 243 K and after addition of TEA at 243–313 K in [D$_2$]dichloromethane. The descriptors (i) and (ii) denote protons in the areas defined in Figure 1 b. b) Schematic representation of the switch in the meshing of the two rotors upon the addition of TEA and TFA. The asterisk (*) denotes the signal of added TEA.

In this paper, we prepared synthetic molecular bevel-gear-shaped rotors (**1** and **2**) in which the intrinsic rotational rate of one rotor differs from the other, with the two distinct top and side rotor(s) being mounted on rotational axes aligned at an angle of almost 90°. The rotational activities of these top and side units are partially transmitted through mechanical interactions between the two rotors. In the case of systems **1** and **2**, it was possible to switch the frequency of the rotary motion from a meshing state ($E_{top} \approx E_{side}$) to an independent state ($k_{top} \ll k_{side}$), and back again to the original state, through chemical stimulation.

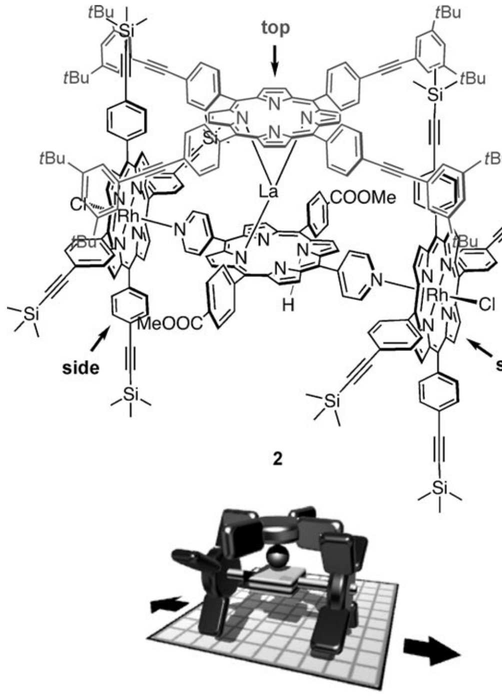

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Figure 4. Molecular structures of **2**.

Experimental Section

General methods and materials: All starting materials and solvents were purchased from Tokyo Kasei Chemicals or Wako Chemicals and used as received. ^{1}H NMR spectra were recorded on a Bruker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane, the internal standard. UV/Vis spectra were recorded by using a Shimadzu UV-2500 PC.

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Keywords: molecular gears · molecular devices · porphyrinoids · supramolecular chemistry

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[14] Compound **1** was purified through size exclusion column chromatography, and during the purification process no decomposition into the corresponding LaDD and porphyrinatorhodium(III) took place. In the temperature range 193–353 K, complexation–uncomplexation dynamics between the pyridine and the porphyrinato Rh^{III} in [D$_2$]dichloromethane (193–298 K) and [D4]tetrachloroethane (353 K) was not observed from VT ^{1}H NMR spectroscopy. These observations suggests that these complexation–uncomplexation dynamics should be much slower than the NMR time scale if they exist, which indicates that even if a complexation–uncomplexation process takes place in this system, the side rotor can rotate within the lifetime of the pyridine−Rh^{III} coordination bond. Under the conditions we applied in this study, we deduce that this dynamic behaviour in the complexation–uncomplexation of the pyridine−Rh^{III} bond is negligible and the pyridine−Rh^{III} coordination bond can be regarded as the robust rotational axis of the side rotor (also see Figure S4 in the Supporting Information).

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[17] To obtain direct structural information on **1**, we have been trying to obtain single crystals that are suitable for X-ray analyses with and without TEA, but unfortunately we have been unsuccessful at the present stage. As far as we know, there is no report of the single-crystal analysis of lanthanum(III) bis(porphyrinate). Instead, we utilised a computer-generated model to discuss the mechanical interaction between top and side rotors (see Figure S9 in the Supporting Information).

[18] We assume that the slippage would still occur although the activation energies for the rotations of the top and side rotors are almost same.

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