Control of Rocking Mobility of Rotaxanes by Size Change of Stimulus-responsive Ring Components

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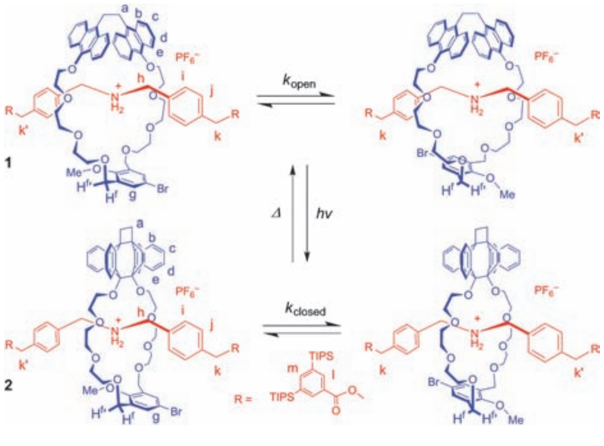
A rotaxane having a ring molecule composed of a metaphenylene unit which swings as a pendulum and a dianthrylethane unit which undergoes isomerization in response to external stimuli was synthesized. The rates of the rocking motion were switched reversibly and changed substantially in response to photo and thermal stimuli by changing the size of the ring component.

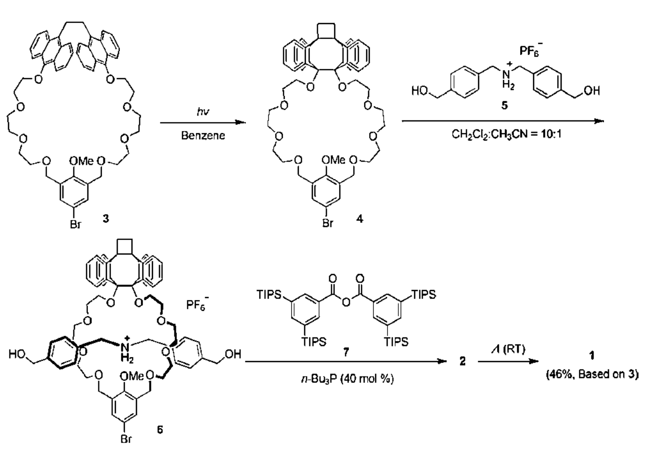
Rotaxanes[1] are thought to be prime candidates for the construction of artificial molecular machines[2] and molecular electronic devices,[3] since the ring and dumbbell components of rotaxanes are capable of exchanging the position of one component relative to that of the other by their motions such as shuttling[4] (linear motion), circumrotation[5] (rotary motion), and rocking[6] (pendular motion). These motions can in principle be controlled by external impetus such as on chemical,[7] electrical,[8] or photochemical[9] stimuli. The exchanges by shuttling motions have been studied most extensively aiming at the application to molecular electronic devices. In contrast to control of relative position by the shuttling motion, control of rocking mobility has not been studied.[10] If a ring component of a rotaxane has large dipole moment, and its direction or oscillation frequency is controlled, the rotaxane can be applied to switching devices in a molecular scale. Indeed, it is reported that efficiency of photoinduced electron transfer is differentiated appreciably by the direction of dipole moment of helical peptides immobilized on substrate.[11] In this connection, we report here the syntheses of rocking-rate controllable rotaxanes **1** and **2** and effective switching of the rates of the rocking motion by 20 times (**1** vs **2**).



Scheme 1. Switching of rocking rates (k) of rotaxanes **1** and **2** based on the change of the size of the ring component.

Rotaxanes **1** and **2** that we designed are shown in Scheme 1. We planed to control the rates of rocking motion (oscillation) of the metaphenylene unit, by changing the size of the ring component.[12] We expected that the barrier to the quasi-rotation of the phenylene moiety would change between open (**1**) and closed (**2**) states of the rotaxanes. In order to induce appropriate steric barrier, a methoxy group was attached at the flanked position of the metaphenylene unit. Since, it is well known that dianthrylethane derivatives undergo reversible photodimerization and thermal reversion reaction quantitatively, the size of the ring molecules can be changed by employing this protocol.[13,14] For the preparative reason, dibenzyl ammonium ion was used as the axle component. Finally, 3,5-bis(triisopropylsilyl)phenyl group was employed as a stopper component because it is bulky enough to prevent the dethreading of the axle in the open form. The synthetic route of rotaxanes **1** is shown in Scheme 2. By irradiation of crown ethers **3**[15] in benzene with a high-pressure mercury lamp, closed form **4** was formed by photodimerization of the anthracene moieties. After solvent exchange into a mixture of dichloromethane and acetonitrile (10:1), pseudorotaxanes **6** were formed by association of **4** with secondary ammonium salt **5** at −10 °C. The acylation end-capping reaction[16] of **6** with anhydride **7** afforded the corresponding rotaxane **2** which then reverted to the respective open type rotaxane **1** during the work-up and isolation procedures. The yield of rotaxane **1** from **3** (4 steps) was 46%.

The photochemical ring closure and the thermal reversion of the anthracene units took place reversibly between the open rotaxane **1** and its closed form **2**. Upon irradiation of a solution of **1** in CD_3CN in an ice-water bath with a high-pressure mercury lamp, the ^1H NMR signal of **1** assigned to the ethylene protons of the dianthrylethane unit disappeared, while a characteristic



Scheme 2. Synthesis of rotaxane **1**.

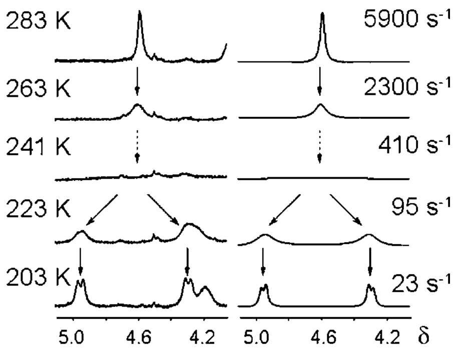


Figure 1. Experimental (left) and simulated (right) partial VT-NMR (270 MHz, THF-d_8) spectra of H^f of **2**.

Table 1. Rates of rocking and kinetic parameters of **1** and **2**

	T_c/K	$\Delta H^{\ddagger}$ /kJ mol^{-1}	$\Delta S^{\ddagger}$ /J K^{-1} mol^{-1}	k_{203K}/s^{-1}
1	nd[a]	nd[a]	nd[a]	>470[b]
2	241	31 ± 1.2	−65 ± 5.0	23

[a]Not determined. [b]Estimated from the Gutowski's equation assuming that the $\Delta\nu$ value of H^f signals of **1** is same as that of **2**.

signal of the cyclobutane protons of **2** appeared as shown in Supporting Information,[17] indicating that the ring closure proceeded efficiently. The spectrum of **2** reverted to that of **1** when the NMR solution of **2** was stood at room-temperature overnight, implying that the thermal reversion **2** to **1** proceeded quantitatively. The rate of the thermal reversion of **2** was determined following the change of the UV–vis absorption spectra. The rate constant of **2** at 30 °C was determined to be 49.7×10^{-5} s^{-1} (the half life: 23 min).

The rate of the oscillations of the rotaxanes **2** was determined by the line-shape analysis of their VT-NMR spectra in THF-d_8. Figure 1 shows partial experimental ^{1}H NMR spectra of H^f on the axle component of **2** between 283 and 203 K and the simulated spectra assuming the rate constants shown. The rates of oscillations of **2** were estimated on the basis of the line-shape analysis of the VT-NMR spectra. The kinetic parameters were determined from the Eyring plot as listed in Table 1.

In the case of **1**, the room-temperature spectrum indicates that the rocking motion of the phenylene unit is rapid on the NMR time scale and the spectrum did not change when the solution was cooled to 165 K. Therefore, the minimum rate of oscillation (k_{203}) of **1** was estimated to be >470 s^{-1}. Table 1 summarizes the kinetic parameters and the oscillation frequencies at 203 K of rotaxanes **1** and **2**.

As shown in Table 1, the rate of oscillation of open **1** ($k_{203} > 470$ s^{-1}) is at least 20 times larger than that of closed **2** ($k_{203} = 23$ s^{-1}). These results demonstrate clearly that the rate of oscillation was substantially changed by the external stimuli.

In conclusion, we synthesized rotaxane having a dianthrylethane moiety in the ring unit of which ring size was changed reversibly and quantitatively by photochemical cycloaddition and thermal reversion. Substantial difference between the oscillation rates of open and closed rotaxanes was observed, demonstrating that the rocking motion was controlled effectively by the external stimuli.

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