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A pseudorotaxane-based molecular machine controlled by light and thermal stimuli†

Kyu-Sung Jeong,* Kyoung-Jin Chang and Young-Jae An

Department of Chemistry, Yonsei University, Seoul 120-749, S. Korea. E-mail: ksjeong@yonsei.ac.kr; Fax: (+)82-2-364-7050; Tel: (+)82-2-2123-2643

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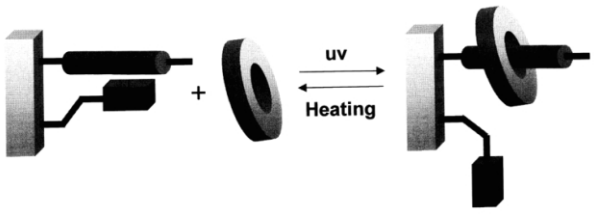
A new pseudorotaxane-based molecular machine exhibits extremely efficient switching between assembly and disassembly mode, controlled by the combination of light and thermal stimuli.

A large variety of molecular-level machines have been developed over the last decade,[1] accompanying a remarkable advance of supramolecular chemistry. A common and fundamental feature of these machines is the reversible switching of their physicochemical properties or states according to the applied stimulation. Pseudorotaxanes have been proven to be highly useful entities for the construction of artificial molecular machines.[1,2] This is because their assembly and disassembly can be conveniently and reversibly controlled by chemical, electrochemical and photochemical methods. Herein we report a new pseudorotaxane-based machine that displays nearly complete, light-induced interconversion between assembly and disassembly states.

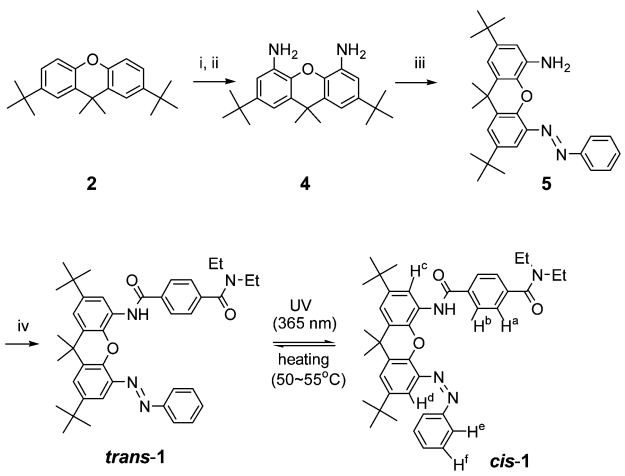
As depicted in Scheme 1, the assembly–disassembly switching of the molecular machine designed here stems from the *cis*–*trans* isomerisation of the N=N bond in the threading molecule.[3] In the *trans* isomer (left), the diaryldiazenyl moiety sterically blocks the above binding site and the macrocycle cannot encircle it. In the *cis* isomer (right), however, the binding site is opened to allow for the formation of the pseudorotaxane complex between two molecular components with the aid of hydrogen bonding interactions. To maintain these structural features of the *cis* and *trans* isomers, the binding site should be in parallel with the light-responsive diaryldiazenyl moiety. For this purpose, the xanthene skeleton was found to be an ideal one owing to its conformational rigidity.

Synthesis of the threading molecule (thread) **1** is outlined in Scheme 2. Diaminoxanthene **4** was prepared by nitration of 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene (**2**),[4] followed by reduction. Reaction of **4** with 1 equivalent of nitrosobenzene provided a diazo compound **5**.[5] Terephthaloyl dichloride was sequentially coupled in one pot with **5** and diethylamine to give the thread **1**. As the binding partner of **1**,[6] a tetralactam macrocycle **6** has been prepared because the nitro substituents at the *para* position greatly increase the strength of hydrogen bonding interactions.[7] The ^{1}H NMR spectroscopic analysis indicates that the thread **1** mainly exists as the thermally more stable *trans* isomer with a ratio of approximately 94 : 6 (*trans*-**1**/*cis*-**1**) at 23 °C in $CDCl_3$, based on the ^{1}H NMR integration. The population of *cis*-**1** was increased to approximately 78% upon irradiation with UV light (365 nm).[8] The ^{1}H NMR spectra of *cis*-**1** and *trans*-**1** are noticeably different from each other. Especially, the aromatic signals, H^d, H^e and H^f, of the diaryldiazenyl moiety in *cis*-**1** were considerably upfield shifted ($\Delta\delta$ = ~ 1 ppm) relative to those in *trans*-**1**. These spectral behaviors are consistent with model structures of the thread **1**; upon the isomerisation of *trans*-**1** into *cis*-**1**, two aryl rings of the diaryldiazenyl moiety become stacked together (see Electronic Supplementary Information†), which results in large upfield shifts of the aromatic signals due to the shielding by the adjacent ring current.

The relative binding strengths of *cis*-**1** and *trans*-**1** to the macrocycle **6** can be clearly noticed in Fig. 1. Addition of the thermally stable *trans*-**1** (2 equiv.) to a $CDCl_3$ solution containing **6** (2×10^{-3} mol L^{-1}) induced only a small downfield shift ($\Delta\delta$ = 0.1 ppm) of the lactam NH signal of **6** (Fig. 1b), indicating that the hydrogen bonding interaction between *trans*-**1** and **6** is negligible. However, the signal was strongly downfield shifted from 8.9 to 10.0 ppm when the solution was simply irradiated with UV light[8] and consequently the relative amount of *cis*-**1** was raised to 77% (Fig. 1c). This experiment provides direct evidence for the macrocycle **6** binding much more strongly to *cis*-**1** than to *trans*-**1**. Moreover, the signals for aromatic hydrogens, H^a and H^b, of *cis*-**1** were significantly upfield shifted ($\Delta\delta$ > 2 ppm) on complex formation. This strongly supports the proposal that the terephthalamido plane of *cis*-**1** is threaded inside the cavity of **6**, surrounded by aryl surfaces, to form a pseudorotaxane-type complex. The NH signal moved back to the original position on



Scheme 1 Schematic representation of working principle of a new pseudorotaxane-based machine.



Scheme 2 *Reagents and conditions*: i, HNO_3, acetic acid, room temp. (49%); ii, Raney Ni, H_2 gas, THF, room temp. (93%); iii, nitrosobenzene, acetic acid, $CHCl_3$ (61%); iv, terephthaloyl dichloride, diethylamine, Et_3N, $CHCl_3$ (26%).

† Electronic supplementary information (ESI) available: synthesis of thread **1** and macrocycle **6**; ^{1}H–^{1}H NOESY spectra of *trans*-**1** and *cis*-**1**; model structures of *trans*-**1** and *cis*-**1**; UV–visible spectral change of thread **1** upon irradiation; ^{1}H NMR spectral changes of thread **1** induced by irradiation and heating. See http://www.rsc.org/suppdata/cc/b3/b303269h/

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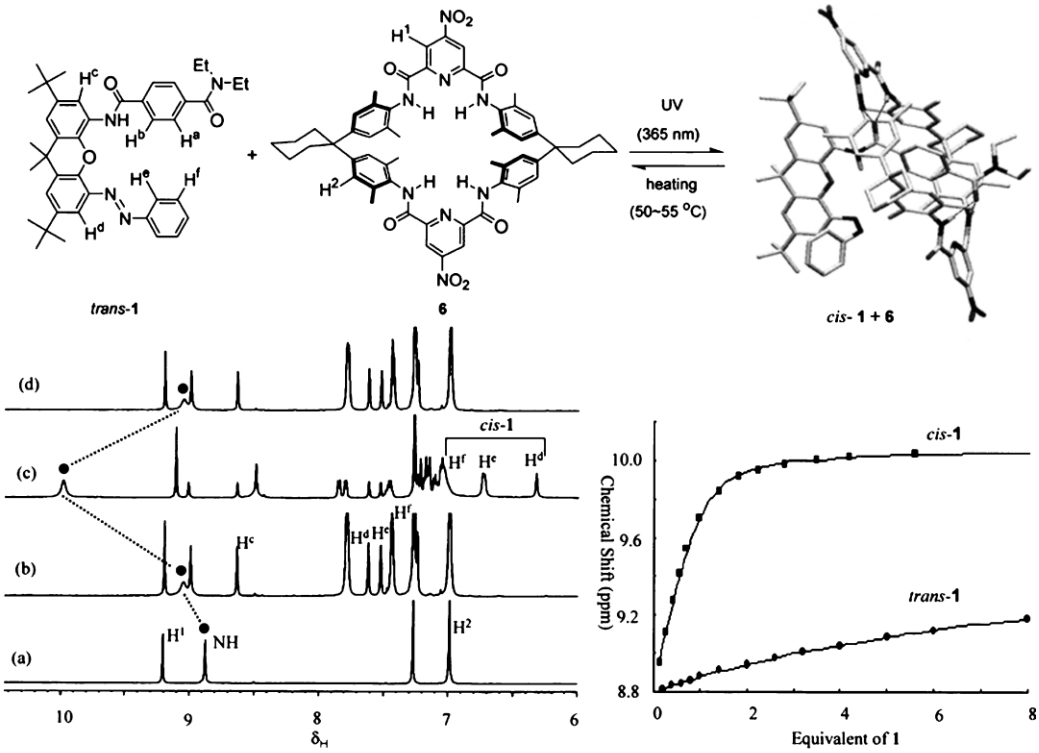

Fig. 1 Partial ^{1}H NMR spectra (left) in $CDCl_3$ at 5 °C of (a) macrocycle **6** (2 mM); (b) macrocycle **6** (2 mM) + *trans*-**1** (4 mM); (c) after irradiation for 3 h with UV light (365 nm) [8]; (d) after heating (50–55 °C) for 12 h, and ^{1}H NMR titration curves (right) plotting NH chemical shift of macrocycle **6** against equivalent of **1** (*trans*-**1** and *cis*-**1**).

heating the solution that causes the isomerisation of *cis*-**1** into *trans*-**1** (Fig. 1d). This cycle can be repeated by continuously alternating irradiation and heating, which results in reversible switching between assembly and disassembly modes.

The association constants between the thread **1** (*cis*-**1** and *trans*-**1**) and the macrocycle **6** were determined and compared by ^{1}H NMR titration experiments. The experiments were performed in $CDCl_3$ at a low temperature, 5 °C, to prevent possible thermal isomerisation of the thread **1**. Under these titration conditions, time-averaged resonances for the free and the complexed species were always observed. As demonstrated in Fig. 1 (right), the NH chemical shift changes of **6** induced by *trans*-**1** are very small compared to those induced by *cis*-**1**. Even these small changes may be attributed to a small amount ($\sim$ 6%) of *cis*-**1** existing in the stock solution of *trans*-**1**. The association constants (K_a) were calculated by nonlinear least squares fitting methods[9] and found to be $\leq 1\ M^{-1}$ for *trans*-**1** and $5200 \pm 100\ M^{-1}$ for *cis*-**1**,[10] respectively. The difference in binding affinities is nearly four orders of magnitude, one of the highest exhibited by light-driven molecular machines developed to date.

In conclusion, we have described a new molecular machine based on a pseudorotaxane whose assembly occurs only with the *cis* isomer of the threading molecule. On the other hand, the pseudorotaxane is completely disassembled into its molecular components on isomerisation to the *trans* isomer caused by an external stimulus.

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Notes and references

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