

ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for

Advanced Functional Materials, adfm.200600981

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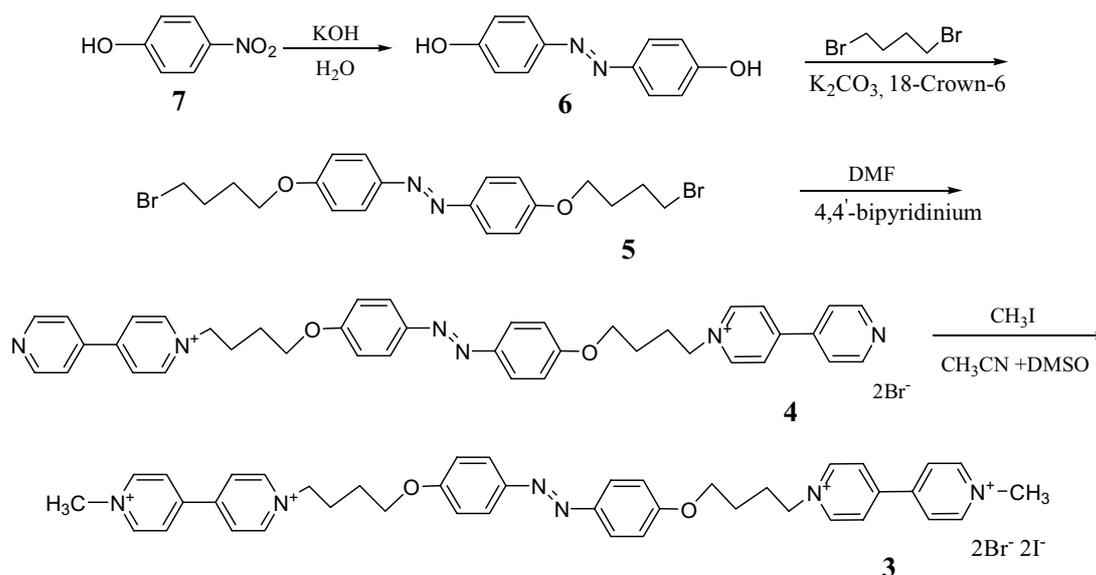
Supporting Information

A Light-driven Pseudo[4]rotaxane Encoded by Induced Circular Dichroism in Hydrogel **

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Dedicated to Professor J. Fraser Stoddart on the occasion of his 65th birthday

Scheme S1. Synthesis route of dumbbell 3. ^[1]



UV absorption spectra

Aqueous UV spectra: The UV absorption spectra of aqueous pseudo[4]rotaxanes **1** and pseudo[2]rotaxanes **2**, as well as the corresponding reference pseudo[3]rotaxanes **2'** and dumbbell **3** solution are shown in **Figure S1**. The absorption maxima at around 365 nm for **1**, **2**, **2'** and **3** are attributed to the azobenzene units. It can be observed that the four absorption spectra of pseudorotaxanes **1**, **2**, and **2'**, as well as the dumbbell **3**, are very similar, which means that the encircling of α -CyD on the dumbbells and the inclusion of CB[7] on the viologen moieties influence the absorption spectra little.

It has been found that the irradiation on an azobenzene-based rotaxane would induce E/Z photoisomerization, which results in absorption spectral changes. ^[2, 3] For the α -CyD pseudorotaxanes **1** and **2**, the same characteristic spectral changes in aqueous solution (1.44×10^{-5} M) were also found, as also shown in **Figure S1**. The irradiation on the aqueous pseudo[4]rotaxanes **1** solution at 360 nm for 60 min results in

photoisomerization to give a E/Z mixture, characterized by a decrease of the absorption at around 364 nm and the presence of two isobestic points at 324 and 443 nm (**Figure S1 A**). The aqueous pseudo[2]rotaxanes **2** solution, irradiated at 360 nm for 60 min, results in photoisomerization to give a E/Z mixture similarly, showing by a decrease of the absorption at about 365 nm and the presence of two isobestic points at 322 and 435 nm as illustrated in **Figure S1 B**. After the photoisomerization of α -CyD pseudorotaxanes **1** and **2** from the E to Z form, the equilibrium can be shifted reversibly by irradiation at 430 nm (**Figure S1 A** and **Figure S1 B**).

The corresponding aqueous solution of pseudo[3]rotaxanes **2'** and dumbbell **3** also undergo E/Z photoisomerization after the irradiation at 360 nm for 15 min to reach the photostationary state (**Figure S1 C** and **S1 D**), showing also by a decrease of the absorption at about 365 nm. Their original states can be shifted back by irradiation at 430 nm as well.

In α -CyD pseudorotaxanes **1** and **2**, the photoinduced shuttling of the α -CyD ring can be realized repeatedly with reversible UV signal changes owing to the reversibility of the photoisomerization process. And the CB[7] pseudorotaxanes **2'** and the dumbbell **3** can also be photoisomerized reversibly. However, cyclodextrin-based pseudorotaxanes **1** and **2** take more time to realize the E/Z photoisomerization than the cyclodextrin-free **2'** and **3**, as is shown in **Figure S1**. Pseudorotaxanes **1** and **2** are irradiated at 360 nm for around 60 min to reach the photostationary state (from $A \approx 0.2$ to $A \approx 0.05$). And pseudorotaxanes **2'** and dumbbell **3** take only about 15 min to reach the photostationary state (from $A \approx 0.2$ to $A \approx 0.05$). These results demonstrate that the cyclodextrin-free systems undergo easier E/Z photoisomerization than the corresponding cyclodextrin-based ones and the fact that E/Z isomerization becomes more difficult in the presence of the α -CyD ring.

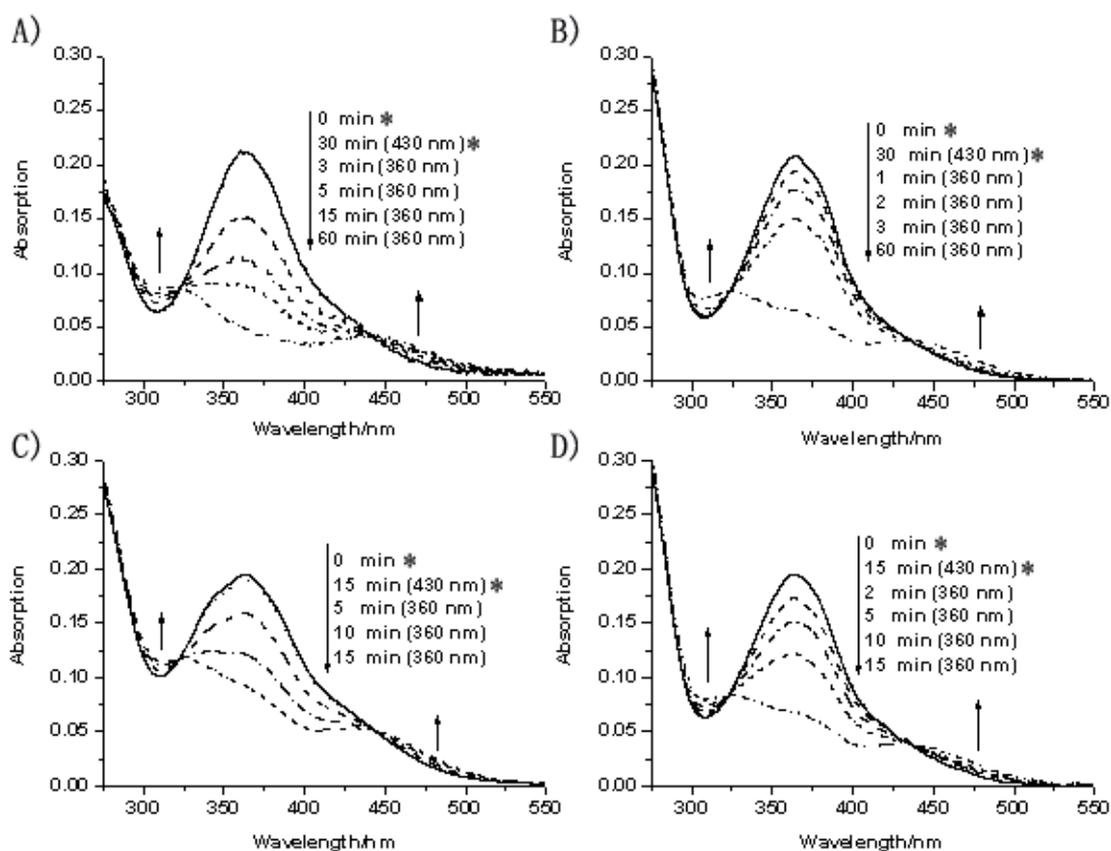


Figure S1. UV absorption spectra of pseudo[4]rotaxane **1** (A), pseudo[2]rotaxane **2** (B), pseudo[3]rotaxane **2'** (C) and dumbbell **3** aqueous solution (25 °C, 1.44×10^{-5} M), and the spectral changes can be shifted back by the irradiation at 430 nm. Legends show the irradiation wavelengths and times in experiments, and the arrows stand for the sequential order by comparing the respective peaks of curves (Curves marked with * coincide basically in each figure.).

Variable-temperature UV spectra of pseudo[4]rotaxane 1 and pseudo[2]rotaxane 2: Temperature increase can induce isomerization of azobenzene from Z form to E form.^[4] UV measurements along with temperature variance of pseudo[4]rotaxane **1** and pseudo[2]rotaxane **2** were shown in **Figure S2**. With an opposite variance from the variable-temperature ICD spectra, a gradual increase of the absorption maxima at about 365 nm exists when the aqueous pseudo[4]rotaxane **1** was heated from room temperature to 50 °C, 60 °C, 70 °C. The temperature raise increases the proportion of E-1 in the usual mixture conformation of pseudo[4]rotaxane **1**. And the vibrancy of the active α -CyD ring at higher temperature affects the absorption spectra of azobenzene moiety little. The spectra change can be shifted back by natural cooling to

room temperature (**Figure S2 A**). Aqueous pseudo[2]rotaxane **2** experiences similar variable-temperature UV absorption as shown in **Figure S2 B**.

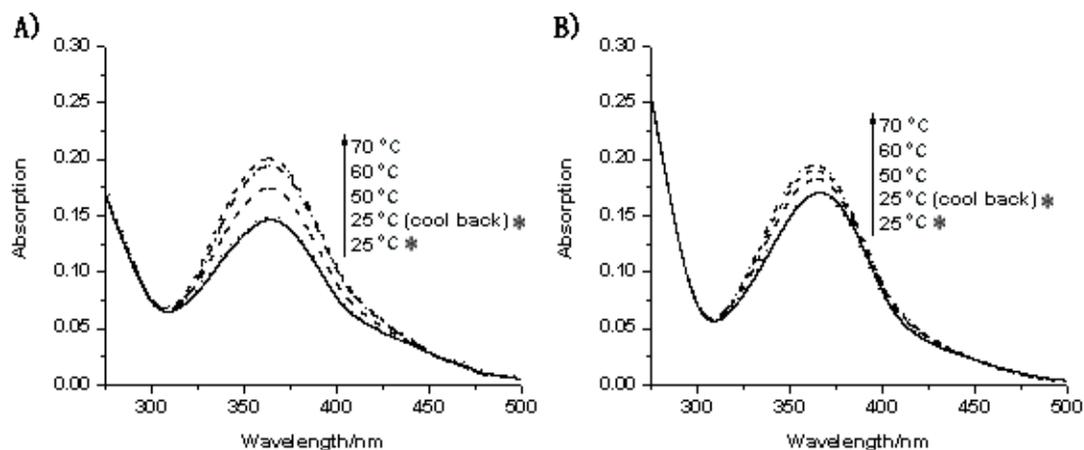


Figure S2. Variable-temperature UV absorption spectra of pseudo[4]rotaxane **1** (**A**) and pseudo[2]rotaxane **2** (**B**) aqueous solution (1.44×10^{-5} M), and the spectral change can be shifted back when cooling to 25 °C. Legends show the temperature in experiments, and the arrows stand for the sequential order by comparing the respective peaks of curves (Curves marked with * coincide basically in each figure.).

References:

- [1] J. W. Lee, K. Kim, K. Kim, *Chem. Commun.* **2001**, 1042.
- [2] D.-H. Qu, Q.-C. Wang, J. Ren, H. Tian, *Org. Lett.* **2004**, *6*, 2085.
- [3] C. A. Stanier, S. J. Alderman, T. D.W. Claridge, H. L. Anderson, *Angew. Chem. Int. Ed.* **2002**, *41*, 1769.
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