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Light-driven molecular shuttles modified on silicon nanowires†

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Immobilization of light-driven molecular shuttles onto the surface of the silicon nanowires (SiNWs) was realized. The α -cyclodextrins as the shuttles could be reversibly translocated along the thread by the optical stimuli. Such SiNWs-based molecular shuttles also exhibited sequential logic with optical stimuli as the input and fluorescence as the output.

Inspired by biological motors, including Adenosine Triphosphate (ATP) synthase-a molecular rotary motor participating in the synthesis and hydrolysis of ATP,¹ various molecular machines, including walkers,² elevators,³ rotors⁴ and shuttles⁵ have been fabricated and exciting results have been achieved. Most of these molecular machines are operated by a chemical or optical stimulation. Compared with a chemical driving force,⁶ light signals as stimuli could operate the molecular machine without direct touch. Moving a macrocycle as a molecular shuttle back and forth between two or more stations in response to external optical stimuli has been realized in solution.⁷ However, such molecular shuttles are disordered, which might cause the molecular shuttles to not be rationally controlled. As a precondition for their practical application, molecular shuttles are required to be immobilized onto the surface of the carriers.⁸ In this study, in order to meet the demand of miniaturizing molecular shuttles in microenvironments and integrating more molecular machines into a chip in the future, silicon nanowires (SiNWs) were selected as the carrier due to their good compatibility with the prevalent Si-based integration technology. By covalently attaching the N,N-2-((4-formyl-biphenyl)–(4-methyl-phenyl)–diazene) dansylamide (S4, Scheme 1) with α -cyclodextrins (α -CDs) onto the surface of the SiNWs, SiNWs-based light-responsive molecular shuttles were realized. The present molecular shuttles consisted of four components; the SiNWs stopper, dansylamide stopper (fluorescence unit), molecular track and the α -CD (Fig. S1⁺). The α -CD was locked between the SiNWs stopper and the dansylamide stopper. The translocation of the α -CD was triggered by the external optical stimuli.

The SiNWs were prepared by a typical chemical vapor deposition method.⁹ The as-prepared SiNWs have a crystalline Si core of about 8 nm in diameter and a silica shell of about 2 nm in thickness, as shown in Fig. S2 \dagger . The synthesis of the (N,N-2-((4-formyl-biphenyl)-(4-methyl-phenyl)-diazene) dansylamide (S4) and the modification on the surface of the SiNWs are described in detail in the Supporting Information[†]. The 3-aminopropyltriethoxylsilane (APTES)-modified SiNWs are abbreviated as APTES-SiNWs.¹⁰ The final products were named S4-CD-SiNWs. For comparison, a parallel product without α-CD was synthesized and abbreviated as S4-SiNWs. The modifications on the SiNWs were characterized by the X-ray photoelectron spectroscopy (XPS), the results of which are shown in Fig. S3a⁺. It was found that no nitrogen was detected from the bare SiNWs, while the APTES-SiNWs contained 3.05% nitrogen. The results indicate that the APTES were modified onto the surface of the SiNWs.9 Reactions between the APTES-SiNWs and the S4 or S4-CD simultaneously were verified by a further increase of the nitrogen content and a variation of the sulfur content (Fig. S3b⁺). The relative content of the oxygen in the S4-SiNWs and S4-CD-SiNWs was also compared. The oxygen content in the S4-SiNWs was 26.41%, while that in the S4-CD-SiNWs was 29.85% (Fig. S3c⁺). The additional oxygen was attributed to the α -CD, suggesting that the α -CD was locked onto the SiNWs. Furthermore, infrared spectroscopy (IR) was carried out (Fig. S4[†]). It was found that the characteristic peak of aldehydes at 1685 cm^{-1} appeared in the IR spectrum of S4, but not in that of S4-CD-SiNWs, which means that all of the aldehydes were coupled. Combining the synthesis route and above characterizations, the construction of the molecular shuttle could be fully confirmed. The S4-CD-SiNWs consist of the fluorescence unit, thread, α -CD and SiNWs. The α -CD was interlocked between the two stoppers, *i.e.* the fluorescent unit and SiNWs.

When the α -CD is located near to the fluorescent unit, the vibrations and rotations of the bonds in the dansylamide unit would be weaken, which results in an increase of fluorescence emission from the dansylamide.^{7e} Conversely, the fluorescence emission of the dansylamide would be restrained when the α -CD



Scheme 1 The structure of S4.

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moves away from the fluorescent unit. Thus, there is a correlation between the fluorescence intensities of the dansylamide and the locations of the α -CD. Accordingly, the movement of the α -CD on the SiNWs-based molecular shuttles can be monitored by the change in the fluorescence intensity. It was observed that the fluorescence intensity of the S4-CD-SiNWs excited by 365 nm in 5% ethanol aqueous solution could increase to 274% of the initial value (Fig. S5a⁺) after the system was irradiated continuously with the UV light of 254 nm for 10 min. Further durative irradiation with the visible light of 420 nm for 10 min can increase the fluorescence intensity to 513% of the initial value. Then, the fluorescence intensity can be regressed to 308% of the initial value if the system is further irradiated with UV light of 365 nm for 10 min. Moreover, it is worthwhile to notice that the fluorescence intensity cannot be increased by the durative irradiation of UV light of 365 nm or visible light of 420 nm, unless the system was previously irradiated by UV light of 254 nm. However, it was found that, after a durative irradiation with UV light of 254 nm, alternate irradiation with light of 420 nm and 365 nm can switch the fluorescence intensities of the system (Fig. 1). Furthermore, it was observed that the fluorescence intensity of the system cannot reach the initial value once it has been irradiated by UV light of 254 nm, only when the system is placed in the dark again for more than 24 h. The parallel experiment showed that no significant fluorescence changes were observed from the S4–SiNWs without the α -CD when it was separately or combinatorially irradiated by 254 nm, 420 nm, or 365 nm lights (Fig. S5b⁺). It indicates that the existence and position of the α -CD determine the changes in the fluorescence intensities. These phenomena demonstrate that sequentially irradiating the system with light of 254 nm and 420 nm can gradually drive the α -CD closer to the dansylamide part. Further irradiation with light of 365 nm will drive the α-CD away from the dansylamide part. After the system was irradiated with the light of 254 nm, alternate illumination with light of 420 nm and 365 nm can reversibly drive the α-CD to move between the two stoppers, *i.e.* the fluorescent unit and SiNWs. Thus, light-driven molecular shuttles were realized on SiNWs.

The movement of the α -CD within the molecular shuttles can be understood based on the variation of the configurations of the **S4**-CD-SiNWs under the different light illuminations (Fig. 2). Considering the initial low fluorescence intensity, it



Fig. 1 Fluorescence intensity of S4–CD–SiNWs sequently irradiated with 254 nm light, 420 nm light and 365 nm light.

can be determined that the α -CD was originally located at the carbon-nitrogen double bond site due to the thermal stability of the α -CD and carbon-nitrogen double bond. Illumination by 254 nm UV light can isomerize the carbon-nitrogen double bond from state 1 ($E_{C=N}$, $E_{N=N}$) to state 2 ($Z_{C=N}$, $Z_{N=N}$).¹¹ These isomerizations will drive the α -CD to the biphenyl unit, accompanied by the fluorescence increase of the dansylamide. Further irradiation by 420 nm light will lead to the isomerization of the nitrogen-nitrogen double bond ($Z_{N=N}$ to $E_{N=N}$) and, simultaneously, the carbon-nitrogen double bond will not be excited.¹¹ Such isomerizations can shift the α -CD gradually close up to the dansylamide group (state 3) and, as a result, the fluorescence intensities are further enhanced. Illumination with 365 nm light could relocate α -CD at biphenyl under the isomerization of the nitrogen-nitrogen double bond from the state 3 ($Z_{C=N}, E_{N=N}$) back to state 2 ($Z_{C=N}, Z_{N=N}$). The alternate illumination with light of 420 nm and 365 nm can control the isomerization of the nitrogen-nitrogen double bond and, consequently, results in the movement of the α-CD along the S4 chain. Furthermore, the system will be recovered to initial state 1 ($E_{C=N}$, $E_{N=N}$) after being settled in the dark for more than 24 h (Fig. S6[†]).

To confirm the mechanism of the α -CD movement, the ¹HNMR spectra of the **S4**–CD and **S4** in *d*-DMSO and CDCl₃ were recorded under various conditions. By comparing the ¹HNMR spectra of the **S4** and **S4**–CD (Figs S7a and b†), it can be found that the H_g exhibited a chemical shift by $\delta = 0.02$ ppm, H_a and H_b by 0.05, H_c, H_e, H_f by 0.02 ppm, H_d by 0.16 ppm from the original chemical shift of **S4**. These results suggest that the α -CD located at the azobenzene site. Comparing the ¹H NMR spectra of the **S4**-CD before and after the irradiation (Figs S7b and c†) of 365 nm light, 0.5 ppm chemical shift for H_d, 0.03 ppm for H_a and 0.15 for H_b and 0.02 for H_g were produced. Finally, the chemical shift of the 420 nm-stimulated **S4**–CD can be recovered by irradiation of the 420 nm light



Fig. 2 A schematic illustration of the molecular shuttle.



Fig. 3 The fluorescence intensity of **S4**-CD–SiNWs under irradiation of 254 nm, 420 nm and 365 nm light in different orders. The dashed line corresponds to the threshold value. a, b, c is the sequence of irradiation.

(Figs S7b and d†). These shifts of H are attributed to the variation of the α -CD position.⁷⁷ The above information further confirmed that the α -CD was first located at the azobenzene group and then transferred to the biphenyl part by the optical stimuli, which is in accordance with the analysis based on the observation of the fluorescence intensities.

Interestingly, it was also found that the fluorescence emission from the system was related to the order of the irradiation with 254 nm, 420 nm, 365 nm light. However, without the premier irradiation with 254 nm light, any irradiation cannot alter the fluorescence intensities. These results indicate that the fluorescence intensity changes not only depend on the present irradiation, but also relate to the history of the irradiation. These repeated phenomena could be used as sequential logic¹² (sequential logic is a type of logic circuit, the output of which depends on both the present input and the history of the input) by defining the 254 nm, 420 nm and 365 nm light as inputs and the fluorescence emission of the system as the output. The absence and presence of the light stimuli is defined as 0 and 1, respectively. The threshold of output is shown in Fig. 3. It is clearly shown in Fig. 3 that the SiNWs-based molecular shuttle could mimic the sequential logic in which only the proper order of inputs can result in the output being 1.

In conclusion, the SiNWs-based molecular shuttles driven by suited light stimuli were realized. The α -CD can reversibly move back and forward at tri-states by the external light stimulations. The configuration changes between the *cis* and *trans* isomers resulted from light illuminations with different wavelengths provide the driving force for the α -CD movement. Furthermore, the molecular shuttle can mimic a sequential logic by defining the 254 nm, 420 nm and 365 nm light as inputs and the fluorescence of molecular shuttles as the output. This method paves a way to miniaturize molecular shuttles and could be extended to make other molecular machines with multiple functions.

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