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Photoisomerization of Spiropyran for Driving a Molecular Shuttle

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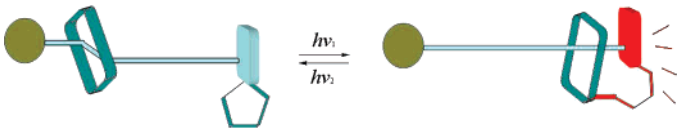
ABSTRACT



A novel light-powered molecular shuttle was synthesized which can switch the movement of a macrocycle between two distinct stations—dipeptide and zwitterionic ME—by exploiting the photoisomerization of spiropyran. The macrocycle resides selectively in the dipeptide station in the SP form and moves to the ME station under the irradiation of UV light. This movement process of the macrocycle is accompanied by reversible absorptive output signals which can be detected by the naked eye.

With the great development of biotechnology and biochemistry in the past decades, scientists have been encouraged to construct molecular motors for simulating natural motors.[1] Considering the extreme complexity of the natural motors, what can be done, at present, is to construct simple prototypes of artificial molecular motors, consisting of a few components capable of moving in a controllable way, and to investigate the associated problems. Mechanically interlocked molecules, such as catenanes and rotaxanes, have become typical candidates in the design of artificial molecular machines because they consist of a few noncovalently interacting components with the ability to move reversibly between two or more stations on application of external stimuli.[2−5] Various stimuli have been employed to induce such switching, including metal binding,[2] configurational changes,[3] and alteration of the oxidation state[4] or protonation level[5] of the molecule. Among them, the chemical fuel-powered artificial motors described so far are not autonomous because, after the mechanical movement induced by a chemical input, they need another, opposite, chemical input to reset, which also implies generation of waste products. Light and electricity powered artificial motors are now under prominent consideration in the construction of molecular devices due to the convenience of energy input and the absence of waste products.[6]

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Spiropyran (SP), a typical photoisomerizable compound, has been widely exploited for the construction of various logic gates and optical switches due to the remarkable difference of the two isomers and their high reversibility under the irradiation of different light. As shown in Figure 1, the colorless SP does not show absorption bands at

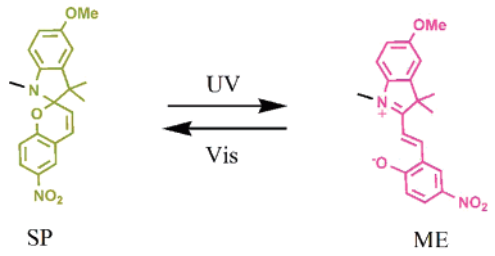


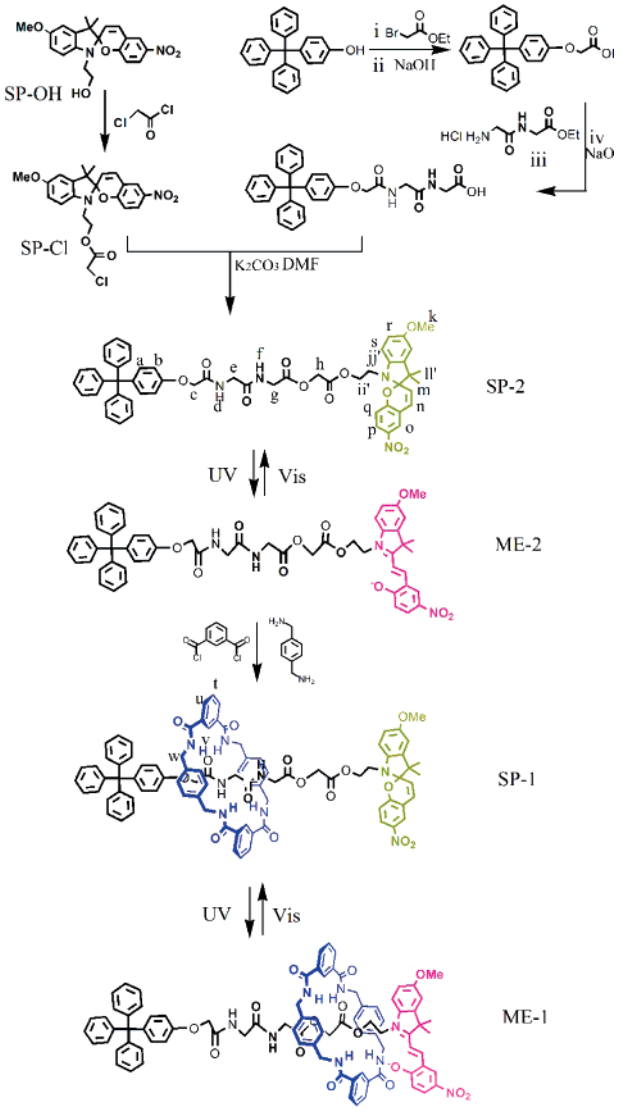
Figure 1. Photoisomerization process of spiropyran (SP).

wavelengths greater than 400 nm. When it is irradiated by ultraviolet light, it switches to the purple merocyanine (ME), accompanied by the appearance of an absorption band at 568 nm and an emission band at 640 nm.[7] These bands disappear when the solution is irradiated with visible light, as ME switches completely to SP. Both transformations are highly reversible and can be detected by the naked eye, even without the help of spectral equipment. As indicated in the structural drawing, the open form exhibits a zwitterionic structure with a nitrogen cation and a phenolic anion. This suggests that ME has strong electronic donor ability and can function as a favorable metal ion ligand and a hydrogen bond acceptor.[8]

Amide−amide hydrogen bonding of short peptide units with isophthalamide macrocycles has been well studied by the Leigh group for template-induced synthesis of rotaxanes.[9,10] Recently, Leigh has successfully demonstrated that strong anion hydrogen bonding translocates the isophthalamide macrocycle from a neutral hydrogen-bonding station in a molecular shuttle, though there is limited data or theory with which to compare the hydrogen-bonding ability of anions with neutral functional groups.[9]

Here, we describe a [2]rotaxane in which the light powered isomerization of the SP in the thread induces the movement of the macrocycle along the thread. The molecular shuttle **SP-1/ME-1** consists of an isophthalamide-based macrocycle mechanically locked onto a thread, **SP-2/ME-2**, featuring two potential H-bonding stations - short peptide unit and an open form ME unit. The short peptide unit has previously been shown[10] to be an excellent geometrical and electronic fit for isophthalamide macrocycles. The second station is related to the SP group which is a weakly hydrogen bonding acceptor as the ester group in the SP form (gray) but a powerful hydrogen-bond acceptor as the phenolate anion in the ME form (purple) (Scheme 1). So, the macrocycle resides

Scheme 1. Synthesis Route of the Molecular Shuttle



selectively in the dipeptide station in the SP form, and moves to the ME station under the irradiation of UV light. The macrocycle will return to the dipeptide station with the isomerization of ME to SP upon the irradiation of visible light.

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The shuttle was synthesized according to Scheme 1. What surprised us is that the hydroxyl group in SP-OH did not react with normal acid under the catalysis of EDCI and DMAP or even the benzoyl chloride, which might be due to the passivation effect from the SP unit. In fact, the yield is less than 40% even when it reacts with one equiv of super active chloroacetyl chloride under the base of Et_3N. The target rotaxane **SP-1**, incorporating glycylglycine and SP unit in the thread and an isophthalamide macrocycle, was synthesized through a template induced clipping strategy. Treatment of the thread **SP-2** with 10 equiv of both *p*-xylylene diamine and isophthaloyl dichloride (CH_2Cl_2, Et_3N, 4 h, high dilution) provided [2]rotaxanes **SP-1** in 20% yields.

Since the xylylene parts of the macrocycle shields encapsulated regions of the thread, the position of the macrocycle could be determined by comparing the chemical shift of the protons in the rotaxane with those of the corresponding thread.[9] The ^{1}H NMR spectra (Figure 2) of thread **SP-2** and rotaxane **SP-1** confirm the interlocked nature of **SP-1** and show that, in the form of **SP-1**, the macrocycle is largely localized on the dipeptide region of the thread (Scheme 1). The upfield shifts of the methylene resonances of the dipeptide station (H*e* 1.078, H*c* 0.402) in **SP-1** are characteristics[9] of aromatic shielding by the encapsulating macrocycle. The ester carbonyl is a weaker hydrogen bond acceptor than the amides and does not appear to contribute significantly to the intercomponent binding.

The thread amide resonances, H*d* and H*f*, are shifted downfield by 0.505 and 0.513 ppm, respectively, in the rotaxane as a result of the collective influences of (i) aromatic shielding (upfield shift) and (ii) inductive effects of hydrogen bonding to the thread amide groups from macrocycle (downfield shift). There is no evidence of any interaction between the macrocycle and the SP group.

UV light irradiation (365 nm, high press mercury lamp, 100W) of **SP-1** for 3 min results in significant changes to the ^{1}H NMR spectrum in CD_3CN (Figure 2c). The opened structure **ME-1** is approximately 26% of the total isomers according to the analysis of the ^{1}H NMR spectrum[7] (see the Supporting Information). When the thread **SP-2** is irradiated under the same conditions, the opened form **ME-2** is so active that it returns to **SP-2** during the process of ^{1}H NMR measurement, though the change of color can be detected. Kinetic studies indicate that the rate constant of **ME-2** to **SP-2** is about 6 times as large as that of **ME-1** to **SP-1** (see the Supporting Information). This increased stability of **ME-1** indicates an interaction between the macrocycle and the ME unit in the [2]rotaxane, which stabilizes the zwitterionic **ME-1**. The upfield shifts of the methylene resonances adjacent to the ME station (H*ii′* 0.89, Figure 2c) in **ME-1** are characteristics of aromatic shielding by the encapsulating macrocycle, because the signals of H*ii′* would downfield shift with the isomerization in the free SP unit.[7e] Twenty-six percent of the integral area of the signals assigned to H*e* downfield shifts to 4.00 ppm, which is strong evidence for the movement of the macrocycle away from the dipeptide during isomerization of the SP unit. That is, about 26% of the cyclic tetraamide moves from the peptide to the ME station on irradiation. In addition, 26% of two signals belonging to H*ll′* shifted downfield to a single signal due to the equalization in the isomerization process, which indicates that 26% of the spiropyran opens up on irradiation. Both features indicate that the cyclic tetraamide is highly selective around the ME station in **ME-1** (near 100%) (Scheme 1). As shown in Figure 2d, all ^{1}H NMR signals of **ME-1** return to those of **SP-1** upon irradiation with sunlight, which indicates the cyclic tetraamide moves back to the dipeptide end when ME is isomerized to SP and supports the reversibility of this shuttle.

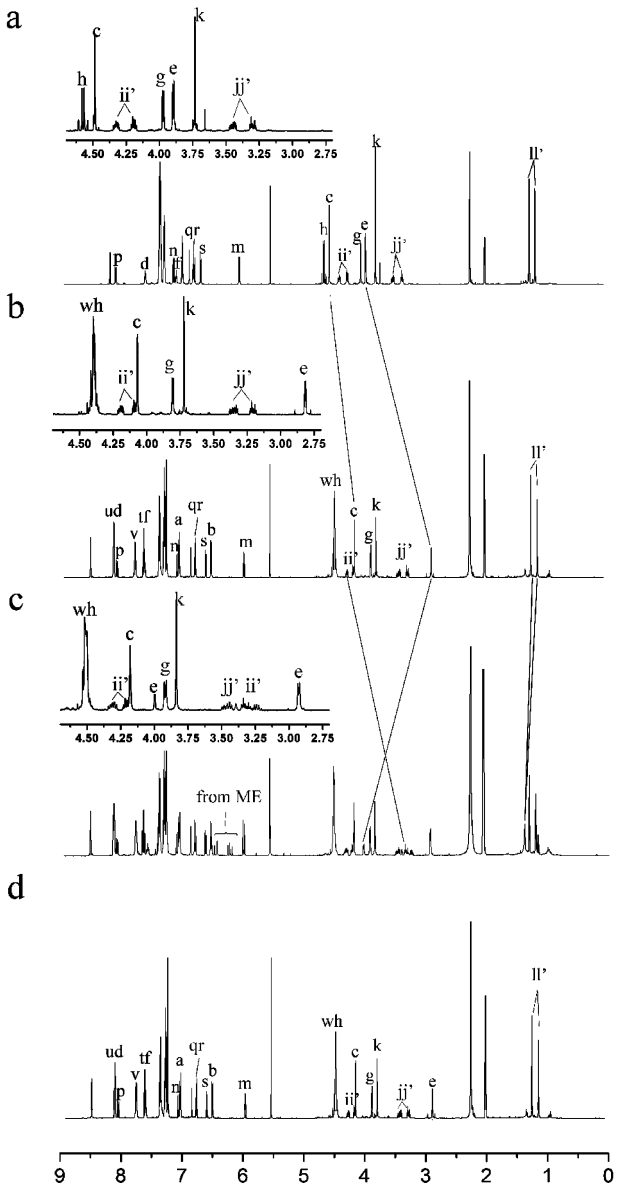

Figure 2. Partial ^{1}H NMR spectra (600 MHz, 298 K, CD_3CN, 1 $\times$ 10^{-3} M) of the **SP-2** (a), **SP-1** (b), **ME-1** (gained from irradiation of **SP-1** with 365 nm UV light for 3 min) (c), and **SP-1**(gained from irradiation of **ME-1** with sunlight for 3 min) (d).

The absorption spectra of colorless solutions **SP-2** and **SP-1** (Figure 3) do not show bands at wavelengths greater

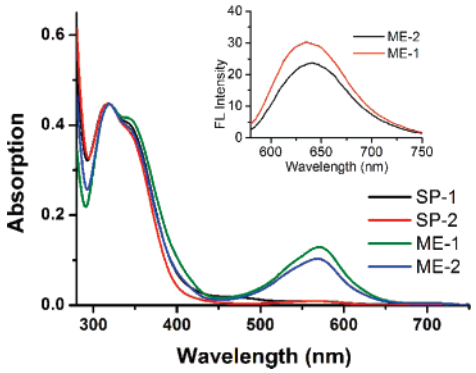

Figure 3. Absorption spectra of **SP-1**, **SP-2**, **ME-1**, and **ME-2** (5×10^{-5} M, CH_3CN, 25 °C). Insets are the emission spectra of **ME-1** and **ME-2** (5×10^{-5} M, CH_3CN, 25 °C). **ME-1** and **ME-2** were gained from the irradiation of **SP-1** and **SP-2** with 365 nm UV light for 3 min.

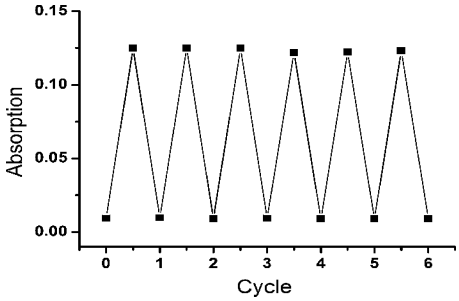

Figure 4. Absorption spectrum of **SP-1** (5×10^{-5} M, CH_3CN, 25 °C) at 568 nm under irradiation of alternate light (UV light at 365 nm and sun light) for six cycles.

than 400 nm. Upon irradiation of both solutions with ultraviolet light, an absorption band at 568 nm and an emission band at 640 nm appeared, which revealed the colorless **SP-2** and **SP-1** switched to purple **ME-2** and **ME-1**, respectively.[7] As shown in Figure 3, the absorption and emission wavelength of **ME-1** is similar to that of **ME-2,** but the intensity of absorption at 568 nm and emission at 640 nm from **ME-1** is larger than that from **ME-2**. Though the change of absorption spectra does not reflect the movement process of the macrocycle directly, the stronger absorption of **SP-1** than **SP-2** at 568 nm after the same irradiation of UV light verifies the fact that the macrocycle promotes the isomerization of **SP-1** to **ME-1**.

Different photostationary states exist for **SP-1** and **ME-1** (relative percentage of **SP-1**/**ME-1** was alternated from 100:0 to 74:26), and evident absorptive and fluorescent changes could be achieved by irradiating with light of different wavelengths. Because of the good reversibility of the photoisomerization process, the photoinduced shuttling motion of the macrocycle could be repeated remarkably well many times without obvious degradation at room temperature (Figure 4). This movement of the macrocycle is accompanied by reversible absorptive output signals which can be detected even by the naked eye.

In conclusion, we have synthesized a novel photopowered molecular shuttle that can switch the movement of a macrocycle between two distinct stations—dipeptide and zwitterionic ME—by exploiting the photoisomerization of spiropyran. The highly reversible shuttle of the macrocycle was accompanied by an obvious absorption output signal, which can be detected by the naked eye. The incorporation of one switchable unit in the molecular shuttle as a bulk stopper and an interaction site will introduce more understanding on the construction of future molecular shuttles.

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Supporting Information Available: Full experimental details pertaining to the preparation and characterization of **SP-1**/**ME-1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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