Lewis acid and base triggered molecular switch

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A new kind of trigger for molecular switch has been developed using a photochromic spirooxazine derivative as a template system. It is found that the ring-opening and ring-closing interconversion of spirooxazine derivative can be performed by Lewis acid and base trigger instead of photoinducement. With Lewis acid trigger, the ring-closing species converts to ring-opening species *via* formation of a complex, and the complexed ring-opening species is thermal stable and photoinactive. Meanwhile, the complexed ring-opening species converts completely back to ring-closing species by decomplexation with Lewis base trigger, and the interconversion between ring-opening and ring-closing species can be cycled.

Introduction

Great interest is currently devoted to bistable molecules presenting two forms whose interconversion can be modulated by an external stimulus.[1] The design of such molecular-level switching devices is directly linked to the chemistry of signal generation, transfer, conversion, storage and detection. Molecules with switchable properties are of considerable practical and fundamental interest as the development of robust systems will open up new avenues and possibilities for regulating cellular processes and potential applications to drug delivery systems, optical devices and sensors.[2]

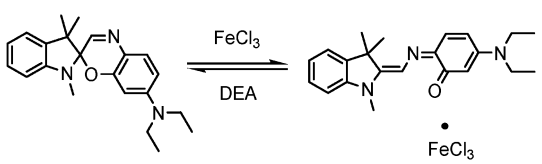
Typical bistable molecules are the so-called photochromic compounds, which is defined as a reversible change induced by light radiation, between two states of a molecule having different absorption spectra.[3] Of all potential applications of photochromic compounds, photoswitch is one of important and attractive application fields.[4] The basic requirements for photoswitch are bistability and nondestructive detection.[5] For most photochromic spirooxazines, thermal fading after UV irradiation is one of their intrinsic characteristics,[6] and it is useless for switching purposes since the information is spontaneously erased after a relatively short time. Another shortage of photochromic compounds for photoswitch is destructive detection because two states are photochemically active. The approach to avoid destructive detection is usually to build dual-mode systems in which two reversible processes can be addressed by means of two different stimuli.[7]

The ring-opening and ring-closing interconversion of spirooxazines are usually triggered by photoinduction. Although acidichromism of spirooxazines has been reported by using strong acids, such as HCl, AcOH and CF_3COOH, as triggers,[8] the reversal of ring-opening isomers is usually inhibited because addition of strong base NaOH results in the damage of spirooxazines and limits the cycling of ring-opening and ring-closing interconversion. In this paper, we report a new kind of trigger for ring-opening and ring-closing interconversion of spirooxazine derivative. It is found that the ring-opening and ring-closing interconversion of spirooxazine derivative can be performed by Lewis acid and base trigger *via* complexing and decomplexing. Moreover, the inhibited interconversion between the ring-opening and ring-closing species of spirooxazine derivative in some solvents by phototrigger can be accomplished with Lewis acid and base trigger, which provides a promising way of manipulating ring-opening and ring-closing interconversion for spirooxazine derivatives. The principle of ring-opening and ring-closing interconversion with Lewis acid ($FeCl_3$) and base (diethanolamine, DEA) trigger is outlined in Scheme 1.

Experimental

General

^1H NMR spectra were recorded at 400 MHz with TMS as an internal reference and $CDCl_3$ as solvent. MS spectra were recorded with a GC-TOF MS spectrometer. UV absorption spectra were measured with an absorption spectrophotometer (Hitachi U-3010). All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reactions were monitored by TLC silica gel plate (60F–254). Column chromatography was performed on silica gel (Merck, 70–230 mesh). A low-pressure mercury lamp (30W) and a Xeon light (500W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively.



1c **1o • $FeCl_3$**

photoactive photoinactive

Scheme 1 The principle of ring-opening and ring-closing interconversion of spirooxazine derivative **1c** with Lewis acid and base trigger.

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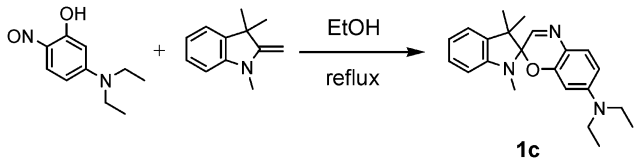


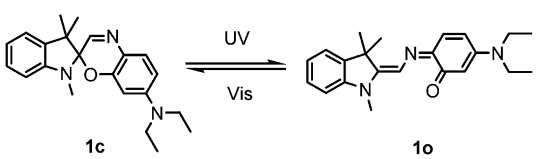
Scheme 2 Synthesis of spirooxazine derivative **1c**.

Material

Spirooxazine **1c** was synthesized according to the synthetic route presented in Scheme 2, and the detailed procedures and spectra data were as follows: a mixture of 1-nitroso-4-N,N-diethylamino-2-phenol (3.88 g, 20 mmol) and 1,3,3-trimethyl-2-methyleneindoline (3.5 ml, 20 mmol) in EtOH (50 ml) was refluxed. After no starting material was detected by TLC plate, the mixture was cooled. The resulting solution was concentrated and purified by flash column chromatography with petroleum/acetone (3:1) as eluent to afford target compound **1c** (orange solid) in 18% yield. M.p. = 143–145 °C. ^{1}H NMR ($CDCl_3$): 7.36 (s, 1H), 7.21 − 7.18 (m, 2H), 7.07 (d, $J = 7.2$ Hz, 1H), 6.86 (t, $J_1 = 7.4$ Hz, $J_2 = 7.4$ Hz, 1H), 6.57 (d, $J = 7.8$ Hz, 1H), 6.24 (dd, $J_1 = 2.7$ Hz, $J_2 = 2.7$ Hz, 1H), 6.05 (d, $J = 2.7$ Hz, 1H), 3.32 − 3.27 (q, 4H), 2.77 (s, 3H), 1.36 (s, 3H), 1.29 (s, 3H), 1.30 (t, 6H). ^{13}C NMR ($CDCl_3$): 149.4, 148.7, 148.1, 147.4, 136.4, 129.1, 128.0, 121.6, 120.6, 119.7, 107.2, 104.2, 98.9, 97.2, 51.7, 44.6, 29.8, 25.7, 20.8, 12.8. HRMS (TOF-MS EI, *m/z*) [M^+] calcd. for $C_{21}H_{27}N_3O$: 337.0443, found: 337.0440.

Results and discussion

Spectral photochromic properties of spirooxazine **1** were studied in dichloromethane (DCM) solution. **1** showed ring-opening and ring-closing photoisomerization with UV/Vis light irradiation. The photoisomerization of **1** was described in Scheme 3, and absorption spectra changes were presented in Fig. 1. Before irradiation, the absorption maximum of **1c** at 343 nm ($\varepsilon = 1.6 \times 10^4$). Upon irradiation with UV light, a new band at 607 nm, which corresponded to the ring-opening isomer **1o**, appeared, and absorption intensity increased with increasing the irradiation time till photostationary state was reached. The process was accompanied by color change of the solution from colorless to blue. The new band at 607 nm decreased and disappeared when the sample was irradiated with visible light ($\lambda_{max} \geq 450$ nm) or kept in the dark, and accompanying this process the color change of solution from blue to colorless. This coloration and decoloration can be cycled with UV/Vis light irradiation. It was worth noting that no color change was observed when spirooxazine **1c** was dissolved in some solvents such as acetonitrile, tetrahydrofuran, benzene and cyclohexane with UV light irradiation.



Scheme 3 Ring-opening and ring-closing photoisomerization of **1c** with UV/Vis light irradiation.

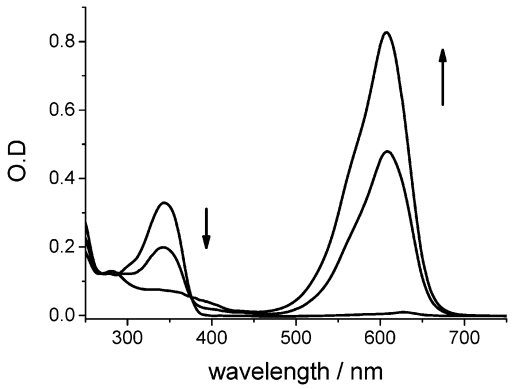


Fig. 1 Absorption changes of **1c** (20 μM, DCM) with 365 nm light irradiation (periods: 0, 10, 20 s).

It seemed that photochromism is inhibited in those solvents although the mechanism is not known.

Some interesting results were obtained when Lewis acid was added to the solution of **1c**. It is found that addition of $FeCl_3$ (0.01M, DCM) to the solution of **1c** promoted a color change of solution from colorless to blue immediately, as shown in Fig. 2, the absorption band at 628 nm increased with increase of amount of $FeCl_3$ till 5.0 equiv. of $FeCl_3$ was added. Further investigation found that the blue solution was attributed to the absorption of

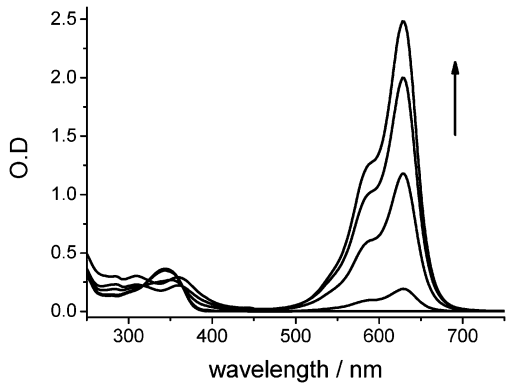


Fig. 2 Absorption changes of **1c** (20 μM, DCM) with addition of $FeCl_3$ (0, 13, 40, 100 μM, DCM).

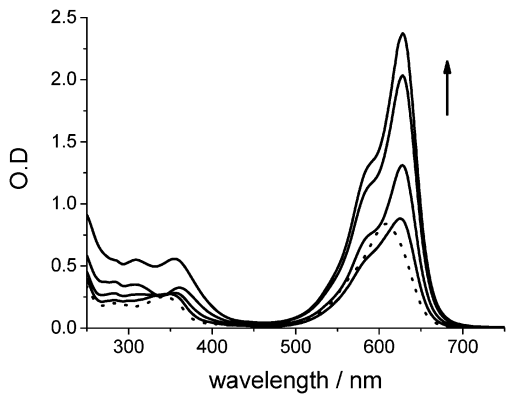


Fig. 3 Absorption changes of **1o** (dot) with addition of $FeCl_3$ (solid) (13, 25, 50, 100 μM, DCM).

complex **1o**·$FeCl_3$. As presented in Fig. 3, addition of $FeCl_3$ (0.01M, DCM) to the solution of **1o** produced an absorption band of **1o** at 607 nm bathochromic shifted to 628 nm. Comparing the absorption bands in Figs 2 and 3 found that both the profile of band and absorption wavelength are the same, which indicated that the absorption at 628 nm corresponded to complex **1o**·$FeCl_3$. The investigation of decoloration found that the complex **1o**·$FeCl_3$ is photoinactive upon irradiation with visible light, the blue solution of **1o**·$FeCl_3$ could not be bleached to colorless solution, and no absorption change was detected in absorption spectrum. Moreover, complex **1o**·$FeCl_3$ also showed thermal stability and the blue solution was not faded when the temperature is over 60 °C.

The bleaching of the complex **1o**·$FeCl_3$ is explored by using Lewis base as trigger It is found that the blue solution of **1o**·$FeCl_3$ was bleached quickly when diethanolamine (DEA) was added and the decoloration of **1o**·$FeCl_3$ could be performed completely. As presented in Fig. 4, the absorption band at 628 nm was disappeared completely with addition of DEA, and the absorption band at 344 nm, which corresponding to **1c**, reappeared. These indicated that the addition of DEA transferred **1o**·$FeCl_3$ to **1c**. The mechanism of bleaching probably combined two processes in which $FeCl_3$ bound with DEA and deviated from **1o**·$FeCl_3$. Switching properties exhibited that coloration and decoloration between **1c** and **1o**·$FeCl_3$ could be cycled with $FeCl_3$ and DEA trigger although the optical density of **1o**·$FeCl_3$ was decreased significantly after 5 cycles (Fig. 5).

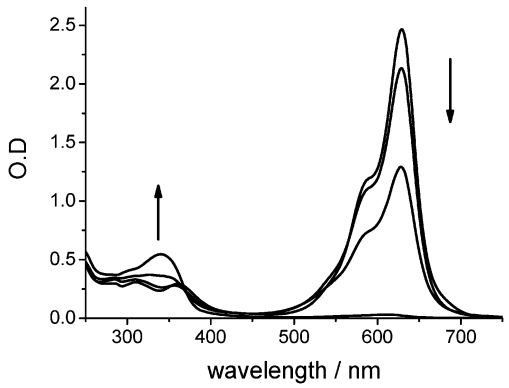


Fig. 4 Absorption changes of **1o**·$FeCl_3$ with addition of DEA (0, 66, 100, 166 μ M, DCM).

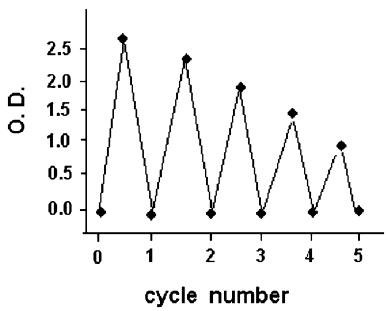


Fig. 5 Cycle number of coloration and decoloration with $FeCl_3$ and DEA trigger in solution.

Similar results were obtained when other Lewis acids were employed as triggers. It is found that using $AlCl_3$, $SnCl_4$, BF_3 Et_2O, and $ZnCl_2$ as triggers, the colorless solution of **1c** could also be converted to blue solution of complex **1o**·X. Like **1o**·$FeCl_3$, the blue solution of **1o**·X could be bleached to a colorless solution of **1c** with addition of DEA, and coloration and decoloration could be cycled. Fig. 6 showed the absorption changes of **1c** with addition of $AlCl_3$ solution, both absorption profile and absorption wavelength of **1o**·$AlCl_3$ are similar to those of **1o**·$FeCl_3$.

Different solvents were employed in the investigation of ring-opening and ring-closing interconversion of spirooxazine **1** with Lewis acid and base trigger. No color change was observed when **1c** dissolved in acetonitrile (CH_3CN) with UV light irradiation, and it seemed that the ring-opening and ring-closing photoconversion of **1** was inhibited in CH_3CN. By using Lewis acid and base trigger instead of phototrigger, the ring-opening and ring-closing interconversion of spirooxazine **1** was, however, accomplished in CH_3CN. As presented in Fig. 7, the absorption band at 613 nm, which corresponded to complex **1o**·BF_3 Et_2O, appeared when BF_3 Et_2O (0.01M, CH_3CN) was added to the solution of **1c** in CH_3CN and the absorption increased with increase of amount of BF_3 Et_2O till about 10 equiv. BF_3 Et_2O was added. The addition of DEA could also bleach the blue solution of **1o**·BF_3 Et_2O back to the colorless solution of **1c**, and the color switching could

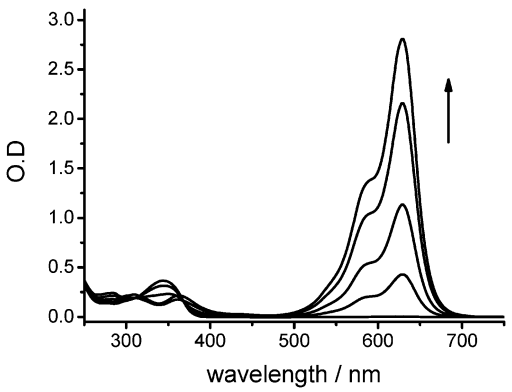


Fig. 6 Absorption changes of **1c** (20 μM, DCM) with addition of $AlCl_3$ (0, 40, 80, 160, 240 μM, DCM).

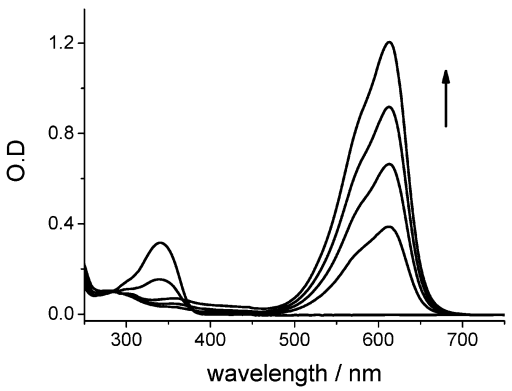
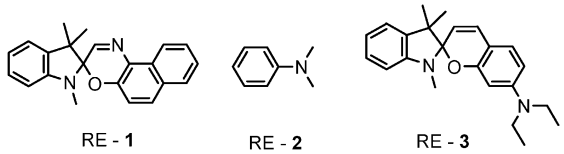
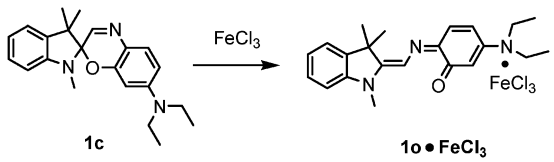


Fig. 7 Absorption changes of **1c** (20 μM, CH_3CN) with addition of BF_3 Et_2O (0, 66, 106, 160, 213 μM, CH_3CN).



Scheme 4 Compounds employed in control experiments.



Scheme 5 A probable mechanism of ring-opening conversion with Lewis acid trigger and the structure of the resulting complex.

be cycled with Lewis acid and base trigger. Similar results were obtained when other solvents were employed.

In order to study the mechanism of ring-opening conversion with Lewis acid trigger and the binding site of **1c** with $FeCl_3$, the following control experiments were carried out. First, it is found that other spirooxazine derivatives such as compound RE-**1** (Scheme 4) did not preform ring-opening conversion with $FeCl_3$ trigger, suggesting that an imino group (=N–) of spirooxazine derivatives may not play a key role in ring-opening conversion. Second, addition of $FeCl_3$ to the ring-opening isomer of RE-**1**, which obtained by irradiation of RE-**1** with UV light, did not produce the absorption red-shifted, indicating the ring-opening isomer of RE-**1** probably did not bind with $FeCl_3$. Third, it is found that the absorption of *N,N*-dimethylaniline (RE-**2**) occurred red-shift when $FeCl_3$ was added and recovered back with the addition of DEA, which indicated that *N,N*-dimethylamino substitute group may play a key role in ring-opening and ring-closing interconversion of **1c**. To further confirm the *N,N*-dimethylamino substitute group plays a key role in ring-opening and ring-closing interconversion, a spiropyran derivative containing a *N,N*-dimethylamion substitute group (RE-**3**) was prepared and investigated. It was found that spiropyran derivative RE-**3** also performed ring-opening and ring-closing interconversion with Lewis acid and base triggers, and similar results were obtained with addition of $FeCl_3$ and DEA, respectively. Based on the above results, the mechanism of ring-opening conversion with Lewis acid trigger is probably as follows: the *N,N*-dimethylamino substitute group bound with $FeCl_3$ to form a complex, the latter performing ring-opening conversion spontaneously (Scheme 5).

Conclusion

In summary, a Lewis acid and base triggered molecular switch has been developed by employing a spirooxazine derivative as a model compound. It has demonstrated that the interconversion between ring-opening and ring-closing species can be performed and cycled *via* complexing and decomplexing. The colored complex species shows thermal stability and photoinactivity, and can be bleached back to colorless species. This provides a promising way of manipulating ring-opening and ring-closing interconversion for spirooxazine derivatives, especially when photoinduced interconversion is inhibited.

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