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Mercury ion induced activation of the C—O bond in a photo-responsive spiropyran

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The conversion of 7-hydroxy-BIPS in solution from colourless form to colored form can be induced using both light and the addition of Hg^{2+} ion. No significant color change is observed when other ions (Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, K^+, Na^+, Li^+, and Ag^+) were used.

1. Introduction

Great interest currently attends bi-stable molecules that presenting two forms whose inter-conversion can be modulated by an external stimulus [1–3]. The design of such molecular-level switching devices is directly linked to the chemistry of signal generation, transfer, conversion, storage and detection. Molecules with switching 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 [4–7], optical devices [8–11] and sensors [12–19].

Typical bi-stable molecules are the so-called photochromic compounds, which undergo a reversible change induced by light radiation, through the existence of two states of the molecule which posses different absorption spectra [20]. Spiropyrans are one of important photochromic compounds that have attracted much interest from the viewpoints of both fundamental elucidation of photochemical reactions [21–26] and their potential application for optical devices and sensors [27–34]. The photochromism of spiropyrans usually results from photo-cleavage of the C—O bond under UV irradiation, creating a ring-opened merocyanine form which displays broad absorption in the visible region and which can be converted back to the (colourless) ring-closed form by visible light irradiation or heating (Fig. 1) [35].

Currently, simple and efficient multi-addressable switching systems are of interest, especially in a single molecule [36–39] from the viewpoint of potential applications in molecular sensing and switch [40]. Since multi-input systems are prototypes of molecular-level logic operators [41,42], the addition of a multi-output response would endow such systems with the ability to act as parallel operating logic elements. This paper concerns a multi-addressable switching system based on a photochromic spiropyran derivative **1a** (Fig. 2) in which the activation of theC—O bond of **1a** can be induced not only by a traditional light trigger, but also by metal ion. The metal recognition and signaling molecule inversely provides a colorimetric sensor for metal ion detection.

2. Experimental

2.1. General

^{1}H NMR spectrum was recorded at 400 MHz with TMS as an internal reference and $CDCl_3$ as solvent. MS spectra were recorded with TOF-MS spectrometer. Absorption spectra were measured with an absorption spectrophotometer (Hitachi U-3010). Anhydrous ethanol was obtained from "absolute" methanol by passage

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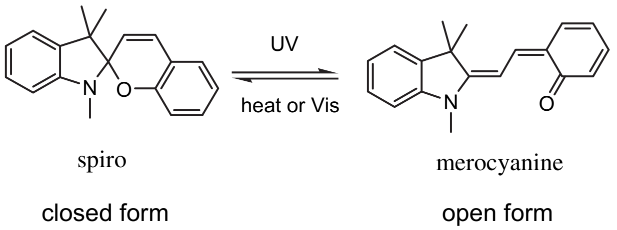
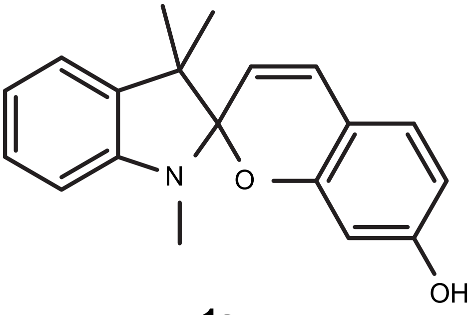


Fig. 1. Photochromism of a typical spiropyran.



1a

Fig. 2. Chemical structure of photochormic spiropyran **1a**.

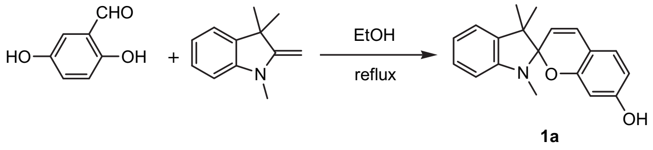


Fig. 3. Synthesis of **1a**.

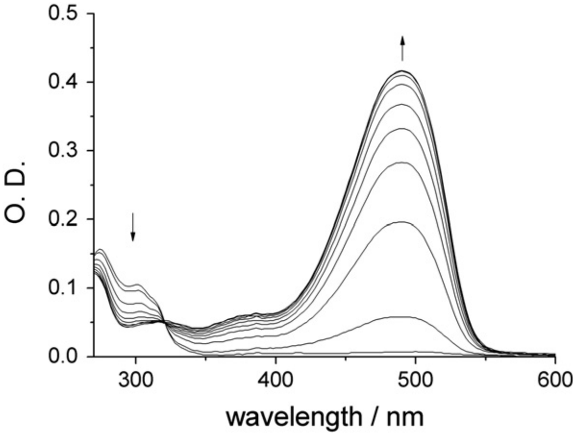


Fig. 4. Absorption changes of **1a** (10 μM, in DCM) with 254 nm light irradiation (periods: 0, 10, 20, 30, 40, 50, 60, 70, 80 s).

through type 4A molecular sieve and distilled over calcium hydride [43].

2.2. Chemical

All chemicals for synthesis were purchased from commercial suppliers, reaction monitored by TLC silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh). **1a** was prepared according to traditional synthetic route presented in Fig. 3, and the detailed procedures and spectra data were as follows: a mixture of 2,5-dihydroxybenzaldehyde (0.7 g, 5 mmol) and 1,3,3-trimethyl-2-methyleneindoline (0.87 g, 5 mmol) were dissolved into 50 ml anhydrous ethanol. 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 – ethyl acetate (4:1) as eluent to afford target compound **1a** in 40% yield. ^{1}H NMR ($CDCl_3$): 7.19 (t, $J_1 = 7.4$ Hz, $J_2 = 7.6$ Hz, 1H), 7.07 (d, $J = 7.2$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 6.84 (t, $J_1 = 7.3$ Hz, $J_2 = 7.3$ Hz, 1H), 6.79 (d, $J = 10.2$, 1H), 6.53 (d, $J = 7.7$ Hz, 1H), 6.40 (s, 1H), 6.31 (d, $J_1 = 8.1$ Hz, 1H), 6.20 (s, 1H), 5.54 (d, $J = 10.2$ Hz, 1H), 2.73 (s, 3H), 1.30 (s, 3H), 1.15 (s, 3H). HRMS (TOF-MS EI, m/z) [M^+] calcd. for $C_{19}H_{19}NO_2$: 285.1545, found: 285.1548.

2.3. Source of metal ions and preparation of metal ions in methanol

All metal ions for binding experiments used acetate salts as sources except for Fe^{2+}, Li^+ and Ag^+. Both Fe^{2+} and Li^+ used $Fe(ClO_4)_2$ and $LiClO_4$ as sources, Ag^+ used $AgNO_3$ as sources respectively. Rare-earth metal ion used nitric salts as sources. Metal ions in methanol were obtained by dissolution of the metal salts (0.1 mmol) in methanol (10 ml). Metal ions in methanol were added to the ligand solution by syringe.

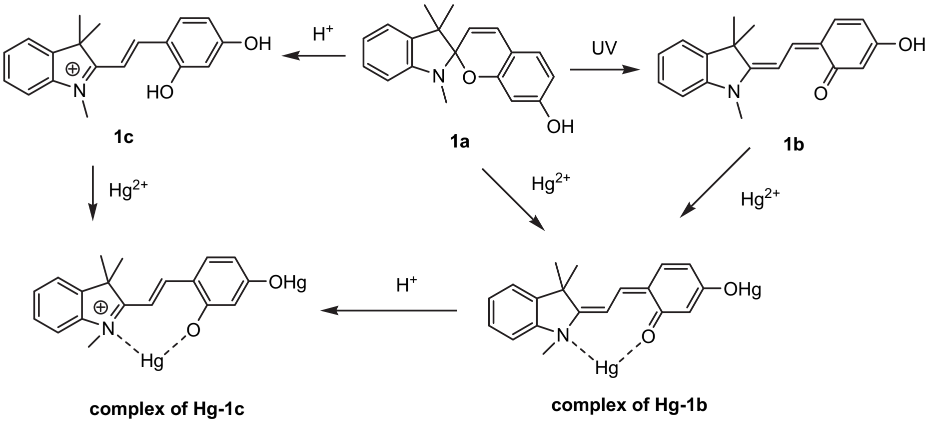


Fig. 5. Isomerization of open form and closed form and a possible mechanism of metal-induced conversion.

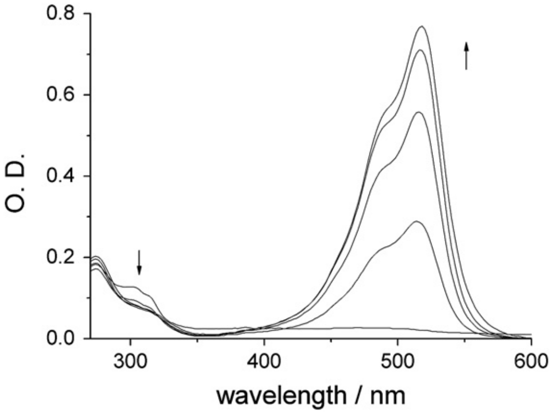


Fig. 6. Absorption changes of **1a** (10 μM, in DCM) with addition of Hg^{2+} (amount: 0, 5, 10, 15, 20 μM).

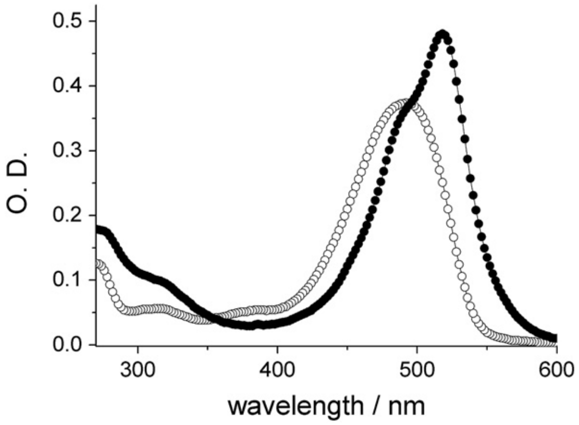


Fig. 7. Absorption change of **1b** with addition of Hg^{2+} (20 μM, in DCM. white: **1b**; black: Hg^{2+}-**1b**).

3. Results and discussion

3.1. Photochromic behavior of spiropyran *1a*

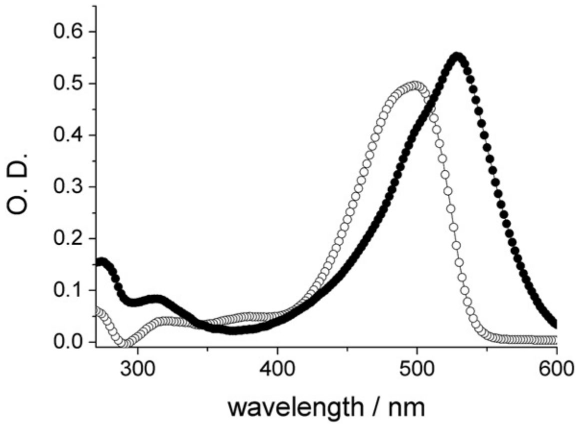


Fig. 9. Absorption change of **1c** with addition of Hg^{2+} (20 μM, in DCM. white: **1c**; black: Hg^{2+}-**1c**).

Dissolution of **1a** in dichloromethane (10 μM) produced a colorless solution with absorption band at 300 nm. Upon irradiation with UV light, the absorption at 300 nm decreased, and a new band appeared at 490 nm (Fig. 4), which corresponded to open form **1b** (Fig. 5), was increased until the photostationary state is reached. The clear isobestic points in Fig. 4 showed that **1a** converted to **1b** when the solution of **1a** underwent the photo-induced reaction. It is worth noting that **1b** could not be completely bleached back to **1a** with visible light (≥400 nm), and the oxygen in the air had little effect on the reversible transformation.

3.2. Metal-induced activation of spiropyran *1a*

Addition of Hg^{2+} ($Hg(OAc)_2$,) to the solution of **1a** (10 μM, in dicholormethane) produced the color change of solution from colorless to colored. Further study found that the absorption at 300 nm decreased when Hg^{2+} was added, and a new band at 517 nm appeared. As presented in Fig. 6, the absorption intensity at 530 nm was increased significantly with addition of Hg^{2+} till around 2 equiv. of Hg^{2+} was added. The new band at 517 nm was red-shifted around 27 nm by comparison with **1b**, and the red-shift probably resulted from the complexation of Hg^{2+} with **1b**. Photo-stability experiments showed that the complex of Hg^{2+}-**1b** was stable in darkness, and not marked change was observed when the colored solution was kept in darkness for several days. But a significant photo-degradation was detected when the

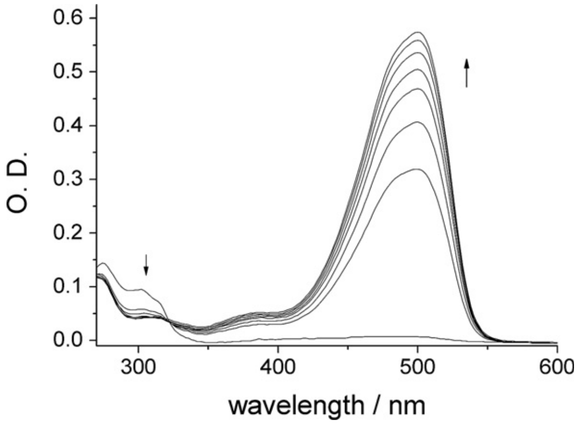


Fig. 8. Absorption changes of **1a** (10 μM, in DCM) with addition of CF_3COOH (amount: 0, 20, 30, 40, 50, 60, 70, 80 μM).

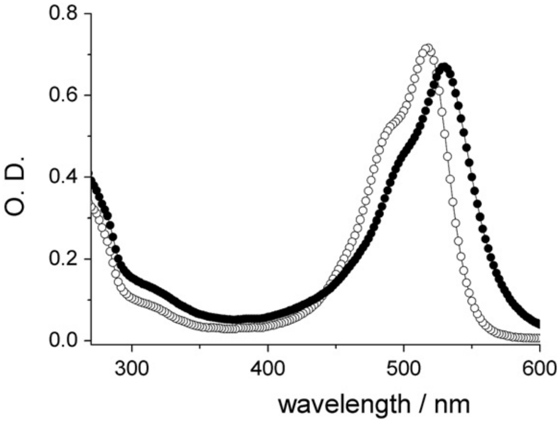


Fig. 10. Absorption change of Hg^{2+}-**1b** with addition of CF_3COOH (80 μM, in DCM. white: before addition of acid; black: after addition of acid).

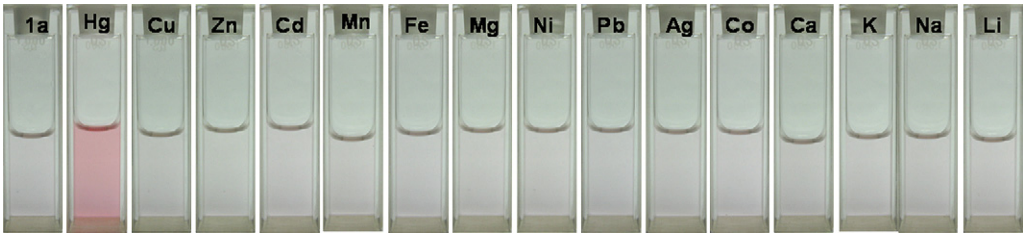


Fig. 11. Photographs of **1a** (10 μM, in DCM) with addition of different metal ions (100 μM).

colored solution of Hg^{2+}-**1b** was irradiated with both UV light (254 nm) and visible light (≥400 nm), and the mechanism is not known.

The mechanism of metal-induced conversion was elucidated by the following control experiments. First, addition of Hg^{2+} to the solution of **1PPS** produced the absorption of 490 nm red-shifted to 517 nm. As presented in Fig. 7, the absorption profile at 517 nm was similar to that in Fig. 6, and only difference between them is the O.D. (optical density) at 517 nm. It was found that the O.D. of 517 nm in Fig. 7 (0.42) was smaller than that in Fig. 6 (0.74) with the same concentration of **1a**. The smaller O.D. of 517 nm in Fig. 7 was due to the photo-degradation of **1b** during the photocyclization of **1a** with UV light irradiation. Second, addition of acid (CF_3COOH) to the solution of **1a** produced open form **1c** (Fig. 5) by acid-induced conversion [35], whose absorption appeared at 500 nm (Fig. 8). **1c** could be recovered back to **1a** by neutralization of acid with addition of base, and **1a** was damaged with excess base. Addition of Hg^{2+} to **1c** also produced the absorption of 500 nm red-shifted to 530 nm (Fig. 9), which corresponded to complex of Hg^{2+}-**1c** (Fig. 5). Further study found that the absorption of Hg^{2+}-**1b** at 517 nm was red-shifted to 530 nm with addition of acid (Fig. 10), and the absorption profile at 530 nm in Fig. 10 was similar to that in Fig. 9. All results suggested that Hg^{2+} induced the activation of C—O bond in **1a** and produced a **complex** with **1b** when Hg^{2+} was added to solution of **1a**. A possible mechanism is illustrated in Fig. 5.

3.3. *Colorimetric detection of Hg^{2+}*

1a used as a probe for colorimetric Hg^{2+}-detection was explored. Preliminary investigation found that no significant color change was observed by the addition of other metal ions (Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Ag^{+}, Pb^{2+}, K^{+}, Na^{+}, Li^{+}) (100 μM) and rare-earth ions such as Nd^{3+}, Ce^{3+}, and La^{3+} (100 μM) to the solution of **1a** (Fig. 11). Further studies showed that no marked absorption change of **1a** was detected when other metal ions were added. In addition, no obvious interference was observed when a competition experiment was conducted in which a mixture solution containing all above metal ions was added to the solution of **1a**. All suggested that **1a** used as a probe for Hg^{2+}-detection has some advantages such as high selectivity, anti-interference, and visualization.

4. Conclusions

In summary, a metal recognition induced activation of C—O bond in photo-responsive spiropyran system has been built. In such a system, the activation of C—O bond can be induced by metal ion, resulted in the conversion of colorless form to colored form. This “recognition and signaling” molecule provides a colorimetric sensor for metal ion detection.

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