

# Reversible regulation of pyrene excimer emission by light and metal ions in the presence of photochromic spiropyran: toward creation of a new molecular logic circuit

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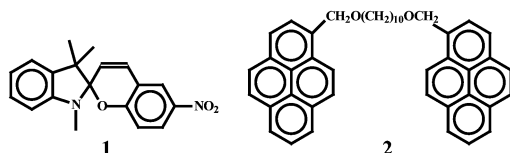
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The excimer fluorescence of a bis-pyrene molecule can be reversibly regulated by ultraviolet light, metal ions and visible light in the presence of spiropyran. Based on this result, a new molecular logic circuit is proposed.

Photochromic spiropyran, which responds to different external stimulations such as light, proton and metal ions to undergo reversible structural interconversions and modulation of photo-physical properties, has spawned extensive research toward its application.<sup>1</sup> Efficient strategies to convert chemical, light, and thermal inputs into specific output signals can be designed by exploiting the mutual interaction between different states of spiropyran and a compatible molecule or molecular unit. Moore *et al.*,<sup>2</sup> by attaching spiropyran to porphyrin, showed it possible to control the excited states of porphyrin by intramolecular energy transfer from porphyrin unit to the two states (SP and ME) of spiropyran unit under light irradiation. Raymo and his coworkers<sup>3</sup> demonstrated the modulation of pyrene fluorescence in the presence of spiropyran under three external inputs (UV, proton and visible light) by taking advantage of the different absorption properties of the three states (SP, ME and MEH) of spiropyran. They proposed the multichannel signal communication employing a similar mechanism.<sup>3</sup> One of the unique properties of pyrene is the formation of excimer.<sup>4</sup> Saika *et al.* studied a pyrene-thioindigo compound and found that the fluorescence modes of this compound were controlled by photoisomerization process.<sup>5</sup> In this report, we present for the first time the reversible regulation of pyrene excimer fluorescence by light and metal ions in the presence of spiropyran. This report provides another new example of energy transfer from the chromophore to the multistates of spiropyran component controlled by more than two types of external inputs.<sup>6</sup> Based on this result, a new molecular logic circuit is proposed.

Spiropyran **1** (Scheme 1) was synthesized by the condensation of 2-methyleneindoline with 5-nitrosolicaldehyde in the presence of Et<sub>3</sub>N. Bis-pyrene **2** (Scheme 1) was prepared through the reaction of 1,10-dibromodecane with 2 equiv. of 1-pyrenemethanol in the presence of excess sodium hydride in anhydrous tetrahydrofuran. Both of them were fully characterized by NMR and elementary analysis.<sup>†</sup>



Scheme 1 The structures of **1** and **2**.

As expected, spiropyran **1** shows the corresponding photo-switching behavior as indicated in the inset (curves *a* and *b*) of Fig. 1A. Bis-pyrene **2** displays the typical excimer fluorescence with  $\lambda_{\text{max}} = 478$  nm (not shown). For the mixture solution of **1** and **2**, it does not absorb light with wavelength longer than 400 nm (curve *a*, Fig. 1A), and it shows a strong excimer emission with  $\lambda_{\text{max}} = 478$  nm (curve *a*, Fig. 1B). Upon irradiation with ultraviolet light,<sup>‡</sup> the closed form of spiropyran (SP) is

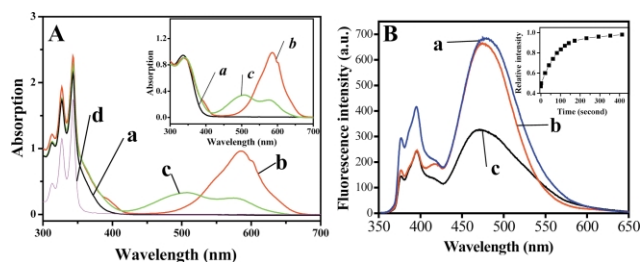
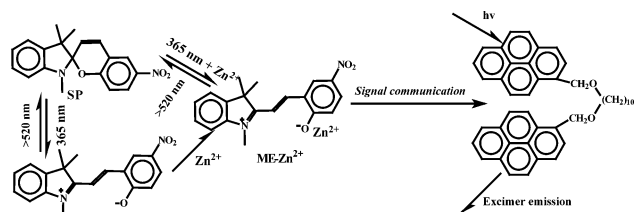


Fig. 1 A: The absorption spectra of the mixture solution of **1** and **2** (a) before and (b) after irradiation with ultraviolet light, (c) upon addition of 20 equiv. of ZnCl<sub>2</sub> immediately after irradiation with ultraviolet light and (d) the solution of pure **2**. Inset curves show the absorption spectra of the pure solution of **1** (a) before and (b) after irradiation with ultraviolet light and (c) upon addition of 20 equiv. of ZnCl<sub>2</sub> immediately after irradiation with ultraviolet light. B: The emission spectra of the mixture solution of **1** and **2** (a) before and (b) after irradiation with ultraviolet light and (c) upon addition of 20 equiv. of ZnCl<sub>2</sub> immediately after irradiation with ultraviolet light. Inset curve shows the gradual intensity change of excimer fluorescence at 478 nm of the mixture kept in the dark after UV light irradiation.

photoisomerized to the open form of spiropyran (ME) (see Scheme 2) as indicated by the appearance of its characteristic absorption band with  $\lambda_{\text{max}} = 585$  nm (curve *b*, Fig. 1A). Owing to the structural transformation from SP to ME, the fluorescence intensity of the mixture solution<sup>7</sup> in the range of 350–390 nm is decreased (curve *b*, Fig. 1B). This is due to the fact that the ME form has relatively stronger absorption in this wavelength region as compared to the SP form, which increases reabsorption efficiency of ME. Hence, the fluorescence intensity of bis-pyrene **2** is reduced in this wavelength range. On the contrary, the excimer fluorescence intensity of bis-pyrene nearly remains constant (curve *b*, Fig. 1B). This can be ascribed to the rather small spectral overlap between the excimer emission band and the absorption band of ME form. Consequently, the energy transfer process from the pyrene-excimer to the ME form can not take place efficiently.

It has been reported that addition of suitable metal ions to the ME solution can cause the blue-shift of the absorption spectrum.<sup>1</sup> For example, addition of 20 equiv. of Zn<sup>2+</sup> to the pure solution of spiropyran **1** immediately after irradiation with ultraviolet light results in the appearance of two distinct absorption bands: one corresponding to the free ME with  $\lambda_{\text{max}} = 585$  nm, and the other to ME–Zn<sup>2+</sup> complex with  $\lambda_{\text{max}} = 500$

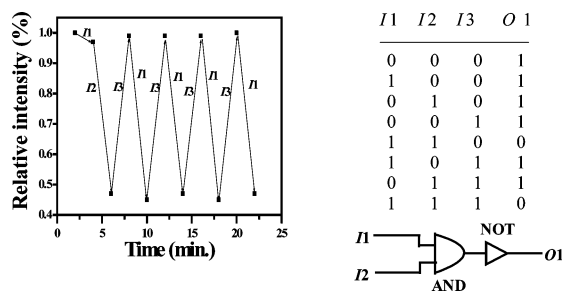


Scheme 2 Signal communication pattern between spiropyran **1** and bis-pyrene **2**.

nm as showed in the inset (curve *c*) of Fig. 1A. This can substantially increase the spectral overlap between the excimer emission band of bis-pyrene and the absorption band of the ME-Zn<sup>2+</sup> complex. As a result, the energy transfer from excimer to ME-Zn<sup>2+</sup> complex would occur more efficiently, and the excimer fluorescence would be quenched to some extent. This assumption is confirmed by similar experiments with the mixture solution of spirocyan 1 and bis-pyrene 2. As for the pure solution of spirocyan 1, the absorption spectrum of the mixture solution, formed by UV light irradiation followed by addition of 20 equiv. of Zn<sup>2+</sup>, is blue-shifted (see curve *c*, Fig. 1A) in the range of 400–700 nm. As a result of this spectral hypsochromic shift, the excimer fluorescence intensity of bis-pyrene 2 is reduced to *ca.* 47% of the initial value at 478 nm while the fluorescence intensities of the bands with maxima shorter than 400 nm remain nearly constant (curve *c*, Fig. 1B). Thus, the addition of Zn<sup>2+</sup> ion leads to opening up an efficient pathway for the mutual interaction between pyrene excimer and the ME form of spirocyan. When the above solution is treated by visible light irradiation, the ME-Zn<sup>2+</sup> complex and pure ME form are rapidly switched back to the SP form (Scheme 2). The absorption spectrum of the mixture solution is restored (not shown). Concomitantly, the fluorescence intensity in all spectral region recovers to its initial value (not shown). Therefore, the pyrene excimer fluorescence can be reversibly switched *on* (*ca.* 100%) or *off* (*ca.* 47%) consecutively in such a way. As an example, Fig. 2 shows several reversible cycles of the excimer fluorescence intensity alteration at 478 nm regulated by ultraviolet light, visible light and Zn<sup>2+</sup> ion. Even in the dark, the conversion of the ME-Zn<sup>2+</sup> complex and pure ME form to the SP form can take place. Inset curve in Fig. 1B shows the gradual intensity change of excimer fluorescence at 478 nm of the mixture, which was first treated by UV light and then kept in the dark.

Similar experiments with other metal ions including Mn<sup>2+</sup>, Ce<sup>3+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, Cd<sup>2+</sup> and La<sup>3+</sup> reduce the excimer fluorescence intensity of bis-pyrene 2 to 65%, 64%, 82%, 80%, 85%, and 87% of the initial value at 478 nm, respectively. Obviously, only three of the seven metal ions, Zn<sup>2+</sup>, Mn<sup>2+</sup> and Ce<sup>3+</sup>, can effectively change the pyrene excimer fluorescence intensity. In other words, these three metal ions have an important effect on the efficient pathway for intermolecular energy transfer between the communicating components (the ME form of spirocyan 1 and bis-pyrene 2) of the solution. Control experiments were performed by injection of 20 equiv. of each metal ion (of the seven metal ions) separately into the solution of pure bis-pyrene 2 ( $2.3 \times 10^{-5}$  M), and the results indicated that these metal ions had negligible influence on the excimer fluorescence.

The above result can be interpreted by binary logic.<sup>8</sup> The ensemble of the interacting molecules (spirocyan 1 and bis-



**Fig. 2** Demonstration of the reversible excimer fluorescence intensity alteration, the truth table and the corresponding logic circuit. *I1*, *I2* and *I3* are UV, metal ions and visible light, respectively. The output signal (*O1*) is *off* when the relative emission intensity at 478 nm is *ca.* 47% of the initial value, and it is *on* when the relative intensity is *ca.* 100% of the initial value. Because *I3* has no influence on *O1*, the combinational logic circuit includes only the two inputs: *I1* and *I2*.

pyrene 2) can “read out” three kinds of binary inputs: *I1* (UV), *I2* (Zn<sup>2+</sup> or Mn<sup>2+</sup> or Ce<sup>3+</sup>) and *I3* (visible light), and “write” a specific binary output: *O1* (excimer emission at 478 nm). Based on the above result, the truth table is constructed (see Fig. 2). For example, when both *I1* and *I2* are *on*, and *I3* is *off*, the input string is 110. Under these condition, the excimer fluorescence intensity of bis-pyrene 2 was reduced to *ca.* 47% of the initial value at 478 nm. Thus the output signal is *off* and the digit is 0. The entries in the truth table where *I1* and *I3* are 1 imply that the sample is irradiated simultaneously with UV and visible light. The corresponding combinational logic circuit incorporating two logic gates is illustrated in Fig. 2.

In summary, by taking advantage of the fact that suitable metal ions can induce hypsochromic shift of the absorption spectrum of ME form, the efficient energy transfer (and intermolecular mutual communication) is realized for the solution containing spirocyan 1 and bis-pyrene 2 together with metal ion (*e.g.* Zn<sup>2+</sup> or Mn<sup>2+</sup> or Ce<sup>3+</sup>) under UV light irradiation. Consequently, the excimer fluorescence of bis pyrene 2 can be reversibly switched *on* or *off* in the presence of spirocyan 1 by light and metal ions.

Besides, the present results also demonstrate that the extent of the excimer fluorescence quenching is dependent on what kind of metal ions are used. Thus, the present system may be useful in construction of new metal ion sensors in future.

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## Notes and references

- † Spirocyran 1:  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.22 (s, 3H), 1.33 (s, 3H), 2.78 (s, 3H), 5.88 (d, 1H), 6.48 (d, 1H), 6.60 (d, 1H), 6.92 (m, 2H), 7.13 (d, 1H), 7.24 (t, 1H), 8.05 (m, 2H). Elemental analysis: calc. for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>: H, 5.63; C, 70.79; N, 8.69. Found: H, 5.74; C, 70.50; N, 8.62%. Bis-pyrene 2:  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.22–1.38 (m, 12H), 1.68 (m, 4H), 3.64 (t, 4H), 5.25 (s, 4H), 8.08 (m, 10H), 8.20 (m, 6H), 8.42 (d, 2H). Elemental analysis: calc. for C<sub>44</sub>H<sub>42</sub>O<sub>2</sub>: H, 7.02; C, 87.67. Found: H, 7.14; C, 87.52%.
- ‡ A THF solution of 1 ( $1.1 \times 10^{-4}$  M) and 2 ( $2.1 \times 10^{-5}$  M), and aqueous solutions of metal halide salts (ZnCl<sub>2</sub>, MnCl<sub>2</sub>, CeCl<sub>3</sub>, CaCl<sub>2</sub>, BaCl<sub>2</sub>, CdCl<sub>2</sub>, and LaCl<sub>3</sub>) were prepared for the experiments. For the light irradiation experiments, the solutions were treated by 140 W high-pressure mercury lamp ( $\lambda = 365$  nm) for 2 minutes, and 2 minutes by visible light ( $\lambda > 460$  nm). When the sample was simultaneously irradiated by UV and visible light, the two light sources were held by the same distance from the sample.
- § The degree of this spectral blue-shift is dependent on the quantities of metal ions added to the solution. For the present experiment, in order to induce large spectral shift 20 equiv. (*vs.* SP) of metal ion was used.
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