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Concatenation of Two Molecular Switches via a Fe(II)/Fe(III) Couple

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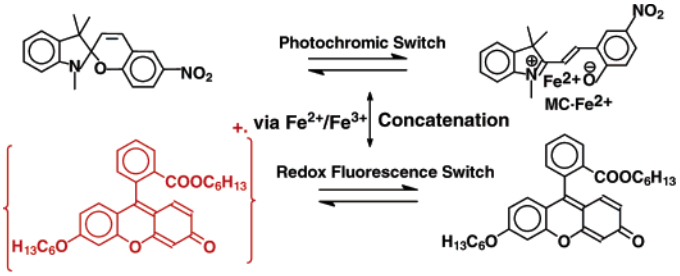
ABSTRACT



Modulation of the fluorescein fluorescence in the presence of spiropyran and ferric ion by light was observed. Such fluorescence modulation was due to the low oxidation potential of complex MC·Fe^{2+}, which made the electron transfer from MC·Fe^{2+} to Flu$^{+\bullet}$ thermodynamically favorable. As a result, the communication between two molecular switches based on fluorescein and spiropyan, respectively, was realized via the reversible Fe(III)/Fe(II) redox couple. The communicating behavior corresponds well to the function of an INHIBIT logic gate.

Concatenation of the environmental events at the molecular level plays a crucial role in the human central nervous system, ensuring the exact transfer of information from the environment to our brain.[1] To shed light on these complicated processes, studies of artificial models, which can produce detectable signals when addressed with chemical, electrical, or optical stimulations, are needed. Moreover, mimicking the processes and operating mechanisms in biological systems makes it possible to find new strategies for the design of logic gates and integrated logic circuits suitable for information processing at the molecular level.[2−8] It should be noted that these logic gates and circuits might have potential applications in the area of molecular-level devices. Recently, several examples of signal communication between molecules and communication (and even concatenation) among molecular switches have been proposed and inves-

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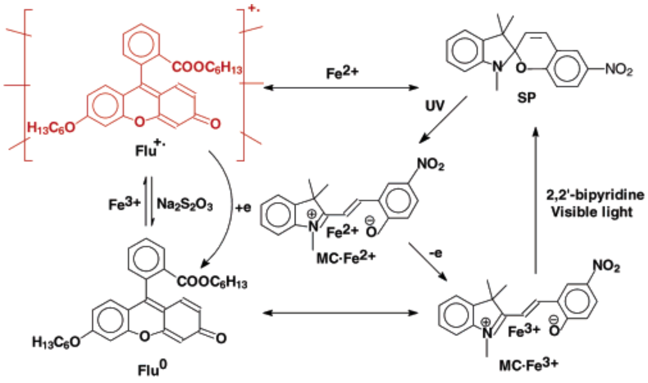
tigated. For instance, information communication between molecular switches based on photochromic spiropyrans (SP) via proton transfer or energy transfer has been described.[2c,9,10] However, exploiting such spiropyan systems to realize communication between molecular switches via electron transfer has thus far received little attention.[11] Herein we demonstrate the first example of a substantial fluorescence change between two communicating molecular switches via a reversible redox reaction.

We have just recently reported[11b] that the oxidation potential of Fe^{2+} was significantly reduced after coordination with the open form of spiropyran (**MC**), and as a result, the electron transfer between the tetrathiafulvalene (TTF) unit and Fe^{3+} can be photocontrolled in the presence of **SP**. Through our continuing research in this vein, we have found that the radical cation of fluorescein (**Flu**) formed by oxidation with ferric ion can be reduced to the corresponding neutral species upon UV light irradiation in the presence of **SP** (Scheme 1), just like the $TTF^{+\bullet}$. As compared to the neutral fluorescein, its radical cation shows strong emission at 480 nm when excited at 410 nm. Hence, a promising redox fluorescence switch based on fluorescein can be constructed. In this communication, we demonstrate an efficient strategy for the communication between a redox fluorescence switch based on fluorescein and a photochromic molecular switch based on spiropyran through the Fe(II)/Fe(III) redox couple. The concatenation of these two molecular switches can mediate the transduction of two kinds of external inputs into one kind of optical output, which corresponds to the function of an INHIBIT logic gate.

Scheme 1. Transformation Patterns of the Communicating Ensemble of Two Molecular Switches



First, we show the redox fluorescence switch based on fluorescein (**Flu**, Scheme 1). **Flu** was synthesized according to a previous report.[10d] Addition of 1 equiv of $Fe(ClO_4)_3$ to the THF solution of **Flu** led to the disappearance of the characteristic absorption bands at 430, 456, and 486 nm ascribed to the neutral molecule **Flu** and concomitantly the emergence of the strong absorption band with $\lambda_{max} = 445$ nm. But, further addition of 1 equiv of $Na_2S_2O_3$ to the above solution resulted in nearly complete recovery of its initial absorption spectrum (inset curve in Figure 1A). On the basis of these results,[12] it could be concluded that **Flu** was oxidized to its radical cation (**Flu**$^{+\bullet}$) after addition of 1 equiv of $Fe(ClO_4)_3$, and Fe^{3+} was reduced to Fe^{2+} simultaneously. The oxidative $Flu^{+\bullet}$ could be reduced to its neutral species by addition of 1 equiv of $Na_2S_2O_3$. These results are in agreement with the fact that **Flu** is a moderate electron donor with $E_{ox}^{1/2} = 0.89$ V (vs SCE).[13] The new absorption band with $\lambda_{max} = 445$ nm of the solution of Flu after treatment with $Fe(ClO_4)_3$ should be ascribed to $Flu^{+\bullet}$.

Figure 1A shows the gradual increase of the fluorescence intensity of the solution of fluorescein with increasing amounts of $Fe(ClO_4)_3$ added to the solution. Addition of 1 equiv of $Fe(ClO_4)_3$ to the solution of **Flu** resulted in a significant increase of the fluorescence intensity at 480 nm of the solution excited at 410 nm, accompanied by a 45 nm hypsochromic shift of the fluorescence spectrum. Quantitatively, the fluorescence quantum yield of the solution after addition of 1 equiv of $Fe(ClO_4)_3$ increased from that of the original solution ($\Phi_F = 0.022$) to 0.235.[14] Addition of $Na_2S_2O_3$ to the above solution led to the gradual decrease of the fluorescence intensity as shown in Figure 1B. The fluorescence spectrum nearly returned to its original spectrum after addition of 1 equiv of $Na_2S_2O_3$, due to the

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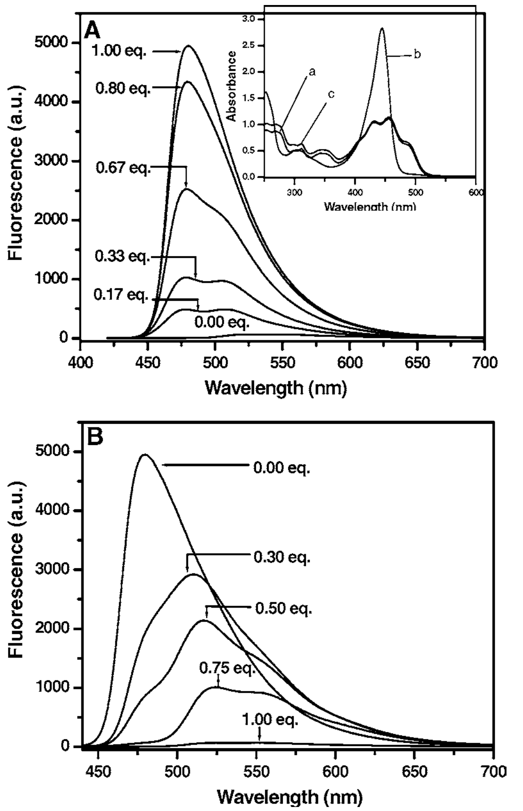

Figure 1. (A) Fluorescence spectra of **Flu** in THF (5.0×10^{-5} M, 25 °C) upon addition of increasing amounts of $Fe(ClO_4)_3$; the excitation wavelength is 410 nm. Inset curves show the absorption spectra of **Flu** in THF (5.0×10^{-5} M, 25 °C) (a) before and (b) after addition of 1 equiv of $Fe(ClO_4)_3$ and (c) then upon further addition of 1 equiv of $Na_2S_2O_3$. (B) Fluorescence spectra of **Flu** in THF (5.0×10^{-5} M, 25 °C) upon addition of increasing amounts of $Na_2S_2O_3$ after treatment with 1 equiv of $Fe(ClO_4)_3$; the excitation wavelength is 410 nm.

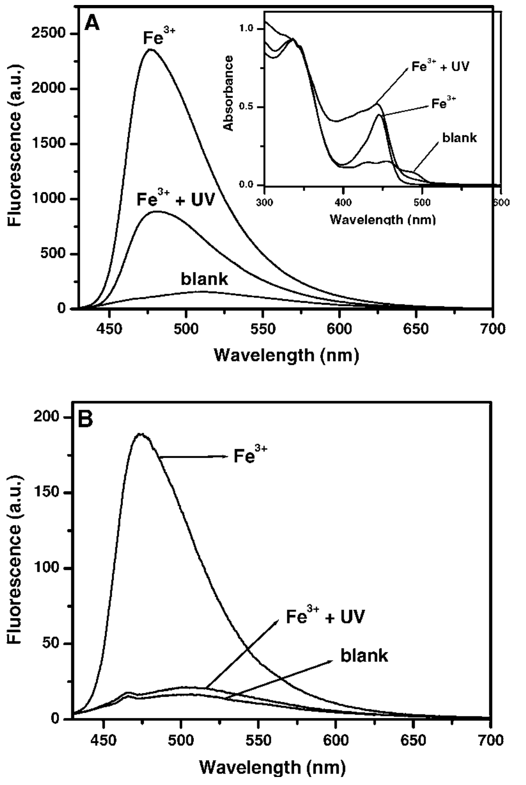

Figure 2. (A) Fluorescence spectra of the ensemble of **Flu** (1.0×10^{-5} M, 25 °C) and **SP** (1.0×10^{-4} M, 25 °C) in THF before and after addition of 1 equiv of $Fe(ClO_4)_3$ (vs **Flu)** and then upon further irradiation of UV light at 365 nm; the excitation wavelength is 410 nm. Inset curves show the absorption spectra of the above solution with the same operations. (B) Fluorescence spectra of the ensemble of **Flu** (1.0×10^{-6} M, 25 °C) and **SP** (1.0×10^{-4} M, 25 °C) in THF with the same operations as above.

reduction of $Flu^{+\bullet}$ by $Na_2S_2O_3$. Consequently, the sequential actions of $Fe(ClO_4)_3$ and $Na_2S_2O_3$ could reversibly modulate the fluorescence intensity of the solution of fluorescein. These results demonstrated a reversible fluorescence switch based on the electroactive fluorescein.

Second, we demonstrate the communication between the fluorescence switch based on fluorescein and the photochromic switch based on SP via the Fe(II)/Fe(III) redox couple. Figure 2A shows the variation of the fluorescence and absorption spectra of the solution of **Flu** (1×10^{-5} M) in the presence of **SP** (1×10^{-4} M) under the actions of Fe^{3+} and UV light. Addition of 1 equiv of $Fe(ClO_4)_3$ (vs **Flu**) led to the emergence of the absorption band with $\lambda_{max} = 445$ nm (inset curve in Figure 1A), indicating the formation of $\mathbf{Flu}^{+\bullet}$ as mentioned above. Concomitantly, the fluorescence intensity of the solution at 480 nm was significantly increased, due to the formation of $\mathbf{Flu}^{+\bullet}$. After irradiation with UV light for 5 min, the fluorescence intensity of the above solution was reduced greatly, but it was still stronger than that of the initial solution before treatment of Fe^{3+} and UV light (Figure 2A). Similarly, the absorption spectrum of the solution after UV light irradiation did not return to that of the initial solution before treatment of Fe^{3+} and UV light. However, by increasing the relative molar ratio of **SP** vs **Flu**, complete fluorescence restoration could be realized for the solution of **SP** and **Flu** after consecutive actions of Fe^{3+} and UV light irradiation. For example, Figure 2B shows the fluorescence spectra of the mixture solution of **Flu** (1×10^{-6} M) and **SP** (1×10^{-4} M) under the actions of Fe^{3+} and UV light irradiation. Interestingly, consecutive actions of 1 equiv of $Fe(ClO_4)_3$ (vs **Flu**) and UV light irradiation led to almost the same fluorescence spectrum as that of the initial solution (Figure 2B).

These results can be interpreted as follows (Scheme 1): Addition of $Fe(ClO_4)_3$ to the mixture solution of **SP** and **Flu** resulted in the oxidation of **Flu** to $\mathbf{Flu}^{+\bullet}$ and the reduction of Fe^{3+} to Fe^{2+}, accompanied by a significant enhancement of the fluorescence of the solution. Upon UV light irradiation, **SP** was transformed to its open form (**MC**), which would coordinate with Fe^{2+} to produce a $\mathbf{MC}\cdot Fe^{2+}$ complex. According to our previous results,[11] it is thermodynamically favorable for the electron-transfer reaction from the $\mathbf{MC}\cdot Fe^{2+}$ complex (0.48 V vs SCE) to $\mathbf{Flu}^{+\bullet}$ (0.89 V vs SCE). This electron-transfer reaction would lead to the reduction of **Flu**$^{+\bullet}$ to the neutral species and the formation of the MC·Fe^{3+} complex. This is fully in accordance with the fact that the fluorescence of the solution was decreased after UV light irradiation. Only a partial amount of **SP** was transformed to **MC** in the photostationary state as reported previously.[2b,c] Thus, if only 10 equiv (vs **Flu**) of **SP** was present in the solution, the amount of MC·Fe^{2+} species was not sufficient for the complete reduction of **Flu**$^{+\bullet}$ generated by oxidation with Fe^{3+}. As a result, the fluorescence and absorption spectra of the solution could not return to the initial spectra of the mixture solution before the actions of Fe^{3+} and UV light (Figure 2A). As expected, if more than 20 equiv of **SP** (vs **Flu**) was used, more **MC** and hence sufficient **MC**·Fe^{2+} can be generated. Accordingly, complete reduction of **Flu** was achieved, which is in excellent agreement with the results mentioned above (Figure 2B). It should be noted that addition of 2,2′-bispyridine, followed by visible light irradiation will lead to the transformation of **MC**·Fe^{3+} to **SP**.[11] Therefore, the fluorescence modulation for the solution of **Flu** in the presence of **SP** can be reversibly performed under the combined actions of Fe^{3+} and light irradiation.

The communicating ensemble of two molecular switches can transmit one chemical input (Fe^{3+}, $I1$) and one optical input (UV light, $I2$) into a single optical output ($\lambda_{\text{flu.}} = 473$ nm, $O1$). On the basis of the results mentioned above, the output ($O1$) is 1 only when $I1 = 1$ and $I2 = 0$. For other combinations of the two inputs, the output ($O1$) is always 0. Thus, the communicating behavior of these two molecular switches corresponds to the function of an INHIBIT logic gate.[2c]

In summary, we have demonstrated the fluorescence modulation of the ensemble of spiropyran and fluorescein in the presence of ferric ion by light. Essential to understanding this spectral alteration is the low oxidation potential of complex **MC**·Fe^{2+}, which made the electron transfer from **MC**·Fe^{2+} to **Flu**$^{+\bullet}$ thermodynamically favorable. As a result, communication between two molecular switches based on fluorescein and spiropyan, respectively, has been realized via the reversible Fe(III)/Fe(II) redox couple. The communicating behavior corresponds well to the function of an INHIBIT logic gate. This new strategy of concatenation of independent molecular switches through electron transfer may not only add new merits to the chemistry of photochromic spiropyrans but also find potential application in the construction of new molecule-based devices.

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