

Photocontrolled Electron Transfer Reaction between a New Dyad, Tetrathiafulvalene–Photochromic Spiropyran, and Ferric Ion

Xuefeng Guo,^{†,‡} Deqing Zhang,^{*,†} and Daoben Zhu^{*,†}

Organic Solids Laboratory, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China, and Graduate School, Chinese Academy of Sciences, Beijing 100080, China

Received: August 27, 2003

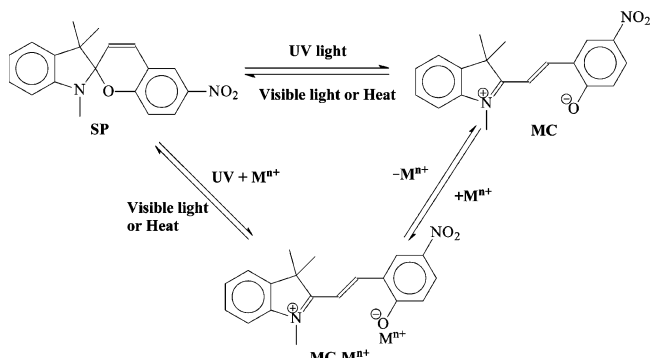
Photocontrolled electron transfer reaction is important not only for understanding the complicated biological processes such as photosynthesis and respiration but also for the design and studies of molecular electronics. This paper presents the synthesis and spectral and electrochemical studies of a new dyad **1** containing an electroactive unit (tetrathiafulvalene, TTF) and a photochromic unit (spiropyran, SP). Spectral studies showed that the redox states of the TTF unit of dyad **1** in the presence of ferric ions were dependent on the photoswitching process of the spiropyran unit upon UV light irradiation. Electrochemical investigations indicated that the oxidation potential of ferrous ion was largely reduced after coordination with MC (the open form of SP). As a result, the electron-transfer reaction from MC•Fe²⁺ to TTF^{•+}, which act as electron donor and acceptor, respectively, is thermodynamically favorable. Therefore, the electron-transfer reaction between the TTF unit and ferric ion can be photocontrolled in the presence of the SP unit. The present result shows the possibility to design new electron donor–acceptor supramolecules containing spiropyran units to photoregulate the electron-transfer reaction.

Introduction

Electron donor–acceptor supramolecules have been extensively investigated in recent years not only for a better understanding of many complicated biological processes such as photosynthesis and respiration¹ but also for the potential applications in the construction of efficient and fast-responding electronic/photonic devices at the molecular level.² In particular, much effort is currently devoted to regulating electronic communication and thus controlling electron-transfer reactions among electroactive components through photoisomerization³ and redox reactions.⁴

Spiropyran molecules, as one of the promising families of photochromic compounds, undergo reversible structural transformations in response to external inputs such as light, heat, proton, and metal ions (Scheme 1).⁵ By using the special photoswitching properties of spiropyran molecules, complex integrated logic gates and communication networks have been constructed.^{6,7} We also reported previously new logic gates for information processing and communication at the molecular level, by taking the advantage of the photochromic behaviors of spiropyran and the energy-transfer mechanism.⁸ However, to the best of our knowledge, there has been no report that deals with photoregulation of electron-transfer reaction for the electron donor–acceptor (D–A) dyad with photochromic spiropyran as one of the units. This is probably because both the closed form (SP) of spiropyran and the corresponding open form (MC) are weak electron donors and they have similar oxidation potentials.^{7,9} It should be noted that the MC form is able to coordinate with suitable metal ions and as a result the absorption spectrum of MC form is hypsochromically shifted, while the corresponding SP form does not show this behavior.^{5h,i,8a} Therefore, if the

SCHEME 1: Illustrations of the Reversible Structural Transformations of Nitrospiropyran in Response to Light, Heat, and Metal Ions



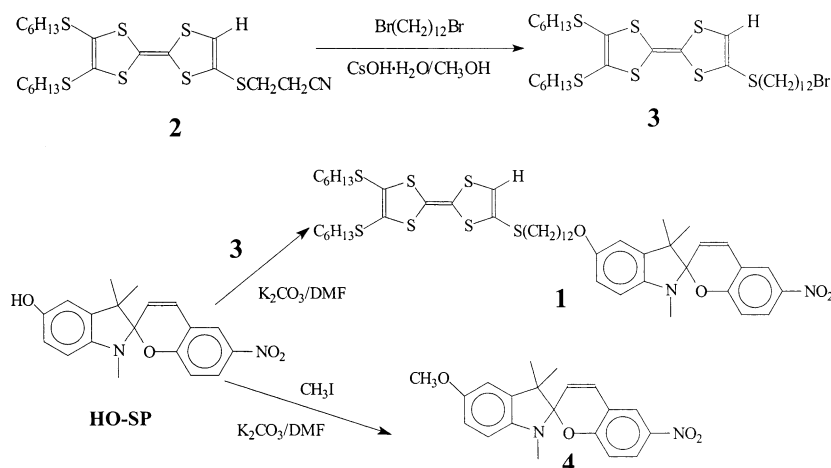
metal ions such as the ferric and the ferrous ions, which show redox behaviors, are used, it seems possible to alter their redox potentials by light in the presence of photochromic spiropyran.

Tetrathiafulvalene (TTF) and its derivatives are good electron donors for studies of organic conductors (as well as superconductors),¹⁰ and the construction of electron donor–acceptor supramolecules.¹¹ They can be oxidized by some metal ions such as the ferric ion to form TTF^{•+} and even TTF²⁺.¹² Therefore, it would be interesting to investigate whether it is possible to alter the redox states of the TTF unit of a new dyad TTF–SP (dyad **1**, Scheme 2) in the presence of ferric ion by light. With these in mind, we initiated studies of photocontrolled electron-transfer reaction for a new dyad **1** in the presence of ferric ion. In this paper, we will report the synthesis and spectral and electrochemical investigations of dyad **1**. The results show that the redox states of the TTF unit of dyad **1** are dependent on the photoswitching process of the SP unit in the presence of ferric ion. Namely, the electron-transfer reaction between the

* Corresponding author. E-mail: dqzhang@iccas.ac.cn.

[†] Institute of Chemistry.

[‡] Graduate School.

SCHEME 2: Synthetic Route to Dyad 1, as Well as the Structures of Reference Compounds 2 and 4

TTF unit and ferric ion can be controlled by light in the presence of the SP unit.

Results and Discussion

Synthesis. The preparation of dyad **1** was depicted in Scheme 2. Compound **2** was prepared according to the procedures developed in our laboratory recently.¹³ Using the standard deprotection/alkylation method,^{13,14} deprotection of cyanoethyl group of compound **2** generated the corresponding thiolate, which further reacted with $\text{Br}(\text{CH}_2)_{12}\text{Br}$ to afford compound **3**.^{13b} Compound **HO-SP** was synthesized according to refs 8b and 15. Finally, the reaction of compound **3** with **HO-SP** in DMF at room temperature in the presence of anhydrous K_2CO_3 yielded the target compound **1** in 73% yield after separation with column chromatography. The reference compound **4** was prepared in the same way as that for dyad **1**.^{8b}

Spectral Studies. The absorption spectrum of dyad **1** (curve a) is shown in Figure 1A, together with those of compounds **2** (curve c) and **4** (curve b). The absorption spectrum of dyad **1** is approximately the sum of the absorption spectra of compounds **2** and **4** (Figure 1A). As reported by Buncel and Raymo et al.,^{5b,6a} upon UV light irradiation¹⁶ at 365 nm, the SP unit of dyad **1** was photoswitched to its open form (MC) with the appearance of its characteristic absorption band with $\lambda_{\text{max}} = 580 \text{ nm}$ (curve a, Figure 1B), and dyad **1** was transformed to dyad TTF-MC (see Scheme 3). Similarly, reference compound **4** was photoswitched to its open form (curve b in Figure 1B) under the same condition. As shown in Figure 1B, the absorption peaks of the dyad TTF-MC are almost identical to those observed for the reference compound **2** and the open form of **4**. On the basis of the above results, it can be concluded that there exists no strong electronic interaction between the TTF unit and the SP unit in dyad **1**, and the SP unit also exhibits the characteristic photochromic property in the presence of the TTF unit.

But the presence of the TTF unit has a weak effect on the photoswitching process of the SP unit of dyad **1**. For example, the absorption intensity at 580 nm (due to MC form) for dyad **1** is relatively low compared with that of the MC form of **4**, probably because of the coabsorption of the TTF unit at 365 nm. In particular, the thermal cyclization of MC to SP in the TTF-MC dyad in the dark is slowed compared with that of the reference compound **4**. The inset curve of Figure 1B shows the variation of the absorption intensity at 580 nm (due to the MC form) with time for the solution of dyad **1** that was first irradiated by UV light and then kept in the dark at room

temperature. Similar experiments were performed for reference compound **4**, and the result was shown in the inset curve of Figure 1A. Quantitatively, it took 95 s for the absorption intensity at 580 nm to be reduced to half of the initial value for the case of dyad **1** ($\tau_{1/2} = 95 \text{ s}$), while it needed only 58 s for the case of reference compound **4** under the same conditions ($\tau_{1/2} = 58 \text{ s}$). Accordingly, the rate constants for the conversion

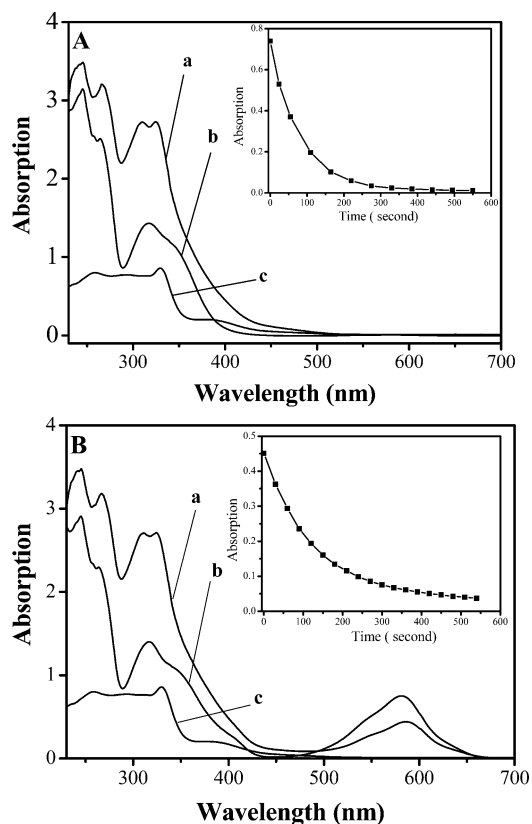
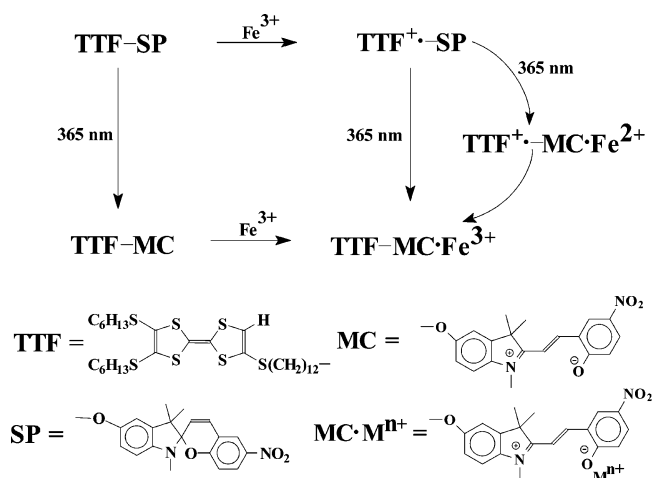


Figure 1. Panel A: The absorption spectra of dyad **1** ($1.0 \times 10^{-4} \text{ M}$, THF, 25 °C) (a), reference compound **4** ($1.0 \times 10^{-4} \text{ M}$, THF, 25 °C) (b), and reference compound **2** ($5.0 \times 10^{-5} \text{ M}$, THF, 25 °C) (c). Inset curve shows the decay of the absorption intensity at 580 nm with time for the solution of **4** after irradiation with UV light for 5 min and then being kept in the dark. Panel B shows the absorption spectra of dyad **1** after irradiation with ultraviolet light at 365 nm ($1.0 \times 10^{-4} \text{ M}$, THF, 25 °C) (a), reference compound **4** after irradiation with ultraviolet light at 365 nm ($1.0 \times 10^{-4} \text{ M}$, THF, 25 °C) (b), and reference compound **2** ($5.0 \times 10^{-5} \text{ M}$, THF, 25 °C) (c). Inset curve shows the decay of the absorption intensity at 580 nm with time for the solution of **1** after irradiation with UV light for 5 min and then being kept in the dark.

SCHEME 3: Transformation of Dyad 1 under the Action of UV Light and Ferric Ion.


of MC to SP were determined to be $6.85 \times 10^{-3} \text{ s}^{-1}$ for dyad **1** and $1.20 \times 10^{-2} \text{ s}^{-1}$ for reference compound **4**, respectively. The different behavior of dyad **1** from the reference compound **4** is likely due to the intimacy of the MC unit with the TTF unit within a covalently linked dyad TTF-MC (see Scheme 3), facilitating the π - π and the charge-transfer interactions by folding the alkylchain $(-\text{CH}_2)_{12}$. Consequently, the MC form in the TTF-MC dyad becomes more stable.

As described above, upon UV light irradiation at 365 nm, the SP unit of dyad **1** was photoswitched to its open form (MC) (Scheme 3) with the appearance of its characteristic absorption band with $\lambda_{\text{max}} = 580 \text{ nm}$ (curve a in Figure 1B and curve b in Figure 2). Further addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ to the solution of dyad **1** after irradiation with UV light (dyad **1** was converted to TTF-MC as shown in Scheme 3) led to the emergence of a new strong absorption band with $\lambda_{\text{max}} = 424 \text{ nm}$ (curve c in Figure 2) with the concomitant disappearance of the characteristic absorption band at 580 nm ascribed to the MC form. Moreover, addition of $\text{Fe}(\text{ClO}_4)_3$ to the solution of the TTF-MC dyad (Scheme 3) did not lead to oxidation of the TTF unit because the characteristic absorption band of TTF^+ ($\lambda_{\text{max}} = 610 \text{ nm}$)¹⁷ was not observed. If $\text{Fe}(\text{ClO}_4)_2$ instead of $\text{Fe}(\text{ClO}_4)_3$ was employed for the above reaction, only a much weaker absorption band at about 424 nm (curve d in Figure 2) was detected. On the basis of previous reports that the MC form can coordinate with suitable cations (M^{n+}) to induce the significant hypsochromic shift of the MC absorption band,^{5h,5i,8a} the new strong absorption band with $\lambda_{\text{max}} = 424 \text{ nm}$ was ascribed to the coordination of the MC unit of the TTF-MC dyad with Fe^{3+} ion. As a result, dyad **1** was transformed to TTF-MC-Fe^{3+} (see Scheme 3) after sequential reaction with UV light and Fe^{3+} . Control experiments with the reference compound **4** supported this assignment: UV light irradiation of the solution of **4** induced the formation of MC with the appearance of its characteristic absorption band with $\lambda_{\text{max}} = 580 \text{ nm}$ (inset curve b in Figure 2). Further addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ to the solution led to a strong absorption band with $\lambda_{\text{max}} = 424 \text{ nm}$ with the complete disappearance of the characteristic absorption band at 580 nm of MC (inset curve c in Figure 2). Similarly, further addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_2$ to the solution also led to a much weaker absorption band around 424 nm (inset curve d in Figure 2). Thus, it is clear that the appearance of the strong absorption band with $\lambda_{\text{max}} = 424 \text{ nm}$ after addition of $\text{Fe}(\text{ClO}_4)_3$ to the solution of MC was due to the formation of $\text{MC}\cdot\text{Fe}^{3+}$ rather than $\text{MC}\cdot\text{Fe}^{2+}$.

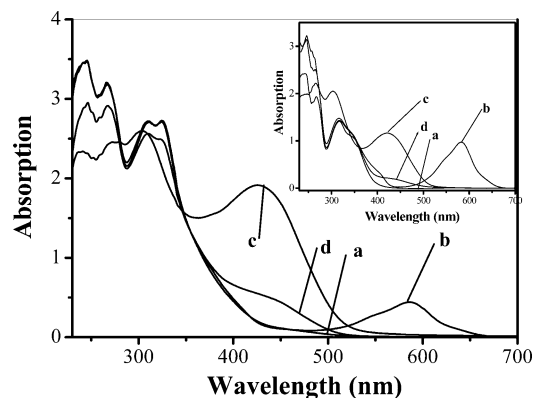


Figure 2. The absorption spectra of dyad **1** ($1.0 \times 10^{-4} \text{ M}$, THF, 25 °C) before (a) and after irradiation with ultraviolet light (b), upon addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ immediately after irradiation with ultraviolet light (c), and upon addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_2$ immediately after irradiation with ultraviolet light (d). Inset curves show the absorption spectra of reference compound **4** ($1.0 \times 10^{-4} \text{ M}$, THF, 25 °C) before (a) and after irradiation with ultraviolet light (b), upon addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ immediately after irradiation with ultraviolet light (c), and upon addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_2$ immediately after irradiation with ultraviolet light (d).

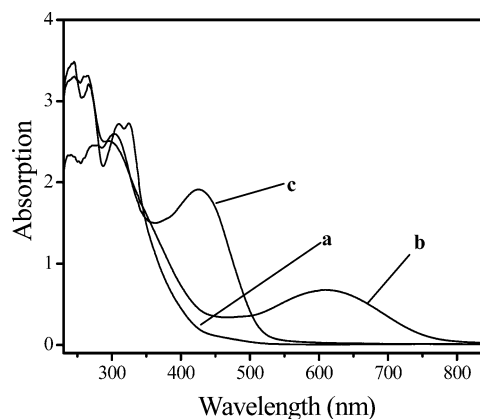
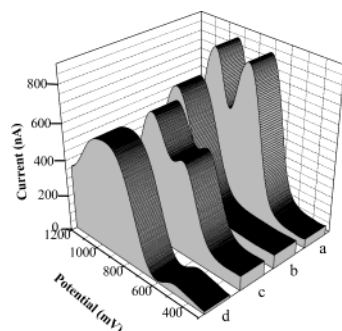


Figure 3. The absorption spectra of dyad **1** ($1.0 \times 10^{-4} \text{ M}$, THF, 25 °C) before (a) and after addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ (b) and after UV light irradiation of the solution that was first treated with 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ (c).

On the other hand, addition of 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ to the solution of **1** resulted in the appearance of the broad absorption band with $\lambda_{\text{max}} = 610 \text{ nm}$ (curve b in Figure 3), which should be ascribed to radical cation TTF^+ rather than SP^+ .¹⁷ The formation of TTF^+ was due to the oxidation of the TTF unit by ferric ion, and as a result, ferric ion was reduced to ferrous ion. The following experiment was performed to provide support for this assumption: addition of the aqueous solution of $\text{K}_3\text{Fe}(\text{CN})_6$ to the solution of dyad **1** that had been treated by 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ afforded a dark-blue precipitate immediately, indicating the presence of ferrous ion in the mixture solution.

Interestingly, irradiation of the above solution with ultraviolet light at 365 nm led to nearly the same absorption spectrum (curve c in Figure 3) as that of the solution of dyad **1** that was first treated by UV light followed by addition of $\text{Fe}(\text{ClO}_4)_3$ (curve c in Figure 2). As shown in Figure 3, the strong absorption band of the radical cation TTF^+ disappeared and the distinct absorption band with $\lambda_{\text{max}} = 580 \text{ nm}$ ascribed to the MC form was not observed. However, a new strong absorption band with $\lambda_{\text{max}} = 424 \text{ nm}$ appeared in the meantime. Furthermore, no dark-blue precipitate was formed after addition of the aqueous solution of $\text{K}_3\text{Fe}(\text{CN})_6$ to the solution of dyad **1** that had been treated by 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ and UV light,



| Compound | $E_{1/2}$ [V vs. SCE] | |
|---------------------|-----------------------|--------------|
| | X/X^+ | X^+/X^{2+} |
| dyad 1 | 0.66 | 0.86 |
| 2 | 0.69 | 0.91 |
| 4 | 0.94 | — |
| MC·Fe ²⁺ | 0.48 | — |

Figure 4. Differential pulse voltammograms (left) of the THF solutions of **2** (a), **4** (b), dyad **1** (c), and **4** after consecutive treatment with UV light and $\text{Fe}(\text{ClO}_4)_2$ (d). Potentials are relative to SCE. The potentials of all compounds are listed in the table (right).

indicating the absence of ferrous ion. As discussed above, the new absorption band with $\lambda_{\text{max}} = 424$ nm was ascribed to the formation of coordination complex between the MC unit and ferric ion. These results indicated that UV light irradiation of the solution of dyad **1** that had been treated by 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ induced the reduction of the radical cation $\text{TTF}^{+\bullet}$ unit to the neutral TTF unit and the formation of $\text{TTF-MC}\cdot\text{Fe}^{3+}$. This is in excellent accordance with the disappearance of the absorption band at about 610 nm and the appearance of the absorption band at about 424 nm. Further evidence for the reduction of the $\text{TTF}^{+\bullet}$ unit to the neutral TTF unit came from the following experiment: further addition of $\text{Fe}(\text{ClO}_4)_3$ to the solution of dyad **1** that had been consecutively treated by 1 equiv of $\text{Fe}(\text{ClO}_4)_3$ and UV light led to the emergence of the characteristic absorption band of $\text{TTF}^{+\bullet}$ again. This was obviously due to the oxidation of the TTF unit in $\text{TTF-MC}\cdot\text{Fe}^{3+}$ by the additional ferric ion. In another approach, if the solution of dyad **1** was first treated by excess $\text{Fe}(\text{ClO}_4)_3$, the characteristic absorption band ascribed to $\text{TTF}^{+\bullet}$ was still observed (albeit with reduced intensity) after further UV light irradiation.

In addition, the intermolecular electron transfer between $\text{MC}\cdot\text{Fe}^{2+}$ and $\text{TTF}^{+\bullet}$ can also take place. Upon mixing the solution containing $\text{2}^{+\bullet}$ formed by electrochemical oxidation of **2** and the solution of $\text{MC}\cdot\text{Fe}^{2+}$ prepared by UV light irradiation of the solution of **4** followed by addition of $\text{Fe}(\text{ClO}_4)_2$, the typical absorption of $\text{TTF}^{+\bullet}$ in the range of 500–800 nm disappeared and a strong absorption band with $\lambda_{\text{max}} = 424$ nm due to $\text{MC}\cdot\text{Fe}^{3+}$ was detected instead.

To conclude, upon either first reaction with UV light and then with ferric ion or first with ferric ion and then with UV light, dyad **1** was transformed to $\text{TTF-MC}\cdot\text{Fe}^{3+}$. The results demonstrate that the electron-transfer reaction between the TTF unit and ferric ion can be controlled by UV light irradiation in the presence of the SP unit. Moreover, the results also showed that intermolecular electron transfer between $\text{MC}\cdot\text{Fe}^{2+}$ and $\text{TTF}^{+\bullet}$ could also take place efficiently. Differential pulse voltammetric experiments detailed below indicated that the electron-transfer reaction between the $\text{TTF}^{+\bullet}$ and $\text{MC}\cdot\text{Fe}^{2+}$ units was thermodynamically favorable, which was crucial for understanding the transformation of dyad **1** to $\text{TTF-MC}\cdot\text{Fe}^{3+}$ under the consecutive action of UV light and ferric ion.

Differential Pulse Voltammetric Studies. Figure 4 shows the differential pulse voltammograms of dyad **1**, reference compounds **2** and **4**, and the solution containing $\text{MC}\cdot\text{Fe}^{2+}$. Two redox potentials of dyad **1** were found to be 0.66 and 0.86 V (curve c in Figure 4). The transformation of the SP unit to the MC form induced by UV light irradiation of the solution of dyad **1** resulted in no observable change in its redox behavior, consistent with the previous reports.^{7,9} Compound **4** possessed

only one redox potential at 0.94 V (curve b in Figure 4), while two redox waves for compound **2** were observed at 0.69 and 0.91 V (curve a in Figure 4). Under the same conditions, irradiation of the solution of compound **4** with UV light at 365 nm also resulted in no observable change in its redox behavior. By reference to those of reference compounds **2** and **4**, the first oxidation peak of dyad **1** at 0.66 V should be ascribed to the oxidation of the TTF unit to $\text{TTF}^{+\bullet}$ and the second oxidation peak at 0.86 V of dyad **1** should be the result of two-electron oxidation because $\text{TTF}^{+\bullet}$ and SP possess similar oxidation potentials.

Differential pulse voltammetric experiment with the solution of reference compound **4** in the presence of $\text{Fe}(\text{ClO}_4)_2$ upon UV light irradiation at 365 nm was also carefully performed. As shown in Figure 4 (curve d), a new oxidation peak at about 0.48 V for the solution of compound **4** after consecutive UV light irradiation and addition of $\text{Fe}(\text{ClO}_4)_2$ was recorded, which should be ascribed to the oxidation of $\text{MC}\cdot\text{Fe}^{2+}$ to $\text{MC}\cdot\text{Fe}^{3+}$, and the second oxidation peak at about 0.94 V was due to the oxidation of free SP (or MC) to SP^+ (or MC^+). Importantly, after coordination with MC, the oxidation potential of iron(II) was significantly reduced.¹⁸ The reduction of $\text{TTF}^{+\bullet}$ to neutral TTF occurred at about 0.66 V (see curve a in Figure 4). Thus, it is thermodynamically favorable for the electron-transfer reaction from $\text{MC}\cdot\text{Fe}^{2+}$ (as electron donor) to $\text{TTF}^{+\bullet}$ (as electron acceptor¹⁹). This important result is crucial to interpret the photocontrolled electron-transfer reaction between the TTF unit and ferric ion in the presence of the SP unit as shown in Scheme 3. For the solution containing $\text{TTF-MC}\cdot\text{Fe}^{3+}$, two oxidation potentials at 0.68 and 0.89 V were recorded from differential pulse voltammetric measurements, which were very close to those of dyad **1** and **2**, indicating that the TTF unit in $\text{TTF-MC}\cdot\text{Fe}^{3+}$ was in the neutral state. This result is in accordance with those of the spectral studies as discussed above.

The interesting behaviors of $\text{MC}\cdot\text{Fe}^{2+}$ and $\text{MC}\cdot\text{Fe}^{3+}$ may be qualitatively interpreted by considering the HOMO and LUMO orbitals. The phenoxide group of the MC form as a good electron-donating fragment may be involved in the formation of the coordination bonds. Compared with the energies of the frontier orbitals of the free Fe^{2+} and Fe^{3+} ions, the HOMO energy and LUMO energy of $\text{MC}\cdot\text{Fe}^{2+}$ and $\text{MC}\cdot\text{Fe}^{3+}$ will be increased, respectively, because of the coordination with MC form. Consequently, compared with the free Fe^{2+} , the oxidation potential for the reaction of $\text{MC}\cdot\text{Fe}^{2+}$ to $\text{MC}\cdot\text{Fe}^{3+}$ will be decreased. Similarly, the reduction potential for the reaction of $\text{MC}\cdot\text{Fe}^{3+}$ to $\text{MC}\cdot\text{Fe}^{2+}$ will also be decreased.

Mechanism Discussion. Based on the results of the above electrochemical studies, mechanisms for the conversion of dyad **1** to $\text{TTF-MC}\cdot\text{Fe}^{3+}$ after first UV light irradiation and addition of $\text{Fe}(\text{ClO}_4)_3$ (see Scheme 3) can be proposed as follows: (1)

UV light irradiation generated the TTF–MC dyad, followed by direct coordination of the MC unit with Fe^{3+} . Oxidation of the TTF unit did not take place, probably because after coordination with the MC form the oxidation potential of Fe^{3+} was largely reduced as discussed above. (2) Oxidation of the TTF unit by free Fe^{3+} ion and coordination of MC form with Fe^{3+} may occur simultaneously. Oxidation of the TTF unit would lead to the formation of $\text{TTF}^{+\bullet}$ and Fe^{2+} , which would be coordinated by the MC form, and consequently, the intermediate dyad $\text{TTF}^{+\bullet}\text{--MC}\cdot\text{Fe}^{2+}$ was generated. Further intramolecular electron transfer from $\text{MC}\cdot\text{Fe}^{2+}$ to $\text{TTF}^{+\bullet}$ led to the formation of $\text{TTF}\text{--MC}\cdot\text{Fe}^{3+}$.

The sequential reaction of dyad **1** with first Fe^{3+} and then UV light can be described as follows (see Scheme 3): oxidation of the TTF unit of dyad **1** led to $\text{TTF}^{+\bullet}\text{--SP}$. Because the absorption coefficient of dyad **1** ($\epsilon_{\text{SP}} = 10\,973\text{ cm}^2\cdot\text{L}^{-1}$) at 365 nm was much larger than those of Fe^{3+} ($\epsilon_{\text{Fe}^{3+}} = 497\text{ cm}^2\cdot\text{L}^{-1}$) and Fe^{2+} ions ($\epsilon_{\text{Fe}^{2+}} = 480\text{ cm}^2\cdot\text{L}^{-1}$), the presence of Fe^{3+} and Fe^{2+} ions in the solution was not able to block the photoisomerization of the SP unit to the MC unit. Accordingly, upon UV light irradiation $\text{TTF}^{+\bullet}\text{--SP}$ was transformed to $\text{TTF}^{+\bullet}\text{--MC}$, which would coordinate with Fe^{2+} to generate the intermediate dyad $\text{TTF}^{+\bullet}\text{--MC}\cdot\text{Fe}^{2+}$. The further intramolecular electron transfer between the $\text{TTF}^{+\bullet}$ and $\text{MC}\cdot\text{Fe}^{2+}$ units led to $\text{TTF}\text{--MC}\cdot\text{Fe}^{3+}$ as discussed above.

As mentioned above, if the solution of dyad **1** was first treated by excess $\text{Fe}(\text{ClO}_4)_3$, followed by UV light irradiation, the characteristic absorption band of $\text{TTF}^{+\bullet}$ could still be observed. This can be interpreted as follows: The MC unit in dyad $\text{TTF}^{+\bullet}\text{--MC}$ was first coordinated with iron(II) because iron(III) complexes are usually thermodynamically favored but are kinetically unstable. Consequently, electron transfer from $\text{MC}\cdot\text{Fe}^{2+}$ to $\text{TTF}^{+\bullet}$ took place, and then $\text{TTF}^{+\bullet}$ was reduced to neutral TTF, which can be oxidized back to $\text{TTF}^{+\bullet}$ by excess $\text{Fe}(\text{ClO}_4)_3$ quickly. As a result, $\text{TTF}^{+\bullet}\text{--MC}\cdot\text{Fe}^{3+}$ was formed at last. Another possible route was that iron(II) in the $\text{TTF}^{+\bullet}\text{--MC}\cdot\text{Fe}^{2+}$ unit was first replaced by iron(III) to form iron(III) complexes $\text{TTF}^{+\bullet}\text{--MC}\cdot\text{Fe}^{3+}$ because iron(III) is more strongly bonded than iron(II) before the electron-transfer reaction between $\text{MC}\cdot\text{Fe}^{2+}$ to $\text{TTF}^{+\bullet}$ took place. Thus, no matter which pathway took place, the ultimate state of dyad **1** was $\text{TTF}^{+\bullet}\text{--MC}\cdot\text{Fe}^{3+}$ under this condition.

Finally, it's interesting to note that the solution of $\text{MC}\cdot\text{Fe}^{3+}$ did not exhibit photochromism upon irradiation of visible light ($\lambda > 460\text{ nm}$) and even in the presence of $\text{Na}_2\text{S}_2\text{O}_3$, while $\text{MC}\cdot\text{Fe}^{2+}$ can be reversibly converted to SP and free Fe^{2+} upon irradiation with visible light. The solution of $\text{TTF}\text{--MC}\cdot\text{Fe}^{3+}$ and $\text{TTF}\text{--MC}\cdot\text{Fe}^{2+}$ showed the same behaviors. This means that $\text{MC}\cdot\text{Fe}^{3+}$ is more stable than $\text{MC}\cdot\text{Fe}^{2+}$. Such unique property of $\text{MC}\cdot\text{Fe}^{3+}$ makes the complete conversion of SP to $\text{MC}\cdot\text{Fe}^{3+}$ possible. It should be noted that only an equilibrium between SP and MC forms can be reached in the absence of ferric ion under the same conditions.

Conclusion

Spectral and electrochemical studies of a newly well-designed dyad containing an electroactive TTF unit and a photoactive spiropyran unit were presented. Compared with the free Fe^{2+} , its oxidation potential was largely reduced after it was coordinated to MC. Consequently, the electron-transfer reaction from $\text{MC}\cdot\text{Fe}^{2+}$ to $\text{TTF}^{+\bullet}$ can take place thermally. Owing to this peculiar property of $\text{MC}\cdot\text{Fe}^{2+}$, the electron-transfer reaction between the TTF unit and ferric ion can be photocontrolled in the presence of the photochromic SP unit. In other words, the

redox state of the TTF unit of dyad **1** in the presence of ferric ion was dependent on the photoswitching process of the SP unit, and thus dyad **1** provides a good example of photoregulation of the electron transfer between an electroactive unit and an oxidant in the presence of a photoactive unit. The present result shows the possibility to design new electron donor–acceptor supramolecules containing the spiropyran unit to regulate the electron-transfer reaction by light.

Experimental Section

General. Melting points were measured with an XT4-100X apparatus and uncorrected. ^1H NMR spectra were recorded with Bruker 300 MHz spectrometers. Infrared spectra were obtained on a Perkin-Elmer System 2000 FT-IR spectrometer. Mass spectra were determined with MALDI-TOF-MS. Elemental analysis was performed on Carlo-Erba-1106 instrument. Absorption spectra were measured with Hitachi (model U-3010) UV–vis spectrophotometer. Fluorescence measurements were carried out with a Hitachi (model F-4500) spectrophotometer in a 1-cm quartz cell. Differential pulse voltammetric experiments were performed on an EGDG PAR 370 system at a scan rate of 100 mV in THF using Bu_4NPF_6 as electrolyte, platinum as counter and work electrodes, and SCE as reference electrode.

THF was dried over sodium/benzophenone before use. DMF was predried by standing over molecular sieves (4 Å) for at least 3 days before use. All other reagents and solvents (standard grade) were used as received unless otherwise stated.

For the ultraviolet light irradiation experiments, a 140 W high-pressure mercury lamp at 365 nm was used.

Compounds **2**, **3**, HO–SP, and **4** (see Scheme 2) were synthesized on the basis of the reported procedures.^{8b,13b}

Dyad 1. To a solution of HO–SP (0.19 g, 0.56 mmol) in DMF (20 mL) was added compound **3** (0.20 g, 0.28 mmol) and anhydrous K_2CO_3 (0.81 g, 5.90 mmol). Then the mixture was stirred at room temperature for 2 days before 150 mL of H_2O was added. The aqueous solution was extracted with dichloromethane ($3 \times 70\text{ mL}$), and the combined extracts were washed with H_2O ($2 \times 40\text{ mL}$) and saturated aqueous NaCl (20 mL), dried (MgSO_4), and concentrated in vacuo. After column chromatography on silica gel with dichloromethane/petroleum ether (60–90 °C, 1:2 v/v) as eluant, dyad **1** was obtained as an orange oil in 73% yield. ^1H NMR (CDCl_3) δ 0.88 (6 H, t, $J = 6.8\text{ Hz}$, 2CH_3), 1.19 (3 H, s, CH_3), 1.37 (29 H, br, $13\text{CH}_2\text{--CH}_3$), 1.61 (8 H, m, 4CH_2), 1.76 (2 H, m, CH_2), 2.68 (3 H, s, CH_3), 2.77 (6 H, m, 3SCH_2), 3.91 (2 H, t, $J = 6.5\text{ Hz}$, CH_2O), 5.83 (1 H, d, $J = 10\text{ Hz}$, CH), 6.30 (1 H, s, olefinic), 6.45 (1 H, d, $J = 9\text{ Hz}$, Ar–H), 6.74 (3 H, m, Ar–H), 6.89 (1 H, d, $J = 10\text{ Hz}$, CH), 7.99 (2 H, m, Ar–H). MALDI-TOF m/z 972.5; FT-IR(KBr) 2925 and 2853 (alkyl C–H), 1473 and 1337 (NO_2); Anal. Calcd for $\text{C}_{49}\text{H}_{68}\text{N}_2\text{O}_4\text{S}_7$: H, 7.04; C, 60.46; N, 2.88. Found: H, 6.98; C, 60.29; N, 2.73.

Acknowledgment. The present research was financially supported by NSFC (Grant 90101025), Chinese Academy of Sciences, and State Key Basic Research Program. D.-Q. Zhang thanks National Science Fund for Distinguished Young Scholars.

Supporting Information Available: Electronic absorption spectra of **2**, **2**⁺, **4**, and **4**⁺. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860. (b) De Vault, D.; Chance, B. *Biophys. J.* **1966**, *6*, 825. (c) Armitage, B. *Chem. Res.* **1998**,

- 98, 1171. (d) Schuster, G. B. *Acc. Chem. Res.* **2000**, *33*, 253. (e) Fukuzumi, S.; Okamoto, K.; Imahori, H. *Angew. Chem., Int. Ed.* **2002**, *41*, 620. (f) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369. (g) Tollin, G. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 4, pp 202–231.
- (2) For reviews, see: (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim, Germany, **1995**. (b) Otsuki, J. *Recent Res. Dev. Pure Appl. Chem.* **1998**, *2*, 427. (c) De Cola, L.; Belser, P. *Coord. Chem. Rev.* **1998**, *177*, 301. (d) Barigelli, F.; Flamigni, L. *Chem. Soc. Rev.* **2000**, *29*, 1. (e) Joachim, C.; Gimzewski, J. K.; Aviram, A. *Nature* **2000**, *408*, 541. (f) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. (g) Ward, M. D. *Chem. Ind.* **1997**, *18*, 640. (h) De Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515.
- (3) (a) Liu, Z. F.; Hashimoto, K.; Fujishima, A. *Nature* **1990**, *347*, 658. (b) Tsuchiya, S. *J. Am. Chem. Soc.* **1999**, *121*, 48. (c) Endtner, J. M.; Effenberger, F.; Hartschuh, A.; Port, H.; *J. Am. Chem. Soc.* **2000**, *122*, 3037. (d) Myles, A. J.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 177. (e) Liddell, P. A.; Kodis, G.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2002**, *124*, 7668. (f) Malval, J.-P.; Gosse, I.; Morand, J.-P.; Lapouyade, R. *J. Am. Chem. Soc.* **2002**, *124*, 904.
- (4) (a) Kurihara, M.; Hirooka, A.; Kume, S.; Sugimoto, M.; Nishihara, H. *J. Am. Chem. Soc.* **2002**, *124*, 8800. (b) Otsuki, J.; Tsujino, M.; Iizaki, T.; Araki, K.; Seno, M.; Takatera, K.; Watanabe, T. *J. Am. Chem. Soc.* **1997**, *119*, 7895. (c) Akasaka, T.; Otsuki, J.; Araki, K. *Chem.—Eur. J.* **2002**, *8*, 130. (d) Murata, M.; Yamada, M.; Fujita, T.; Kojima, K.; Kurihara, M.; Kubo, K.; Kobayashi, Y.; Nishihara, H. *J. Am. Chem. Soc.* **2001**, *123*, 12903. (e) Kurihara, M.; Matsuda, T.; Hirooka, A.; Yutaka, T.; Nishihara, H. *J. Am. Chem. Soc.* **2000**, *122*, 12373. (f) Kurihara, M.; Sano, H.; Murata, M.; Nishihara, H. *Inorg. Chem.* **2001**, *40*, 4.
- (5) (a) Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, *100*, 1741. (b) Kawata, S.; Kawata, Y.; *Chem. Rev.* **2000**, *100*, 1777. (c) Collins, G. E.; Choi, L.-S.; Ewing, K. J.; Michelet, V.; Bowen, C. M.; Winkler, J. D. *Chem. Commun.* **1999**, 321. (d) Inoue, M.; Akamatsu, K.; Nakazumi, H. *J. Am. Chem. Soc.* **1997**, *119*, 9160. (e) Dvornikov, A. S.; Malkin, J.; Rentzepis, P. M. *J. Phys. Chem.* **1994**, *98*, 6746. (f) Raymo, F. M. *Adv. Mater.* **2002**, *14*, 401. (g) Shipway, A. N.; Willner, I. *Acc. Chem. Res.* **2001**, *34*, 421. (h) Wojtyk, J. T. C.; Kazmaier, P. M.; Buncel, E. *Chem. Commun.* **1998**, 1703. (i) Wojtyk, J. T. C.; Kazmaier, P. M.; Buncel, E. *Chem. Mater.* **2001**, *13*, 2547. (j) Wojtyk, J. T. C.; Wasey, A.; Kazmaier, P. M.; Hoz, S.; Buncel, E. *J. Phys. Chem. A* **2000**, *104*, 9046.
- (6) (a) Raymo, F. M.; Giorgani, S. *J. Am. Chem. Soc.* **2001**, *123*, 4651. (b) Raymo, F. M.; Giorgani, S. *J. Am. Chem. Soc.* **2002**, *124*, 2004. (c) Raymo, F. M.; Giorgani, S. *Org. Lett.* **2001**, *3*, 1833. (d) Raymo, F. M.; Giorgani, S. *Org. Lett.* **2001**, *3*, 3475. (e) Raymo, F. M.; Giordani, S. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4941. (f) Raymo, F. M.; Alvarado, R. J.; Giordani, S.; Cejas, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 2361.
- (7) Bahr, J. L.; Kodis, G.; de la Garza, L.; Lin, S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2001**, *123*, 7124.
- (8) (a) Guo, X.; Zhang, D.; Wang, T.; Zhu, D. *Chem. Commun.* **2003**, 914. (b) Guo, X.; Zhang, D.; Zhou, Y.; Zhu, D. *J. Org. Chem.* **2003**, *68*, 5681. (c) Guo, X.; Zhang, D.; Zhou, Y.; Zhu, D. *Chem. Phys. Lett.* **2003**, *375*, 484.
- (9) (a) Zhi, J.-F.; Baba, R.; Hashimoto, K.; Fujishima, A. *Chem. Lett.* **1994**, 1994, 1521. (b) Zhi, J.-F.; Baba, R.; Hashimoto, K.; Fujishima, A. *J. Photochem. Photobiol., A* **1995**, *92*, 91.
- (10) See, for example: Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carson, K. D.; Geiser, U.; Wang, H. H. A.; Kini, M.; Whangbo, M. H. *Organic Superconductors (Including Fullerenes) Synthesis, Structure, Properties, and Theory*; Prentice Hall: Englewood Cliffs, NJ, 1992; pp 11–64.
- (11) (a) Collier, P. C.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172. (b) Eppesen, J. J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1216. (c) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Hamers, C.; Mattersteig, G.; Montalti, M.; Shipway, A. N.; Spencer, N.; Stoddart, J. F.; Tolley, M. S.; Venturi, M.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 333. (d) Segura, J. L.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372.
- (12) (a) Spanggaard, H.; Prehn, J.; Nielsen, M. B.; Levillain, E.; Allain, M.; Becher, J. *J. Am. Chem. Soc.* **2000**, *122*, 9486. (b) Asakawa, M.; Higuchi, M.; Mattersteig, G.; Nakamura, T.; Pease, A. R.; Raymo, F. M.; Shimizu, T.; Stoddart, J. F. *Adv. Mater.* **2000**, *12*, 1099.
- (13) (a) Jia, C.; Zhang, D.; Xu, W.; Zhu, D. *Org. Lett.* **2001**, *3*, 1941. (b) Guo, X.; Zhang, D.; Zhang, H.; Xu, W.; Ai, X.; Fan, Q.; Fan, L.; Zhu, D. *Tetrahedron* **59**, 4843. (c) Jia, C.; Zhang, D.; Guo, X.; Wan, S.; Xu, W.; Zhu, D. *Synthesis* **2002**, 2177.
- (14) Simonsen, K. B.; Svenstrup, N.; Lau, J.; Simonsen, O.; Mork, P.; Kristensen, G. J.; Becher, J. *Synthesis* **1995**, 407.
- (15) Shragiha, L.; Buchholtz, F.; Ytzechaik, S.; Krongauz, V. *Liq. Cryst.* **1990**, *7*, 643.
- (16) All of the solutions were irradiated with a 140 W high-pressure mercury lamp ($\lambda = 365$ nm) for 5 min.
- (17) Addition of ferric ion to the solution of reference compound **2** led to emergence of a new absorption band ($\lambda_{\text{max}} = 610$ nm), while for the reference compound **4**, a broad absorption band with $\lambda_{\text{max}} = 480$ nm was observed under the same conditions (see Supporting Information).
- (18) The oxidation potential of Fe^{2+} to Fe^{3+} was observed at 0.97 V under the same conditions with SCE as the reference electrode.
- (19) Ashton, P. R.; Balzani, V.; Becher, J.; Credi, A.; Fyfe, M. C. T.; Mattersteig, G.; Menzer, S.; Nielsen, M. B.; Raymo, F. M.; Stoddart, J. F.; Venturi, M.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 3951.