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EXCERPT OF DISSERTATION

Minireview: molecular level devices based on electroactive tetrathiafulvalene and photochromic spiropyran

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Abstract　This Minireview details the design, development, and demonstration of chemical strategies that are used to create molecular level devices and implement digital processing and communication. The design principle here is to integrate two informationally rich but relatively simple nanobuilding blocks with their complements through photoinduced electron transfer, redox processes, conformational changes, photoinduced energy and proton transfer, and supramolecular events into functional molecular devices. Depending on the abundant electrochemical properties of TTF, lots of D-A-D supramolecules and [2]rotaxanes with the different linkages were synthesized for studying photoinduced transient electron transfer and nanorecording abilities. Also detailed below are the methods to take advantage of the distinct abilities of electron, energy, and proton transfer of photochromic spiropyran to design supramolecular ensembles and control their absorption, fluorescence, and conductive properties by light and chemical reagents. Based on the spectral and electrochemical behaviors of these ensembles, a whole bunch of novel molecular switches, logic gates, and molecular circuits were constructed. At last, we present an interesting insight into designing a new type of luminescent spiropyan molecules with stable merocyanine open form in solution as well as in the solid state.

Key words　molecular devices, tetrathiafulvalene, spiropyran, logic circuit

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1　Introduction

Motivated by the intrinsic physical and economic limitations of semiconductor devices,[1,2] one of the major themes in the 21th century research is the miniaturization of conventional silicon-based devices down to the molecular

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scale, which led to the emergence of a new research field, often termed "molecular electronics". Actually, miniaturization of optoelectronic devices has been an essential ingredient in the outstanding progress of information technology over the past fifty years. Transistors, for example, are scaled down at an exponential rate and the feature size is presently 65 nm and the gate length of FETs at this node is 32nm, which is well within the "nano" range.[1~3] The next limit of miniaturization is that of molecules, which are the smallest entities with definite size, shape, and properties. Recent years have witnessed the significant improvements in molecular electronics, exemplified by the comprehensive set of proof-of-concept experiments.[4~9] Despite these remarkable examples, however, this research area is still at an exploratory stage. In this area the big challenge is still the construction, measurements, and understanding of the optical or electronic responses of the circuits in which molecular systems play an important role as pivotal elements.

The essential requirement for telecommunication and internet applications demands the continuous enhancement of the transmission capacity and speed of communication networks.[10] Unfortunately, the interplay between optical and electrical signals is a major "bottleneck" to the development of optical networks.[11,12] The possible solution to this problem is to eliminate the electronic portion of these hybrid devices and to route the traveling optical signals with optical, rather than electrical, stimulations.[13~15] To do this, materials that would permit the manipulation of electrical and optical signals with alternative operating principles must be developed. Organic molecules with complementary functions are promising candidates for the realization of electronic and photonic devices in the future. Their attractive features are the miniaturized dimensions and the high degree of control on molecular design possible in chemical synthesis. Efficient and reliable mechanisms to store, elaborate, and communicate signals with functional molecules can be developed principally and experimentally at the molecular level.

This Minireview illustrates the recent progresses in our lab in the past few years and highlights the chemical strategies that we have developed to implement digital processing and communication.[16~21] The key portion here is to integrate two informationally rich but relatively simple nanobuilding blocks with their complements through photoinduced electron transfer, redox processes, conformational changes, photoinduced energy and proton transfer, and supramolecular events for the purpose of creating functional molecular devices. Electro-active tetrathiafulvalene (TTF) was utilized to synthesize a series of D-A-D supramolecules and rotaxanes with the saliently different linking groups. Time-resolved absorption/fluorescence spectra indicate the correlation of the life-time of the charge separated states of D-A-D with the linkages while STM investigations of rotaxane thin films show the new phenomenon of conformation-related reversible, stable nanorecording for future high-density information storage. Photochromic molecule, spiropyran (SP), was used to modulate the absorption, fluorescence, and conductive properties of its supramolecular ensembles by light and suitable chemical reagents. Based on the spectral and electrochemical behaviors of these molecules, a series of new molecular switches, logic gates, and molecular circuits were constructed through photoinduced electron, energy and proton transfer reactions. In addition, the structure and properties of a new type of fluorescent spiropyran molecule were presented in the end.

2 TTF-based molecular level devices

Tetrathiafulvalene (TTF) and its derivatives have been extensively investigated as components of organic conductors and superconductors.[22] Meanwhile, on account of their reversible redox properties, TTF derivatives have also been used to construct supramolecules for studies of molecule-based devices, especially in recent years.[23~28] Many electron donor-acceptor supramolecules with TTF units have been prepared for studies related to intramolecular photoinduced electron transfer processes, intramolecular charge-transfer interactions and construction of molecular rectifiers.[29] In my dissertation we have conducted two types of work as described below.

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2.1 D-A-D triads

We have synthesized a series of D-A-D triads with tetrathiafulvalene (TTF) units as electron donors and naphthyldiimide (NIm) or perylenetetracarboxylic diimide (PIm) as electron acceptors (TTF-(sp)-NIm/PIm-(sp)-TTFs), [30~33] Intramolecular photoinduced charge-separation and charge-recombination processes of these supramolecules have been investigated by time-resolved absorption and fluorescence techniques. For example, [32] the fluorescence lifetimes of the NIm moiety in TTF-(sp)-NIm-(sp)-TTFs considerably decreased compared with that of the NIm molecule, suggesting the photoinduced intramolecular charge separation via the singlet excited state of the NIm moiety. Based on the charge-separation rate constants (k_{CS}) and quantum yields (Φ_{CS}) of TTF-(sp)-NIm-(sp)-TTF from the observed short fluorescence lifetimes, the k_{CS} values for the triads with the rigid cyclohexyl spacers are larger than that with long flexible alkyl chain spacers. In the nanosecond transient spectra in PhCN, the absorption bands were observed at 480nm and 760nm, which were attributed to the radical anion of NIm suggesting the formation of TTF$^{\cdot+}$-(sp)-NIm$^{\cdot-}$-(sp)-TTF. From the decays of the radical ion-pair, the charge-recombination rate-constants (k_{CR}) were evaluated in the range of $9 \times 10^5 \sim 3 \times 10^7\ s^{-1}$. Longer lifetimes of the radical ion-pair were observed for the triads with the cyclohexyl spacer than that of the long flexible spacer. From the temperature dependence of the k_{CR} values, the reorganization energies and coupling constants were experimentally evaluated in PhCN; small coupling constants of the triads with the cyclohexyl spacers than that of the long flexible spacers support the relatively long lifetimes of the charge separated states of the chyclohexyl spacer. Figure 1 indicates the optimized molecular structures and suggested energy diagram of TTF-(sp)-NIm-(sp)-TTF with the chyclohexyl spacer in PhCN. These data show the strong evidence of the dependence of intramolecular photoinduced electron transfer on the different linkage spacers, thus providing the scientific foundation of fabricating ultrafast picosecond molecular switches.

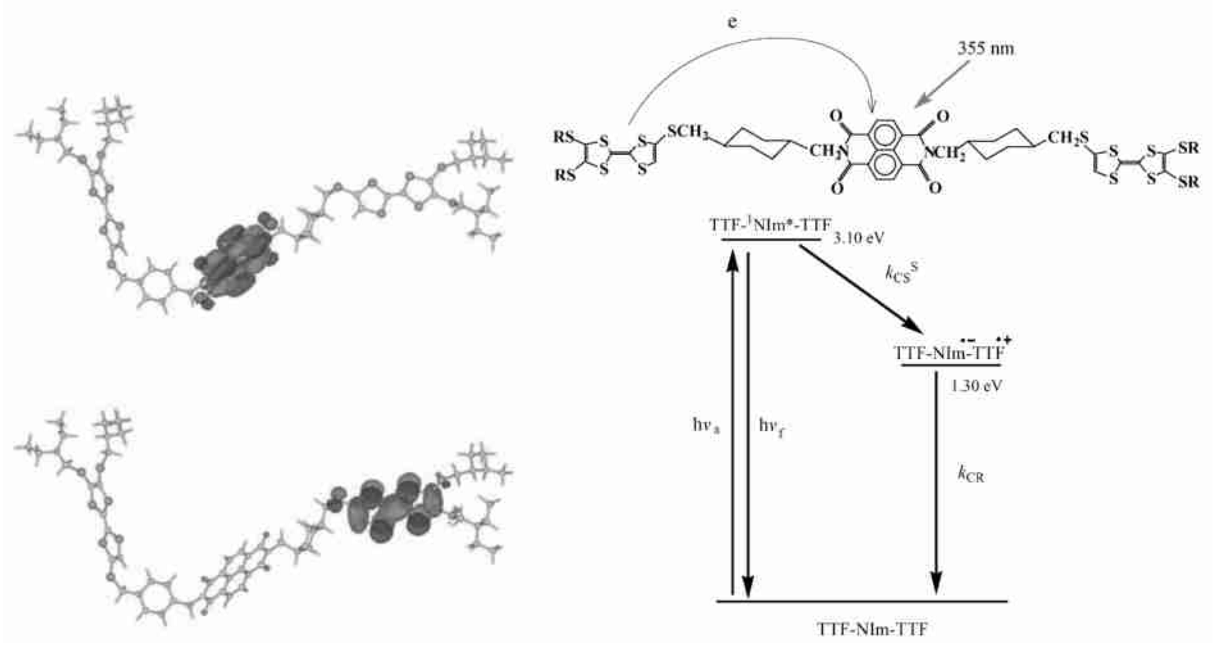

Fig. 1 Optimized molecular structures and energy diagram of triads in PhCN

As to TTF-(sp)-PIm-(sp)-TTFs, [33] UV/vis spectroscopic and cyclic voltammetric results indicate that they all show negligible intramolecular charge transfer interaction in their ground states. Similar to TTF-(sp)-NIm-(sp)-TTFs, these triads display reduced fluorescence and their fluorescence lifetimes suggesting the photoinduced electron

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transfer interactions between the PIm units and TTF units, and the dependence of intramolecular photoinduced electron transfer due to their difference in the spatial separation of TTF and PIm units. It is also preliminarily found that the steric hindrance of the groups attached to TTF units can improve their photostability.

2.2 TTF-based rotaxanes

Rotaxane is a family of interlocked molecules with one or more rings encircling a dumbbell-shaped component. As prime candidates for the construction of artificial molecular machines, rotaxanes have become the subject of intense investigations. The [2]rotaxanes, which contain tetrathiafulvalene (TTF) and 1,5-dioxynaphthalene (DNP) as the two recognition stations and cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) as the cyclic moiety, have been comprehensively investigated by Stoddart and coworkers.[34,35] It is anticipated that structural modification of the TTF moiety would change its electron-donating ability and accordingly the interaction between TTF and $CBPQT^{4+}$ would be affected. Thus, we intended to prepare switchable [2]rotaxanes with new TTF derivatives. In this context, we reported two new TTF-DNP-$CBPQT^{4+}$ [2]rotaxanes with cyclohexyl and alkyl chains as the spacers.[36] In these two [2]rotaxanes, the TTF moiety is the 4,4′(5′)-dialkylthiotetrathiafulvalene that is rather easily accessible based on the synthetic procedure developed by us previously,[26,27] and two different spacers are used: cyclohexyl and alkyl chains (H1 and H2 in Fig. 2). The two stopper units are G2-dendritic moieties. It was found that the $CBPQT^{4+}$ can be switched between the TTF and DNP stations of [2]rotaxanes in solution upon oxidation and reduction and stable monolayers of [2]rotaxanes can be formed at the air-water interface. Then the corresponding multilayer LB films can be fabricated with the normal LB technique. Conducting atomic force microscopy, scanning tunneling microscopy, and two-terminal junction device studies indicated that the LB films of [2]rotaxanes showed electrical bistability behavior resulting from the distinct conformational states. By comparing with the TTF-DNP-$CBPQT^{4+}$ [2]rotaxanes reported by Stoddart, *et al*. previously,[34,35] the present results imply that proper modification of the chemical structures of the TTF unit and the spacer have negligible effect on the electrical bistability behavior of these TTF-DNP-$CBPQT^{4+}$ [2]rotaxanes. These findings will allow for the design and preparation of new multifunctional TTF-DNP-$CBPQT^{4+}$ [2]rotaxanes in the future.

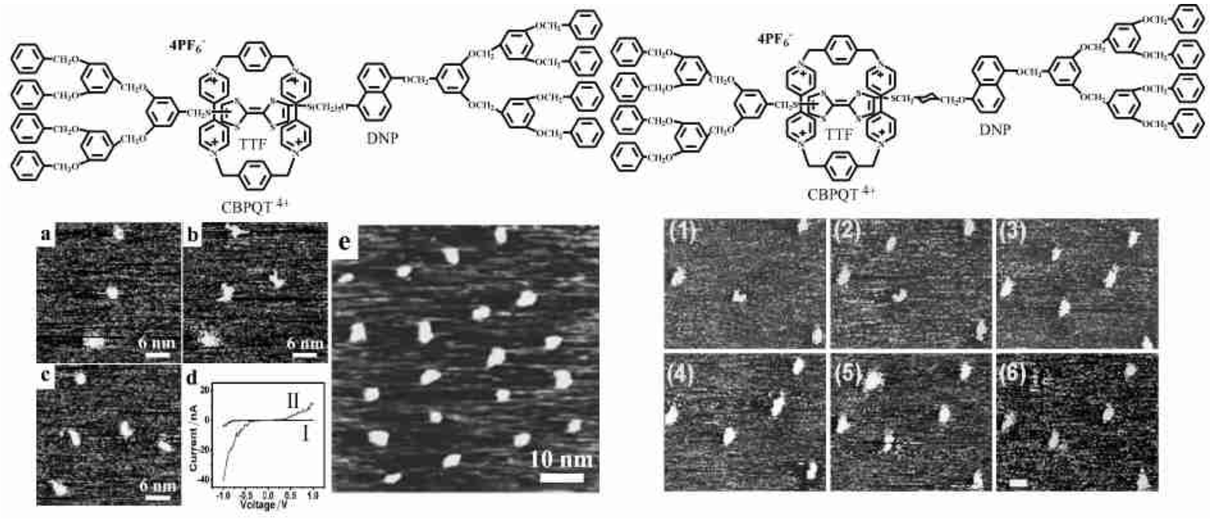

Fig. 2 Molecular structures of H1 (left) and H2 (right) and the corresponding STM images of the recording dots written on their thin films the detailed experiments can be found in the references[37～39]

More interestingly, our preliminary STM experiments[37] demonstrated that the thin films based on H1 molecule with the flexible spacer indicated the stable, reproducible nanorecording (Fig. 2). The thin films exhibited a reversible conductance switching and nonvolatile memory effect with an on/off ratio of about 100. These results show

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for the first time that a rotaxane thin film may be a promising candidate for application in nanorecording. Furthermore, our detailed STM experiments[38,39] clearly showed the erasable and rewritable nanorecording behaviors in thin films of H2 with the rigid spacer as a result of the reversible conductance transition in the H2 rotaxane molecules (Fig. 2). We suggested that the difference of their electrical behaviors between H1 and H2 in thin films resulted from the flexibility of the different spacers. The cyclohexyl chain is relatively rigid compared to the alkyl group. Consequently, the intermolecular interaction of H2 molecules will not be as strong as that in H1 molecules, making the $CBPQT^{4+}$ ring move back and forth possible. This work indicates the potential for the chemical modification of the rotaxane molecules as a promising route toward molecular memories, which have stable electrical properties and a long lifetime suitable for practical applications.

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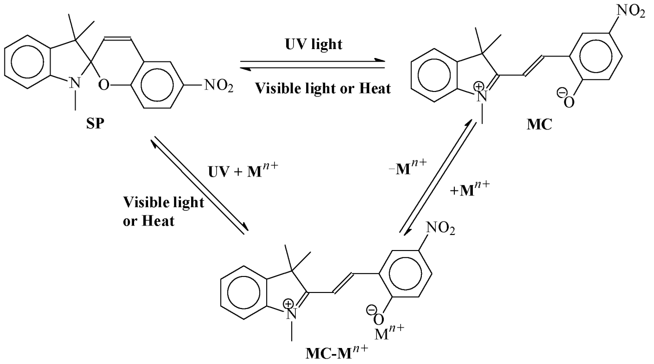
3 SP-based molecular level devices

As one of the most promising families of photochromic compounds, spiropyran molecules (SP) have been extensively investigated, mainly due to their potential application in the area of molecular sensors, switches, and information processors. Uniquely, spiropyran can undergo reversible structural transformation among the three states as shown in Scheme 1, accompanying the significant changes of the characteristic photochemical and photophysical properties, in response to external inputs such as light, proton, and metal ions[40～44]. By taking advantage of these properties of spiropyran, molecular systems with spiropyran have been configured to mimic the functions of several integrated logic gates, and moreover, communication networks have been proposed in recent years[45,46]. In this context, we are going to tell you our own recent progresses and the chemical strategies that we have developed to create molecular switches, molecular sensors, and integrated logic gates through photoinduced electron, energy, and proton transfer mechanisms.



Scheme 1 Illustrations of the reversible structural transformations of nitrospiropyran (SP) in response to light, heat, proton and metal ions

3.1 Electron transfer

First of all, we would like to introduce our first observation of a new phenomenon of photocontrollable electron transfer reaction in a donor-acceptor (D-A) dyad. Then we will move to show our interesting results of further applications based on this finding for creating the integrated molecular logic gates. This discovery and the new strategies for concatenation of complementary molecular components 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.

3.1.1 Discovery of a new phenomenon

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 spiropyan and the corresponding open form (MC) are weak electron donors and they have similar oxidation potentials. 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[47,48]. Therefore, if the metal ions such as the ferric and the

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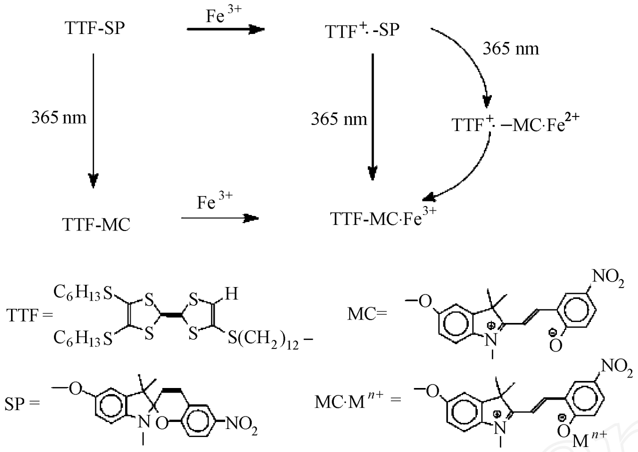

Fig. 3 Transformation of dyad TTF-SP under the action of UV light and ferric ion

ferrous ions, which show redox behaviors, are used, it seems possible to alter their redox potentials by light in the presence of photochromic spiropyran. Keeping this idea in mind, a new dyad containing an electroactive unit (tetrathiafulvalene, TTF) and a photochromic unit (spiropyran, SP) has been synthesized (Fig. 3).[49] Spectral studies showed that the redox states of the TTF unit of dyad 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·Fe^{2+} to TTF$^{+\cdot}$, which act as electron donor and acceptor, respectively, is thermodynamically favorable (Fig. 3). 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 in the applications of molecular electronics.

3.1.2 Intramolecular electron transfer

The first application is to introduce photochromic spiropyrans (SP) into perylene diimide dye system (PI), because of its excellent electron-accepting ability as well as their excellent stability, high molar extinction coefficient and fluorescence quantum yield,[50,51] for the purpose of regulating the photoinduced intramolecular electron transfer (PET) processes with multiple external stimulations.[52] The absorption spectrum of dyad 1 (Fig. 4) indicated that the absorption bands are obviously red-shifted by 21nm and 18nm respectively, compared to those of the reference at λ_{max} = 529nm and 494nm. Also, the electrochemical experiments showed that the first reduction potential was significantly reduced and no distinct oxidation potential was observed for dyad 1. These results consistently suggest

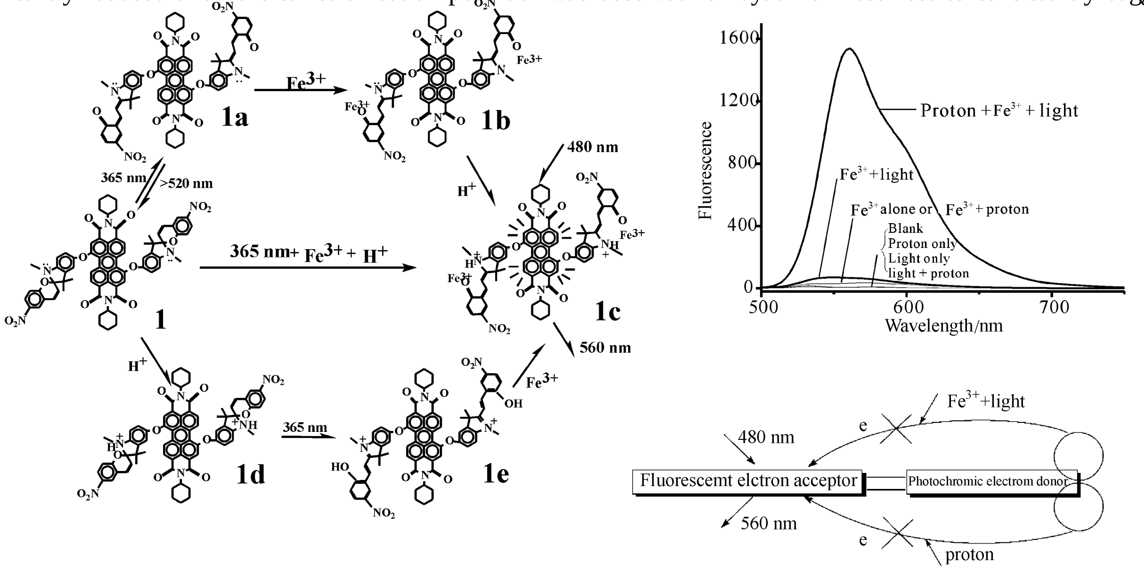

Fig. 4 The mechanism and strategy demonstration and the fluorescence spectrum of logic control of the fluorescence of dyad 1

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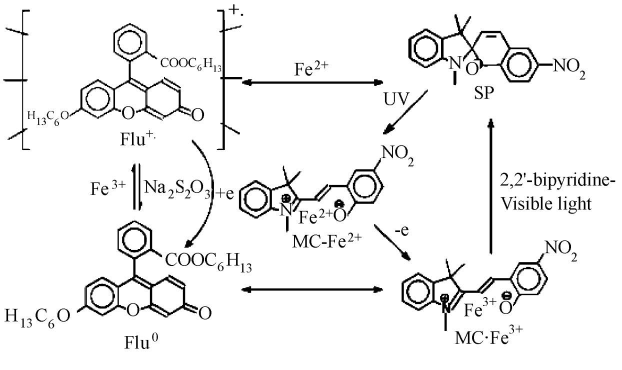
that the PI and SP units in dyad 1 are strongly coupled in the ground state probably due to their intimacy only through one oxygen atom bridge. As a result, the fluorescence of PI unit is completely quenched.

However, we found that the cooperative actions of UV light and ferric ion can decouple the strong electronic interaction between PI unit and SP units in the ground state, as indicated by the hypsochromical shifts of PI unit due to the formation of ME·Fe^{3+} complex units. Further protonation of the *N*-methyl indole moiety of SP units can turn off the PET processes from SP units to PI unit. Consequently, the fluorescence of PI unit can be restored (Fig. 4). Detailed experiments showed that simultaneous or consecutive operations of one or two of these three inputs (UV light, ferric ion and proton) could shut off either of the ways, but not both. Therefore, it is not unexpected that the fluorescence of PI unit of dyad 1 can be significantly enhanced only with the cooperative action of UV light, ferric ion and proton (Fig. 4). These behaviors of dyad 1 can be interpreted by a novel three-input "AND" logic gate. The fluorescence spectrum and working mechanism are illustrated in Fig. 4.

3.1.3 Intermolecular electron transfer

Besides intramolecular electron transfer, intermolecular electron transfer is another important pathway to concatenate the environmental events for information communication in nature. In the research, it is also an important method to build the complex communicating network through the concatenation between independent components. For example,[53] we demonstrated the first example of a substantial fluorescence change between two communicating molecular switches via a reversible redox reaction. What is essential to understanding this communication strategyis the low oxidation potential of complex MC·Fe^{2+}, which makes the electron transfer from MC·Fe^{2+} to $Flu^{+\cdot}$ thermodynamically favorable. Firstly, we showed a novel reversible redox fluorescence switch based on fluorescein through oxidation by Fe^{3+} and reduction by $Na_2S_2O_3$. Secondly, by taking advantage of intermolecular electron transfer from MC·Fe^{2+} to $Flu^{+\cdot}$, we demonstrated the reversible fluorescence modulation of the ensemble of the fluorescence switch fluorescein and the photochromic switch SP via the reversible Fe(Ⅱ)/Fe(Ⅲ) redox couple as shown in Scheme 2. The communicating behavior of this ensemble corresponds well to the function of an INHIBIT logic gate.



Scheme 2 Transformation patterns of the communicating ensemble of two molecular switches

We also found[54] that the fluorescence of pyrene in THF was significantly quenched in the presence of photochromic spiropyran, mainly due to intermolecular photoinduced electron transfer. However, the fluorescence of the ensemble solution restored nearly to the initial value of the original solution of PY after the consecutive operations of external inputs ($Fe(ClO_4)_3$ and UV light). Such photo-controlled PET reaction is due to the formation of MC·Fe^{3+} complex, leading to the modulation of electron-donating ability of SP. It is believed that such photo-controlled PET process will find applications in the construction of molecular-based devices for information communication and memory.

3.1.4 Monomolecular half-adder

One of the great challenges in molecule-based devices is to fabricate highly complex integrated circuits at the molecular level. Therefore, integration of relatively simple logic gates into high-level circuits (e.g., half-adder) is highly important not only for the potential application in molecular level devices but also for the understanding of complex mechanisms of some important biological processes. In this regard, we demonstrate[55] for the first time a novel kind of theoretical "monomolecular" half-adder based on multistate/multifunctional photochromic spiropyrans.

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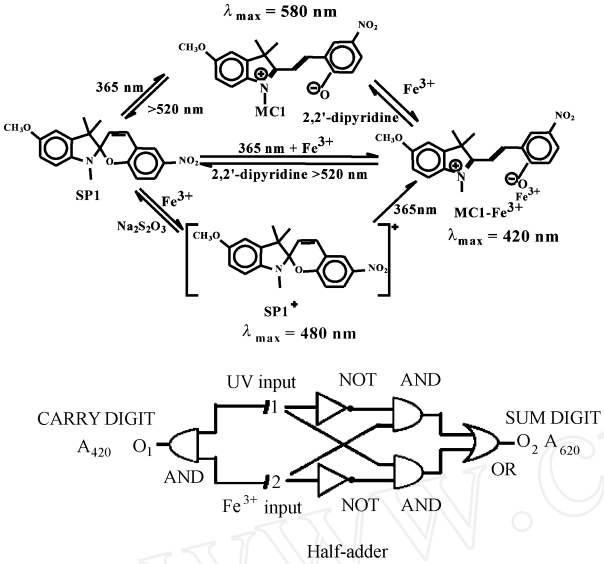


Fig. 5 Intrinsic interconversion network of the four states of SP1 and the corresponding physical electronic symbols of the 2-input logic half-adder circuit

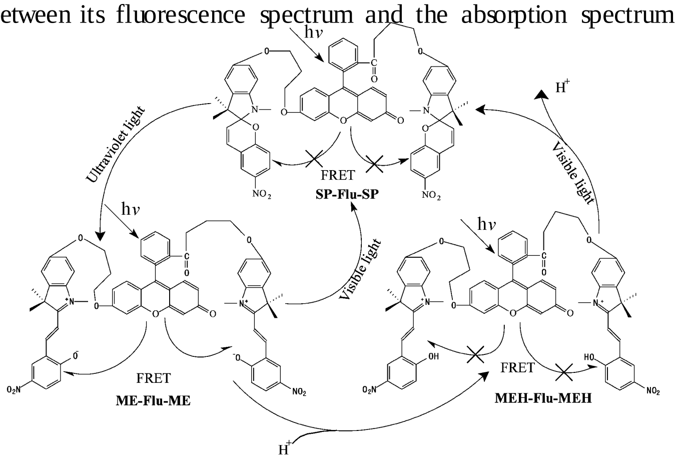
Spiropyran molecule (SP1) can be transformed to MC1, $\mathrm{MC1}\cdot\mathrm{Fe}^{3+}$ and $\mathrm{SP1}^{+\cdot}$ (Fig. 5), each of which shows a characteristic absorption spectrum, under the appropriate actions of I1 (UV light) and I2 (ferric ion). The intrinsic network of the transformations among the four states (SP1, MC1, $\mathrm{MC1}\cdot\mathrm{Fe}^{3+}$, and $\mathrm{SP1}^{+\cdot}$) reveals the distinct and interesting properties. The behaviors of the absorption changes at 420nm and 520nm correspond to those of an "AND" gate and an "XOR" gate, respectively. Since the absorption changes at both 420nm and 520nm are based on the entity of a single molecule of spiropyran (e.g., SP1) and under the same external inputs, the AND and XOR gates can be "operated" in parallel. Therefore, the absorption spectral variations of the solution of spiropyran in response to UV light irradiation and ferric ion mimic the function of a "half-adder" that can perform simple arithmetic addition (Fig. 5).

3.2 Energy transfer

As shown in Scheme 1, photochromic spiropyran can undergo reversible structural transformation among the three states, accompanying the significant changes of the characteristic photochemical and photophysical properties upon exposure to external inputs such as light, proton, and metal ions. The three states of spiropyran SP, MC, and MCH show different absorption spectra, and thus it is possible to regulate the fluorescence intensity of a suitable fluorophore by irradiation of the solution containing both spiropyran and the fluorescent molecule through fluorescence resonance energy transfer (FRET). Indeed, Raymo and Moore, *et. al*. studied the "signal communication" between aromatics or porphyrin and spiropyran, and proposed the corresponding integrated logic gates and communication network.[44～46, 56]

3.2.1 Intramolecular energy transfer

We notice that fluorescein (Flu) shows the emission in the range of 500～650nm, and hence the big overlap between its fluorescence spectrum and the absorption spectrum of MC. There is almost no overlap between the fluorescence spectrum of fluorescein and the absorption spectra of SP and MCH. One remarkable feature here is that fluorescein shows strong absorption around 430nm, at which SP, MC, and MCH have very weak absorption. Thus, excitation of fluorescein at 430nm will perturb none of the three states of spiropyran (SP, ME, and MEH). With these thoughts in mind, a new dyad SP-Flu-SP[57] with two spiropyran units as the photochromic acceptors and one fluorescein unit as the fluorescent donor was synthesized and characterized (Scheme 3). External inputs (ultraviolet light, visible light, and proton)



Scheme 3 The reversible switching cycle for SP-Flu-SP under the action of three external inputs: UV light, visible light and proton

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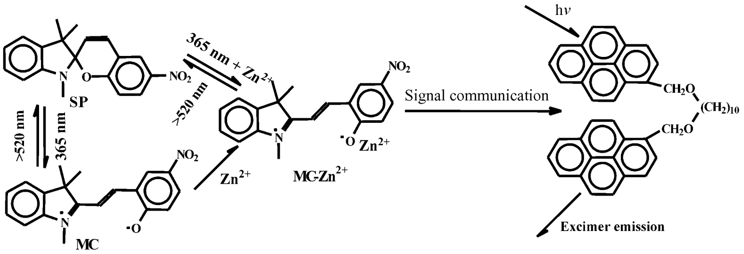
induce the reversible changes of the structure and , concomitantly , the absorption spectrum of SP-Flu-SP due to the presence of two spiropyran units. Only the absorption spectrum of the MC form of the spiropyran units in this dyad has large spectral overlap with the fluorescence spectrum of the fluorescein unit. Thus , the fluorescence intensity of this dyad is modulated by reversible conversion among the three states of the photochromic spiropyran units and the intramolecular fluorescence resonance energy transfer (FRET) between the MC form and the fluorescein unit (Scheme 3) . Based on the fact that SP-Flu-SP could "read out" three external input signals (ultraviolet light , visible light and proton) and "write" a compatible specific output signal (fluorescence intensity) , this molecule described here can be considered to perform an integrated circuit function with one OR and one AND interconnected logic gates. These results demonstrate an efficient strategy for elaborating and transmitting information at the single molecular level.

3.2.2 Intermolecular Energy transfer

To our best knowledge , there is no report about reversible regulation of pyrene excimer fluorescence through energy transfer due to the lack of the suitable chromophores as the energy acceptors. Although there is no obvious spectral overlap between the excimer emission band of pyrene and the absorption band of MC , however , one smart behavior of SP is that addition of suitable metal ions to the MC solution can cause the blue-shift of the absorption spectrum , thus substantially increasing the spectral overlap between the excimer emission band of bis-pyrene and the absorption band of the MC-Zn^{2+} complex. Consequently by taking advantage of the fact that suitable metal ions can induce hypsochromic shift of the absorption spectrum of MC form , the efficient and reversible intermolecular energy transfer (and mutual communication) was realized in solution containing spiropyan and bis-pyrene together with metal ion (e. g. , Zn^{2+} or Mn^{2+} or Ce^{3+}) under UV light irradiation for the first time (Scheme 4) .[58] Based on this result , a new molecular logic circuit containing one "AND" and one "NOT" logic gates is proposed. In addition , 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 the future.



Scheme 4 Signal communication pattern between spiropyran and bis-pyrene

3.3 Proton transfer

Another remarkable feature of spiropyran is that the intrinsic interconversion among the three states (SP , MC and MCH) accompanies the reversible uptake and release of protons upon UV and visible light irradiations as shown in Scheme 1. If this reversible uptake and release of protons regulated by light based on spiropyran is combined with other functional materials , whose properties are dependent on the level of protonation , the corresponding properties of these materials can be reversible regulated. We fortunately found two smart examples : reversible regulation of the conductivity of polyaniline[59] and reversible modulation of the fluorescence of pyrenemethylamine.[60]

The unique property of polyaniline is that its electrical conductivity depends not only on the level of oxidation but also on the degree of protonation. The reversible interconversion of the "base form" and "salt form" can be achieved by employing the principle of acid/base (doping/dedoping) chemistry enabling control over its electrical conductivity (Fig. 6) . As a proof of principle ,[58] we first tested the possibility of photoinduced intermolecular proton

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transfer reaction between MC and polyaniline in solution. We found that absorption spectral studies didn't indicate the observable proton transfer between the salt form of polyaniline and SP before UV light irradiation but did show proton transfer reaction from the "salt form" of polyaniline to the MC form after UV irradiation accompanied by the disappearance of the characteristic absorption band of MC at around 580nm and the salient enhancement of the MCH absorption band at around 420nm. Very similarly, the solid-state absorption spectra of SP-doped polyaniline thin films indicated the gradual proton transfer reaction from the "salt form" of polyaniline to the MC form during UV irradiation and prolonged visible-light irradiation could nearly restore their original absorption spectra, indicating the reversibility of proton transfer reaction between them (Fig. 6). As a result, the electrical conductivity of the thin-film of SP-doped polyaniline can be reversibly controlled by UV and visible lights (Fig. 6). This is the first example of reversible regulation of the electrical conductivity of thin-films of SP-doped electro-active materials by light irradiation. Such conducting materials based on SP-doped polyaniline may find potential application in the field of information recording and processing in the nondestructive manner. To improve the reversibility, recently we also reported another interesting example of reversible photoswitching behaviors of the conductance of isolated semiconducting single-walled carbon nanotube transistors through the combination of microfabrication and noncovalent self assembly.[60]

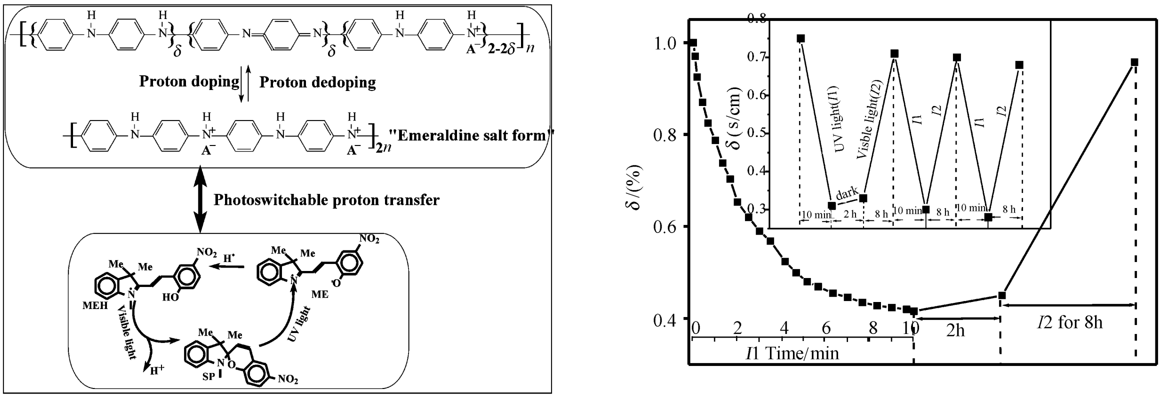

Fig. 6 Illustration of the photoinduced proton transfer between a three-state molecular switch based on SP and the conducting polyaniline and demonstration of the reversible modulation of the conductivity of their thin films

The second interesting example is that the fluorescence of pyrenemethylamine hydrochloride can be reversibly modulated by light in the presence of spiropyran.[60] The key point here is that the reversible interconversion between pyrenemethylamine and protonated pyrenemethylamine is accompanied by the change of fluorescence intensity due to the quenching effect of photoinduced electron transfer, constituting the basis for a proton-dependent fluorescence switch. The interconversion of SP among three states induced by ultraviolet light, visible light, and proton inputs can efficiently controls the level of protonation of pyrenemethylamine and thus demonstrate the signal communication between two molecular switches through proton transfer bridge.

4 A new photochromic spiropyran molecule

As described above, by fully utilizing these different properties of spiropyran, molecular systems related to spiropyran have been developed to mimic the functions of several molecular switches, molecular sensors, integrated logic gates and moreover communication networks. However, the application of spiropyran in these areas is still hindered by the fact that its open merocyanine form (MC in Scheme 1) is thermally unstable. Thus, stabilization and clear elucidation of their real meta-stable structure are one of the crucial topics in this context. In this regard, a new spiropyran SP2 with the stable merocyanine form both in solution and in the solid state at room temperature

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was designed and synthesized.[61] The design principle is to introduce the strong electron-withdrawing groups into the proper positions of the molecule. ^1H NMR spectra indicate that the ratio of the open form vs the closed form of SP2 is dependent on the polarity of solvents. Figure 7 indicates the molecular crystal structure of the stable merocyanine form with *s*-trans, *s*-cis conformation. It should be noted that this is the first report of the X-ray crystal structure of the pure open form of spiropyran. The stability of MC2 is believed to be due to the electron-withdrawing effect of both the quinoline and the trifluoromethyl groups. The spectral properties of SP2/MC2 in the presence of different metal ions are also studied, and the results show the potential application of SP2/MC2 in sensing metal ions.

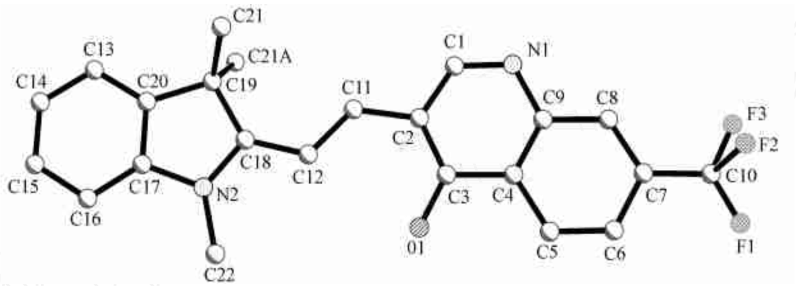

Fig. 7　Molecular crystal structure of MC2 with *s*-trans, *s*-cis conformation

5　Summary and perspectives

In summaries, this minireview details the design, development, and demonstration of chemical strategies that allow us to create molecular level devices and implement digital processing and communication. The design principle here is to integrate two informationally rich but relatively simple nanobuilding blocks with their complements through photoinduced electron transfer, redox processes, conformational changes, photoinduced energy and proton transfer, and supramolecular events into functional molecular devices. On the one hand, a series of D-A-D supramolecules and [2]rotaxanes based on TTF with the different linkages were synthesized. Transient absorption/fluorescence spectra indicated the correlation of the life-time of the charge separated states of D-A-D with the linkages and STM investigations of rotaxane-based thin films showed the new phenomenon of conformation-related reversible, stable nanorecording for future high-density information storage. On the other hand, photochromic spiropyran (SP) was used to modulate the absorption, fluorescence, and conductive properties of its supramolecular ensembles by light and chemical reagents. Based on the spectral and electrochemical behaviors of these ensembles, a whole bunch of novel molecular switches, logic gates, and molecular circuits were constructed through photoinduced electron, energy and proton transfer reactions. At last, a new fluorescent spiropyran with the stable merocyanine form both in solution and in the solid state at room temperature was presented and showed *s*-trans, *s*-cis conformation in single crystals.

These researches cover the broad fields of chemical and materials science including molecular electronics (molecular switches, molecular sensors, logic gates, molecular computing, and so on), dye chemistry and photochemistry, not only broadening and enriching the chemistry of tetrathiafulvalene and photochromic spiropyran, but also providing some insights into molecular level optoelectronic devices. However, at the present stage our studies still remain the rudimentary examples, but encouraged us to continue our efforts in this area. In the future, practical applications in electronics and photonics might emerge only after considerable fundamental studies on various aspects of this research area. One of the major challenges is in great need of more prototypes and strategies of integrating isolated molecular switches to chemical networks, ensuring the fast information processing and transportation. Another major challenges is the demonstration of methods to incorporate these functional molecules into solid-state devices while maintaining their signal transduction abilities. Also the construction of nano-electronic

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circuits and all-optical networks from molecular components is needed to lead the development of a new generation of digital devices for information technology. So, we have many opportunities at the bottom of molecules in this burgeoning field.

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功能分子设计合成及原理性的分子尺寸器件研究

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摘 要 详细综述了一些用于制备分子尺寸器件的化学策略的设计、发展和演示.其设计思想是通过各式各样的光诱导的电子、能量和质子转移机理,氧化还原反应,构象变化以及超分子原理,分别将2个信息量丰富而结构又比较简单的四硫富瓦烯和光致变色的螺吡喃分子,与它们性质互补的不同组分集成在一起来构建功能分子器件,用于完成快速的数字处理和传输.首先凭借四硫富瓦烯丰富的电化学性质,大量的D-A-D超分子和环轴烃分子已经被设计并成功合成.时间分辨的吸收和荧光光谱研究表明,这些D-A-D超分子发生分子内的光诱导的电子转移反应的能力,可以通过不同的桥联基团进行有效调控.STM研究则首次发现并开辟了环轴烃分子在纳米记录和高密度信息储存方面的应用研究.同时,也详细描述了如何充分利用光致变色的螺吡喃分子独特的电子、能量和质子转移能力去设计超分子组合,并通过光和适当的化学试剂来控制这些组合的吸收、荧光和导电性质的方法.根据这些组合的光谱和电化学行为,构建了一系列新型的分子开关、逻辑门和分子回路.最后,展示了用于设计合成新类型开环结构稳定的荧光螺吡喃分子的独特见解.

关键词 分子器件,四硫富瓦烯,螺吡喃,逻辑回路

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