ADVANCED MATERIALS

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Organic Functional Molecules towards Information Processing and High-Density Information Storage**

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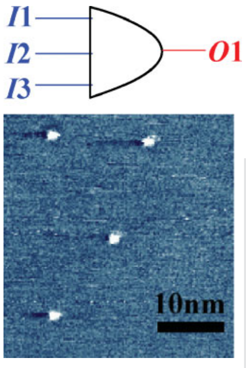

In this Progress Report, we discuss our recent achievements in design and synthesis of new functional molecules towards information processing at the molecular level and high-density information storage. These include: 1) new molecular switches, logic gates, and combinational logic circuits based on molecules and ensembles with photochromic spiropyran units that undergo reversible structural transformation among multistates, in response to external inputs such as light, protons, and metal ions; 2) high-density information storage, mainly focusing on nanometer-scale electrical recording based on the conductance transition of organic molecules, and multimode data storage on multiresponsive molecules. Relevant progress and an outlook in this area are also discussed.

1. Introduction

Two philosophically different approaches have been proposed for information processing at the molecular level. The first mimics the operational principles of solid-state computers presently in use at the nanometer scale. This approach is based on molecular electronics, in which both input and output signals are electronic (electron fluxes). Molecular photonics based on photon fluxes can be of help for this line of research. The second approach, which takes inspiration from information processing in living organisms, is based on chemionics,[1a] in which molecules and ions can be used as input/output signals to process information by using a molecular substrate. Chemionics usually operates in solution and can be complemented by photonics since chemical and light input/output signals can be easily coupled. Within each aspect of molecular electronics, photonics or chemionics, information processing takes place at logic gates and data manipulation relies on the binary digital (bit) nature of these input and output signals that are elaborated by means of the Boolean logic.

Although significant progress has been achieved for molecular electronics in recent years thanks to the advance of nanotechnology, photonics and chemionics have also received more and more attention.[1a] In fact, information processing in nature is usually based on exchange of chemical signals, exemplified by neurons in our brain, which process signals relying on the behaviors of ions in solution. A number of functional molecules and supramolecules have been reported to mimic functions of switches and logic gates. Various interesting molecular switches and logic gates have been described for information processing at the molecular level.[1]

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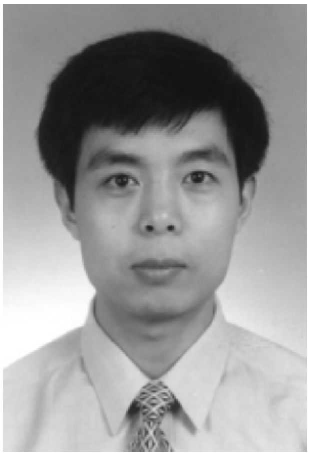
In the meantime, information storage has become a central issue in this digital age. The past few decades have shown an explosive increase in information and a remarkable miniaturization of electronic devices. Such trends will continue to demand an increase of the bit areal density and storage capacity in order to overcome the intrinsic physical limitations of memory-device components. To fulfill this, vast efforts have been devoted to exploring and developing new recording technologies and materials that combine high density, fast response time, long retention time and rewriting capability etc.

Among the various recording media for high-density data storage, organic materials have been especially attractive in recent years because of their low cost, simplicity, good stimuli-responsive properties, and versatility in molecular design; therefore, they have been suggested as promising candidates for future application development. In principle, the basic requirements for recording materials are that they should possess at least two distinct stable states via an external stimulus, where each state can represent "0" or "1" of a digital mode, and the states can be clearly distinguished during read-out. Furthermore, as an ideal recording media, several important performance parameters of a memory device include: 1) chemical stability; 2) film-forming properties; 3) storage capacity; 4) transition time (a short transition time between two states is intrinsically indicative of a fast writing); 5) retention ability (the ability to remain in the stored state is necessary for stable and secure recording); and 6) the on-off ratio (a high on-off ratio is crucial for memory devices in order to realize high-resolution and low-error-rate data storage). In addition, low power consumption, ease of fabrication, and competitive cost are also important for practical application.

In this *Progress Report*, we will discuss our recent results regarding the development of new organic functional molecules for information processing and high-density information storage at the molecular level. The results include two parts: 1) new molecular switches and logic gates based on photochromic spiropyran derivatives; 2) design and synthesis of new functional molecules and their application in high-density information storage.

2. New Molecular Switches and Logic Gates Based on Photochromic Spiropyran Derivatives

As one of the most promising families of photochromic compounds, spiropyran (SP) molecules have been extensively investigated, mainly because of their potential applications in the area of molecular sensors, switches, and information processors. Uniquely, SP can undergo reversible structural transformation among multistates, in response to external



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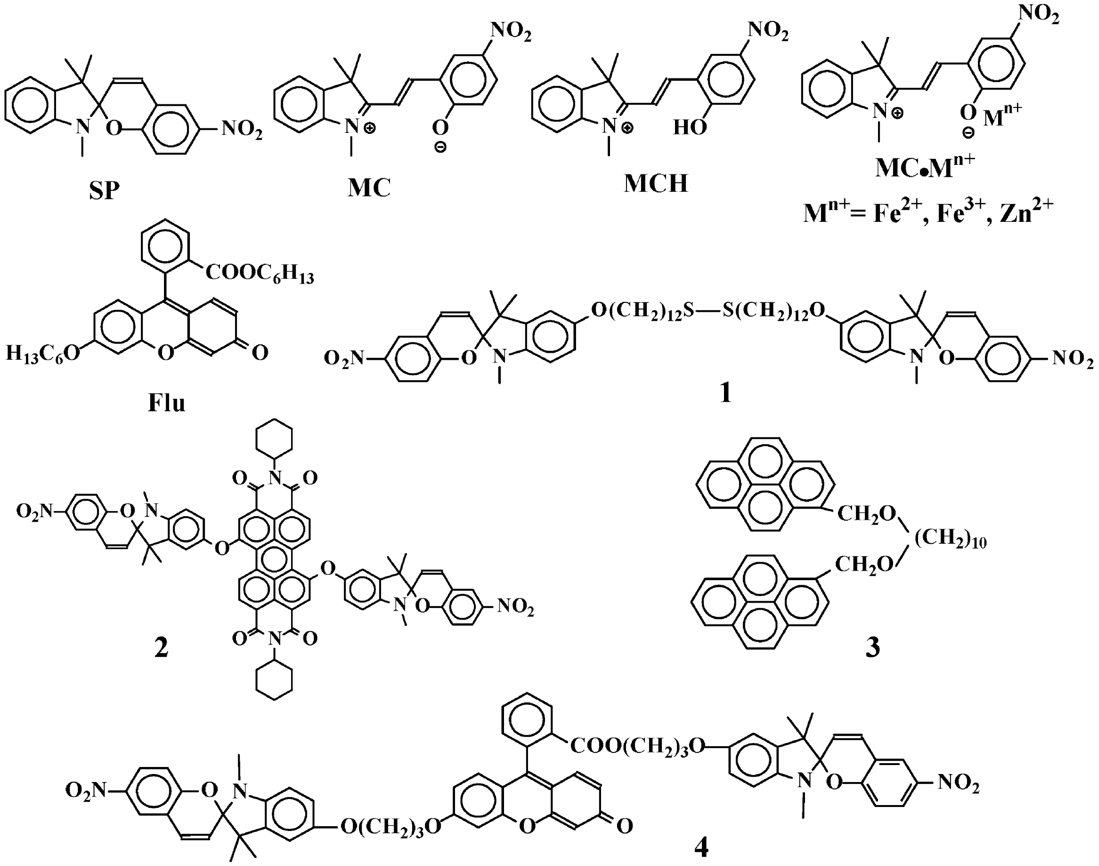
inputs such as light, protons, and metal ions. By taking advantage of this property of spiropyran, molecular systems with spiropyran have been configured to mimic the functions of molecular switches, elementary logic gates and integrated logic gates.[2] In the following we will report some recent achievements in the development of new molecular switches, elementary logic gates, and combinational logic circuits based on functional molecules with SP moieties by manipulating the corresponding photoinduced electron/energy/proton transfer processes.

2.1. Molecular Switches with SP Molecules

2.1.1. Molecular Switches Based on Electronic Transduction of Optical Signals[3a]

SP and the corresponding open form of spiropyran (MC) can be reversibly interconverted upon irradiation with UV and visible light. One of the unique features of SP is that the MC form is able to coordinate with metal ions[3] and that the SP form does not show such a property. Compound **1** (Scheme 1) with two SP and one –S–S– units was designed and synthesized to generate a Au electrode modified with a self-assembled monolayer (with SP units), which can be regarded as a membrane electrode. It is anticipated that the electrode potential recorded with this spiropyran-modified Au electrode can be reversibly modulated by UV/visible light irradiation of the electrode when this electrode is immersed into an electrolyte solution with metal ions (e.g., Zn^{2+}). This is based on the following consideration: the MC form can coordinate with metal ions present in the solution. As a result, the concentration of ions in the membrane will be altered, leading to a variation of the membrane potential of the modified electrode, after the UV light irradiation. Further visible light irradiation will cause the conversion of the MC form into the SP form; concomitantly, the coordinated-metal ions will be released, leading to the restoration of the membrane potential.

The electrode (immersed in conducting electrolyte solution containing Zn^{2+}) potential increased after irradiation with UV light (365 nm): the maximum enhancement (ca. 35 mV) in the potential was achieved after continuous UV-light irradiation of the modified electrode for 200 s. Further visible light irradiation led to the reduction of the potential, and the initial potential was restored after irradiation with visible light for 300 s. Such an electrode-potential variation can be reversibly performed for at least five cycles. Consequently, electronic transduction of the optical signals was realized, and a new molecular switch was established with UV/visible light and the electronic potential as the input and output signals, respectively.



Scheme 1. Chemical structures of SP-containing molecules and relevant compounds for studies of molecular switches and logic gates.

2.1.2. *Photocontrolled Electrical Switches*[4a]

Another remarkable feature of SP is that the open form of SP (MC) can uptake protons to generate the MCH form (protonated MC) and then release protons upon further visible light irradiation.[4a,b] By making use of this feature, several interesting switchable systems have been described.[4] For instance, it was reported that the electrical conductivity of SP-doped polyaniline thin films could be modulated reversibly by alternating UV and visible-light irradiations.

The electrical conductivity of polyaniline 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. If polyaniline and spiropyran were mixed, the following photoinduced proton-transfer processes would occur: 1) the MC form generated by UV-light irradiation of SP will uptake protons from the "salt form" of the polyaniline, leading to the reduction of the protonation degree; 2) upon visible-light irradiation, the MCH form will release protons that will be captured by the polyaniline to restore the protonation degree. As a result, the electrical conductivity of polyaniline can be reversibly photocontrolled as illustrated in Figure 1.

The electrical conductivity of the polyaniline thin film doped with SP decreased by ca. 50% after UV-light irradiation for 10.0 min. The conductivity reduction for this thin film was surely due to the proton-transfer process from the "salt form" of the polyaniline and the MC form of the SP. The electrical conductivity of the thin film (after exposure to UV-light irradiation) varied very little after the thin film was kept in the dark for 2 h. After further irradiation with visible light for 8 h, the electrical conductivity of the thin film was almost restored to its initial value (before the UV-light irradiation) (Fig. 1). The reversible variation of the electrical conductivity of the SP-doped polyaniline thin film upon UV-light (*I*1) and visible-light (*I*2) irradiation constitutes the base of a new photocontrolled electrical switch with the electrical conductivity (*O*1) as the output signal.

2.2. "AND" and "IHIBIT" logic gates with SP molecules

2.2.1. *"AND" Logic Gates with Three Inputs*[5]

Compound **2** (Scheme 1), a perylene diimide (PI) derivative with two SP units, shows rather-weak fluorescence. This is likely to be due to the photoinduced electron transfer (PET) between the SP and PI units. The SP units of **2** can be reversibly transformed into the corresponding MC units. The fluorescence intensity of **2** became even weaker after UV-light irradiation at 365 nm. It was reported that MC is able to form a coordination complex with Fe^{3+}, resulting in a reduced electron-donating ability. After addition of Fe^{3+}, MC-Fe^{3+} complex units were generated, based on studies of the absorption spectra. However, the fluorescence of the PI unit was just slightly increased. After further addition of CF_3COOH to the solution, the fluorescence of PI unit was significantly enhanced. The fluorescence-intensity difference between the original solution of **2** and after sequential actions of UV light, Fe^{3+} and H^+ can be clearly distinguished by the naked eye.

Moreover, experimental results indicated that the reaction sequence of UV light, Fe^{3+} and H^+ with the solution of **2** had no influence on the final fluorescence spectrum of the solution. Simultaneous or consecutive operations of one or two of the three inputs (UV light, Fe^{3+} and H^+) could not induce significant fluorescent enhancement. The fluorescence of the PI unit of **2** can be significantly enhanced only with the cooperative action of UV light, Fe^{3+} and H^+. Accordingly, the fluorescence variation of **2** in response to UV light (*I*1), Fe^{3+} (*I*2) and H^+ (*I*3) can be represented by an "AND" logic gate with three inputs.

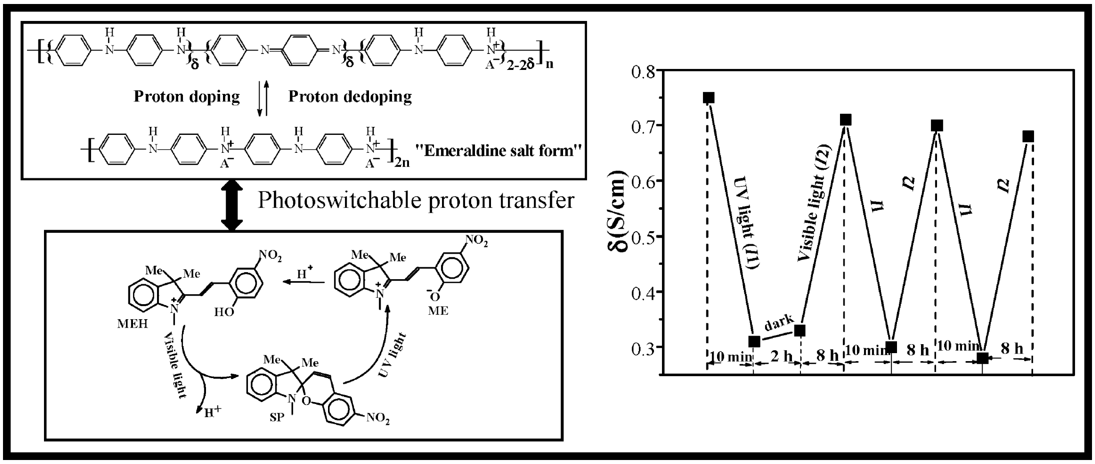


Figure 1. Illustration of the photoinduced proton transfer between a three-state molecular switch based on SP and conducting polyaniline; the graph shows the variation of the electrical conductivity of the SP-doped polyaniline thin film under the influence of UV-light input (*I*1) and visible-light input (*I*2) for three consecutive switching cycles.

2.2.2. INHIBIT Logic Gates[6]

This new INHIBIT gate is based on the fluorescence variation of an ensemble of fluorescein (Flu) (Scheme 1) and SP upon addition of Fe^{3+} and UV-light irradiation at 365 nm. The fluorescence of Flu ($\lambda_{max} = 473$ nm) increased after oxidation with $Fe(ClO_4)_3$ (formation of $Flu^{+\bullet}$); further reaction with $Na_2S_2O_3$ would restore the fluorescence spectrum of Flu. As a result, the fluorescence of Flu can be modulated reversibly by oxidation and reduction. For the ensemble of Flu and SP, fluorescence enhancement was also observed after addition of Fe^{3+}. After UV light irradiation at 365 nm, the fluorescence intensity of the ensemble was reduced to a large extent, and the initial fluorescence spectrum of the ensemble (before addition of Fe^{3+} and UV light irradiation) can be almost recovered.

These results can be interpreted as follows: addition of $Fe(ClO_4)_3$ to the mixture solution of SP and Flu resulted in the oxidation of Flu 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 then coordinate with Fe^{2+} to produce $MC{\bullet}Fe^{2+}$ complexes. According to our previous report,[3b] it is thermodynamically favorable for the electron-transfer reaction from the $MC{\bullet}Fe^{2+}$ complex (0.48 V vs. saturated calomel electrode (SCE)) to $Flu^{+\bullet}$ (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 $MC{\bullet}Fe^{3+}$ complex. This is fully in accordance with the fact that the fluorescence of the solution was decreased after UV-light irradiation.

The communicating ensemble of SP and Flu can transmit one chemical input (Fe^{3+}, $I1$) and one optical input (UV light, $I2$) into a single optical output ($\lambda_{max} = 473$ nm, $O1$). Based on 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 a new "INHIBIT" logic gate.

2.3. Combinational Logic Circuits with SP Molecules

2.3.1. Combinational Logic Circuits Incorporating "AND" and "NOT" Logic Gates[7]

We studied an ensemble of compound **3** (Scheme 1), which contains two pyrene units, and SP for the creation of a new combinational logic circuit. As anticipated, compound **3** displays the typical pyrene-excimer fluorescence with $\lambda_{max} = 478$ nm. The pyrene-excimer fluorescence intensity of ensemble of **3** and SP remains nearly constant after UV- and visible-light irradiation, which can induce the reversible transformation between SP and MC as discussed earlier. This is understandable since there is a rather-small spectral overlap between the pyrene-excimer emission band and the absorption band of the MC form; consequently, the energy-transfer process from the pyrene excimer to the MC form cannot take place efficiently.

It has been reported that a blue shift of the absorption spectrum occurs after the coordination of the MC form with metal ions. For example, addition of 20 equiv. of Zn^{2+} to the pure solution of SP immediately after UV-light irradiation results in the appearance of two distinct absorption bands: one corresponding to the free MC with $\lambda_{max} = 585$ nm, and the other to an $MC\text{-}Zn^{2+}$ complex with $\lambda_{max} = 500$ nm. This can substantially increase the spectral overlap between the pyrene-excimer emission band and the absorption band of the $MC\text{-}Zn^{2+}$ complex. As a result, the energy transfer from the excimer to the $MC\text{-}Zn^{2+}$ complex would occur more efficiently and the excimer fluorescence would be quenched to some extent. This assumption is confirmed by similar experiments with the ensemble of **3** and SP. The excimer fluorescence intensity of the ensemble of **3**, SP and Zn^{2+} is reduced to ca. 47% of the initial value at 478 nm. Further visible-light irradiation led to the restoration of the fluorescence spectrum of the ensemble. Therefore, the pyrene-excimer fluorescence can be reversibly switched *on* (ca. 100%) or *off* (ca. 47%) consecutively in such a way for several reversible cycles.

The above results can be interpreted by binary logic. The ensemble of the interacting molecules (compound **3** and SP) can "read out" three kinds of binary input: $I1$ (UV), $I2$ (Zn^{2+}) and $I3$ (visible light), and "write" a specific binary output: $O1$ (excimer emission at 478 nm). Based on the fluorescence spectral results, the truth table can be constructed. The truth table corresponds to a combinational logic circuit incorporating two logic gates ("AND" and "NOT").

2.3.2. Combinational Logic Circuits Incorporating "AND" and "OR" Logic Gates[8]

Fluorescein (Flu) shows emission in the range of 500–650 nm. Thus, there is a big overlap between the fluorescence spectrum of Flu and the absorption spectrum of MC (open form of SP), while there is no overlap between the fluorescence spectrum of Flu and the absorption spectra of SP and MCH (protonated MC form). One remarkable feature here is that Flu absorbs strongly at around 430 nm, at which SP, MC, and MCH exhibit very-weak absorption. With these considerations in mind, compound **4**, a Flu derivative flanked by two SP units, was examined for fluorescence modulation in response to UV- and visible-light irradiations and addition of acid; such fluorescence variation behavior mimics a combinational logic circuit incorporating "AND" and "OR" logic gates.

Before UV-light irradiation, compound **4** shows a broad emission band in the range 500–650 nm. Upon UV-light irradiation, the fluorescence intensity at 550 nm decreased. This is simply due to the photoinduced energy transfer between the Flu and MC units, which are generated after UV light irradiation. Further visible-light irradiation led to fluorescence enhancement. Also, the fluorescence intensity of the solution could be restored to its initial value after addition of

CF_3COOH to the solution of compound **4** after UV-light irradiation. This fluorescence intensity alteration can be repeated consecutively for several switching cycles.

The fluorescence variation of compound **4** in response to UV light, visible light and protons can be interpreted by Boolean logic. The three input signals are *I*1 (ultraviolet light), *I*2 (visible light) and *I*3 (protons). The output signal is *O*1, the emission band of the fluorescein moiety at 550 nm. The corresponding truth table is established based on fluorescence spectral studies with compound **4**, and the truth table can be represented by the combinational logic circuit including one "OR" and one "AND" logic operations with two inputs *I*1 and *I*3.

2.3.3. Monomolecular Half Adder[9a]

Rational integration of relatively simple logic gates into high-level circuits (for example, the "half adder" which, as the basis of electronic calculators and computer machines, requires two binary inputs and two binary outputs to perform simple arithmetic addition) is highly important not only for the potential application in molecular electronics, but also for the understanding of the complex mechanisms of important biological processes. To the best of our knowledge, there are only a few reports dealing with a "half adder".[9,1b-e]

SP can be transformed to MC and MC-Fe^{3+} under the appropriate actions of *I*1 (UV light) and *I*2 (Fe^{3+}) as discussed above. SP can be also oxidized to the corresponding radical cation (SP^+) by Fe^{3+}. Each species of SP, MC, MC-Fe^{3+}, and SP^+ displays a distinct absorption spectrum. MC-Fe^{3+}, formed only after sequential UV-light irradiation and addition of Fe^{3+}, shows strong absorption at 420 nm. Therefore, variation of the absorbance at 420 nm (*O*1) in response to I1 (UV light) and I2 (Fe^{3+}) mimics the function of an "AND" logic gate. The absorption spectrum of MC and that of SP^+ have a cross-point at 520 nm, at which both SP and MC-Fe^{3+} have a rather-weak absorption. Accordingly, the absorption change at 520 nm (*O*2) after the actions of *I*1 (UV light) and *I*2 (Fe^{3+}) corresponds to an "XOR" gate. Since the absorption changes at both 420 and 520 nm are based on the entity of a single molecule of SP and are under the same external inputs, the "AND" and "XOR" gates can be "operated" in parallel. Therefore, the absorption spectral variations of the SP solution in response to UV-light irradiation (*I*1) and Fe^{3+} (*I*2) mimic the function of a "half adder" and can perform simple arithmetic addition.

3. High-Density Information Storage with Organic Functional Materials

According to different external stimuli in data recording, data storage usually includes three types: magnetic data storage, optical data storage and electrical data storage. In addition, to overcome the shortages of single-mode magnetic, optical or electrical storage, and also to perform complex information processing, multifunctional data storage based on multiresponsive materials has been proposed. In this *Progress Report*, we present a brief overview of recent progress in organic recording materials for high-density information storage, especially focusing on organic materials for scanning probe microscopy (SPM)-based electrical data storage and multimode data storage.

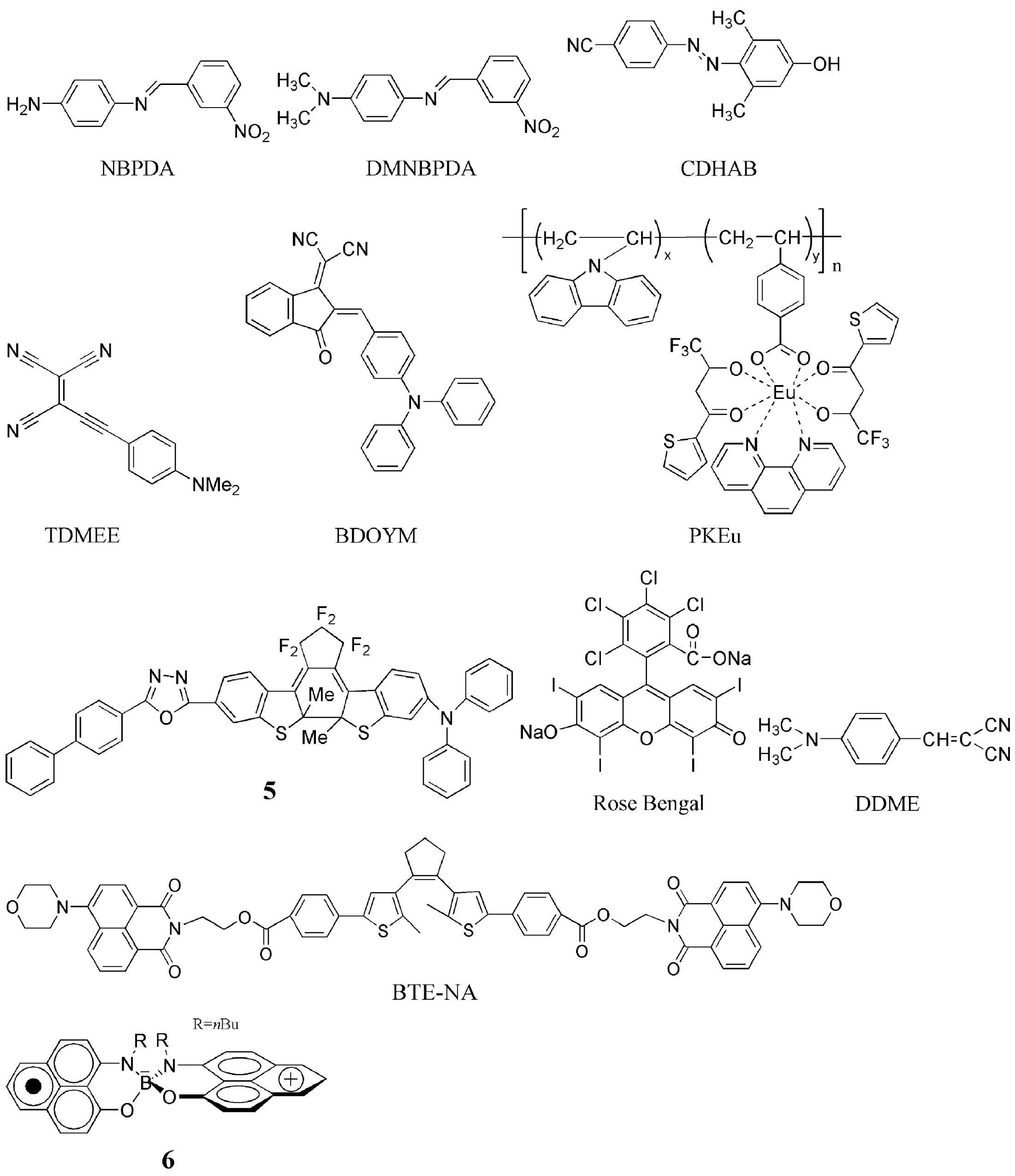
3.1. Electrical Data Storage

Electrical data storage is a powerful approach to achieve high-density data recording. It has no superparamagnetic limitations in comparison to magnetic storage, and no optical diffraction in contrast to optical storage. In electrical data storage, the data is stored based on the high- and low-conductivity response to an applied voltage (electrical bistability). So far, various organic electric-responsive materials based on different bistable mechanisms including charge transfer, oxidation-reduction, and conformational change etc. have been developed. SPM-based techniques represented by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been demonstrated as being powerful for conducting data storage at the nanometer scale or the molecular scale.[10] To improve the writing/reading speed, parallel recording techniques[11a] and crossbar nanocircuits[11b] have further been developed.

3.1.1. Charge-Transfer Materials for Conductance Transitions

Since Coleman[12a] and Ferraris et al.[12b] reported a highly conducting complex, tetrathiofulvalene (TTF)-tetracyano-*p*-quinodimethane (TCNQ), in the 1970s, charge-transfer materials have been one of the most attractive candidates for high-density electrical data storage.[13,14] Initially, organic films for data recording based on charge transfer were mainly metal/organic complexes represented by silver tetracyanoquinodimethane (Ag-TCNQ) and copper tetracyanoquinodimethane (Cu-TCNQ). Compared with metal-organic complex films, all-organic films have good and uniform physico-chemical properties. Therefore, organic donor compounds have been proposed to replace metal donors, and a series of organic electron-donor and electron-acceptor materials were explored to prepare the organic composite thin films for electrical recording.[15]

In this context, *N*′-(3-nitrobenzylidene)-*p*-phenylene-diamine (NBPDA) (Scheme 2) was synthesized, whose characteristic is that an electron acceptor –NO_2 and an electron donor –NH_2 coexist in one molecule.[16a] Due to the component's homogeneity and the molecular interaction, large-area orderly films can be obtained. On this basis, nanometer-scale high-density data storage in the NBPDA thin film was demonstrated. For NBPDA, the –NH_2 donor is sensitive to air and not stable enough. To improve its thermal stability, another organic material *N*,*N*′-dimethyl-*N*′-(3-nitrobenzylidene)-*p*-phenylene-diamine (DMNBPDA) (Scheme 2) was synthesized, in which the donor –NH_2 of NBPDA is protected by two



Scheme 2. Chemical structures of organic functional molecules for high-density information storage.

–CH_3 groups. Furthermore, –$N(CH_3)_2$ is a better electron donor than –NH_2, so charge transfer could occur more easily in the DMNBPDA system than in the NBPDA system. By controlling the deposition rate, an ordered monolayer of DMNBPDA was prepared by vacuum vapor deposition, in which stable nanoscale data recording was successfully achieved by STM with a storage density of about 10^{13} bits per cm^2.[16b]

To enhance the film-forming and electronic properties, a number of self-assembling functional groups can be combined into the charge-transfer molecules. Motivated by this, an organic donor-acceptor molecule, 4′-cyano-2,6-dimethyl-4-hydroxy azobenzene (CDHAB) (Scheme 2) has been synthesized for STM-based data storage.[17] In a single CDHAB molecule, a hydroxyl group and a cyano group are combined, which act not only as electron donor and acceptor groups respectively, but also as hydrogen-bonding recognition subunits. By molecular self-organization, CDHAB molecules can be assembled into a highly ordered crystalline thin film on a freshly cleaved, highly ordered pyrolytic graphite (HOPG) substrate. Reversible nanometer-scale data storage was realized on such thin films by applying pulsed voltages between the STM tip and the HOPG substrate (shown as (1) in Figure 2a).

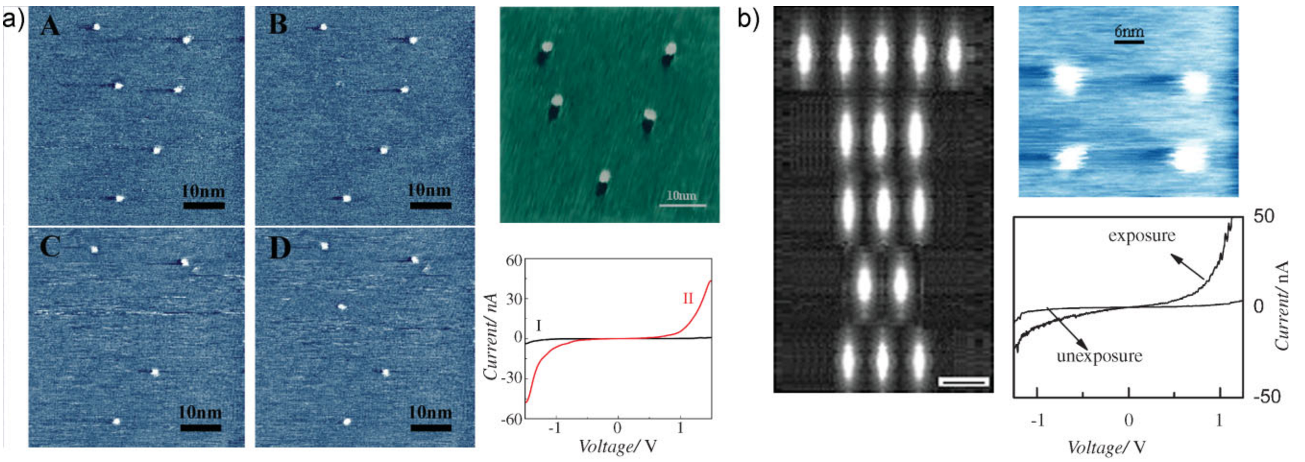


Figure 2. a) (1) STM images of the CDHAB film during the information-recording experiments. Tunneling conditions: $V_{bias}=0.38$ V, $I_{ref}=0.28$ nA, 0.2 Hz per image, constant-current mode. A) A recorded pattern (letter "y"), voltage pulses: +2.6 V, 3.0 ms; area shown is 60 nm × 60 nm. The average dot is about 1.8 nm in diameter. B, C) Patterns after erasing one and two marks, respectively; voltage pluses: −2.2 V, 3.0 ms. D) Pattern after rewriting one mark, voltage pulse: +2.6 V, 3.0 ms. (2) STM image of a nanoscale "v" pattern recorded on the TDMEE thin film by applying a pulse voltage of 2.64 V, 10 ms. STM was performed in constant-height mode with set points of $V_{bias}=0.34$ V and $I_{ref}=0.06$ nA. The average diameter of the marks is about 2.1 nm. (3) Typical STM current–voltage (I–V) curves in the unrecorded (curve I) and recorded region (curve II). b) Five-layer optical information storage based on two-photon excitation (Left, scale bar is 5 μm) and nanoscale electrical data recording (top right corner) by scanning tunnelling microscopy, demonstrated in DDME thin films. Bottom right is the typical local I–V curves of the DDME thin films before and after exposure to UV light. The curves were obtained by scanning tunneling spectroscopy (STS).

Besides the requirement of forming high-quality thin films, the efficiency of charge transfer is the key to achieve a stable and efficient electrical recording. In collaborating with Diederich et al.,[18] we prepared high-quality crystalline thin films based on the self assembly of 1,1,2-tricyano-2-[(4-dimethylaminophenyl)ethynyl]ethene (TDMEE) (Scheme 2) molecules using the vacuum-deposition method. The molecules undergo π-stacking in the crystalline thin films, and the packing adopts regular alternate donor/acceptor stacks. Experimental and theoretical studies showed that such an ordered, antiparallel packing mode of the dipolar donor-acceptor molecules in the film is favorable for efficient electron transfer and the subsequent nanoscale recording by electrical stimulus. The recording pattern is shown as (2) in Figure 2a.

The on-off current ratio is another important parameter because a high on-off current ratio is the basis of high resolution and low error rate. Recently, a new D-A molecule, 2-((Z)-2-(4-diphenylamino)benzylidene)-1,2-dihydro-1-oxoinden-3-ylidene) malononitrile, (BDOYM) (Scheme 2), with a triphenylamine unit as the electron donor and two cyanovinyl groups as the electron acceptor, has been designed and synthesized.[19] The triphenylamine unit, a large conjugated tertiary amine system, can not only behave as a strong electron donor in its initial state, but also stabilizes the charge-transferred state. Furthermore, because of the good hole-transporting ability of the triphenylamine group, it can be expected to modify the electrical conductivity of the material effectively. In electrical measurements, two distinctive conductivity states have been observed in BDOYM thin films, and the on-off current ratio was determined to reach as high as 10^4. On this basis, stable and reversible data storage has been demonstrated using STM.

Due to their flexibility, mechanical strength and ease of processing, polymer materials possessing donor and acceptor groups have been considered as promising electronic components for data storage and molecular devices. Ling et al.[20] designed and synthesized a novel copolymer, poly[*N*-vinylcarbazole-*co*-Eu(vinylbenzoate)(2-thenoyltrifluoroacetone)$_2$ phenanthroline] (PKEu) (Scheme 2), of which the carbazole group was used as the electron donor, and the Eu complex acts as an electron acceptor. By using this material as the active medium, a metal/insulator/metal sandwich memory device was fabricated; switchable electrical bistable behavior with a high on-off current ratio and fast switching time was observed.

3.1.2. Conductance Transitions based on Conformational Changes

The conductivity of a molecule relates to its chemical structure and electronic structure. In some cases, the electrical properties of a molecule can be tuned by changing its conformation via electrical stimulus. As one of the best candidates for optical memory and switches, photochromic diarylethenes have been extensively studied during the past few decades because of the thermal stability of both isomers and their fatigue resistance. Tsujioka and Kondo[21] presented an organic memory device using a bistable photochromic diarylethene as the active media. The diarylethene is a non-symmetrical bipolar molecule with a triphenylamine group as the electron donor and an oxadiazole group as the electron acceptor (compound **5** in

Scheme 2). The device is based on an isomerization reaction of the diarylethene molecule via its excited state by an electrical carrier injection. It should be noted here that the excitation is via the encounter of a hole injected from the anode and an electron injected from the cathode (named electron-mode recording), not via photon absorption (photon-mode recording).

In recent years, interlocked molecules and supermolecular complexes such as rotaxanes, catenanes, and pseudorotaxanes have received much attention. Upon external stimuli, rotaxanes and catenanes can undergo coconformational changes. The switching between two conformations can lead to the switching of conductance, which makes rotaxanes and catenanes promising candidates for high-density electrical data storage. Gao and coworkers[22a] prepared a rotaxane film on an indium tin oxide (ITO)-based glass substrate using the Langmuir-Blodgett (LB) deposition technique. In electrical measurements, the thin films exhibit a reversible conductance switching and non-volatile memory effect with an on-off ratio bout 100. On this basis, stable, reproducible nanorecording in the rotaxane film was demonstrated by STM. Recently, the structural and conductance transition of another rotaxane molecule (H2) was directly observed using low-temperature STM at 77 K,[22b] and reversible, erasable, as well as rewritable nanorecording on H2 rotaxane thin films was further achieved.[22c] Earlier, Heath and coworkers[22d] reported pioneering work on a solid-state, electronically addressable, [2]-catenane-based molecular switching device. The device exhibits bistable current/voltage characteristics and robust operation under ambient conditions.

3.1.3. Conductance Transitions based on Oxidation and Reduction Reactions

Attaching redox-active molecules to an electroactive surface such as gold or silicon provides an attractive approach for molecular-based electrical recording.[23] Driven by the external voltage, the molecules undergo reversible oxidation and reduction reactions, and information is stored in the distinct oxidation states of the molecules. Also, the reactions result in a change of the conductivity, so the information can be read based on the difference of the conductivity. Such writing, reading and erasing of information is accomplished electrically under ambient conditions, and multiple bits of information can be stored through the molecules or molecular arrays that afford a set of distinct oxidation states. The storage density depends on the oxidation states that the molecules can afford. The more oxidation states they have, the higher the density that could be achieved.

Several scientific issues should be taken into account for electrically addressable molecular-based information storage, among which the charge-retention properties of the media are of particular importance. To address this, many electroactive porphyrin-based molecules have been synthesized, and the electrochemical behavior of the molecules self assembled on the substrate have been comprehensively investigated by Lindsey and coworkers.[24] The preliminary studies showed that the self-assembled monolayers (SAMs) of momomeric porphyrins retain their charge for hundreds of seconds after disconnection of the applied potential, and the charge-retention time of porphyrin monomers bearing phenyl or alkylphenyl linkers can be altered by ~10-fold through structural modification of the linkers. The studies also showed that the length of the linkers played a significant role in determining the charge-retention characteristics of the porphyrin SAMs; that is to say, long linkers generally give longer charge-retention time.

As mentioned above, for an electrical recording medium, the on-off ratio is an important parameter because it determines whether or not the supporting electronic circuitry can distinguish between “0” and “1”. The route to increase the on-off ratio is to either increase the ON-state current or decrease the OFF-state current. To achieve a low conducting OFF-state, Bandyopadhyay and Pal[25] chose Rose Bengal (Scheme 2), a molecule with many electron and acceptor groups, and fabricated memory devices based on spin-cast and layer-by-layer electrostatic self-assembled films. In these devices, a large electrical conductance switching with an on-off ratio of 10^5 was obtained. Such a high on-off ratio in a single layer-sandwich structure is due to the low OFF-state leakage current. It was also shown that by introducing the supramolecular matrix in conducting switching, the ON- and OFF-state device currents and the on-off ratio can be tuned by the resonance between the density of states and the electrode’s Fermi level.

3.2. Multimode Data Storage

For practical applications in high-density data storage and also to enhance the multifunctionality of molecular devices, it is better to combine multiple physical channels (such as optical, electrical, and magnetic multifunctionality) on a single device for recording and transmitting information.[2a,26] Furthermore, when two different physical channels are simultaneously involved, new applications and even new research fields will be brought on, such as optoelectronics, magneto-optics, and spintronics.[27] As far as the recording medium is concerned, a molecule that can undergo different transformations depending on the type of external stimuli can be expected to have significant applications in multimode and complex information processing.[28]

In multimode data storage, optoelectrical dual-mode storage that combines optical and electrical properties within a single component is of great interest in that it may allow for high-density storage as well as non-destructive readout. Photoresponsive conducting systems have been developed, and the mechanism involves the photoinduced modulation of the π-conjugated lengths of the molecules, resulting in a change in the electrical conductivity.[29]

Photo- and electro-dual-responsive molecules, such as some diarylthenes mentioned in Section 3.1.2., are also effective molecular systems for optoelectrical dual-mode data storage. Recently, another dual-responsive organic compound, 1,1-dicyano-2,2-(4-dimethyaminophenyl) ethylene (DDME) (Scheme 2), which is a stable conjugated system with a strong electron donor, -N(CH$_3$)$_2$, and two electron acceptors, -CN, was reported.[30] Mechanism analysis suggests that the optical- and electrical-responsive properties of the material result from the same conformational change induced by light or an electric field. Accordingly, nanoscale electrical data recording by STM and three-dimensional optical information storage based on two-photon excitation was achieved in the DDME thin films (Fig. 2b).

Multimode data storage also has important applications in security data storage. Recently, we reported a photo- and proton-dual-responsive fluorescence switch based on a bisthienylethene-naphthalimide dimer (BTE-NA).[31] Based on the photoresponsive property of the BTE-NA thin film, information can be written optically. Based on the proton-responsive characteristic, the stored data can be concealed by acid treatment and recovered by deprotonation if needed. On the basis of fluorescence with the use of a light and a proton source, the overall write-conceal-display process of information in security data storage can be successfully demonstrated.

Haddon and coworkers[26a] reported that electrical, optical, and magnetic properties can be simultaneously switched between two states in a phenalenyl-based neutral radical by thermal control of two neutral alkyl-substituted spirobiphenalenyl radicals(compound **6** in Scheme 2). By analysis of the bond length as a function of temperature, it is concluded that the intradimer separation (indicative of molecular arrangement) varied from 3.2 Å to 3.3 Å with increasing temperature, resulting in a reduction in the electronic interaction. Such temperature-dependent movement of the unpaired electrons and the electronic interaction lead to a structural alternation and significant changes in conductivity, magnetic and optical properties of the material. This work represents a big step forward and demonstrates that materials with three useful properties for future devices can be made.

4. Summary and Outlook

In this *Progress Report*, we have mainly summarized our recent achievements in design and synthesis of new functional molecules towards information processing at the molecular level and high-density information storage. On the one hand, we describe molecules and ensembles with photochromic spiropyran units and their spectral tuning by manipulating the corresponding photoinduced electron/energy/proton transfer processes. Such spectral tuning in response to external stimuli mimics the functions of molecular switches and logic gates, which are interesting for information processing at the molecular level. On the other hand, high-density information storage based on the conductance transition of organic molecules and multimode data storage with multifunctionality on multiresponsive organic molecules are presented. Relevant progress in this area is also discussed.

For molecular switches and logic gates, our studies still remain rudimentary examples at the present stage, but they have encouraged us to continue our efforts in this area. In the future, practical applications in electronics and photonics may 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 fast information processing and transportation. Also, it is of great challenge to develop new methods to incorporate these functional molecules into solid-state devices while maintaining signal transduction abilities. Looking to the future, there are many opportunities for molecules in this burgeoning field.

The ever-growing demand for higher storage density is encouraging the exploration of novel recording technologies and innovative materials for future large-capacity memories. As two powerful approaches to this end, electrical and multimode data storage have received increasing attention. In the past few years, great progress in organic electrical recording media with improved film-forming characteristics and electrical properties has been achieved, and nanometer- and even molecular-scale data storage has been realized. Multifunctional molecules that can undergo different transformation depending on the type of external stimulus can be expected to have significant applications in higher-density, multimode and complex information processing. However, to realize the practical application of electrical and multifunctional recording media, there is still a long way to go. For example, the intrinsic active mechanisms are still indistinct for many molecular systems: how to amplify molecular responsive properties in the solid state and further incorporate them into solid-state devices are still the major challenges. These problems put further demands on the deep understanding of functional material design, assembly techniques, device fabrication and the recording mechanism. To achieve this, broad interdisciplinary collaborations that include chemists, physicists, material scientists, and electrical engineers will be required.

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