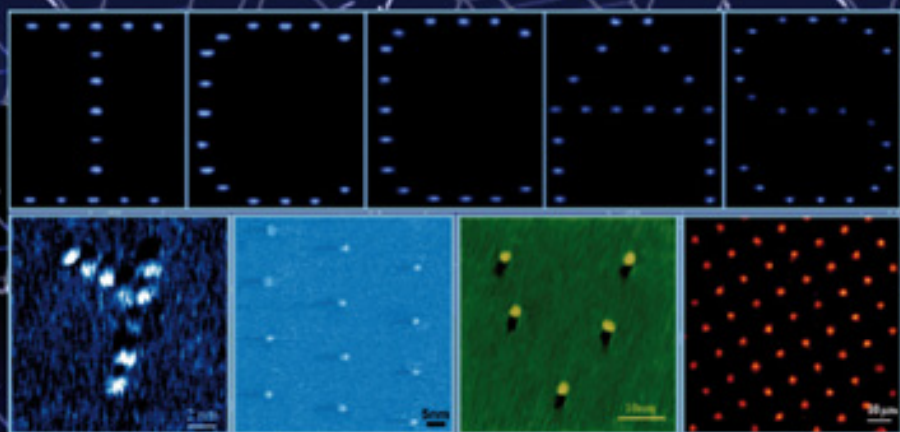




HIGH DENSITY DATA STORAGE

Principle, Technology, and Materials

Edited by

Yanlin Song

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PREFACE

Information storage has been becoming an essential issue in this digital age. The past couple of decades witnessed the explosive increase of the capacity of the information and the remarkable miniaturization of electronic devices. Those trends continue to demand new recording technologies and materials that could combine the virtues of high density, fast response, long retention time, and re-writing capability. They aim at overcoming the current physical limitations in memory device components.

The research on information storage is highly interdisciplinary as various disciplines are involved, like physics, chemistry, materials, and electrical engineering. The realization of high density data storage relies on the clear understanding and effective integration of functional material, assembly techniques, device fabrication and recording mechanism. In recent years, tremendous progress has been made in magnetic/optical/electrical data storage. The development of scanning probe techniques enables the realization of nanometer even molecular scale data storage. Recent insight into the multi-mode data storage on multi-responsive molecules will undoubtedly initiate new horizons for the future data storage, and will also bring on new applications and research fields. In multi-mode data storage, multiple physical-channels like optical, electrical and magnetic multifunctionality are simultaneously involved for recording and transmitting information. The synergetic effect of different channels as well as characteristics in multi-responsive recording media can be intensively exploited. As far as recording medium is concerned, a molecule, which undergoes different transformations with the type of external stimuli, can be expected having significant applications in high density data storage and complex information processing.

This book reviews extensively the most recent achievements on high density data storage based on magnetic, optical, or electrical bistability,

with emphasis on the advances of nano or molecular-based recording materials and technologies. Particular attention was paid to the motivation and the design of new materials and their recording mechanism, which represent some of the most exciting results in this field. Finally, the emerging technologies as well as the future development of high density data storage have also been discussed.

Here I would like to thank my co-workers and friends for their contribution to this book. Especially, Prof. Fushi Zhang (Tsinghua University) and Prof. Andong Xia (Institute of Chemistry, Chinese Academy of Sciences) have reviewed the manuscript of chapter 2 and give their valuable suggestion to the contents for optical recording. Dr. Liping Ma (University of California, Los Angeles, USA) and Dr. Shih-Yuan Wang (Hewlett-Packard Laboratories, USA) have read our original draft of chapter 3 and chapter 4, and made comments for the revision. I would extend my gratitude to my collaborators for research: Prof. Hongjun Gao (Institute of Physics, Chinese Academy of Sciences), Prof. He Tian (East China University of Science and Technology), Prof. François Diederich (ETH Zurich, Switzerland) , and Prof. Daoben Zhu (Institute of Chemistry, Chinese Academy of Sciences) for his kind help for these years. I should also thank my students: Dr. Huimeng Wu, Dr. Yongqiang Wen, Dr. Guiyuan Jiang, Dr. Wenfang Yuan, Dr. Junping Hu, Dr. Fengyu Li and Dr. Yanli Shang for their hard work in my group. Finally, I am grateful to the Natural Science Foundation of China, the Ministry of Science and Technology of China, and the Chinese Academy of Sciences for continuous financial support. The National Science Fund for Distinguished Young Scholars is especially acknowledged for the work in this book.

Yanlin Song

Beijing

August 2008

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CHAPTER 1

HIGH DENSITY MAGNETIC DATA STORAGE

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Areal density in magnetic data storage can be increased by the scaling method. However, the increase cannot continue indefinitely, due to the limit of fabrication technology and thermal stability. To postpone the onset of thermal instability, materials with high magnetic anisotropy are required for recording media in conventional longitudinal magnetic data storage. Nevertheless, this method is limited in further increasing the recording density because it requires extremely huge write field for high anisotropy media. Therefore, to achieve ultrahigh density magnetic data storage, alternative methods has to be explored. This chapter highlights recent advanced technologies and research work proposed for ultrahigh density magnetic data storage, including perpendicular recording, patterned media storage, self-assembling media and molecule-based magnets.

1. Introduction

In order to meet the rapid growing capacity of data storage, ever-increasing areal densities and data rates are needed. Magnetic recording, as one of the most important technologies in data storage, has received enormous

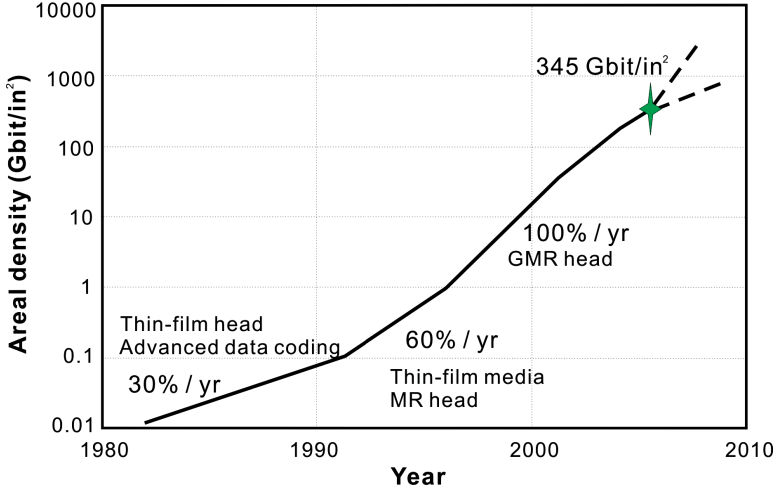


Fig. 1. Areal density for magnetic data recording. (Adapted from Ref. 1 with permission, © 1999, Academic Press).

attention. Figure 1 shows the trend in areal density of magnetic data storage during the past 30 years. Before 1990, the data storage capacity increased at about 30% per year, which arose from the introduction of the thin-film head and advanced data coding. Then a 60% growth rate began in 1991, which was caused by the applications of the magnetoresistive head (MR) and thin-film recording media.¹ During the late 1990s, the areal density of the hard disk increased by over 100% per annum through the introduction of a giant magnetoresistive (GMR) reading sensor.

Since then, higher areal density has been achieved by scaling the components of the disk drive and/or using high K_u (magnetic anisotropy) alternative recording media. Scaling methods can decrease the dimension of recording media, the geometry of the read–write head and the head–media spacing. However, scaling cannot continue indefinitely because of the limit of fabrication technology and thermal stability. Higher K_u materials maintain thermal stability at smaller grain size, but require stronger magnetic field to switch the magnetization of bits, which could be beyond the capability of the write head. In fact, we are already approaching the limitation of thermal stability for the conventional longitudinal recording method.^{3,4} In order to further increase the areal density of magnetic data storage, alternative method must be explored for ultrahigh density data

storage. In September 2006, an areal density of 345 Gbits/in² in perpendicular recording was demonstrated in laboratory by Hitachi Global Storage Technologies.² Nonetheless, this still cannot fulfill the rapidly increasing requirement of information capacity. The pursuit of ultrahigh density data storage still continues. Furthermore, other approaches are proposed besides perpendicular recording.

This chapter will begin with the basic theory of magnetic recording. This will be followed by the current magnetic recording technologies and the limitation set by the thermal instability. Then, some of the recently implemented and promising technologies and research work for ultrahigh density data storage will be reviewed. This chapter focuses primarily on the recording media and some recording mechanisms will also be discussed.

2. Theory of Magnetic Recording

2.1. *Magnetic states of matter*

Magnetic moment of electrons originates from two kinds of electron moments. One, associated with an intrinsic angular momentum of the electron, is called the intrinsic spin magnetic dipole moment. The other, associated with the electron orbit surrounding the nucleus, is called orbital magnetic dipole moment. The total moment of the electron is the combination of those two. Typically, spin magnetic dipole moment is much greater than the orbital one. Consequently, the orbital magnetic dipole moment may be neglected. The magnetic moment of an atom is the total magnetic moments of all the electrons inside the atom. Finally, all the atoms' magnetic moments in a substance combine collectively to produce the magnetic moment of the substance. Therefore, the differences in electron configurations determine the different magnetic properties of a substance. Based on various electronic configurations, magnetic materials can be categorized into several types: diamagnets (e.g. copper and gold), paramagnets (e.g. aluminum and manganese), ferromagnets (e.g. iron, cobalt, nickel, gadolinium, dysprosium and permalloy), ferrimagnets (e.g. Fe₃O₄) and antiferromagnets (e.g. MnO).

Diamagnetic materials have paired electrons and compensated electron moments. When an external magnetic field is applied, their magnetic

moments prefer to align opposite to the field and create a weak, negative magnetic susceptibility. Magnetic susceptibility χ is defined by $\chi = M/H$, where M is magnetization of the material, a measure of the magnetic moment per unit volume; and H is the external magnetic field. The value of χ is the extent to which a material may be magnetized in response to a given applied magnetic field. Typically, diamagnetic molar susceptibilities are very small and independent of the strength of the external magnetic field and temperature.

Unlike diamagnets, other magnets contain unpaired electrons. The alignment of the unpaired electrons spinning through the exchange interaction in each magnetic domain generates a spontaneous magnetization. The interaction between the two unpaired electrons can be described by the following equation:

$$E_{\text{ex}} = -2J_{ij} \vec{s}_i \cdot \vec{s}_j$$

where $\vec{s}_i$ and $\vec{s}_j$ are electron spin vectors of atoms i and j respectively, and J_{ij} is the exchange integral determined by an integration over the overlapping wave functions of those two electrons. If $J_{ij} = 0$, there is no interaction and the substance exhibits the paramagnetic property. If $J_{ij} > 0$, the spins tend to be parallel, leading to ferromagnetism. If $J_{ij} < 0$, the spins are in antiparallel, leading to anti-ferromagnetism.

For paramagnets, each dipole on each atom or ion does not interact with other one in the absence of an external field. When placed in a field, those random oriented dipoles will align and result in a net magnetization. However, when the field is removed, the alignment will be quickly disrupted by thermal perturbation, resulting in a zero net magnetization. Paramagnetic susceptibility is temperature-dependent. When the temperature increases, the magnetic susceptibility χ will decrease because the thermal agitation makes aligning the individual magnetic moments difficult. When the temperature is fixed and the applied field is increased, the magnetization will increase because the external field can suppress thermal agitation and align magnetic moments. Generally, magnetic susceptibility of paramagnets is weak.

For ferromagnets, individual atomic spin moments interact with each other and align spontaneously in the absence of an external field. In each

magnetic domain, the spin moments align in the same direction and create a net magnetization. But the alignment of spin moments varies in different domains, resulting in an unmagnetized bulk sample in most cases. When an external field is applied, the magnetic domains line up with each other and a magnetic field will be generated inside the material. The internal magnetic field can be even stronger than the external applied one. This signifies that these materials have a large positive magnetic susceptibility. Unlike paramagnets, when the applied field is removed, ferromagnets will still keep a portion of magnetization in the direction of the external field. However, when the temperature increases to a certain point (called the Curie temperature, T_C), the thermal energy exceeds the spin coupling (exchange) energy, and the arrangement of magnetic domains breaks down. Thus, at high temperature, ferromagnets will lose their ferromagnetism and behave like a paramagnet.

Since the exchange coupling of individual atomic spin moments in each magnetic domain does not always lead to parallel alignment of all spins, antiferromagnets and ferrimagnets should also be considered.

In antiferromagnets, each atomic spin moment is opposite to adjacent ones spontaneously. As a result the net magnetic moment of the material is zero. But due to spin canting, lattice defects and frustrated surface spins in nanoscale particles, antiferromagnetic materials may exhibit a weak net magnetization. The spontaneous antiparallel coupling of atomic magnets can be disrupted by heating. At a very low temperature, an antiferromagnetic material exhibits no response to the external field, because the antiparallel ordering of atomic spin moments is rigidly retained. But at higher temperature, some atomic magnetic moments break free from the orderly arrangement and align with the external field. When temperature further increases to the transition temperature (called the Néel temperature, T_N), the material reaches a maximum magnetization. Beyond this temperature, thermal energy progressively prevents alignment with the magnetic field. Then the magnetism caused by the alignment of atomic magnetic moments continuously decreases as temperature is increased. The typical Néel temperatures are low, e.g. T_N of MnO is 122 K. While some antiferromagnetic materials can have very high Néel temperatures, even several hundred °C above the room temperature.

The exchange interactions in ferrimagnets lead to parallel alignment of atomic spin moments in some crystal sites and antiparallel alignment in others. Unlike antiferromagnets, the opposing moments in ferrimagnets are not equal and generate a net magnetization. Compared with a ferromagnetic material, a ferrimagnetic material has a very similar magnetic behavior, but a different magnetic ordering. Actually, ferrimagnetism is observed only in some compounds that have complex crystal structures. One important example is magnetite (Fe_3O_4), in which two trivalent iron ions align with opposite moments and cancel each other, and so the net moment arises from the divalent iron ion.

2.2. Magnetic hysteresis

As mentioned before, a ferromagnetic material can keep its magnetization to some extent in a given direction after removal of the external magnetic field. This property is displayed by a magnetic hysteresis loop (M - H loop).

A typical M - H loop is shown in Fig. 2, which describes the change of the magnetization (M) of a ferromagnetic material with the variation of the intensity of an external magnetic field (H). If the initial magnetic state of a material is never magnetized or fully demagnetized ($M = 0$), the

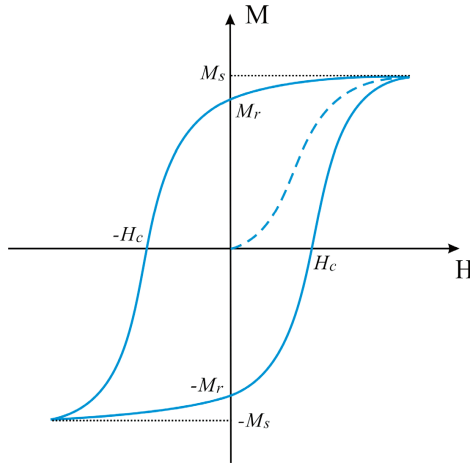


Fig. 2. A typical M - H loop for a ferromagnetic material.

magnetization will increase with increase of H , following the dashed line (called the initial magnetization curve). The maximum value of M is M_s (called saturation magnetization). At this point, all magnetic moments in the material are aligned and the material is magnetized to saturation. When H drops to zero, M will follow the solid line and have a little decrease. At the point where the external field is zero ($H = 0$), some magnetization will still remain in the material. This is called remnant magnetization (M_r), which is very important for magnetic memory devices. Then H goes to the opposite direction, and the magnetization will keep decreasing until it reaches zero. The external force required to remove all of the remnant magnetization from the material is called the coercive force, or coercivity ($-H_c$). After this point, H continues to increase in the negative direction, and magnetization in the opposite direction will be generated until it reaches another magnetic saturation ($-M_s$). Then H reduces to zero, and the magnetization will decrease to another remnant magnetization ($-M_r$). When H increases to H_c in the positive direction, the magnetization of the material will be removed again. After that, if H keeps increasing, the curve will take a different path (the solid line) to the saturation point to complete the loop. Generally, the M - H loop of a magnetic material is symmetrical relative to the center origin point O, i.e. the absolute values of M_r , M_s and H_c in both the positive and the opposite direction are the same.

As mentioned above, the M - H loop is characterized by remnant magnetization (M_r), saturation magnetization (M_s) and coercivity (H_c), which are all crucial magnetic properties of a material. M_r is the remaining magnetization of a ferromagnetic material when the applied magnetic field is removed. M_s is the maximum magnetization that a material could generate. Both M_r and M_s are dependent on the composition of the magnetic material and the processing, such as the nature of the atoms and electron structures of materials and also the crystal structures. H_c is the intensity of the external field required to remove all the magnetization of a material after saturation. Rotation and domain wall motion are two primary processes of magnetization reversal. The value of H_c is determined by these processes.⁵ Magnetic materials with $H_c < 10$ Oe are usually called soft materials; if $H_c > 100$ Oe, called hard magnetic materials. Since high H_c means that the materials are hard to demagnetize (good stability), high H_c magnetic materials are naturally used as magnetic

recording media. On the contrary, low H_c magnetic materials are good candidates for the recording head, because it is easy to reverse the magnetization by external field.

Besides, the M - H loop also provides a great deal of other information about magnets. The shape of the initial magnetization curves displays the magnetic characteristics of materials. The curve also shows the processes of domain wall motions. There are two different modes of domain wall motions: nucleation and pinning.⁶ In the nucleation-type, magnetic saturation is reached quickly at a low field. This shows that the domain wall can be easily moved and not pinned significantly. In the pinning-type, the saturation magnetization is reached only when a strong field is applied. Here domain wall is substantially pinned and a relatively strong field is needed to remove pinning sites.

Remnant squareness (S) and coercive squareness (S^*) are used to measure how square the loop is.

$$S = \frac{M_r}{M_s}, \quad S^* = 1 - \frac{M_r/H_c}{\left. \frac{dM(H)}{dH} \right|_{H_c}}.$$

Usually, large S and S^* are required for magnetic recording media since the parameter S characterizes the flux available for reading and the parameter S^* characterizes the ability of the medium to sustain sharp transition.^{7,8}

2.3. Magnetic anisotropy

The magnetization of magnetic materials always exhibits direction-dependence. This is called magnetic anisotropy, which comes from the different internal energies of the magnetization of a material in different directions. The direction, where the lowest field is required to reach the saturation magnetization is the easy axis. The direction where the highest magnetic field is required is the hard axis. Magnetic anisotropy has a strong effect on the properties of magnetic materials, such as coercivity and remnant magnetization. Therefore it is essential in the design of commercial devices based on magnetic materials.

Generally, magnetic anisotropy is influenced by the structure and symmetry of a material, known as magnetocrystalline anisotropy, which is

generated by the coupling between the electron orbital and the lattice (spin orbit coupling). Thus magnetization will be coupled to electron orbitals, resulting in the lowest or highest energy state along certain symmetry axes.¹ This can be easily determined from the different magnetization curves along different directions. For example, for a single crystal hexagonal closed-packed (hcp) cobalt, the magnetization along the [0001] direction (i.e. the c -axis) is much easier than along other directions; while in the basal plane ($\langle 1010 \rangle$, 90° from the easy direction) the magnetization is much more difficult. So the c -axis is the easy axis and the $\langle 1010 \rangle$ type directions are the hard axis.⁹ The energy required to deflect the magnetization from the magnetocrystalline easy axis to other directions is called magnetocrystalline anisotropy energy.

Also, magnetic anisotropy can be related to the mechanical stress in the system and the external magnetic field. This effect is known as magnetostriction, defined by the change of physical dimensions of materials in response to the magnetization change. The process is dominated by the migration of domain walls and the rotation of domains within the material in response to an external field, which in turn causes the change of dimensions.⁸ The inverse effect is the change of magnetization of a material when it is subjected to a mechanical stress. One example of magnetostriction application is that the easy axis of the face-centered tetragonal (fct) FePt nanoparticle can be expected to align after annealing in the presence of a magnetic field.¹⁰

The shape of magnetic grains is the third factor that affect the magnetic anisotropy. At the surface of a magnetized material, there are magnetic charges or poles, and a demagnetizing field forms in an opposite direction to the original magnetization. The magnitude of the demagnetizing field is related to the shape of the grain, resulting in the shape anisotropy. For example, considering a long needle-shaped grain, the demagnetizing field is weaker along the long axis than that along the other directions. So the magnetization easy axis is along the long axis of the grain.

2.4. Temperature dependence

The hysteresis curve mentioned above measures the magnetization of a magnetic material by varying the applied field. From the curve, a lot of

important information about the system can be obtained. Besides the hysteresis curve, the variation of temperature can also provide other important information. Temperature affects the thermal motion of atoms, which leads to the disruption of the alignment of molecular magnetic moments.

2.4.1. Curie's law

The dependence of the magnetic moment on temperature for paramagnetic materials is known as Curie's law:

$$\chi = \frac{M}{H} = \frac{C}{T}$$

Here χ is the magnetic susceptibility, M the resulting magnetization, H the applied magnetic field, C a material-specific Curie constant, and T is the absolute temperature in Kelvin. The Curie constant can be determined through experiments by plotting a χ vs. $1/T$ curve. Curie's law is valid only for materials whose magnetic moment is localized at the atomic or ionic sites and where there is no interaction between neighboring magnetic moments. This law indicates that the paramagnetic susceptibility decreases as temperature increases.

2.4.2. Curie-Weiss law

For paramagnetic materials, the relationship between magnetic moment and temperature can be described by Curie's law. The Curie constant C is the slope of the line, which is proportional to the effective magnetic moment for paramagnets. However, the law will not be valid when intermolecular interactions, such as ferromagnets, are involved. In such a system, the susceptibility obeys the Curie-Weiss law:

$$\chi = \frac{C}{T - \theta}$$

Here θ is the Weiss constant. When $\theta = 0$, the Curie-Weiss law becomes the Curie's law. When $\theta \neq 0$, the magnitude of θ indicates the strength of

the intermolecular interaction among neighboring magnetic moments. If θ is positive, the material is ferromagnetic when the temperature is below the transition temperature (called the Curie temperature, T_C , which is equal to θ); if θ is negative, the material is antiferromagnetic when the temperature is below the transition temperature (called the Néel temperature, T_N). The Curie temperature is important in magnetic recording, which indicates on the energy required to disrupt the long range magnetization ordering in the material.

2.4.3. Van Vleck's equation

The total magnetic moment of electron is composed of both spin magnetic moment S and orbital magnetic moment L . Typically, only spin is considered since the spin moment is much greater than the orbital moment like transition metal ions: high spin Mn^{2+} or Fe^{3+} ; Ni^{2+} , Cr^{3+} or Mn^{4+} in an octahedral field; Cu^{2+} and Mn^{3+} as Jahn–Teller distortion.¹¹ However, for some other ions, such as octahedral Co^{2+} , the orbital contribution is significant to the magnetic moment. In that case, Van Vleck's equation is applied.

To derive the equation, the energy term can be expressed as a power series of the applied field (H_0):

$$E_n = E_n^{(0)} + E_n^{(1)}H_0 + E_n^{(2)}H_0^2 + \dots$$

Here $E_n^{(0)}$ is the energy of state n when $H_0 = 0$; $E_n^{(1)}$ is the first order Zeeman coefficient (a measure of change in the energy of state n due to interaction with H_0); $E_n^{(2)}$ is the second order Zeeman coefficient (a measure of change in the energy of state n due to field-induced interaction of state n with higher energy states). After several approximations, the magnetic susceptibility can be described as:

$$\chi = N \frac{\sum_n \left[\frac{(E_n^{(1)})^2}{kT} - 2E_n^{(2)} \right] \exp\left(\frac{-E_n^{(0)}}{kT}\right)}{\sum_n \exp\left(\frac{-E_n^{(0)}}{kT}\right)}.$$

From this equation, the magnetic susceptibility is determined by taking a population-weighted average of the specific level susceptibility. (Van Vleck's work^{12,13} is recommended for further reading.)

3. Conventional Magnetic Storage Technology and Its Challenge

In current magnetic hard disk drives (HDDs), longitudinal recording is employed as the basic method. In this recording mode, the magnetization of recorded bits is parallel to the surface of the disk, as shown in Fig. 3. The recording head moves over the medium at a small fly height. Nowadays, the performance of longitudinal recording has been improved by the giant magnetoresistive (GMR) head. The new recording head consists of separate reading and writing elements, which can be optimized individually. Using the inductive ring type write head can record data along a track with either positive or negative direction in the medium. The resulting stray field pattern is read back by a GMR reading sensor that is located in a narrow gap between two magnetic shields. The shields are used to decrease the interference of the undesired magnetic fields generated from the medium. GMR sensor can therefore “read” only the magnetic field from the desired data bit.¹⁴

The GMR effect can be explained by the interaction of electron spin and magnetic field. It is well known that an electron can either spin up or spin down. If the spin direction of conduction electrons is parallel to the

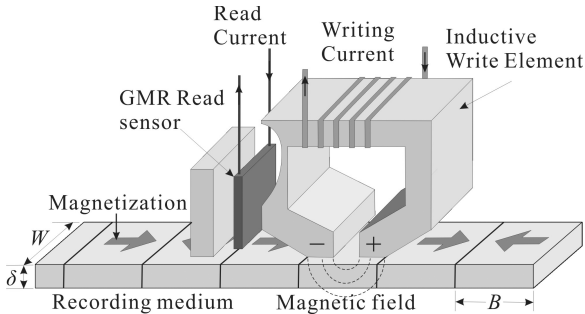


Fig. 3. A typical longitudinal recording model. δ is the medium thickness, W is the track width and B is the bit length. (Adapted from Ref. 9 with permission, © 2000, IBM)

magnetic orientation of the material, it will move with less resistance. On the contrary, if the spin direction of conduction electrons is opposite to the magnetic orientation, it will collide with atoms frequently, resulting in a high resistance. This phenomenon is called the GMR effect, which was first discovered in the Fe/Cr multilayer¹⁵ and later also found in other inhomogeneous materials, such as the Co/Cu multilayer.¹⁶

The application of the GMR effect led to a new development — the spin-valve read head, with a multilayer structure. Generally, it consists of the following layers. The first is an antiferromagnetic exchange film (e.g. FeMn). It is used to “pin” the Co layer magnetization in a certain direction. The ferromagnetic Co layer is called a pinned layer. Next is a copper spacer layer, followed by the second ferromagnetic layer, called a free layer. Typically CoFe or NiFe is used as a free layer because it is magnetically soft and can be aligned parallel or antiparallel by very small fields. Finally, there is an underlayer (e.g. Ta), which gives a good surface to grow on and a cap to avoid oxidization in air.¹⁷ The exchange coupling between the two ferromagnetic layers can be mediated by conduction electrons in the spacer layer. When a strong external field is applied, the direction of the magnetization in both magnetic layers will be aligned, from an antiparallel to a parallel configuration, which will exhibit a distinct change in resistance, with a concomitant change in current (for a constant applied voltage). For the Fe/Cr multilayer, the experiment demonstrated that the change of resistance is more than 50%.¹⁵ (For the physical description of GMR, please check Ref. 7.)

The discovery and application of the GMR effect in the read head improved the ability to sense a change in the magnetic field that occurs within a very small distance. Thus the GMR read head can detect small recorded bits and read them at higher data rate. It creates more room to reduce the size of bits and increase the areal density of magnetic recording. However, the optimization of the areal density is still limited by the material of the recording media.

As the candidate of magnetic recording media, several aspects must be considered: high signal-to-noise ratio (SNR), high thermal stability, very smooth surface and small magnetic grains with uniform size. The most common one is a thin film medium, with complex multilayers. The structure, material and function of each layer are shown in Table 1. Underlayer

Table 1. Schematic illustration of the layer structure, material and function of thin film used for longitudinal magnetic recording.^{21,22}

Layer structure	Material	Function
Lubricant	Perfluoropolyether	Lubrication
Overcoat	Carbon	Protection
Magnetic layer	Co alloy	Recording
Underlayer	Chromium (Cr)	Orientation control
Sublayer	NiP	Hardness
Substrate	AlMg/glass	

can promote the growth of a particular crystallographic texture, grain size and morphology in the magnetic layer. As a result, it increases the coercivity and squareness of the magnetic layer. Because of the similar atomic orientation and size relationships between hcp Co grains and bcc Cr grains, Co alloy films can grow with a significant degree of heteroepitaxy on the Cr underlayer.¹⁸ The crystallographic texture of Co alloy can be controlled by modifying the microstructure of the Cr underlayer, which depends on growth process conditions, such as the base vacuum, the temperature of the substrate, the pressure of the sputter gas and the film thickness.¹⁹ Besides the Cr underlayer, NiAl is used as an alternative underlayer because it produces finer grains in the magnetic layer.²⁰ The carbon overcoat is used to protect the magnetic film from mechanical damage and corrosion during the start and stop point of the reading and writing processes. A layer of NiP, deposited on the substrate, is used to enhance the durability of the combined film structure.

The magnetic layer is essential in the recording system. The requirements for hard magnetic media to obtain very sharp transitions and high readback signal are the following: high remnant magnetization (M_r), saturation magnetization (M_s), coercivity (H_c), magnetic anisotropy, and small thickness (δ).²¹ So far, several materials have been selected as magnetic recording media, such as γ -Fe₂O₃, Co alloy,²³ CrO₂ and barium ferrite.

To obtain a high areal density, one employs the scaling method by shrinking the relevant head and medium dimension (including bit

length, track width, medium grain size, medium thickness, fly height and head gap) by a factor s , which causes an increase of areal density by s^2 . However, this approach cannot continue indefinitely, for several reasons. First, current technologies are unable to achieve such dimensions. Second, the scaling will lose the amplitude of the signal and decrease the SNR rapidly, which has to be compensated for by a more sensitive reading head design. Third, when the size is smaller than a critical value, the electronic and magnetic properties of the grain will change dramatically. Moreover, when the distance between the head and the medium becomes too short, the tunneling effect and surface roughness will have to be considered. Finally, in recording bits, if the size of the grain is too small, the medium will no longer be thermally stable and data loss will occur. The distribution of grain size affects areal density. If the size is not uniform, but spreads in a range, the information stored in smaller ones will decay more quickly than that in larger ones. Therefore, decreasing the distribution of grain size will improve the SNR. An ideal magnetic medium should contain small grains with a narrow distribution of the size.

According to the physics of magnetics, two key factors must be considered in order to achieve very high areal density: (1) the superparamagnetic effect (thermal stability) in recording media; (2) the finite sensitivity of the readback head. In both cases, the limitation arises because the signal energy becomes too small to be comparable with the ambient thermal energy.²⁴

Thermal stability sets an upper limit on the areal density of the medium in magnetic recording. The Arrhenius equation indicates the relationship between the relaxation time τ and the activation energy barrier of magnetization reversal E_B :^{23,25}

$$\tau_{\pm} = \tau_0 \exp\left(\frac{E_B^{\pm}}{k_B T}\right).$$

In the absence of an external field H , $E_B^0 = K_u V$, where K_u is the magnetic anisotropy and V is the volume of grains, $+$ and $-$ mean the “upward” and the “downward” magnetization direction respectively, and τ_0 is

the characteristic relaxation time, determined by the intrinsic properties of the recording medium. When the grain gets smaller, the energy barrier in each grain ($K_u V$) becomes so close to the thermal energy ($k_B T$, where k_B is Boltzmann's constant and T is the temperature) that the releasing time decreases dramatically. This is known as the superparamagnetic effect. With the presence of external magnetic field H ,

$$E_B^\pm(H, V) = E_B^0 \left(1 \mp \frac{H}{H_0} \right)^n, \quad E_B \text{ can be either increased or decreased and}$$

the thermal decay will be affected. Here, H_0 is the intrinsic switching field. Generally, in order to avoid thermal instability, $K_u V / k_B T \approx 50\text{--}70$ is required for magnetic media.^{3,23} Several improvements have been tested to increase thermal stability by improving epitaxy²⁶ and perfecting the magnetocrystalline,^{24,27} or using magnetic materials with ultrahigh magnetic anisotropy such as hexagonal close-packed phase CoPt oxide media with high Pt content, L1₀ phase-ordered CoPt and FePt alloys, or (Co/Pd)_n multilayer structures.^{27,28} However, because of the constraint of the writing head, the infinitely high K_u material is not reasonable.

To increase the sensitivity of the reading head, alternatives must be explored to improve areal density. The tunneling magnetoresistance (TMR) sensor may be applied in the future; it consists of an antiferromagnetic layer, a reference layer, a tunneling barrier and a free layer.²⁹ The challenge of applying it in recording systems is to obtain efficiently small resistance. Since the resistance of a tunneling junction increases exponentially with the thickness of the oxide tunneling barrier (e.g. a normal aluminum oxide monolayer), the barrier thickness must be uniform at the atomic level. This presents a huge technical challenge.

In order to accomplish ultrahigh density data recording, the longitudinal recording mode requires an infinitely thin recording layer combined with an excessively high coercive force. However, the former implies a deterioration of the SNR due to a drastic reduction of the reading flux from the medium, and the latter is limited by the writing ability of the inductive write head. In practice, these factors place an upper limit on the areal density. Therefore, this becomes an obstacle to realizing ultrahigh density longitudinal recording.

4. High Density Magnetic Recording

As discussed above, the areal density of the conventional longitudinal recording model is limited by the superparamagnetic effect. New approaches are needed to fulfill the requirements of the rapid growth rate of information. Perpendicular recording is technically the closest alternative to longitudinal recording, in which the magnetization of recorded bits is normal to the plane of the medium. It saves space and increases thermal stability. Patterned media (the location and size of the magnetic features are predetermined by the medium manufacturing process) are used with one grain as one bit, so the capacity is increased. To get even smaller patterned uniform grains, self-assembled magnetic nanoparticle arrays are the most promising method due to their low cost and large area. Besides conventional magnetic materials, new materials are explored. Molecular-based magnets give more room for further increase of areal density data storage.

4.1. *Perpendicular recording*

The perpendicular recording technology was proposed by Prof. Iwasaki in 1975.^{30,31} It is a promising candidate for high density magnetic data storage, since it is technically the closest to conventional longitudinal compared with other technologies and methods. The significant difference between perpendicular and longitudinal recording is that the former orients the magnetization of the recording bit normal to the surface of the medium, thereby saving space in the plane of the medium and increasing thermal stability. Using perpendicular recording technology, an areal density of 345 Gbits/in² was achieved in laboratory demonstration.² Since the maximum areal density achievable by perpendicular recording is expected to be beyond 1 Tb/in²,³² there is room for further improvement. The following discusses the special design of the recording head, media and advantages and challenges of perpendicular recording. Detailed reviews can be found in Refs. 28, 33 and 34.

The typical perpendicular recording model is shown in Fig. 4. There are three key elements in perpendicular recording: a single pole perpendicular write head,³¹ a CoCr anisotropy recording film³⁵ and a soft magnetic underlayer (SUL).³⁶

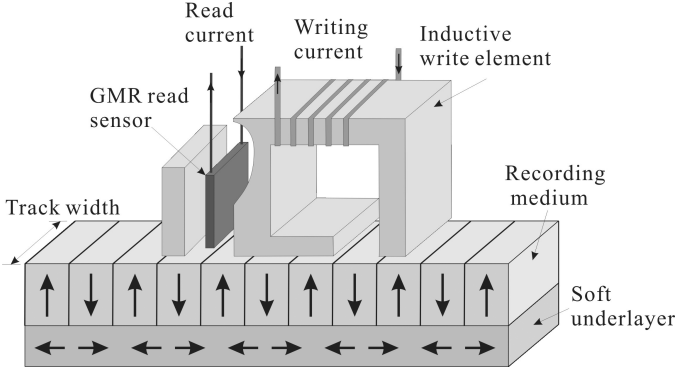


Fig. 4. A typical perpendicular recording model: a magnetic recording medium and a soft underlayer used together with a single-pole head. (Adapted from Ref. 9 with permission, © 2000, IBM)

4.1.1. Single pole write head

In conventional longitudinal recording, the maximum field generated from a ring head (RH) is limited by $2\pi M_s$, where M_s is the saturation magnetization of the write-pole material while in perpendicular recording the write field is generated between the trail pole of a single pole head and a soft underlayer. In this geometry, the upper limit of the write field is $4\pi M_s$, twice the field from the longitudinal recording head. The ability to generate higher fields makes it feasible to record bits on a higher magnetic anisotropy medium, which in turn further delays the superparamagnetic limit to a higher areal density.³⁷ Thereby, to realize higher-resolution writing, a strong and sharp perpendicular field from a single pole type write head is required.^{38–40} This requires that a single pole write head should be designed to energize the recording medium. A recording layer should consist of a single pole head and a double-layered medium. Also, a soft magnetic back-layer is designed to effectively bring out the effect of magneto static interaction between them. Besides, the recording layer of the medium should be made to narrow the dispersion of the grain size and coercivity.

4.1.2. Perpendicular recording media

Perpendicular recording provides a new technique to postpone the limitation of thermal stability. One of the important reasons in the

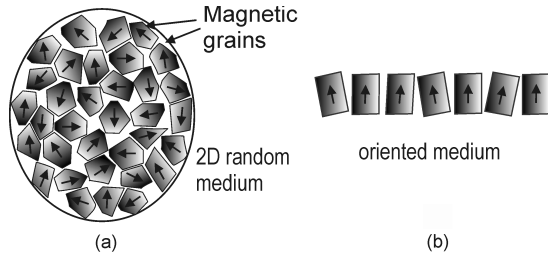


Fig. 5. Schematic diagrams illustrating (a) a longitudinal medium with randomly oriented easy axes and (b) a perpendicular medium with aligned easy axes. (Adapted with permission from Ref. 42, © 2004, Kluwer Academic Publishers)

perpendicular recording mode is the relatively well-aligned easy axis of each magnetic grain in the direction perpendicular to the plane of the disk [see Fig. 5(b)]. Thus, the bit transition in such a highly aligned film relaxes the stringent requirements of the write field for achieving sharp transitions for conventional longitudinal recording, where the magnetization is randomly oriented in the plane [see Fig. 5(a)].^{41,42} Also, the opposite states of magnetization in neighboring bits generate a minimum demagnetization field, making the bits smaller without superparamagnetism and keeping their memory. Since the demagnetization field in perpendicular recording decreases with increasing thickness, thicker media with smaller grain can be applied in perpendicular recording than in longitudinal recording to achieve the same areal density.

An ideal perpendicular recording medium requires:

- (1) Sufficiently small and uniform grains with a small intragranular exchange to increase the SNR
- (2) A high anisotropy and texture control to improve thermal stability
- (3) Unity squareness ($S \approx 1$) of its $M-H$ loop to avoid excess noise in the DC saturated state.

The typical perpendicular recording medium has a double-layered structure composed of a magnetic recording layer (a hard magnetic material with high magnetic anisotropy) and a soft underlayer (a soft magnetic material). The latter is a new component compared with the longitudinal recording model. Its function will be discussed later.

To optimize the specifics, the materials with high magnetic anisotropy are used as magnetic recording layers. So far, two types⁴¹ of recording magnetic materials have been used in the perpendicular recording model:

- (1) Alloy-based media, such as CoCr alloy,³⁵ L1₀ phase FePt⁴³ and CoPt. The magnetic anisotropy is controlled by the magnetocrystalline anisotropy, so it is highly textured.
- (2) Multilayer-based magnetic media, such as CoCr/Pt,⁴⁴ and Co/Pd⁴⁵ multilayered films. The magnetic anisotropy is controlled by the interfacial interaction between a magnetic layer (such as Co) and a high polarization nonmagnetic spacer (such as Pd or Pt). This type of media is weakly textured.

Comparing those two kinds of recording magnetic layers, the latter is preferable because it has a significantly larger anisotropy and a remnant squareness of one. Consequently, the anisotropy field, H_k , which keeps the magnetization in the perpendicular-to-the-disk direction, is larger than the maximum demagnetizing field, $4\pi M_s$. Therefore, the thermal stability can be improved and a higher areal density can be achieved.

4.1.3. *Soft underlayer (SUL)*

The use of the SUL, located below the recording layer, is a critical part of perpendicular magnetic recording. It provides the possibility of recording on media with high anisotropy, which increases the thermal stability of the recorded information in the disk. The effect of the SUL is like a mirror in both the write and the read process. It directs the magnetic flux from the write pole to the collector pole and generates a mirror image of the write pole. This results in almost doubling of the write field and reducing the demagnetizing field, thus recording bits at a higher density than conventional longitudinal recording.

The characteristics of the longitudinal and perpendicular recording models are summarized in Table 2.^{46,47} Perpendicular recording is considered as the promising alternative to conventional longitudinal magnetic recording technology. The highly aligned anisotropy axis of individual grains in perpendicular recording media facilitates recording narrow

Table 2. Complementarity between the longitudinal and perpendicular recording model. (Reprinted with permission from Ref. 47, © 2005, Elsevier)

	(a) Longitudinal model	(b) Perpendicular model
	$\lambda \rightarrow 0, H_d \rightarrow 4\pi M$	$\lambda \rightarrow 0, H_d \rightarrow 0$
Head	Dipole (ring) type	Single pole type
Medium	Longitudinal anisotropy (2D random) Thin δ Low M_s , high H_e Low squareness Recording layer only	Perpendicular anisotropy (uniaxial) Thick δ High M_s , high H_e High squareness Soft underlayer
Thermal stability	Good at low density	Good at high density
Write	Medium outside of write flux path • Narrow spacing required	Medium in write flux path • Efficient writing • High frequency writing • Wide temperature range • Relaxed spacing; sharp transition/narrow erase band • High TPI servo writing
Read	Low output • High head sensitivity required; flux from head-on transition • Wide reading	High output • High SNR • Good tracking servo • Relaxed head sensitivity; flux from coupled transition • Narrow reading

tracks with sharp transitions into a thicker recording layer, reducing noise and increasing readback signal. Moreover, the use of a soft underlayer helps to stabilize the grain. The mirror effect of the SUL produces a double writing field, which allows writing transitions in recording media with higher anisotropy, resulting in more thermal stability.

However, before perpendicular recording can be extensively applied, efforts need to make to resolve technical problems. For example, to overcome the high sensitivity of the SNR to the switching field distribution in perpendicular media, tilted media were proposed^{48,49}; to optimize head

design, heat-assisted magnetic recording (HAMR) and/or thermally assisted magnetic recording were used.⁵⁰ Perpendicular recording defers the superparamagnetic limit in the conventional longitudinal recording system, but still cannot meet the growing requirement of data storage. Further increasing the areal density will be realized by new designs and pathways. The following lists some new designs on the recording media, which are believed as promising candidates for the future data storage.

4.2. Patterned media

In conventional longitudinal magnetic recording media [as shown schematically in Fig. 6(a)], each bit contains 50–1000 grains to control the SNR. And the size of each grain is limited by thermal instability of the thin film medium. Assuming that the grain is about 10 nm (typically, a little larger), the size of a single bit will be 0.5–10 μm in size, corresponding to

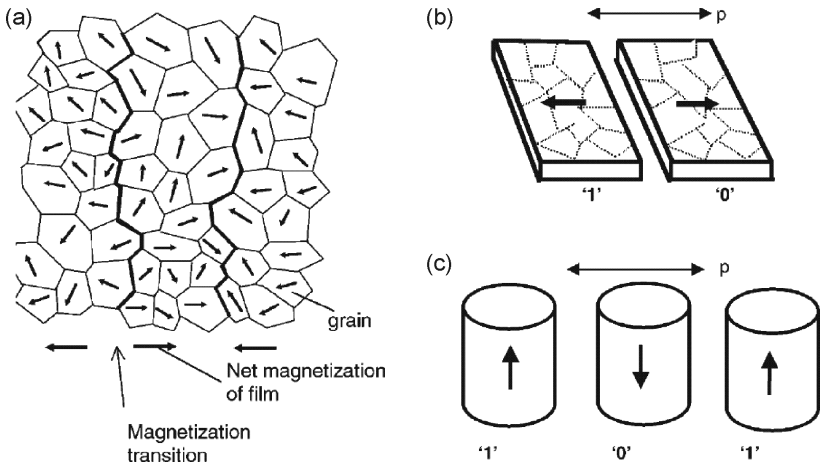


Fig. 6. Schematic drawing of (a) a conventional thin film medium, consisting of single-domain, exchange-decoupled grains. Bits are represented by the transitions between oppositely magnetized regions. Each bit cell contains tens or hundreds of grains. (b) A patterned medium with in-plane magnetization. The single-domain bits are defined lithographically with period p . They can be polycrystalline (indicated by dotted lines) with exchange coupling, or single crystal. (c) A patterned medium with perpendicular magnetization. Binaries 1 and 0 are shown. (Reprinted with permission from Ref. 51, © 2000, Annual Reviews)

an areal density of less than 15 Gbit/in². The simulation predicted that the superparamagnetic limit for longitudinal recording on thin films occurring at the densities is about 200 Gbit/in².^{3,4}

One solution to this problem is patterned magnetic media [as shown in Figs. 6(b) and 6(c)], in which data are recorded in an ordered array of highly uniform magnetic islands separated by a nonmagnetic matrix or material with altered magnets. Each island (also called the switching volume) is capable of storing an individual bit, depending on the direction of magnetization. For example, magnetization up represents “1,” and magnetization down represents “0”.⁵¹ Unlike thin film media, this island may contain one grain, or several exchange coupled grains, and each island behaves as a single magnetic domain. This may effectively eliminate the transition noise and statistical noise problems.^{23,52} Moreover, the transitions are now defined by the patterning and not by the head field. Thus, patterned media are much more stable than the conventional recording media; even those islands are smaller than 10 nm. As a result, the areal density can be increased dramatically compared to conventional recording media. For example, a 50-nm-period patterned medium corresponds to a density of 250 Gbit/in², and a 25-nm-period one corresponds to a density of around 1 Tbit/in².⁵³ Therefore, a patterned medium is a promising candidate for the future recording system with a capacity beyond 1 Tbit/in². However, there are a number of technical problems which need to be resolved, such as fabrication of large-area arrays of magnetic grains with size less than 50 nm at low cost, addressing of the array with high spatial precision, and different recording and writing mechanisms and systems. These issues will be discussed below.

4.2.1. *Fabrication of patterned media by lithography*

Nowadays, significant efforts are devoted to the fabrication of patterned recording media. Many methods have been reviewed to fabricate nanoscale or submicroscale patterned magnetic elements.^{51,55–57} Unfortunately, conventional photolithography no longer meets the requirement for the high resolution of patterned media. In conventional photolithography, a pattern of a geometric shape is created in a mask, and then transferred to a thin radiation-sensitive layer material (called resist), which is placed on the surface of a semiconductor wafer. Finally, the areas which are not protected

by the resist are removed through etching. The resolution in conventional photolithography is limited by the wavelength of light (λ) used and the system numerical aperture (NA) with a minimum feature size of about $\lambda/(2NA)$. For generation of highly ordered arrays of uniform “islands” with dimensions smaller than 50 nm, the conventional optical method cannot work. Instead, some advanced nanolithography techniques, such as E(electron)-beam lithography, X-ray lithography, nanoimprint lithography and interferometric lithography, need to be used.

Among the aforementioned nanolithography techniques, E-beam lithography is widely used to fabricate patterned media. Here, an electron beam is used to write a desired structure directly on a thin resist layer. Although the calculation from diffraction limitation predicts that an E-beam lithography can be obtained as a spot as small as 1 nm by increasing the energy of the electron beam, the secondary electrons produced by high energy electrons⁵⁸ and the following process⁵⁷ limit its resolution. Theoretically, 10 nm spots are possible, and so far the smallest spot demonstrated is an array of 12 nm dots with a 25 nm period by E-beam lithography on a AuPt layer,⁵³ which suggests a potential density of around 1 Tbit/in² for patterned bits. Compared to other methods, E-beam lithography has high resolution, excellent flexibility and reasonable patterning speed. Due to low throughput and expense, when exposing large areas, stitching errors between the different written fields will distort the long range coherence of the array. Therefore, this method is not suitable for the fabrication of large-area samples.⁵¹ However, E-beam lithography can be applied for preparation of masks for master/replication methods, such as nanoimprinting.

In X-ray lithography, UV light is replaced by X-rays, which are produced by synchrotron radiation from a bending magnet in a high energy electron storage ring. The advantage of using X-rays is that diffraction effects can be reduced significantly because the wavelength of X-rays (0.4–5 nm) is much shorter than that of UV light (200–400 nm). Therefore, higher resolution can be achieved. As with high energy electron beams, X-rays have a photoelectron blur problem, which is caused by the excitation of photoelectrons and the associated shower of secondary electrons. Ultimately, this places a limit on the smallest achievable feature.⁵⁸ The resolution limit of X-ray lithography is about 20 nm. However, X-ray

lithography has a high throughput capability because parallel exposure can be adopted.⁵⁷

Nanoimprint lithography (NIL) includes two processes. One is nanoimprinting. In this process, a mold with nanometer scale features is imprinted on a thin resist film and creates a pattern with a thickness contrast in the film. The other process is 'lithography', which transfers the pattern into the entire resist thickness by anisotropic etching.⁵⁹ Although the mold must first be patterned by E-beam lithography or other methods which may be expensive and time-consuming, repeatable use with a long lifetime (depending only on the limit of wear and contamination) will be able to counteract this disadvantage. Therefore, this technique is inexpensive and time-saving. Moreover, the duplicating process of nanostructures on the mold in the resist film is not affected by wave scattering, diffraction and interference in a resist, and backscattering from a substrate. Therefore nanoimprint lithography provides a way to fabricate sub-10-nm structures. In the past few years, it has received considerable attention. For example, metal patterns with a feature size of 25 nm and a period of 70 nm were made with a lift-off process by nanoimprint lithography.⁶⁰

Interference lithography (IL), or holographic lithography, allows periodic arrays of identical particles to be made over several square centimeters. For two-beam interference, two coherent beams interfere at an angle 2ϕ to produce a standing wave, which is recorded in a recording layer (photoresist) with a period of $\lambda/(2 \sin\phi)$. There are also three-beam interference and four-beam interference, which can create different patterns in the photoresist. The minimum spatial period of a pattern is then half the wavelength of the interfering light. Employing UV wavelengths, 200-nm-period gratings can be obtained. For the spatial period of the order of 100 nm, a deep ultraviolet DUV ArF laser ($\lambda = 193$ nm) can be used.⁶¹ But short excimer laser generates too broad a range of wavelengths to produce sufficiently sharp interference patterns. To compensate for the diffraction limit of $\lambda/2$, an achromatic interferometer lithography (AIL) system has been developed, in which the radiation is diffracted by a set of three-phase gratings. The period of the pattern is given by half the period of the gratings, independent of the laser wavelength.^{62,63} For example, an array of a 30 nm nickel-chromium alloy with a period of 100 nm was made.⁶⁴ To further reduce the period, a new generation of the AIL system is under

development for producing 50-nm-period patterns on a substrate, or even as low as 10 nm.⁵⁴

Lastly, one more appealing method, self-assembled block copolymer lithography^{65–67} is discussed. A block copolymer polymerized from two chemically distinct monomers can microphase-separate into a monolayer of nanoscale domains.⁶⁸ Then the structure is used as a template for the following growth of magnetic patterns. The geometry of the template depends on the length of each block. For example, a PS-PFS (polystyrene/polyferrocenyldimethylsilane) copolymer was used to fabricate single domain cobalt dot arrays with the magnetic islands as small as 25 nm.⁶⁹ The approach provides a simple and controllable process for making an array of magnetic nanodots. However, the array lacks long range order. To solve this problem, templated (or guided) self-assembly^{70–73} is proposed, in which a substrate with topographical features or chemical heterogeneities^{74,75} is used to induce orientation and ordering of the self-assembled block copolymer. A 2.5-inch disk patterned medium of Co₇₄Cr₆Pt₂₀ with ~40-nm-diameter islands was prepared via a combination of graphoepitaxy and self-assembly.⁷⁶ A similar method reported for creating nanostructure is to orient a block copolymer under an applied electric field. Here, the block copolymer comprises blocks with different dielectric constants, such as a copolymer of polystyrene-polymethylmethacrylate (PS-PMMA).⁷⁷ Annealing under an applied electric field leads to a hexagonal array of PMMA cylinders oriented parallel to the direction of the field. Then, the removal of PMMA by acetic acid gives an ultrahigh density nanoporous film. By electrodeposition, nanowires with a diameter of 14 nm can grow in the porous template, which will create an ordered array of nanowires, corresponding to an areal density beyond 1 Tbit/in².

Without using a resist, the desired pattern can be directly written on the magnetic film by ion irradiation. When different ions (He⁺, Ar⁺, Ga⁺, N⁺) with varying exposure doses (fluency) interact with the surface, many effects occur. These include radiation damage, elastic reflected ions, implantation and ion etching (milling).⁵⁵ One example is the perpendicular granular CoCrPt media with an ~100 nm period and ~70 nm islands prepared by focused Ga⁺ ion beam (FIB).⁷⁸ Irradiation with light ions typically results in a patterned magnetic structure separated spatially by altered magnetic anisotropy, without changing the surface topography.

The disadvantage here is the lack of throughput and speed to meet the requirement of manufacturing patterned media. Using mask techniques, this issue might be addressed partially. Projection ion beam irradiation has been used to produce a large area of a patterned Co/Pt multilayer.^{79,80} The light ion lithography has been reviewed recently.⁸¹

Some other fabrication processes, such as the AFM (atomic force microscopy)/STM (scanning tunneling microscopy)-based probe lithography system, have been developed. They are suitable for producing small dots, but more efforts need to improve the lithography speed, reproducibility and the ability to produce large-area samples.

4.2.2. *Magnetic properties*

The fabrication is not the only problem associated with patterned media. Integrating patterned media into a disk drive presents another big challenge. When one analyzes the recording process, understanding and modeling the magnetic properties of those small particles are very important. The magnetic properties of nanostructured elements have been reviewed recently.⁵⁶ An ideal patterned medium should be composed of a thermally stable and noninteracting single domain particle with two well-defined remnant states for information storage. Besides, the switching field distribution should be narrow enough to prevent the field gradient of the write head from addressing more than one island, and the saturation magnetization should be turned to optimize recording, thermal stability and read-back signal amplitude.⁵⁷

The coercivity H_c and the remnant-to-saturation magnetization ratio M_r/M_s (also called remnant squareness, S) of magnetic particles are dependent of the size of particles,^{82,83} as shown in Fig. 7. The above two properties have maximum values when the size of particles reaches the critical value, depending on the chemical composition and crystalline structure of the particles. For instance, the critical size is 20~40 nm for the CoNi alloy system,⁸⁴ where the nanoparticles have the highest coercivities.

For polycrystalline particles, there should be exchange coupling existing inside to avoid formation of domain walls. When the size of particles is less than the critical value, single domain remnant behavior is expected. Otherwise, domain structures exist in particles and both coercivity

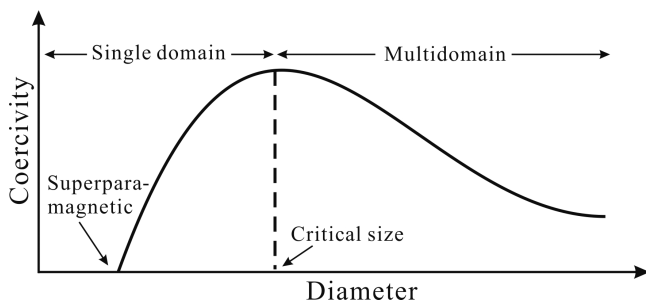


Fig. 7. Schematic curve of coercivity as a function of particle size.

and remnant magnetization of particles will be reduced. On the other hand, when particles are too small, the nanoparticles gradually become superparamagnetic due to random anisotropy. In order to obtain a high areal density for data storage, the size of particles should be within the range where the particles can be expected as a single domain, even in the presence of some defects.

Compared with continuous films, the bit size in patterned media is defined by lithography, not the read/write head. Thus, a high coercivity is not necessary, which provides a wide choice of magnetic materials. Another difference is that in patterned media the structure and shape anisotropies of islands are much more important than others. In particular, shape anisotropy determines the easy axis of magnetic nanoparticles and plays a key role in the process of magnetic reversal. Small variations in the particle's size, shape and microstructure and the magnetostatic interaction between particles lead to changes of coercivity, width of the switching field, etc. Therefore, controlling the size, shape, distribution and array of particles is crucial in the design of patterned media.

4.2.3. Recording data in patterned media

The fabrication of patterned media is not the only issue that needs to be investigated. The methods of recording data in patterned media have also been explored in the last few years. Currently, patterned media can be recorded by scanning probe microscopy (SPM) or MR head technique.

In SPM, an magnetic force microscopy (MFM) tip is used to address patterned particles. The principle of MFM is similar to that of noncontact atomic force microscopy (AFM) except that magnetic materials are used for the sample and tip. Thus, the atomic force and the magnetic interaction are both detected in MFM. Writing data can be realized through the MFM tip (if the magnetization of the tip is strong enough) or by applying an external field. The read-back process can be accomplished by detecting the magnetic states from the change in the oscillation of the cantilever that holds the magnetic tips. To improve the resolution of the writing, the tip should be very close to the patterned element, so that the magnetic field affects only one bit, not other nearby particles. To optimize the writing resolution and prevent inadvertent writing, a method of thermomagnetic writing is used, by passing a current from an MFM tip to a magnetic particle.⁸⁵ To increase the recording rate, there is a new technology called the Millipede (reported by IBM), where arrayed cantilevers are used. Each cantilever is equipped with a heater on its tip and working in parallel. Therefore, the Millipede provides a new approach to storing data at high speed and with an ultrahigh density.⁸⁶

The alternative method is the MR head technique; however, an issue encountered is how to synchronize the writing signal with the physical location of magnetic islands. So far, most experiments have been done using a quasistatic write/read tester together with MFM to study patterned media. The tester consists of a conventional longitudinal inductive write/GMR read head and a piezoelectric x - y stage, which controls the relative position of the sample of the patterned medium.⁸⁷ The synchronization requirements for writing bits in patterned media were investigated on a single row of islands.⁸⁸ The study of the recording system in both longitudinal and perpendicular $\text{Co}_{70}\text{Cr}_{18}\text{Pt}_{12}$ patterned media (see Fig. 8) reveals that a significant “writing window”, where islands can be written 100% correctly, is of about half the island period.⁸⁹ Quantitative analyses show that writing patterned islands correctly in longitudinal media is easier than in perpendicular media, which is consistent with the hypothesis that the window strongly depends on the field gradient of the write head and the switching field distribution (SFD) of islands. Therefore, to expand the writing window or to increase the writing performance of patterned media, narrowing the SFD and increasing the high head field gradients are required.⁸⁹

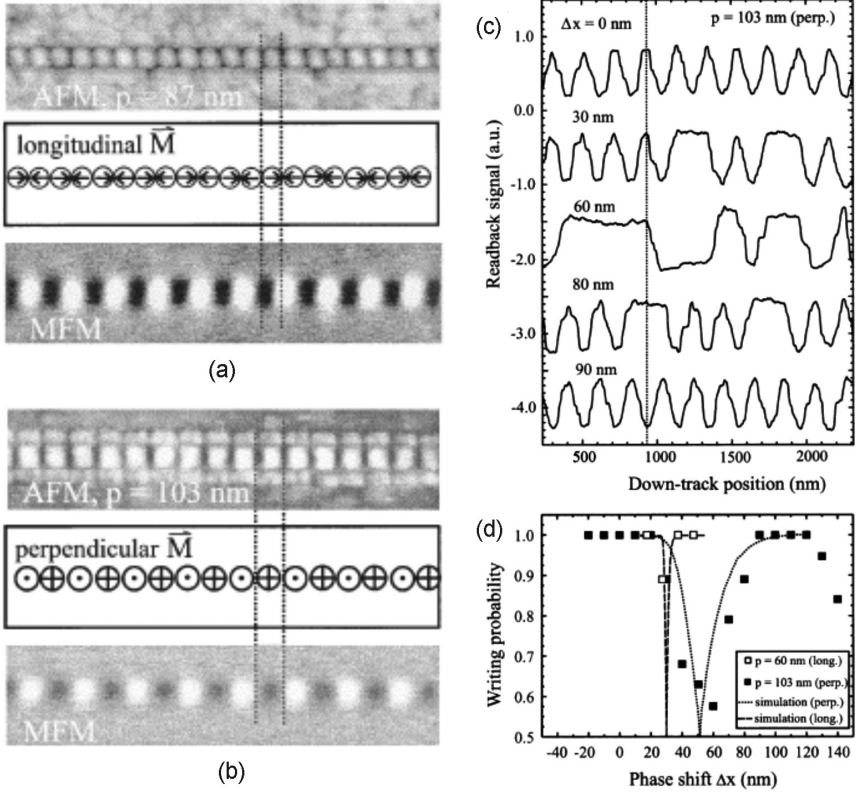


Fig. 8. (a) Longitudinal Co (1010) medium. Top: AFM image of an island row with a period of 87 nm. Bottom: MFM image after in-phase writing. (b) Perpendicular $\text{Co}_{70}\text{Cr}_{18}\text{Pt}_{12}$ medium. Top: AFM image of an island row with a period of 103 nm. Bottom: MFM image after in-phase writing. For the perpendicular case, the islands in the MFM image are either black or white, depending on their magnetization, while for the longitudinal medium each island appears as a dipole with a black-and-white contrast on either side of the island. (c) Perpendicular CoCrPt medium: GMR readback signals, obtained after applying different phase shifts. (d) Probability to address islands correctly as a function of the phase shift for patterned longitudinal ($p = 60$ nm) and patterned perpendicular ($p = 103$ nm) media. Corresponding results obtained from a simulation are indicated by dotted and dashed lines. (Reprinted with permission from Ref. 89, © 2003, IEEE)

Patterned media present an intriguing possibility for ultrahigh density data recording further delay of the limitation of superparamagnetic effect. Several fabrication methods of nanoscale patterned particles have been proposed. In addition, recording systems have been investigated on some

key issues, such as read/write methods, synchronization and noise. However, whether patterned media are practically adopted depends on whether this set of complex fabrication, addressing and integration problems can be solved economically. Also, it is crucial to understand the magnetic properties of patterned nanoparticles completely. More explorations and systematic studies are needed and new fabrication methods and recording techniques are expected in the future.

4.3. Self-assembly of magnetic nanocrystal media

Patterned media present a potential application for ultrahigh density magnetic storage. One of the challenges for patterned media is whether economical methods exists to prepare nanoscale patterned particles, especially the fabrication of ultrafine, uniformly ordered nanoparticles. To obtain the areal density of 1 Tbit/in², a period with a spacing of 25 nm is required. For 10 Tbit/in², this spacing is reduced to 8 nm. It will be difficult to realize such small spacing periods by the nanofabrication methods. In addition, the high-cost and low throughput limit their application. Therefore, new methods are needed. Chemical synthesis and self-assembly on the substrate of the recording medium may be the most cost-effective method. Compared with lithography, self-assembly of magnetic nanoparticles is inexpensive with a rapid process. Also, by this method, particles with smaller size can be well arrayed. By varying synthesis conditions, different sizes (as small as 2 nm) and shapes of magnetic dots can be prepared. And then, by controlling the conditions of deposition, these monodisperse magnetic nanoparticles can self-organize onto the surface of substrates with two-dimensional (2D) or three-dimensional (3D) superlattice structures. Here, we will focus on synthesis approaches and self-assembly process.

4.3.1. Chemical synthesis of nanoparticles

Monodisperse magnetic nanoparticles are of interest as promising candidates to extend the density of data storage media into the range of terabits per square inch.⁹⁰ By careful selection of synthesis conditions, nanocrystals with different shapes and sizes can be fabricated.

So far, many magnetic nanoparticles have been made by the methods above, such as Co,⁹¹ FePt,⁹² FeCo, CoPt, FePd,⁹³ MnFe₂O₄,^{94,95} and Fe₃O₄ (see Fig. 9). Among them, L1₀ FePt is particularly desirable because of its high magnetic anisotropy, small domain wall width (2.8–3.3 nm), small minimal stable grain sizes (2.9–3.5 nm) and chemical stability. In the ordered intermetallic phase, the magnetic anisotropy K_u can reach values as high as 10⁸ erg/cm³, indicating that the magnetic anisotropy energy $K_u V$ (V is the volume of the grain) is much larger than the thermal energy $k_B T$ at ambient temperature. The first successful demonstration of monodisperse FePt nanoparticles was synthesized by decomposition of iron pentacarbonyl [Fe(CO)₅] and reduction of platinum acetylacetonate [Pt(acac)₃] in the presence of surfactant molecules, followed by the high temperature annealing process.⁹² However, the chemical composition is difficult to control because of the loss of Fe(CO)₅ during the synthesis.⁹⁶ Without using Fe(CO)₅, monodisperse FePt nanoparticles [shown in Fig. 9(a)] can be made by reducing the reaction of iron(II) and platinum(II) acetylacetonates with 1,2-hexadecanediol⁹⁷ as the reducing reagent. The stoichiometry can be adjusted by controlling the molar ratio of Fe(acac)₃ to Pt(acac)₃. Among them, annealed Fe₅₅Pt₄₅ nanoparticles have very high coercivity, $H_c = 9500$ Oe.⁹⁸ The smallest size of FePt nanoparticles can be around 2 nm.⁹⁹ To get larger nanoparticles, seed-mediated growth can be employed, where smaller nanoparticles are used as seeds and more FePt is coated over the seeds.⁹²

Actually, the synthesis of nanoparticles can be controlled by the balance between the nucleation rate and growth rate. If the nucleation period is concurrent with the growth process, the final particle size and shape will be poly-disperse. To realize the separation of the nucleation and growth processes, different methods have been tested. One method is called “injection method”. After injection, fast nucleation occurs, and this is followed by a relatively long growth period. Upon nucleation, the concentration of reactant in solution drops below the critical concentration for nucleation, and further material can only add to the existing nuclei. Growth rate is controlled by the rate of diffusion of reactants to the particles and/or by the reaction rate. Ultimately, the growth will be balanced by the solubility. The size, composition and shape of the particles are controlled by varying the synthesis parameters, such as the molar ratio of stabilizers to metal precursors, the addition sequence of the stabilizers and metal precursors, the heating rate, the heating temperature, the heating duration¹⁰⁰ and the solvent.

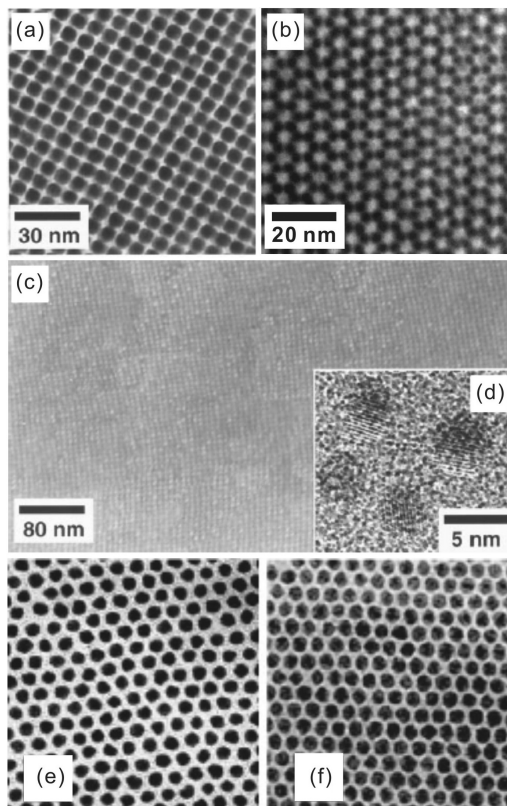


Fig. 9. (a) 3D assembly of a 6 nm $\text{Fe}_{50}\text{Pt}_{50}$ sample after replacing oleic acid/oleyl amine with hexanoic acid/hexylamine.⁹² (b) Monodisperse FePt particles with a 3.01 nm diameter and a standard deviation of 0.29 nm.⁹⁷ (c) HRSEM image of an ~ 180 -nm-thick, 4 nm $\text{Fe}_{52}\text{Pt}_{48}$ nanocrystal assembly annealed at 560°C for 30 min under 1 atm of N_2 gas. (d) High resolution TEM image of 4 nm $\text{Fe}_{52}\text{Pt}_{48}$ nanocrystals annealed at 560°C for 30 min on a SiO-coated copper grid.⁹² (e) Transmission electron microscope image of a Co nanocrystal superlattice before annealing, show in an ~ 4 nm interparticle distance (the nanocrystal diameter is 10 nm). (f) Co nanocrystal superlattice after annealing (~ 2 nm interparticle distance).⁹¹ (Reprinted with permission from Refs. 91 and 92, © 2000, American Association for the Advancement of Science)

The first problem encountered in the synthesis process is the aggregation of nanoparticles, caused by van der Waals force of attraction existing in the nanoparticle system. Magnetic interactions between magnetic nanoparticles make this aggregation more serious. The result generates a nondispersed fine powder. In order to avoid this problem, a repulsive or

stabilizing force is needed. Organic ligands bearing long chain hydrocarbons chains (surfactants) provide a steric repulsion to increase the stability of nanoparticles. Another way is to take advantage of the electrostatic repulsion on the surface of nanoparticles.

Another problem is to prepare nanoparticles with the desired crystallinity. Thermal annealing is necessary to achieve the chemically ordered, high anisotropy ferromagnetic $L1_0$ phase. The high temperature annealing process can lead to nanoparticle agglomeration and sintering. It makes aligning the nanoparticles along the easy axis difficult.^{101,102} In other words, the high temperature annealing process limits the technological applications. One way to decrease the $L1_0$ phase transformation temperature is through addition of Ag to the FePt nanoparticles; yet, 350° C is still necessary for annealing.¹⁰³ Other work included addition of Co to the FePt nanoparticles to improve their physical and magnetic properties.^{103,104} A gas-phase-based process was used to prepare FePt nanoparticles, where the preparation technique allows annealing of the particles in the gas phase prior to their deposition. Higher coercivity was obtained by enhancing the degree of the $L1_0$ order in the gas-phase sintered particles.¹⁰⁵

The solution phase synthesis mentioned above causes the nanoparticles to be encapsulated by organic ligands (such as oleic acid and oleylamine) to prevent aggregation. However, the organic ligand shell can affect both the magnetic properties and the electron configuration of the core. Recently, ligand-free FePt nanoparticles were prepared and their electronic and magnetic properties were characterized.¹⁰⁶ Also, the influence of the surface interaction upon the magnetic properties of $MnFe_2O_4$ nanoparticles with a series of ligands was reported.¹⁰⁷

The biomineral strategy is a potential solution to the synthesis and assembly of crystalline inorganic materials under environmentally benign conditions by controlling the size, composition and phase, in which biological interactions control the nucleation of nanoparticles. So far, using biological templates, narrow size distribution nanoparticles of CoPt¹⁰⁸ and FePt¹⁰⁹ have been prepared. Compared with the approach of chemical synthesis, the development of biological routes for the synthesis of magnetic materials provides a “green” and cost-effective synthetic approach under an ambient environment.

4.3.2. Magnetic nanoparticle self-assembly

Self-assembly is an easy way to produce nanoparticle arrays. By mixing all the chemicals together, nanostructure will be generated automatically by the solvent evaporation. The forces involved in self-assembly include generally weak interactions, such as hydrogen bonding and hydrophobic interaction, steric repulsion, magnetostatic interaction, van der Waals interaction and Coulombic interaction and so on. Among them, which one dominates the behavior of self-assembly depends on the size, size distribution, shape of nanoparticles, and also the properties of solvents. Actually, self-assembled arrays can be fine-tuned. Using the same nanoparticles, different packing styles from hexagonal close packing, square packing, to linear chains were achieved by selecting appropriate conditions.¹¹⁰

The problem here is that the arrays could be easily destroyed since the self-assembly process is driven by weak interactions. This limits the availability and reproducibility of the method. To solve this problem, chemical bonds or other strong interactions must be induced. Template-assisted assembly⁹⁰ was used to assemble the nanoparticles in a controlled manner with robust mechanical properties, in which the substrates are functionalized by special molecules or pretreated to get particular surface structure. For example, organosilane compounds can self-assemble on a hydroxylated surface. Sulfur-containing surfactants are readily absorbed on the surface of gold, silver or copper substrate. These strong molecule–substrate interactions result in “chemical absorption.” Then, by exchanging stabilizers bound to the particles with the molecules that selectively bind to the substrate, nanoparticles can assemble robustly on the surface of the substrate. Alternating adsorption of polyethylenimine (PEI) and FePt nanoparticles on a OH-terminated surface via surface ligand exchange leads to 4 nm FePt nanoparticle assemblies with controlled thickness.^{96,111} As mentioned before, the use of biomolecules as templates for nanoparticle assembly has been proposed recently. For example, a DNA molecule was used as a template for the vectorial growth of a 12-mm-long, 100-nm-wide conductive silver wire,¹¹² and proteins have been reported to direct nanocrystal assembly of semiconductors.¹¹³ The Langmuir–Blodgett method¹¹⁴ was also reported to fabricate FePt nanoparticle media.

4.4. Organic and molecular magnets

As mentioned above, all traditional magnetic materials are inorganic materials, such as transition metals and metallic oxides. Their magnetic properties are based on d/f orbital electron spins. The introduction of spins into s/p orbitals opens up the development of molecule-based magnetic materials, which is important for basic and applied research in science and engineering. Compared with conventional inorganic magnets, molecular magnets present several unique features, such as tunability of properties by means of organic chemistry, easy processability, high mechanical flexibility, low density, low environmental contamination, high compatibility with polymers, high biocompatibility, transparency, semiconducting and/or insulating direct current (d.c.) electrical conductivity, high magnetic susceptibilities, high magnetization and low magnetic anisotropy.¹¹⁵

In the last two decades, much attention has already been directed to the research on molecule-based magnets. Based on the orbital in which spins reside, molecule-based magnets can be grouped into two families.¹¹⁶ One is that the organic fragment is an active component with spin sites contributing to both the high magnetic moment and the spin coupling. The first metal-free organic ferromagnet was discovered 15 years ago. It was a derivative of nitronyl nitroxide, the orthorhombic β -phase crystal of p -nitrophenyl nitronyl nitroxide (p -NPNN), which became magnetically ordered at 0.65 K.¹¹⁷ Also, thiazyl radicals exhibit magnetic ordering temperatures in excess of 50 K.¹¹⁸ The other group is that the organic fragment only provides a framework to accommodate the spins (which reside solely on metal ions) and facilitates coupling among the spin-bearing metal ions. In the second family, the molecule-based magnets contain metal ions, but are obviously distinct from conventional metal-based magnets, where the organic fragments in the molecules are very important to their magnetic properties. In the following subsection, the structures, the magnetic properties and some mechanisms of molecular magnets will be discussed.

4.4.1. Magnets with spins only on organic moieties (p orbitals)

4.4.1.1. Organic radicals

Being magnetic, at least one unpaired electron (or unpaired spin) exists in the atom or molecule of materials. In organic magnets, organic free

radicals possess an odd number of electrons. The regular array of organic free radicals results in a net magnetization. Since most organic radicals show very low anisotropy, a three-dimensional network of magnetic interactions is required if the material exhibits bulk magnetic order.¹¹⁹ The magnetic properties of organic magnets strongly depend on the exchange interaction of organic free radicals and the solid state structure.^{120–122} However, most organic radicals are extremely unstable and reactive; therefore, they are unable to be isolated in their solid state. To increase the stability of organic radicals, synthetic chemistry is used. One solution is to delocalize the unpaired electron by introducing aromatic rings or adding bulky substituents. The following provides several important organic ferromagnets.

4.4.1.2. Nitronyl-nitroxide-based organic magnets

The first evidence of pure organic long range ferromagnetism was discovered in the β -phase crystal of *para*-nitrophenyl nitronyl nitroxide [*p*-NPNN; the molecular structure is shown in the inset of Fig. 10(a)].¹¹⁶ *p*-NPNN is a very soft ferromagnet [Fig. 10(a)], which saturates in a very small field below the transition temperature ($T_c = 0.65$ K). The magnetic moment in nitronyl nitroxides comes from the unpaired electron that is delocalized over the O–N–C–N–O moiety.

The spin density map [Fig. 10(b)] shows that the positive spin density is delocalized over the nitronyl nitroxide group and also the nitrogen of the nitro group. The spin polarization effects are responsible for the transfer of the spin density to the nitrophenyl group, which means that the intermolecular ferromagnetic interaction passes through both the nitro and the phenyl fragments. Therefore, the substituent group can affect the interaction between neighboring molecules, resulting in modification of crystal structure and the magnetic interaction between unpaired spins.¹²³ Following this discovery, many other nitronyl-nitroxide-based organic ferromagnets have been found. Figure 11 shows some structures of these magnets. Although the chemical modification of the substituent group provides an efficient method for controlling the crystal structure, these nitronyl-nitroxide-based organic radicals still need a very low temperature (below 1 K) to achieve the ferromagnetic order.

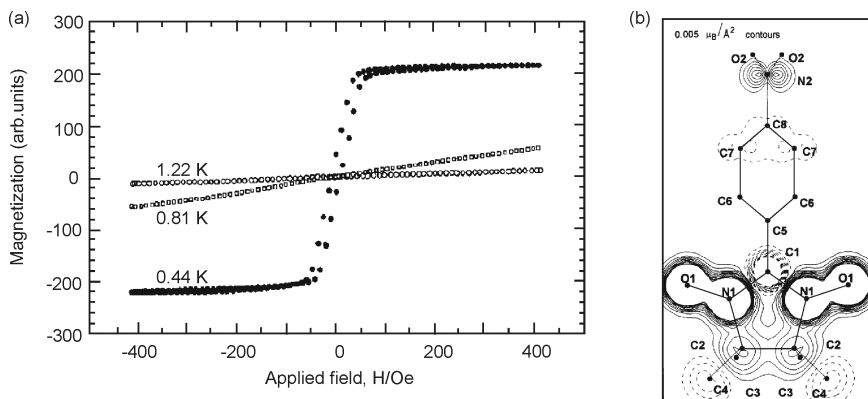


Fig. 10. (a) The magnetization curves of *p*-NPNN, measured at different temperatures ($T_C = 0.65$ K). (Reprinted with permission from Ref. 117, © 1991, Elsevier) The inset shows the molecular structure of *p*-NPNN. (b) The spin density map of *p*-NPNN, obtained from polarized neutron diffraction experiments. (Reprinted with permission from Ref. 123, © 1994, Elsevier)

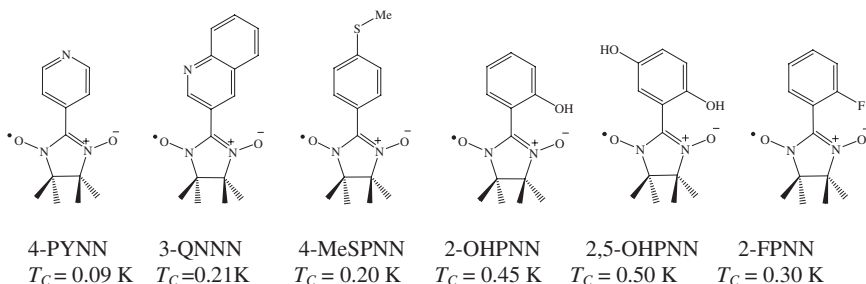


Fig. 11. Some examples of nitronyl-nitroxide-based organic magnets and their transition temperatures.

Other kinds of nitroxide-based radicals exhibiting ferromagnetic interaction have been found, such as the series of 4-(arylmethyleneamino)-2,2,6,6-tetramethylpiperidin-1-oxyls (Ar-CH = N-TEMPO, where Ar = C_6H_5 , 4-Cl- C_6H_4 , 4- C_6H_5 - C_6H_4 , 4-MeS- C_6H_4 , 4- C_6H_5 O- C_6H_4),^{124,125} nitroxide biradical N,N'-dioxo-1,3,5,7-tetramethyl-2,6-diazaadamantane¹²⁶ and

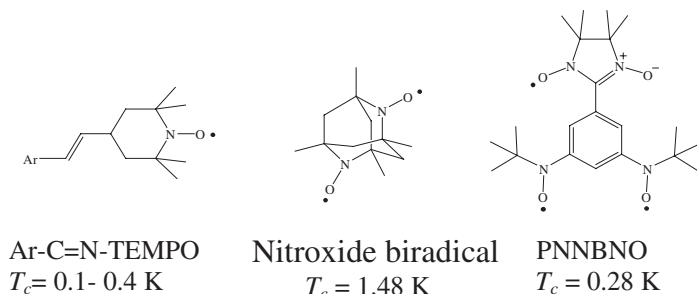


Fig. 12. Some examples of other kinds of nitroxide-based radicals.

asymmetric triradical molecules (2-[3,5-bis(*Ntert*-butylaminoxyl)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1Himidazol-1-oxyl 3-oxide, abbreviated as PNNBNO).¹²⁷ Their molecular structures are shown in Fig. 12. For Ar-C=N-TEMPO, the ferromagnetism transition temperature is also very low, which is believed to be due to the weak dipolar coupling between ferromagnetic layers. The diradical exhibits the highest T_c among them, which order ferromagnetically at 1.48 K.¹²⁶ PNNBNO includes an $S = 1$ and an $S = 1/2$ unit within a single molecule and the two units are connected by intra- and intermolecular antiferromagnetic interactions. The 3D phase transition occurs at 0.28 K.¹²⁷

Besides nitroxide-based radicals, verdazyl radicals and sulfur-based radicals also show ferromagnetic intermolecular interactions. For example, ferromagnetism has been observed in 3-(4-chlorophenyl)-1,5-diphenyl-6-oxoverdazyl (*p*-CdpOV; the molecular structure is shown in Fig. 13) with $T_c = 0.21\text{ K}$.¹²⁸ The β -phase of the dithiadiazolyl radical (*p*-NCC₆F₄CNSSN, the molecular structure is shown in Fig. 13) exhibits noncollinear antiferromagnetism at 35.5 K.¹²⁹ One interesting example is 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA, the molecular structure is shown in Fig. 13). It has a large first order magnetic phase transition over the temperature range of 230–305 K from the high temperature paramagnetic phase to the low temperature diamagnetic phase. The magnetic bistability originates from different molecular arrangement and this property is very helpful in data storage.¹³⁰

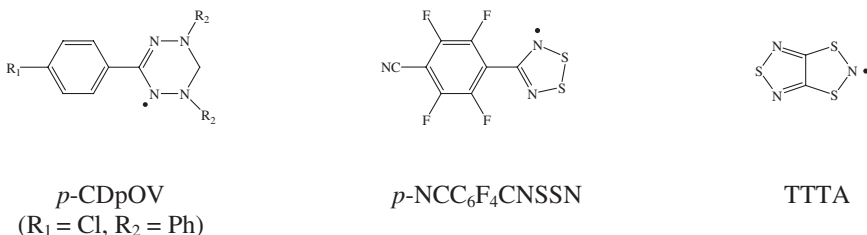


Fig. 13. Some examples of verdazyl radicals and sulfur-based radicals.

4.4.1.3. Fullerenes

Tetrakis(dimethylamino)ethylene-fullerene(60) (TDAE-C₆₀) is a donor-acceptor type magnetic material. The α -phase crystal shows a ferromagnetic state with fully saturated $s = 1/2$ molecular spins at a relatively high Curie temperature, $T_C = 16$ K.¹³¹ The later research results showed that the sample preparation was crucial for the magnetic properties.¹³² Fresh single crystals of TDAE-C₆₀ grown below 10°C (the α -phase), show no ferromagnetic behavior when cooled down to 2 K [Figs. 14(a) and 14(b)].¹³² The different properties between these two crystal forms come from the different orientation of the C₆₀ molecules in the two-phases [Fig. 14(c)]. By annealing at high temperature, the α -phase can turn into the ferromagnetic α -phase. After this discovery, much attention has been given to fullerene and fullerides.

The fullerene-based materials showed a slight increased transition temperature, such as 3-aminophenyl-methano-fullerene(60)-cobaltocene with $T_C = 19$ K.¹³³ But the transition temperatures were still very low until the advent of the rhombohedral C₆₀ polymer (Rh-C₆₀).¹³⁴ The magnetic carbon of Rh-C₆₀ is prepared at high temperature and pressure; the magnetic phase appears when fullerene cages are about to break down and form graphitized fullerene. The formation of the graphitized fullerene is a 2D rhombohedral polymer phase, composed of layers of covalently bonded C₆₀ molecules. The saturation magnetization and Curie temperature are determined by preparation conditions. The highest T_C is 820 K.¹³⁵ Ferromagnetic ordering in a hydrofullerite C₆₀H₂₄ with $T_C = 300$ K has also been found.¹³⁶ The total concentration of magnetic impurities

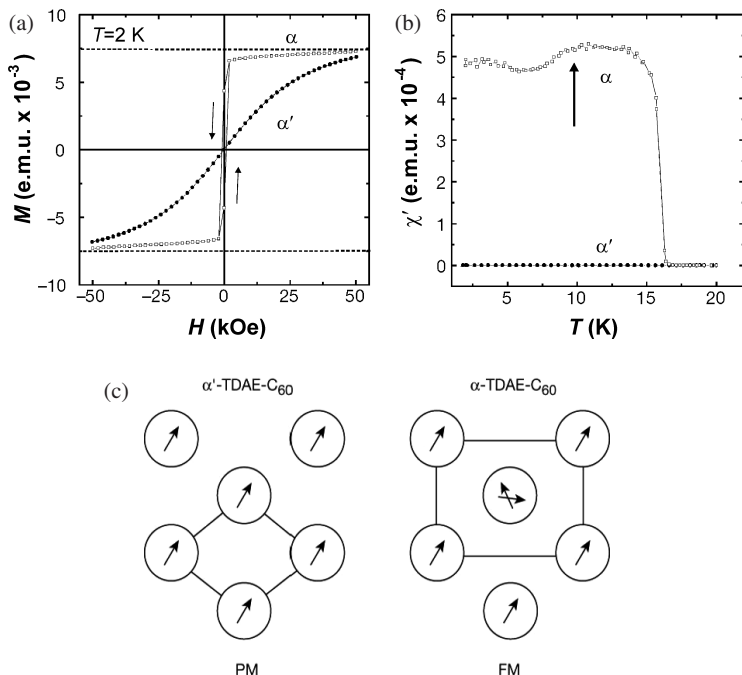


Fig. 14. (a) Magnetization curves of the PM and FM samples of TDAE- C_{60} (dots and squares, respectively). (b) The a.c. susceptibility χ of the PM and FM samples. The arrow shows a dip in the susceptibility due to the onset of glasslike behavior, as suggested by the model. (c) Schematic diagram of the C_{60} molecular orientations in the a - b plane for the PM (left) and FM structures (right). (Reprinted with permission from Ref. 143, © 1987, American Physical Society)

reported in those studies appears to be too low to give rise to the observed magnetization.¹³⁴ However, the new experimental and theoretical results concluded that the rhombohedral distortion of C_{60} itself cannot induce magnetic ordering in the molecular carbon,¹³⁷ and suggested that hydrogen may play an important role in the magnetic ordering found in fullerenes.¹³⁸ To fully understand the mechanism, further experimental and theoretical work is required. Although the mechanism is still unclear and the magnetism is very weak, the discovery of Rh- C_{60} still gives a new perspective in the investigation of organic magnets with highly tunable properties for use in magnetic devices.

4.4.2. Magnets with spins on both metal ions and organic moieties (*p* and *d/f* orbitals)

One route to increase the transition temperature is to prepare hybrid materials, in which organic groups are bonded with transition metals and they both have unpaired spins. This family of magnets includes charge transfer (CT) salts and metal–radical complexes.

4.4.2.1. Charge transfer salts

The most famous type of CT salt ferromagnet is the metallocene-based molecular magnet $[\text{MCp}^*_2][\text{organic acceptor}]$ ($\text{M} = \text{metal}$, $\text{Cp}^* = \text{C}_5\text{Me}_5/\text{pentamethylcyclopentadienide}$). The metallocenes mainly include FeCp^*_2 , MnCp^*_2 and CrCp^*_2 .

The first MCp^*_2 CT salt discovered to have a ferromagnetic ground state was $[\text{FeCp}^*_2][\text{TCNE}]$ with $T_C = 4.8 \text{ K}$ [$\text{TCNE} = \text{tetracyanoethylene}$; the molecular structure is shown in Fig. 15(a)].¹³⁹ The magnetization shows hysteresis as a function of varying applied magnetic field, with a coercive force reaching as high as 1000 G at 2 K [Fig. 15(b)]. Further studies, replacing Fe(III) with Mn(III) ¹⁴⁰ and Cr(III) ,¹⁴¹ yielded new ferromagnets, each having unpaired electrons ($[\text{FeCp}^*_2]^+$, $S = 1/2$; $[\text{MnCp}^*_2]^+$, $S = 1$; $[\text{CrCp}^*_2]^+$, $S = 3/2$). The transition temperatures decrease following the order of $\text{Mn} > \text{Fe} > \text{Cr}$. The organic acceptor, TCNE, is a planar molecule with strong electron withdrawing groups ($-\text{C}\equiv\text{N}$), which helps to stabilize the radical anion formed through accepting an electron. One interesting discovery was $\text{V}(\text{TCNE})_x \cdot y\text{CH}_2\text{Cl}_2$, obtained from the reaction of bisbenzene vanadium with TCNE in dichloromethane, which exhibits a high magnetic ordering temperature, $T_C = 400 \text{ K}$.¹⁴²

The CT salts of MCp^*_2 ($\text{M} = \text{Fe}, \text{Mn}, \text{Cr}, \text{V}, \dots$) and organic acceptors can be synthesized by a simply process, i.e. mixing the donor and acceptor in a polar solvent, and the CT salt can be precipitated by adding a nonpolar solvent (see Fig. 16). The choice of solvent for the synthesis is very important. It is believed that the solvent may affect the donor–acceptor stacking structure.¹³⁸ Considering the stability, synthesis of some CT salts requires an inert atmosphere and a special low temperature. The electron transfers from a metallocene to an organic acceptor and a CT salt forms

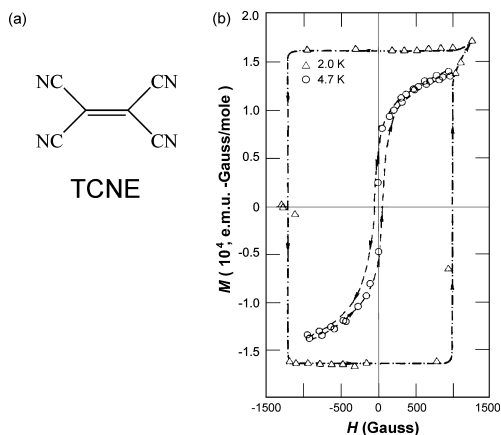


Fig. 15. (a) Molecular structure of TCNE and (b) magnetization data for $[\text{FeCp}^*_2]\text{TCNE}$ at 2.0 K and 4.7 K. (Figure (b) is reprinted with permission from Ref. 143, © 1987, American Physical Society).

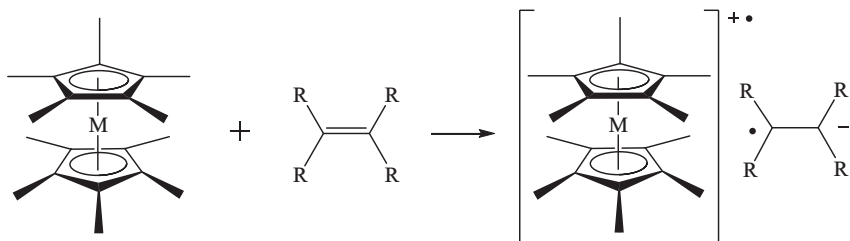


Fig. 16. Formation of CT salt by electron transfer from a metallocene donor to an organic acceptor ($M = \text{Fe}, \text{Mn}, \text{Cr}, \text{V}, \dots$; $R =$ electron withdrawing group, such as $-\text{CN}$).

with unpaired electrons on both the metallocenium ion and the organic radical anion.

Since TCNE was used for the synthesis of CT salts, efforts on the CT salts also resulted in the discovery of other organic acceptors with similar structure. 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) is a typical organic electron acceptor (the molecular structure is shown in Fig. 17). The difference from TCNE is spin in TCNQ was delocalized over more atoms, resulting in lower spin density and weaker spin coupling. Actually,

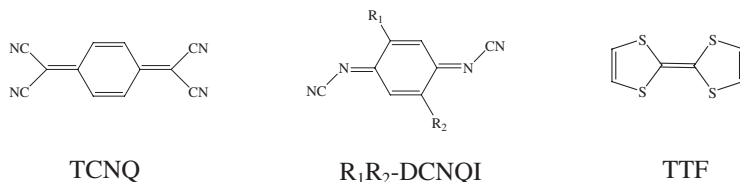


Fig. 17. Some examples of organic acceptors and donors.

the transition temperatures of TCNQ counterparts are lower than that of TCNE salts. R₁R₂-DCNQI (DCNQI = N,N'-dicayanoquinodimine) is another example of an organic acceptor (the molecular structure is shown in Fig. 17). Cu-(Me₂DCNQI)₂ was noted for high conductivity.^{144,145} The strong interlattice interaction between the *d* electrons of Cu and the π electrons in *p* orbitals from DCNQI delocalizes the electron energy. By changing the temperature, pressure or selective deuteration, conductivity and susceptibility can be obtained from metal to insulator, from antiferromagnetic order to ferromagnetic state.¹⁴⁴ Besides organic acceptors, CT salts can also be formed by combining a metal complex with an organic donor, such as tetrathiafulvalene (TTF) as an electron donor. TTF can be combined with metal-anion complexes to form CT salts, such as TTF₁₄(MCl₄)₄ (M = Mn, Co)¹⁴⁶ and TTF₇(FeCl₄)₂.¹⁴⁷

4.4.2.2. Metal-radical complexes

Metal-radical complexes assemble the organic radical centers by means of complexation with paramagnetic transition metal ions. One example is Mn^{II}(hfac)₂-nitroxide system (Mn^{II}(hfac)₂ = bis(hexafluoroacetylacetonato)manganese(II)), where a linear trifunctional nitroxide results in the formation of 2D/3D structure ferro/ferrimagnets.

When [Mn^{II}(hfac)₂] was treated with highly symmetric trinitroxide radical 1 [the molecular structure is shown in Fig. 18)], the expected 3:2 complex with a 2D network structure was obtained. The complex became a magnet with $T_C = 3.4$ K, which was ascribed to the weak intramolecular exchange coupling ($J_{\text{intra}} = 6.8$ K) of 1.¹⁴⁹ When radicals with strong intramolecular exchange coupling were used, such as 2 [Fig. 18(a)] with

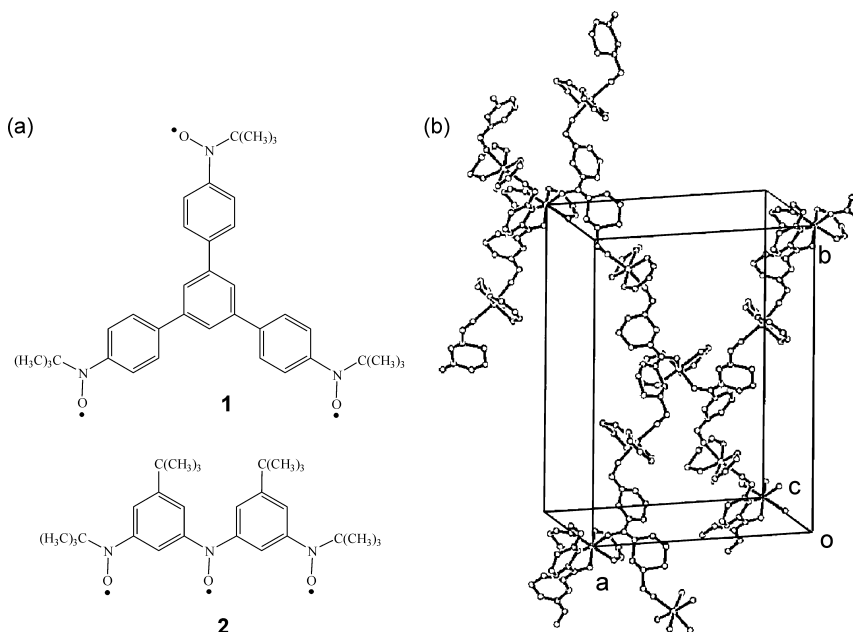


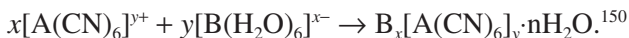
Fig. 18. (a) Molecular structure of radicals 1 and 2; (b) packing structure of the 3D polymer complex $[\text{Mn}^{\text{II}}(\text{hfac})_2]_3 \cdot 2$. (Reprinted with permission from Ref. 148, © 1996, American Chemical Society)

$J_{\text{intra}} = 240 \text{ K}$, a 3D polymeric network was formed and magnetization was obtained at $T_C = 46 \text{ K}$,¹⁴⁸ which arose from ferro- and anti-ferromagnetic coupling (in different directions) [3D packing structure is shown in Fig. 18(b)]. In these complexes, the $2p$ spins of the organic ligands and the $3d$ spins of Mn(II) in ferrimagnetic coupling are the origin for the observed magnetization.

4.4.2.3. Magnets with spins on organic moieties and metal ions providing exchange pathways

Prussian blue, $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$, and its analogues, $\text{A}_x[\text{B}(\text{CN})_6]_y \cdot n\text{H}_2\text{O}$ ($\text{A} = \text{Cu, Ni, Co, Fe, Mn}$; $\text{B} = \text{Cr, Mn, Fe, Co}$), have attracted attention due to their color, as well as their special properties, such as photo-induced magnetic switching and tunable and high Curie temperatures.

These compounds are generally synthesized via Lewis acid–base reactions in water:



Most of these hexacyanometalate-based products adopt a simple face-centered cubic lattice, in which adjacent metals A and B are connected through cyanide bridges forming the linear B–CN–A alignment. The Kahn model applied to such a system realizes that only a t_{2g} (π symmetry) orbital exists on the B site, whereas on the A site both t_{2g} and e_g are present [shown in Fig. 19(a)]. Two kinds of orbital pathways are possible: antiferromagnetic ones, t_{2g} – t_{2g} [Fig. 19(b)], and ferromagnetic ones, t_{2g} – e_g [Fig. 19(c)].¹⁵¹ The coupling constant, J , is the magnitude of the exchange interaction, which can be tuned by tuning the electronic configuration of A. Since $T_C \propto z|J|$,^{126,152} the Curie temperature can be adjusted. For example, crystalline $\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ has a T_C value of 315 K, but the T_C of $\text{K}^{\text{IV}}[\text{Cr}^{\text{III}}(\text{CN})_6]$ is 376 K. Table 3 lists some representatives of Prussian blue analogues, T_C and their magnetic behavior.

4.5. Single molecule magnets

The above molecule-based magnetic compounds normally contain few transition metal ions, such as Mn, Fe, V, Ni, Cr and Co. Another type of molecule-based magnetic compounds is several polynuclear cage metal complexes with a large spin S , resulting from the intramolecular exchange between the transition metal ions in the cluster. This opened up a new area of high spin metal clusters, termed “single molecule magnets” (SMMs).

The first identified SMM was a manganese oxide cluster with acetate ligands, $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4$, which was synthesized by the reaction of $\text{Mn}(\text{O}_2\text{CCH}_3)_2$ with KMnO_4 in CH_3COOH and water solution. This cluster has 4 Mn(IV), 8 Mn(III), 20 unpaired electrons, and crystallizes with tetragonal (axial) symmetry¹⁶² [the structures are shown in Fig. 20(a)]. The studies of the magnetic properties showed the low temperature magnetic susceptibility¹⁶³ and also magnetic hysteresis.¹⁶⁴ The large ground state spin is caused by the exchange interactions between the $S = 2$ spins of the Mn(II) ions and the $S = 3/2$ spins of the Mn(IV) ions. Here the four central Mn(IV)

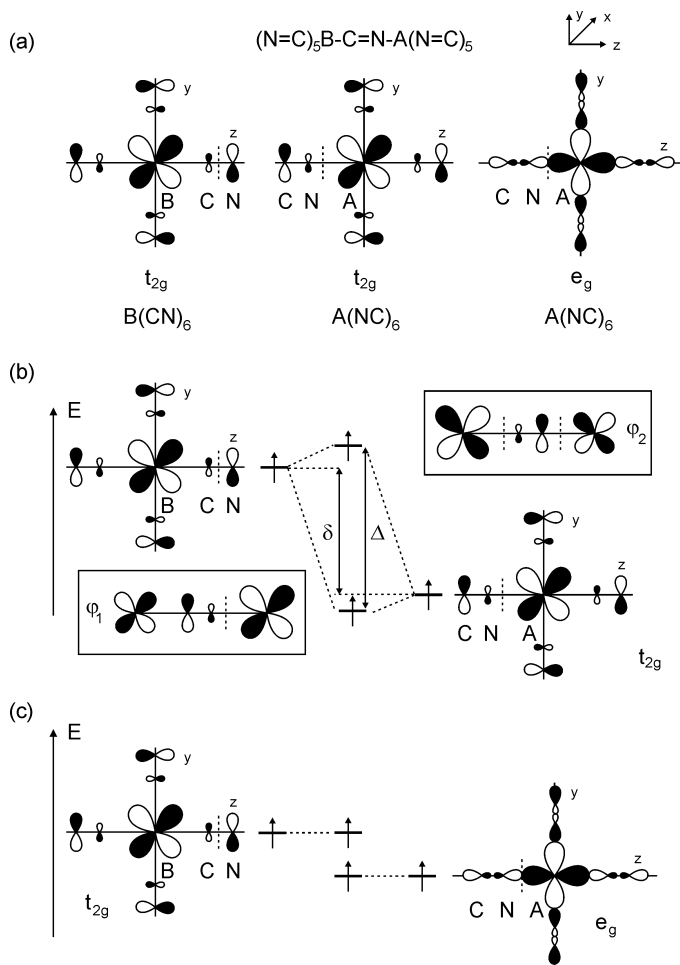


Fig. 19. (a) Magnetic orbitals: (A) t_{2g} in $B(CN)_6$; (B) t_{2g} in $A(NC)_6$; (C) e_g in $A(NC)_6$. (b) Interaction between overlapping t_{2g} magnetic orbitals in $(NC)_5B(CN)A(NC)_5$. (c) Orthogonal t_{2g} and e_g magnetic orbitals in $(NC)_5B(CN)A(NC)_5$. (Reprinted with permission from Ref. 151, © 2001, Elsevier)

centers spin in the opposite direction to those eight outer Mn(III) centers [Fig. 20(b)]. Then the total S is equal to $|(4 \times 2/3) + [8 \times (-2)]| = 10$.^{165,166}

The eight Mn(III) ions on the outer periphery undergo a Jahn–Teller (JT) elongation in the z -direction, which leads to the magnetic moment of an individual Mn_{12} molecule preferentially lying in the z -direction, or the

Table 3. Some representatives of Prussian blue analogues.

Composition	T_C/K	Ordering	Reference
$\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$, Prussian blue	5.6	FO	153
$\text{Cs}^{\text{I}}\text{Ni}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$	90	FO	154
$\text{CsMn}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6] \cdot \text{H}_2\text{O}$	90	FI	155
$\text{Cr}^{\text{III}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.93}[\text{Cr}^{\text{II}}(\text{CN})_6]_{0.05}$	260	FI	156
$\text{V}^{\text{II}}_{0.45}\text{V}^{\text{III}}_{0.53}[\text{V}^{\text{IV}}\text{O}]_{0.02}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.69}(\text{SO}_4)_{0.23} \cdot 3.0\text{H}_2\text{O} \cdot 0.02\text{K}_2\text{SO}_4$	310	FI	157
$\text{Cs}_{0.82}\text{V}^{\text{II}}_{0.66}[\text{V}^{\text{IV}}\text{O}]_{0.34}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.92}[\text{SO}_4]_{0.203} \cdot 3.6\text{H}_2\text{O}$	315	FI	157
$\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$	315	FI	158
$\text{K}^{\text{I}}_{0.058}\text{V}^{\text{II/III}}[\text{Cr}^{\text{III}}(\text{CN})_6]_{0.79}(\text{SO}_4)_{0.058} \cdot 0.93\text{H}_2\text{O}$	372	FI	159
$\text{K}^{\text{I}}\text{V}^{\text{II}}[\text{Cr}^{\text{III}}(\text{CN})_6]$	376	FI	160

FO = Ferromagnet

FI = Ferrimagnet

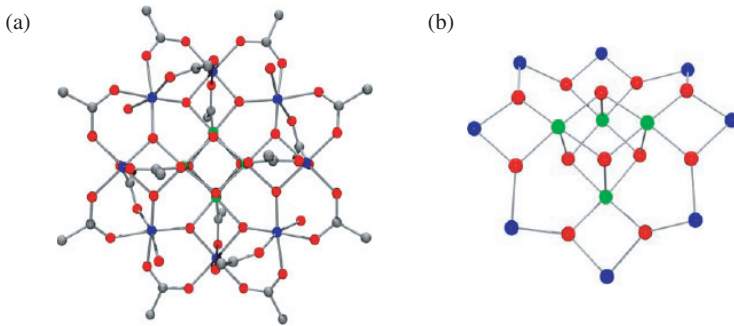


Fig. 20. Structure of (a) the $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]$ complex and (b) the $[\text{Mn}_{12}\text{O}_{12}]^{16+}$ core — Mn(IV), green; Mn(III), blue; O, red; C, gray. (Reprinted with permission from Ref. 161, © 2005, University of Florida)

easy axis. The magnetic anisotropy of this easy axis type is negative, $D = -0.5 \text{ cm}^{-1}$. In zero-field splitting, the $S = 10$ ground state spin is divided into 21 (i.e. $2S + 1$) sublevels, the energy of each sublevel $E = m_s^2 D$ (m_s , spin projection quantum number — $S \leq m_s \leq S$). So when $m_s = \pm 10$ (spin

orientations: spin-up and spin-down), the energy of sublevels is lowest; and when $m_s = 0$, the energy is highest. As a consequence, there is a spin reversal energy barrier, $U = S^2|D|$ (for the Mn_{12} cluster, $U = 100|D| = 50 \text{ cm}^{-1}$), between the two spin orientations of the magnetic moment.

The relationship between the relaxation time τ and U can be given by the Arrhenius equation: $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$. When temperature T is greater than U/k_B , the magnetization can fluctuate. On the contrary, the magnetization is stable. In the case of $T \ll U/k_B$, the magnetization becomes “fixed” because of the exponential in the equation. This is the reason that SMMs exhibit slow (or temperature-independent) magnetization relaxation at low temperature. The a.c. magnetic susceptibility measurements indicate that the slow magnetization relaxation present by an SMM is intrinsic to the molecule itself and not to long range interactions.^{167,168}

The slow relaxation of the magnetization in SMMs also leads to magnetic hysteresis. The magnetic hysteresis loops get narrow when the temperature increases (see Fig. 21),¹⁶⁵ so variation of temperature can strongly affect the coercivity of the sample. The quantum tunneling of magnetization (QTM) through the energy barrier U results in a loss of spin polarization in the molecule. In Fig. 21, this effect is shown as the steps on loops.

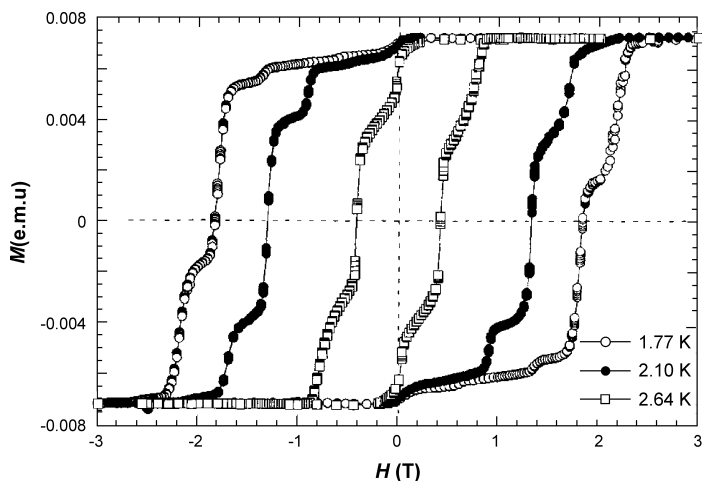


Fig. 21. Magnetic hysteresis loop measured on the Mn_{12} cluster at different temperatures: 1.77 K, 2.10 K and 2.64 K. (Reprinted with permission from Ref. 165, © 1996, Nature Publishing Group)

The discovery of the SMM of Mn_{12} clusters has created great interest in this field. Much work has been done to explore other molecules exhibiting similar magnetic properties. Among them, the Fe_8 cluster is another important SMM.¹⁶⁹ The formula of the Fe_8 cluster is $[\text{Fe}^{\text{III}}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^{8+}$ (tacn = 1,4,7-triazacyclononane), with a ground spin state $S = 10$ (two iron atoms' moments align opposite to the field and the other six parallel to the field, i.e. $S = 6 \times 5/2 - 2 \times 5/2 = 10$), axial anisotropy $D = -0.19 \text{ cm}^{-1}$ and the effective energy barrier $U_{\text{eff}} = 15 \text{ cm}^{-1}$. The weaker anisotropy makes low temperature relaxation measurements experimentally feasible. Compared with Mn_{12} clusters, ground state quantum tunneling (i.e. tunneling between the lowest energy m_s ($m_s = \pm 10$) levels) was first observed in Fe_8 clusters,¹⁶⁹ but the QTM in Mn_{12} clusters occurs between higher energy sublevels ($-10 < m_s < 10$).¹⁷⁰ The latter phenomenon is also called thermally-assisted tunneling. During this tunneling process, molecules on the ground state ($m_s = \pm 10$, either one) sublevel are first thermally activated to higher sublevels, through which tunneling of the magnetization occurs. The difference between these two magnetic relaxations can be attributed to the greater transverse anisotropy, which leads to a high degree of mixing between the $m_s = \pm 10$ levels and facilitates tunneling.

So far in the SMM family, the most salient structure is perhaps the Mn_{84} cluster,¹⁷¹ which is the largest SMM (with an outside diameter of 4.2 nm and a thickness of 1.2 nm), synthesized by the reaction of Mn_{12} acetate clusters with a premanganate salt. The cluster crystallizes in hexagonal arrays, like a holiday wreath. The multiple layers align to form nanotubes that offer various possibilities in future applications. Besides these oxide bridging compounds, other clusters (such as cyanide bridging groups) were also made. Mn_4Re_4 ¹⁷² was the first example of a cube-shaped SMM cluster and the first SMM containing 5d electrons. Table 4 lists some examples of SMMs.

In summary, SMMs have uniform size, readily alterable peripheral ligands and solubility in organic solvents. These properties are not easy to obtain for conventional magnetic recording materials composed of metals, metal oxides or metal alloys. The slow relaxation of the magnetization in SMMs can be applied in data storage as the direction of spin in individual molecules representing “0” and “1” states. To stabilize this bistability, SMMs with larger S values and more negative D values are strongly

Table 4. Examples of single molecule magnets and their properties.

Formula	S	D (cm ⁻¹)	U_{eff} (cm ⁻¹)	Reference
[Mn ₁₂ O ₁₂ (O ₂ CCH ₃) ₁₆ (H ₂ O) ₄]	10	-0.5	42	166
[Fe ₈ O ₂ (OH) ₁₂ (tacn) ₆] ⁸⁺	10	-0.19	15	169
[Mn ₈₄ O ₇₂ (O ₂ CCH ₃) ₇₈ (OCH ₃) ₂₄ (CH ₃ OH) ₁₂ (H ₂ O) ₄₂ (OH) ₆]	—	—	—	171
[Mn ₁₂ O ₁₂ (O ₂ CCHCl ₂) ₁₆ (H ₂ O) ₄][PPh ₄] ₂	10	-0.27	27*	173
[Mn ₁₂ O ₁₂ (O ₂ C- <i>p</i> -CH ₃ C ₆ H ₄) ₁₆ (H ₂ O) ₄]	—	—	—	174
[Mn ₁₂ O ₁₂ (O ₂ CCH ₃) ₈ (O ₂ PPh ₂) ₈ (H ₂ O) ₄]	10	-0.41	42	175
[Mn ₄ (O ₂ CCH ₃) ₂ (pdmH) ₆](ClO ₄) ₂	8	-0.25	12	176
[Mn ₃₀ O ₂₄ (OH) ₈ (O ₂ CCH ₂ But) ₃₂ (H ₂ O) ₂ (CH ₃ NO ₂) ₄]	7	-0.79	39	177
[Fe ₁₉ O ₆ (OH) ₁₄ (methedi) ₁₀ (H ₂ O) ₁₂] ⁺	33/2	-0.035	12	178, 179
[Ni ₁₂ (chp) ₁₂ (O ₂ CCH ₃) ₁₂ (H ₂ O) ₆ (THF) ₆]	12	-0.047	7	180, 181
[{MnCl} ₄ {Re-(triphos)(CN) ₃ }] ₄	8	-0.39	8.8	172

tacn = 1,4,7-triazacyclononane

pdmH = pyridine-2,6-dimethanol

methediH₃ = *N*-(1-hydroxynethylethyl)iminodiacetic acid

chp = 6-chloro-2-pyridonate

triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane

*Estimated value, $U = S^2|D|$

needed. Numerous synthetic strategies aimed at the improvement of these materials have been considered. It is well known that the minimum dimension of a single recording bit is limited by the onset of superparamagnetism. In SMMs, magnetic properties are due only to intramolecular rather than intermolecular interactions. Each single molecule acts as a tiny magnet and stores one bit. This implies a 10,000 times greater storage density capacity than that of the best current computer manufactures.¹⁸²

5. Summary

This chapter provides a broad summary of recent research activities in the area of ultrahigh density magnetic recording. Perpendicular

recording has been explored as the closest alternative to longitudinal recording, where the write head field is enhanced by the combination of a single pole write head and a soft underlayer. Patterned media provides a new way to further increase the storage density and reduce the media noise by lithographic definition of the recording transitions, hence enabling recording with one or several grains per bit. However, advanced nanolithography technologies were limited by high cost and low resolution.

To further decrease the grain size and reduce the cost of preparing patterned nanoparticles, synthesis of magnetic nanoparticles and the self-assembly method are proposed as a promising alternative. However, there are still a number of new problems to be resolved before extensive application, such as the control of the surface roughness, the orientation of the easy axis and the repeatability of the large scale manufacture.

Organic groups in organic and molecular magnets provide new sources of magnetic moments or mediate magnetic exchange interaction, which present several attributes unavailable in conventional inorganic magnets. A self-assembled monolayer of single molecule magnets may be used as a recording medium in the future by storing a single bit in an individual molecule. It will lead to very high surface storage density, since each molecule is only 1–2 nm in diameter. However, it remains a tremendous challenge to read and write on bits with such small magnetic moments.

In a word, superparamagnetic effect is the limitation on magnetic data storage, but the onset can be delayed by using different recording techniques. It is believed that ultrahigh density magnetic recording will be realized by replacing conventional longitudinal magnetic data storage with other alternative methods. Before this comes to fruition, further experimental and theoretical work is required to develop all of these possible methods.

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CHAPTER 2

OPTICAL DATA STORAGE FOR THE FUTURE

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In past decades, optical data storage has undergone great developments, both technically and commercially. However, pushed by the urgent demands for a much higher storage density and a faster data process rate, we still need to put a great deal of effort into exploring new storage media and data process methods so as to overcome the current physical limits on optical data storage devices. So far, among various materials, photochromic compounds are regarded as the promising one, which can be manipulated in all photon modes and processed at the molecular scale with response times ultimately within nano- or pico-second levels. In the technical aspects, the main goals are to overcome the diffraction limit on 2D storage by near-field recording and to take advantage of volumetric storage by adding the third dimension.

1. Introduction

Optical data storage, which appeared after magnetic information storage, is now blossoming. The advantages it provides, such as high storage capacity, removability, compatibility of the formats developed later with the drives already installed, as well as the low costs per Mbyte, have made optical data storage a dominator in multimedia content and software distribution, and even a prime candidate for massive data warehouses.

Eversince it was introduced into the market by Philips and Sony, the optical storage medium has undergone great developments in both the storage capacity and the recording method of the content. On one hand, the storage capacity has increased from the CD with 0.65 GB to the DVD

with 4.7 GB (single layer). The DVD standard offers a higher areal density per layer, and as many as four layers of prerecorded information, providing sufficient readout bandwidth and capacity for distribution of several hours' worth of high quality compressed video. On the other hand, in addition to the great developments of the prerecorded media, the desire of consumers to record information by and for themselves has significantly promoted the appearance of the recordable (R), and rewritable (RW) media, where the data can be “burnt” onto the disks by the users. Figure 1 gives an overview of the different formats.

Despite all those developments, the explosive requirement for much higher capacity and faster data process speed is still driving optical data storage to aim for ever-higher storage densities.² While the limits of magnetic recording are still being debated,³ the limits of conventional optical

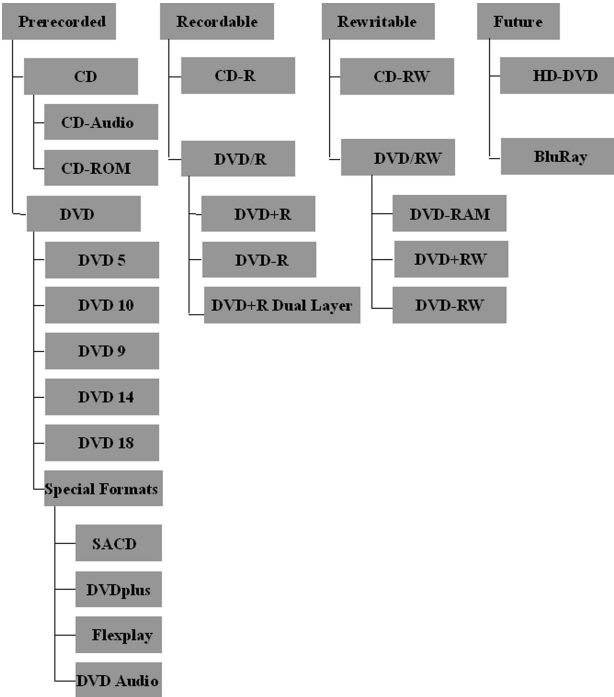


Fig. 1. Overview of the important optical data media formats and their breakdown into prerecorded, recordable (R), and rewritable (RW) media (Reprinted with permission from Ref. 1, © 2006, Wiley-VCH)

recording are well understood.² Based on the fact that the current optical storage technology is already working close to the optical refraction limit, the future development of technology will mainly be focused on taking advantage of the wavelength and/or numerical aperture dependence of the diffraction limit, or going beyond it with near field techniques, or utilizing volume storage. In addition, if the signal-to-noise ratio (SNR) is sufficient, then the gray scale technique will allow the storage of more than one bit per location.⁴

Where materials are concerned, various kinds — from organic to inorganic materials, from synthetic compounds to natural biomaterials, from single-component to hybrid systems — have been extensively explored and some of them have already been applied to certain fields of optical data storage. Among all these materials, photochromic materials have especially been attractive in recent years and have been suggested as promising candidates for future optical data storage with high density and fast data processing rate. These materials have the ability to change between two distinct states; each state can represent “0” or “1” of a digital mode, via irradiation at different wavelengths. In this all-photon-mode recording, the light characteristics, such as wavelength, polarization, and phase, can be multiplexed to enable data storage and thus have the potential to increase dramatically the achievable memory density. Using these materials, it can be expected that the information could be processed at molecular or atomic scales with response times ultimately within nanosecond or picosecond levels. Besides, the rewritability presented by these kinds of materials also makes them attracting candidates for future optical data storage.

This chapter will be focused on the new materials and technologies for the next generation of high density optical data storage devices. It will begin with the new materials, discussing their storage mechanism and presenting new progress in these fields. Then, some main technologies promising to overcome the physical limits on the current optical data storage system will be introduced.

2. Materials for Optical Data Storage

Developing new storage media is indispensable to the development of the next generation of optical data storage devices. In past decades, various

kinds have been explored and some of them have found practical application; for example, some cyanine and phthalocyanine dyes have been used in recordable compact disks (CD-R). Among them, organic materials are prompting ever-increasing attention due to their low cost, simplicity, and ability to design and tune physical and chemical properties. In this section, we will mainly discuss organic materials and biomaterials, including photochromism materials, photorefractive materials, photopolymers, etc.

2.1. *Organic photochromic materials*

Photochromism is defined as a reversible phototransformation of a chemical species between two forms having different absorption spectra. During the photoisomerization, not only the absorption spectra but also various physicochemical properties change, such as the refractive index, dielectric constant, fluorescence emission, oxidation/reduction potential, and geometrical structure. The first finding of photochromic compounds can be tracked back to the middle of the 19th century; however, the concept of photochromism was first proposed by Hirshberg *et al.* in the 1950s. In past decades, photochromic materials have found many applications in various photonic devices, while their application in optical data storage has not been considered because of insufficient reliability. However, the situation is dramatically changing. The worldwide acceptance of CD-R, which uses organic dyes as the memory medium, has changed the situation, and photochromic materials are now anticipated as a promising candidate for erasable memory media of the next generation. In contrast to previous heat mode recording systems, photochromic optical memories are based on a photon mode recording method. Photon mode recording has various advantages in terms of resolution, speed of writing, and multiplex recording capability. In this section, several kinds of photochromic materials, which have been attracting significant attention in recent years, will be introduced, with focuses on the most recent developments and new trends.

2.1.1. *Diarylethenes*

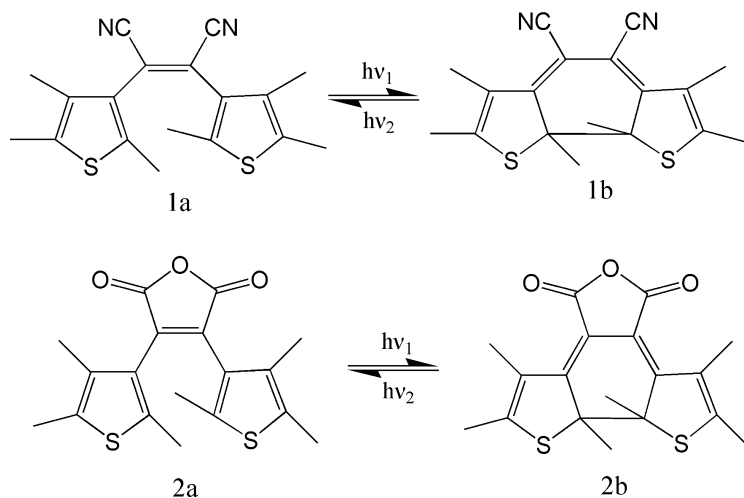
Diarylethenes are well-known thermally irreversible photochromic materials. Their two forms can be interconverted by irradiation with light

sources of appropriate wavelength. In general, the absorption bands of unconjugated open ring isomers of diarylethenes are at shorter wavelength, and those of conjugated closed ring isomers at longer wavelength. Most diarylethenes show very large spectral shifts upon photoisomerization from the open to the closed ring isomers ($> 6500\text{ cm}^{-1}$). It has been found that diarylethenes, in solution as well as in the solid state, display excellent photochromic properties: excellent fatigue resistance, short response time, high quantum yields, absence of thermal isomerization, and large change of the absorption wavelength between the two isomers.⁵⁻⁹ All those outstanding properties have made diarylethenes the most promising photochromic compounds for future optical data storage and optoelectronic devices.

We know that for practical application to erasable high density optical memory, some strict requirements must be met by storage media: (1) thermal irreversibility (the absence of thermal interconversion), (2) fatigue resistance (the ability to be cycled many times without significant degradation), (3) independently addressable absorptions that trigger the photochromic reactions, (4) high sensitivity and rapid response,^{6,10} (5) diode laser susceptibility. For diarylethenes, these requirements can be well fulfilled by proper molecular design.

2.1.1.1. Thermal stability

Thermal stability of the two isomers of photochromic compounds is indispensable for applications to optical data storage; while for common diarylethenes with two phenyl rings, the lifetime of the colored form was very short.¹¹ Such a thermally unstable photochromic system is not useful for optical memories. In the late 1980s, enlightened by the results of Kellogg *et al.*,¹² Irie *et al.* synthesized diarylethenes with thiophene rings in an attempt to construct thermally irreversible photochromic systems (Scheme 1).¹¹ These are the first examples of thermally irreversible photochromic diarylethenes. Later, theoretical studies indicated that the thermal stability of both isomers of diarylethene type photochromic compounds can be attained by introducing heterocyclic aryl groups.¹³ Since then, various types of diarylethenes with thiophene, furan, indole, selenophene, and thiazole aryl groups have been prepared.



Scheme 1. Molecular structure of diarylethenes synthesized by Irie *et al.*¹¹

It is noteworthy that the thermal stability of diarylethenes with various heterocyclic rings is very different. Irie has given a list which summarizes the lifetimes of the closed ring isomers of many diarylethenes in solution in dark.⁶ All the compounds on the list have thermally stable open ring isomers, while the thermal stability of the colored closed ring isomers is dependent on the type of aryl groups. The list shows that diarylethenes with furan, thiophene, selenophene, or thiazole rings, which have low aromatic stabilization energies, have much more thermally stable open ring forms than those with pyrrole, indole, and phenyl rings, which have rather high aromatic stabilization energies. The closed ring forms of those thermally stable diarylethenes even do not return to the open ring forms at 80°C. At the same time, substituents that can weaken the photogenerated central carbon–carbon bonds also may decrease the thermal stability of the closed ring forms.

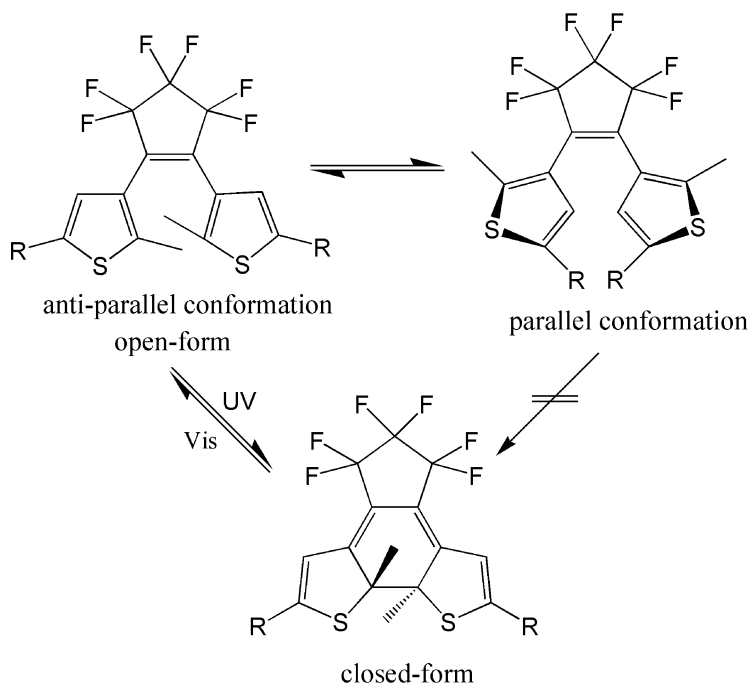
2.1.1.2. Fatigue resistance

Photochromic reactions are always accompanied by rearrangement of chemical bonds. During the rearrangement, undesirable side reactions take place to some extent. This limits the number of cycles of photochromic

reactions. Some derivatives of diarylethenes have excellent fatigue resistance and can undergo $>10^4$ coloration/decoloration cycles.⁶ It is noteworthy that dithienylethenes that have no methyl groups at the 4- and 4'-positions of the thiophene rings are less fatigue-resistant than those with methyl groups at the two positions. This can be attributed to the prevention of formation of byproducts, which is caused by 4- and 4'-methyl groups.

2.1.1.3. Quantum yield

A diarylethene with five-membered heterocyclic rings in the open form may exist as two conformational isomers: antiparallel and parallel conformations.¹³⁻¹⁶ The conformers exchange even at room temperature. The photocyclization reaction can occur only from the antiparallel conformer upon irradiation with UV light, as shown in Scheme 2.



Scheme 2. Photocyclization reaction of diarylethenes.

Therefore, the quantum yield for the cyclization reaction is dependent on the ratio of these conformers. It is crucial to increase the population of the antiparallel conformers in order to increase the photocyclization quantum yield. It has been proposed that the substituents introduced in 2- and 2'-positions strongly influenced the distribution between the parallel and antiparallel conformers present in diarylethene derivatives. It was shown that the cyclization quantum yield increased from 0.35 to 0.52 by introducing bulky isopropyl substituents at the 2- and 2'-positions of the benzothiophene rings.¹⁷ Studies of the effects on the quantum yields of various long alkyl chains at the 2-position indicated that the cyclization quantum yields increase with increasing alkyl chain lengths, while the cycloreversion quantum yields are almost constant.¹⁸

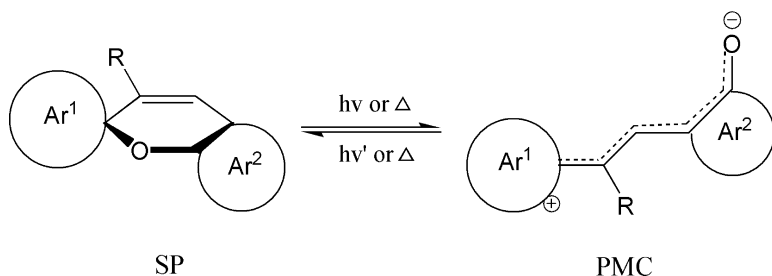
The effects on the quantum yields of radical substituents were studied. The results indicated that the cyclization quantum yields can be reduced greatly by the radical moieties and the main cause is the energy transfer from the diarylethene to the radical substituents.¹⁹

Many other methods were proposed to increase the population of antiparallel conformers by imposing a restricting effect on diarylethenes, such as incorporating the dithienylethenes into a polymer backbone,^{20,21} including the molecule in the confined space of cyclodextrins,²²⁻²⁴ and bridging the dithienylethene to fix the photoactive antiparallel conformation.²⁵

2.1.2. *Spiropyrans and spirooxazines*

2.1.2.1 Spiropyrans

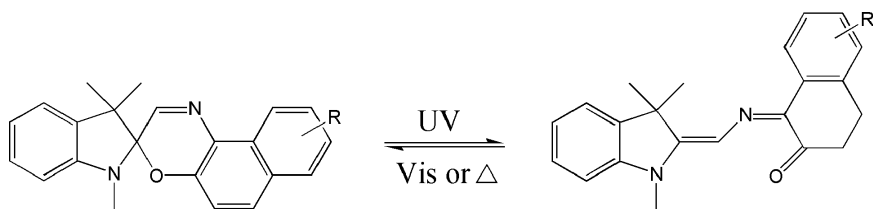
The photocoloration reaction of spiropyrans was first observed by Fischer and Hirshberg²⁶ in 1952, and later, independently by Chaudé and Rumpf,²⁷ the photodecoloration reaction. A few years later, Hirshberg presented the conception of a photochemical binary element for a computer memory, and the possibility of obtaining a variable density optical shutter. Since then an intense research activity has been conducted in both scientific and industrial fields. In 1971 and 1990, Bertelson²⁸ and Guglielmetti²⁹ gave two comprehensive and important reviews respectively. In these reviews, the fundamental aspects of theories and experiments concerning the photochromism of spiropyrans were thoroughly discussed.



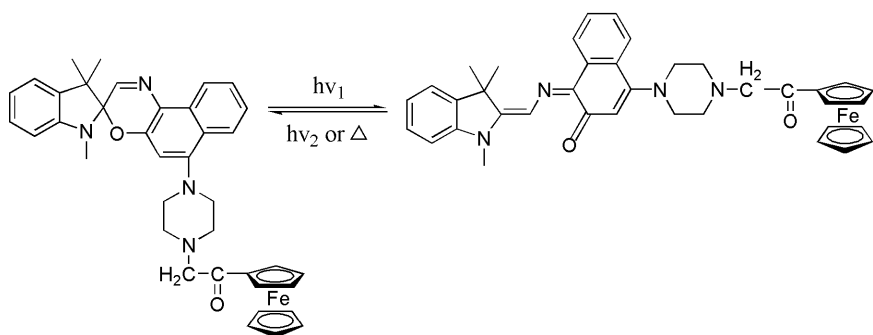
Scheme 3. Photochromism of spiropyran.

Photoisomerization of spiropyrans is shown in Scheme 3. The colorless closed ring form has two heterocyclic parts linked together by a common tetrahedral sp^3 carbon atom. The two halves of the molecule are in two orthogonal planes. The spiro carbon atom prevents direct conjugation between the two halves. The absorption of the closed form is in the UV range of 200–400 nm, with an actinic band mostly situated near 320–380 nm. By cleavage of the carbon–oxygen bond, the colored open ring isomer is formed. Then a conjugation between the two halves of the molecule is made possible, which results in a shift of the absorption from the UV region to the visible region. The open ring form of spiropyrans is often called photomerocyanine, because its structure is quite similar to that of merocyanine dyes. It is noticeable that spiropyrans are usually not photochromic in the solid state, but show this phenomenon in solution and more rigid media such as gels, plasticized resins, films, and bulk plastic solids.

Rentzepis *et al.* presented the three-dimensional optical memory device based on two-photon writing, reading, and erasing of the information in a spiropyran embedded in polymer matrix.³⁰ The structure of the spirobenzopyran used in the experiment is shown in Scheme 4. Simultaneous absorption of either a 1064-nm-photon and a 532-nm-photon (achieving 355 nm excitation) or two 532-nm-photons (corresponding to 266 nm excitation) mutually focused on a certain pixel will “write” information by creating merocyanine in that pixel. This information can be read by monitoring fluorescence emission following irradiation using a 1064 nm laser, as only the merocyanine can be excited by two-photon absorption of this laser.



Scheme 5. Photoisomerization of spirooxazine. Left: Closed form (colorless). Right: Opened form (colored).



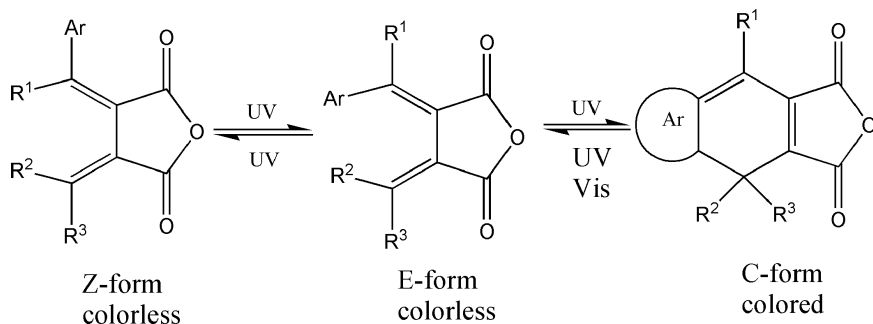
Scheme 6. Photochromism of thermally stable spirooxazine.³¹

The compound was used for both 2D and 3D read, write, and erase data storage experiments, and there was little degradation of fluorescent emission intensity on extended irradiation at the power used by the readout laser.

2.1.3. Fulgides

Fulgides is one of the oldest known groups of organic photochromic compounds. Due to their remarkable properties, such as thermal irreversibility and fatigue resistance, they are still attracting much attention for both fundamental research and practical applications.

Typically, fulgides are yellow or orange crystalline compounds which change to orange, red, or blue upon irradiation with UV light. Photochromism has been observed in crystal, solution, polymers, and glasses



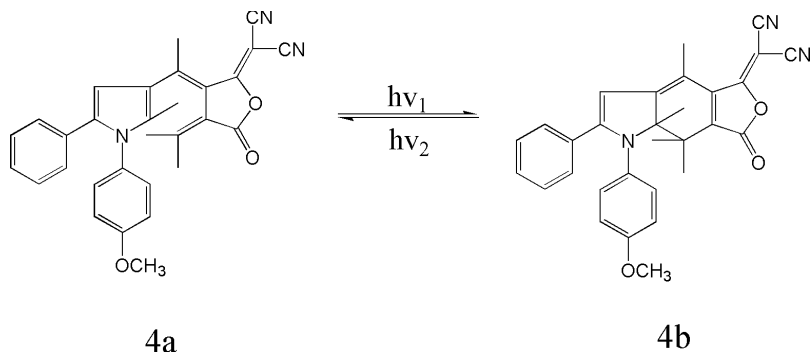
Scheme 7. Photochemical isomerization among three forms of fulgide.

over a wide range of temperatures and conditions.^{35,36} The photochromism of fulgides occurs between one of the colorless open forms (*E*-form) and the photocyclized colored form (*C*-form). However, there is an additional photochemical *E*–*Z* isomerization pathway (Scheme 7). The “*Z*-form,” the geometrical isomer of the *E*-form, is not considered as an important member of the photochromic system, which may not cyclize directly by absorbing one photon to give the *C*-form.

Chen *et al.* studied the photochromism of fulgides with dicyanomethylene 4a, doped in PMMA matrix (Scheme 8).³⁷ Experiments indicated that the material, used as recording media, has advantages: fast response, high sensitivity, and large reflectivity difference between the unrecorded (~ 0.2) and recorded states (~ 0.8). Such a large difference in reflectivity between recorded state and unrecorded state is very useful for multilevel recording. By controlling the laser exposure energy delivered to 4a, the degree of photoisomerization can be finely controlled and four-level signals can be achieved. The destructive readout is not detected after 301 times the readout process.

2.2. Biological material — bacteriorhodopsin

Bacteriorhodopsin (BR), a small, robust protein, is the simplest known photon-driven proton pump.³⁸ It is produced by halobacteria and is the key protein of their photosynthetic capabilities. Since its discovery, BR has been explored in various technical fields and particularly in optical fields.



Scheme 8. Photochromism of fulgide used by Chen *et al.*³⁷

In the area of photochromic applications, BR is much more attractive than other proteins and conventional inorganic or organic photochromic materials due to its special properties. First, the BR wild type — the form which is found in nature — occurs as a two-dimensional crystal, which causes its astonishing stability toward chemical and thermal degradation. Even more important is that the photosensitivity and cyclicity to illumination of this biological photochrome is far beyond that of synthetic materials. Furthermore, BR can be modified to a large extent by genetic and chemical technologies, and can serve as a platform for a whole new class of materials.

2.2.1. Biological function and structure of bacteriorhodopsin

Bacteriorhodopsin (BR) is the key protein of the halobacterial photosynthetic system.^{39,40} Compared to the chlorophyll-based photosynthetic systems, it is extremely simple. BR is found at halobacteria in the form of a two-dimensional crystal integrated into their cell membrane. These patches are called purple membranes (PMs). Up to 80% of the surface may be covered by one or more PM patches, which consist of BR and lipids only. All the BR molecules are uniformly oriented, with their carboxy termini located in the inner portion of the cell. BR consists of 248 amino acids which are arranged in several α -helical bundles inside the lipid membrane and form a cage where a retinylidene residue attached to lysine 216 is located.

Each BR contains one molecule of a linear pigment called retinal, one end of which is attached to the nitrogen atom of a lysine residue in a helix. The other end is wedged deep in the protein.⁴¹ Retinal changes its structure in response to visible light. The inner group of amino acids interacting with retinylidene residue may be considered as an enzyme with a substrate specificity for all-*trans*/13-*cis*-retinal and catalyzes this isomerization at room temperature. Furthermore, the amino acid part of the chromophore is responsible for the suppression of isomerizations which would occur in free retinal, e.g. isomerizations leading to 7-*cis*-, 9-*cis*-, and 11-*cis*-retinal. The rest of the protein moiety carries the proton conduction pathway and shields the photochromic inner group from influences from the outer environment.

The molecular function of BR is that of a light-driven proton pump. The proton transport starts with the release of a proton on the extracellular side and ends with a proton uptake from the cytoplasmatic side. As it does this, the molecule passes through several intermediates, referred to as K, L, M, N, and O, which have well-defined lifetimes and spectral properties.⁴² Figure 2

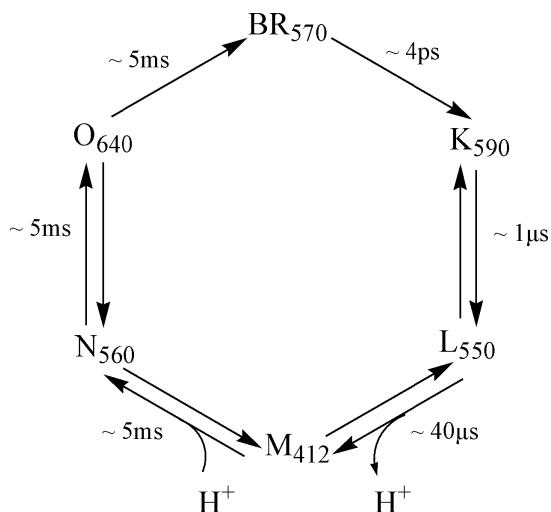


Fig. 2. Schematic representation of the photocycle of BR. The absorption maxima for the ground (BR₅₇₀) and the principal intermedia states (in nm) are shown in subscripts; the respective lifetimes at room temperature, as well as deprotonation and reprotonation, are shown next to the arrows.⁴⁴

shows a simplified model of the BR photocycle. The primary photochemical reaction is the isomerization of retinal, from which a proton's climb against the transmembrane electrostatic potential of the purple membrane follows. An important property of all the intermediates is their ability to be photochemically switched back to BR by shining light at a wavelength that corresponds to the absorption of the intermediate state in question. This property makes BR an ideal material for erasable optical storage.⁴³

2.2.2. *Bacteriorhodopsin as a photochromic molecular material*

During the photocycle of BR, several molecular switches operate sequentially: first the photoinduced isomerization around the C13–C14 double bond (“isomere switch”), then the deprotonation of Asp85 to a more outward-located proton release group (“amino acid protonation switch”), immediately followed by the deprotonation of the Schiff base linkage (“Schiff base protonation switch”), and a conformation change at C15 (“conformation switch”). Isomerization, Schiff base protonation, and conformation switch are reset and the molecule is ready to start a new cycle. The reprotonation of the Schiff base linkage occurs from Asp96 instead of Asp85, reflecting the vectorial proton transport. All of the listed switches have some technical importance, even if it is not possible to separate them completely.

As stated above, photochromic applications with earlier states of the BR photocycle could also be done in principle, but most of the photochromic applications described in the literature use the interconversion of the B and M states at room temperature. The absorption bands of the B and M states are given in Fig. 3. It can be seen that the absorption bands of B and M have only little overlap. For this reason this combination is preferred for photowriting/photoerasing applications. The position of some important laser wavelengths is also indicated. While for lab applications, krypton gas lasers are the best choice for the work with BR — they have emission lines at 568 and 412 nm, which coincide with the maximal absorption wavelengths of the B and M states almost perfectly — technical applications better use solid state lasers, e.g. a diode-pumped frequency-doubled Nd: YAG or laser diodes which are available down to 633 nm from the shelf.⁴⁴

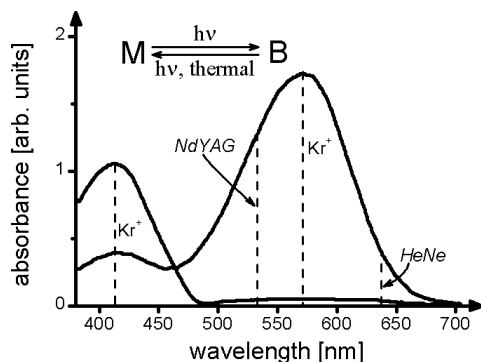


Fig. 3. Absorption spectra of the B and M states of BR. The purple B state is the initial state of BR. The M state is the longest-living intermediate and the most blueshifted from B. For photochromic applications the photochemical interconversion of B and M is preferably used because of the large photochromic shift of about 160 nm. (Reprinted with permission from Ref. 44, © 2000, American Chemical Society)

For the integration of BR into photochromic systems, two hurdles have to be overcome: first, the structuring of the biomaterial itself and, second, the interface of the biocomponent with the rest of the conventional system. Fortunately, the technical level for both criteria is the lowest for photochromic systems in all of the BR applications. No long range order between PM patches, i.e. macroscopic orientation, is required. A homogeneous distribution of PMs in an optically inert matrix material fulfills the needs. They may be sealed completely between protecting glass layers.

It is of considerable significance that the both spectrum and kinetic aspects of the BR photocycle can readily be modified. The modification can be accomplished by changing or modifying one or more of the essential components in BR. Table 1 summarizes the means by which the different components can be modified. All the listed approaches have been implemented already. Amino acid changes are accomplished by genetic engineering of the gene coding for BR and expression of the resulting BR variant in halobacteria. Genetic methods are of great importance to the future development of new BR variants for technical uses. Besides the changes in the molecule itself, alterations of the physicochemical

Table 1. Functional modules in BR and their possible modification and the technologies used for their realization.

Functional modules in BR	Alterations	Technology*
Proton pathways	Chemical additives	Chem
	Amino acid exchanges	Gene
Retinylidene residue	Retinal analogues	Chem
Amino acids in chromophore	Amino acid exchanges	Gene
Schiff base linkage	Attached or free chromophore	Gene
	Different attachment sites	Gene
Protein backbone	Chemical modifications	Chem
	Amino acid exchanges	Gene
External fields	Electric fields	Phys
	Magnetic fields	Phys
Substrate (protons)	PH value	Phys
	Proton availability (drying)	Phys
	Proton mobility (additives)	Phys
	Deuterium	Phys

* Chem = chemical modifications; Phys = physicochemical means; Gene = genetic engineering.

environment of BR and its mutated versions allow its photochemical properties to be influenced to a great extent.

2.2.3. Data storage application

2.2.3.1. 3D data storage

For BR, three different types of volume storage techniques are investigated. The first is page-oriented holographic storage, the second is based on a so-called branched photocycle scheme, and the third uses two-photon excitation of individual data points in the volume of a material.⁴⁴

The third technique is accomplished by the intersection of two laser beams.⁴⁵ Each beam carries photons with just half the energy to switch BR from B to M or vice versa. Two-photon absorption depends on the product of the contributing intensities ($\propto I^2$). In the volume of intersection the probability for two-photon absorption is high enough that a measurable shift in

the population distribution between B and M can be induced. The wavelengths employed must fulfill the condition $1/\lambda_{\text{excite}} = 1/\lambda_1 + 1/\lambda_2$. This may be achieved by choosing $2\lambda_{\text{excite}}$ for both beams, e.g. 820 and 1140 nm, corresponding to one-photon excitations with 410 and 570 nm, respectively.⁴⁶ In the pass of the light beams, undesired two-photon excitations must be taken into account. For this reason it might be advantageous to use two different wavelengths which fulfill the given equation. It is of great advantage that wavelengths can be chosen where the material is almost transparent and one-photon absorption is not a competing reaction. It has been revealed that BR has an astonishing high cross-section for two-photon absorption, and for this reason BR should be considered as a material for volume data storage via two-photon excitation.⁷⁶ The longevity of the stored data is currently possible only if the BR-based storage medium is cooled. Addressing an individual data point in the volume must create a signal which allows the return of information as to whether the photochromic state is a “1” or “0.” For BR its photoelectric properties may be employed for the readout process.

As shown in Fig. 4, writing is done by two beams with wavelengths λ_1 and λ_2 which intersect in the volume. Using $\lambda_1 = \lambda_2 = 1140$ nm, the photochemical transition from B to M can be initiated. The B and M states, or certain ratios of B and M, are assigned to “0” and “1.” Switching from M to B is obtained by overlapping two waves of 820 nm. During the readout, the same procedure is applied. First, two 1140 nm beams are used, and if BR was in the B state it switches now to M. The initial charge separation leads to a photovoltaic effect which can be detected by two electrodes on the outer surface of the volume storage medium.

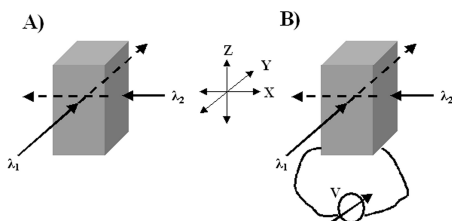


Fig. 4. Principle of 3D data storage in BR using two-photon absorption. (Reprinted with permission from Ref. 44, © 2000, American Chemical Society)

2.2.3.2. Holographic storage and associative memories

The desirable properties of BR compared with other holographic materials are real time writing on microsecond time scales, durability of allowing millions of write/erase cycles without degradation, very high spatial resolution of 2000–5000 line pairs/mm, and good light sensitivity of about 10 mJ/cm^2 .⁴⁷

Dried films of BR suspension or BR embedded into inert matrices like polyvinylalcohol (PVA) or polyacrylamide can be used as holographic media. Use of BR in oriented PVA films as a medium for dynamic holograms has been discussed.⁴⁸ A maximum diffraction efficiency of 11% for a $150 \text{ }\mu\text{m}$ thick film was observed at readout light between 620 and 700. Attempts were also made to generate artificial derivatives of BR to meet the demands of holographic recording processes more closely. Some of these BR variants proved to have superior optical properties for holographic applications compared with BR_{WT} .⁴⁹ The variant BR_{D96N} , which contains an asparagines residue in position 96 instead of aspartic acid, has been chosen and it has a strong retardation of the proton-dependent thermal relaxation $\text{M} \rightarrow \text{B}$. Therefore BR_{D96N} films have an about 50% higher recording sensitivity and a two-fold higher diffraction efficiency compared to wild type films.⁵⁰

2.3. Photorefractive material

The photorefractive effect is defined as the optical modulation of the refractive index of a medium as a result of a number of processes. The interference of two laser beams in a photorefractive material establishes a refractive index grating. The mechanism responsible for the formation of this refractive index grating is the generation of a space charge field (internal electric field) due to charge separation between bright and dark areas of the interference and a subsequent change in the refractive index via an electro-optic effect (Pockels effect).⁵¹ Figure 5 illustrates the photorefractive effect when the crystal is exposed to an interference pattern generated by two plane waves. According to the composition, photorefractive materials can be divided into three categories: (1) inorganic crystals — ferroelectric crystals, e.g. LiNbO_3 , BaTiO_3 , LiTaO_3 , and paraelectric

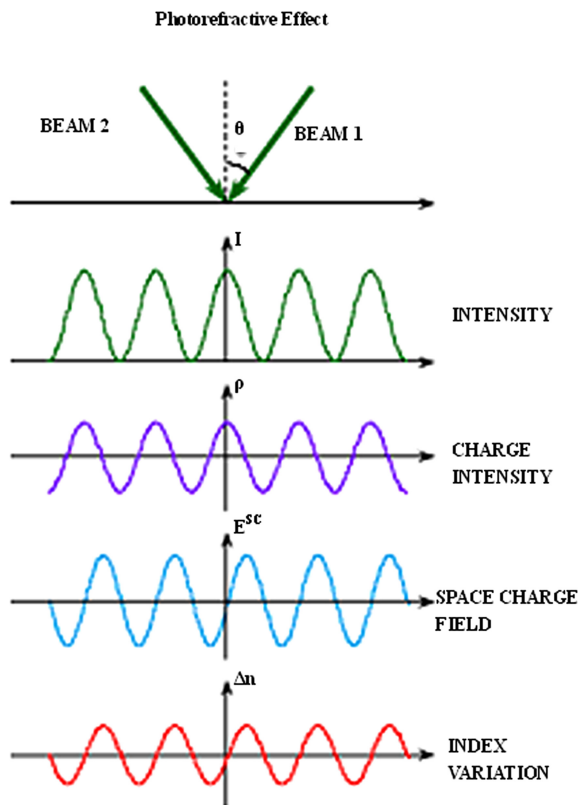


Fig. 5. Formation of an index grating in a photorefractive crystal. (Reprinted with permission from Ref. 52, © 2002, SPIE)

crystals, e.g. $\text{Bi}_{12}\text{SiO}_{20}$ (BSO), $\text{Bi}_{12}\text{GeO}_{20}$ (BGO); (2) semiconductors — e.g. GaAs, InP, CdTe; (3) organic/polymer materials.

The photorefractive effect is an ideal optical effect for 3D bit optical data storage because scattering caused by a change in the refractive index is weak when a beam is focused to a large depth in a recording material and the effect is reversible, allowing for a rewritable optical data storage system.^{53,54} Figure 6 shows the excitation of electrons in a crystal by two-photon absorption. The trapped electrons at donor sites are excited into a conduction band by absorption of two-photons simultaneously.

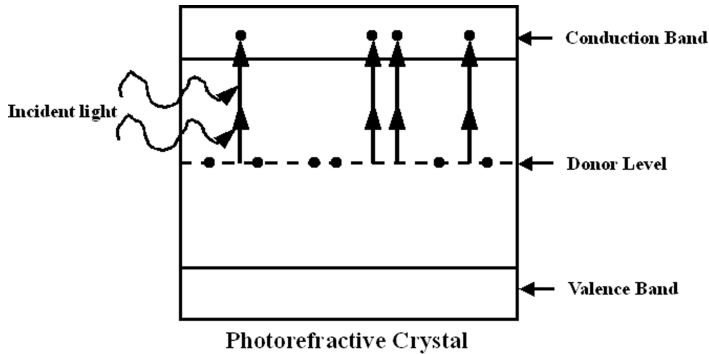


Fig. 6. Excitation of electrons in the donor sites by two-photon absorption. (Reprinted with permission from Ref. 55, © 1998, Optical Society of America)

The energy gap between the conduction band and the donor level is two times smaller than the photon energy. The excited electrons are retrapped in vacant donor sites after movement in the conduction band. The movement of the excited electrons yields a nonuniform distribution of charges. The charge distribution produces an electric field and modulates the refractive index by the Pockels effect. One bit of data can be recorded in the crystal as the refractive index change. By scanning the focused spot in the recording medium, 3D data storage can be realized. Kawata *et al.*⁵⁵ reported two-photon 3D data storage in a LiNbO_3 crystal with a Ti:sapphire laser used as the light source. The wavelength of the laser light was 762 nm, and the pulse width was 130 fs. The recorded bit size was $1.2 \mu\text{m} \times 1.8 \mu\text{m} \times 14.2 \mu\text{m}$ and the attainable storage density was 33 Gbits/cm² with these values.

However, photorefractive crystals are expensive and difficult to manufacture. Gu *et al.*^{53,54} proposed using photorefractive polymers as recording materials for erasable–rewritable 3D bit optical data storage under two-photon excitation. In one case, they successfully demonstrated writing, erasing, and rewriting of multilayered information in a photorefractive polymer consisting of 2,5-dimethy-4-(p-nitrophenylazo) anisole (DMNPAA), 2,4,7-trinitro-9-fluorenone (TNF), 9-ethylcarbazole (ECZ), and poly(N-vinylcarbazole) (PVK). In this system, TNF provides absorption in the UV-to-Vis region of the spectrum, DMNPAA provides absorption

and an electro-optic effect in the UV-to-Vis region, and ECZ reduces the glass transition temperature of the material. A three-dimensional bit density of 5 Gbits/cm³ is achieved by two-photon absorption under pulsed illumination at an infrared wavelength of 800 nm in the recording process.

2.4. Photopolymers

Photopolymers are a class of promising materials for write-once-read-many (WORM) memories. Before exposure to light, the photopolymer recording medium consists of polymerizable monomers dispersed in a matrix. Upon illumination by a light pattern, monomers in the bright areas become polymers. At the same time, the remaining monomers will diffuse to form a uniform distribution throughout the bulk of the medium and form a density grating which can be fixed by a uniform illumination after the diffusion of monomers reaches a steady state. As the index of refraction of the polymer depends on its density, the density grating results in an index grating. The advantages of photopolymers are their relatively large dynamic range and their nonvolatile nature. In recent years, significant efforts have been made to improve the properties of photopolymers, such as higher optical quality, increased thickness, less shrinkage, as well as larger dynamic range and higher photo-sensitivity.^{56–58} Strickler *et al.* demonstrated a 25-layer memory of density 1.3×10^{12} bits/cm³ by two-photon technology. The storage medium used in their experiment was an ~100- μ m-thick film composed of a photopolymer, Cibacool.⁵⁹

But, for two-photon photopolymerization, the photopolymer systems usually exhibit low photosensitivity since the conventional photoinitiators often have small two-photon absorption cross-sections (δ). Consequently, this approach requires high laser power, and its widespread use remains impractical. To solve the problem, Perry *et al.*⁶⁰ developed a class of π -conjugated D- π -D compounds that exhibit large δ (as high as 1250×10^{-50} cm⁴ s per photon) as photoinitiators. Two-photon excitable resins based on these new initiators showed enhanced two-photon sensitivity relative to traditional ultraviolet initiators.

2.5. Photobleaching polymers

In this method, polymers doped with a fluorescent dye that can be excited by photon are used. Under intense laser illumination, dyes in the focused spot are bleached, and thus information is recorded as bleached patterns. The bleached areas do not produce fluorescence. As a consequence, the recorded information can be read out using a fluorescence microscope. The places that have been bleached show up as areas darker than the surrounding fluorescence area. However, optical storage in a photobleaching polymer material is not erasable, as shown in photorefractive and photochromic materials. But, when these polymers are applied to 3D bit data storage, it has been shown that recorded photobleached patterns can be read out using a low cost continuous wave (CW) laser beam rather than an expensive ultrashort-pulsed laser beam.⁶¹ Gu *et al.*⁶² demonstrated recording and reading of six layers of data bits in a photobleaching polymer under CW laser irradiation at 800 nm; the storage density was approximately 3 Gbits/cm³.

3. Progress in Materials for Future Optical Data Storage

There is no doubt that significant developments have been achieved in fields of materials for future optical data storage. Theoretically, researchers can even realize data storage at molecular level.⁶³ However, for practical application, several problems still remain. For example, as far as rewritable materials are concerned, how to read out the stored data nondestructively is still a problem. In order to get a much higher storage density, a faster data processing rate, and to construct nonvolatile devices, much effort is still needed in material design as well as technical innovation. In this section, the focus is placed on the most recent developments in optical data storage materials, and some representative achievements are given an overview. Although they are mainly at the laboratory stage, these results still throw new light on the development of materials for future optical data storage.

3.1. Nondestructive

To successfully place a photochrome in an erasable memory medium, its two photochromic states must be easily identified in a noninvasive manner.

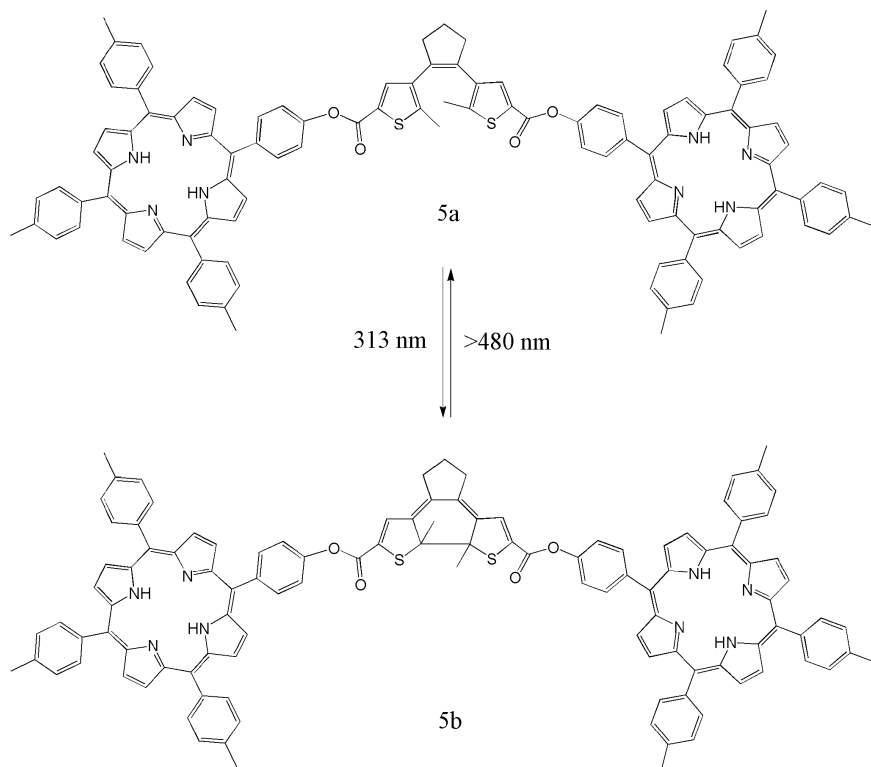
Recording the differences in their ultraviolet-visible (UV-Vis) absorption is the most common detection technique. However, it often has undesired side effects, because the absorption bands of each isomer also can induce the ring-opening and ring-closing reactions. Sampling near these photoactive absorption bands will inevitably cause partial switching of the photochrome and erasing of the stored data. To avoid such inconvenience, it is indispensable to develop nondestructive readout methods.^{10,64}

The approach to solving the problem, while maintaining all-photon-mode erasable memory media, is to discriminate between the two isomers using light which cannot induce the photochromic reactions. For this purpose, change in signals, such as refractive index,⁶⁵ infrared absorption,⁶⁶ optical rotation,⁶⁷ or luminescences⁶⁸ can be employed. Two critical conditions must be met for this strategy to be effective: (1) the photochrome must display varying optical properties dictated by its structural form; (2) the wavelength of light used to stimulate the optical output must not overlap with the photochromic absorptions.¹⁰

3.1.1. *Luminescence*

Recording changes in luminescence is a promising alternative for processing stored data while minimizing the extent to which the information is erased during the detection event. When luminescence is to be used as a detection method in erasable memory media, an important condition must be met, i.e. the wavelengths of light used to produce the luminescence (excitation wavelengths) and the resulting emission wavelengths must reside outside the photochrome's absorption spectral region to avoid any interconversion of the photochrome.

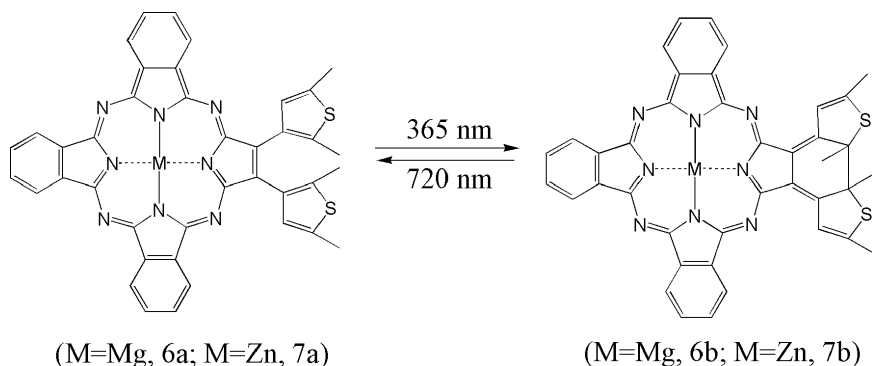
A hybrid dithienylethene has been synthesized, where porphyrin macrocycles are attached to the ends of the 1,2-bis(3-thienyl)cyclopentene backbone (Scheme 9).⁶⁹ The luminescence of the porphyrin macrocycles in 5a and 5b greatly depends on the state of the dithienylethene photo-switch. When 5a is irradiated close to the porphyrin's Soret absorption bands at 430 nm, where both the open and closed forms of the photochrome are transparent, the macrocycles exhibit intense emission at 655 nm. When the photocyclization reaction is carried out by irradiation 5a at 313 nm, the nonfluorescent closed form 5b is produced. Back irradiation



Scheme 9. Photochromism of the hybrid dithienylethene.⁶⁹

at wavelengths greater than 480 nm generates 5a and restores the original emission spectrum. The intensity of the porphyrin's fluorescence can be conveniently regulated by toggling between 5a and 5b through alternate irradiation at 313 nm and greater than 480 nm.

Irradiation of the open form 5a at 430 nm and 650 nm results in no observable ring-closing, because the photochromic fragment of the hybrid is transparent at these wavelengths. Similarly, the photostationary state shows no spectral changes when exposed to light at 650 nm. However, when it is irradiated with 430 nm light, the ring-opening reaction of 5b happens. Since the photochromic fragment is transparent at this wavelength, the authors attributed the cause to the energy transfer from the porphyrin's excited state to the photochromic center. To some extent, the

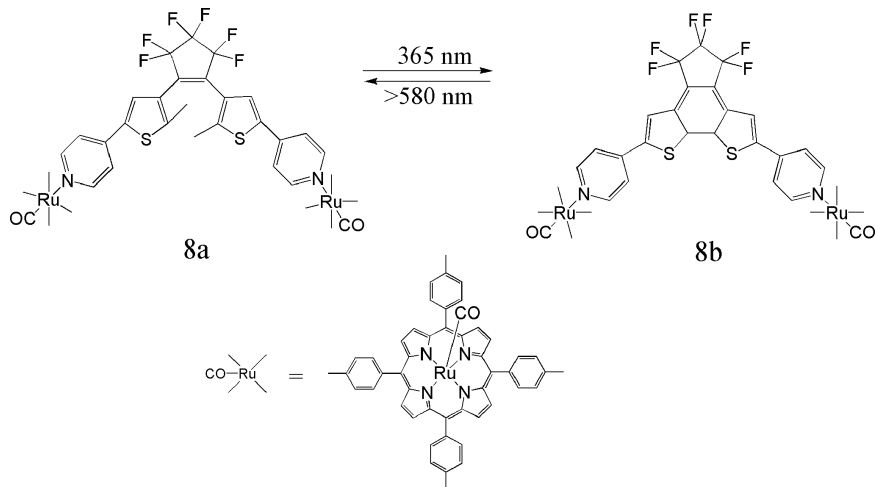


Scheme 10. Photochromism of BTE-uPc synthesized by Tian *et al.*⁷⁰

indirect photochemical interconversion limits the use of 5a in digital data processing applications.

2,3-bis(2,5-dimethyl-3-thienyl) unsymmetrical phthalocyanine hybrids (BTE-uPc's) were synthesized by Tian *et al.* (Scheme 10).⁷⁰ By irradiation with 365 nm and 724 nm light, the hybrids can undergo ring-closing and ring-opening reactions between the two isomers. 445 nm light was employed for excitation of fluorescence, at which the photochemical interconversion of the two states was inactive in either direction. The open rings 6a and 7a emit at 703 nm, which is a wavelength insensitive to the ring-opening reaction, and recyclization of 6b and 7b cannot be induced. The luminescence intensity is proportionally dependent on the content of the closed ring form, so it can be modulated by photochemical regulation between the open and closed forms. Those authors also synthesized a series of bis(thienyl)ethane-based tetraazaporphyrin hybrids which are potentially applicable to the nondestructive readout method.⁷¹

Compared with those of fluorescence, the wavelengths of phosphorescence reside far outside the photochrome's absorption spectral region. Thus, it will be more effective to employ phosphorescence as the readout signal for nondestructive information processing. Branda *et al.*⁶⁸ reported a bis-metalloporphyrin-dithienylalkene hybrid (Scheme 11). In this case, axial coordination of Lewis basic pyridyl heterocycles appended to porphyrinato (ruthenium) building blocks provides a supramolecular assembly



Scheme 11. Photochromism of a bis-metalloporphyrin-dithienylalkene hybrid reported by Branda *et al.*⁶⁸

that phosphoresces far into the visible region and is removed from the photochromic absorption bands.

The two isomers 8a and 8b of hybrid 8 can be interconverted by irradiation with 365 nm and 470–685 nm light, respectively. On excitation of the open isomer at 455 nm, where both forms of the photochromes are transparent, the metalloporphyrin macrocycles phosphoresce intensely at 730 nm. The closed form 8b displays no luminescence. The emission intensity of hybrid 8 can be modulated by interconversion between 8a and 8b through alternate irradiation with 365 and greater than 580 nm light. Prolonged irradiation of the open or closed forms at 455 nm results in no observable spectral changes as monitored by both absorption and emission spectroscopy. This system demonstrates all of the requirements for functioning as a nondestructive read/write/erase system.

3.1.2. Infrared light

For diarylethenes, the C=C stretching region ($1400\text{--}1650\text{ cm}^{-1}$) is highly selective and suitable for detecting the difference. It was reported by Zerbi *et al.* that some diarylethene derivatives having thiophene rings as the aryl

groups exhibited remarkable infrared (IR) spectral changes accompanying the photochromic reaction.⁷² They showed that 1,2-bis[5'-(4''-methoxyphenyl)-2'-methylthien-3'-yl]perfluorocyclopentene has a strong IR absorption peak at 1495 cm^{-1} in the closed ring isomer, while it is absent from the open ring isomer. Conceptually, they proposed that an optical memory system can be constructed in which the information is written and erased by UV and visible photons that activate the photochromic process; the reading is achieved with infrared photons unable to cause any molecular rearrangement.

Later, Uchida *et al.* developed a series of diarylethene derivatives that are suitable for the IR nondestructive readout process.^{73–75} In one case, they prepared two diarylethenes having benzothiophene rings 9 and 10, which showed a remarkable difference in the spectra of the two isomers around 1600 cm^{-1} .⁷³ For compound 9, the closed ring isomer had three strong absorption bands, at 1625, 1585, and 1549 cm^{-1} , which can be attributed to the out-of-plane vibration of the central part of the cyclohexadiene moiety and antisymmetric and symmetric stretching of the double bonds of the benzothiophene rings, respectively. For the closed form of 10, three absorption peaks of the benzene ring in the benzothiophene and the C=C bonds in the central six-member ring at 1545, 1591, and 1624 cm^{-1} were observed. By doping diarylethene 10 into a Zeonex polyolefin polymer, which has no absorption between 1500 and 1700 cm^{-1} , they demonstrated the IR readout of the stored information. A prolonged readout of the image using IR light will not cause a decrease in the SNR.

However, the use of IR light has some disadvantage for high density data storage, due to the longer wavelengths because the light spot diameter cannot be focused shorter than the wavelength of the used light. A possible solution is to employ a multiaddressable recording system which can multiply the data in the same spot. To this end, multifrequency recording using three diarylethene derivatives, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (11), 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (12), and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (13), with different absorption bands not only in the UV/Vis region but also in the IR region, was investigated.⁷⁴ In this system, by using UV and visible light of appropriate wavelengths, writing and erasing the

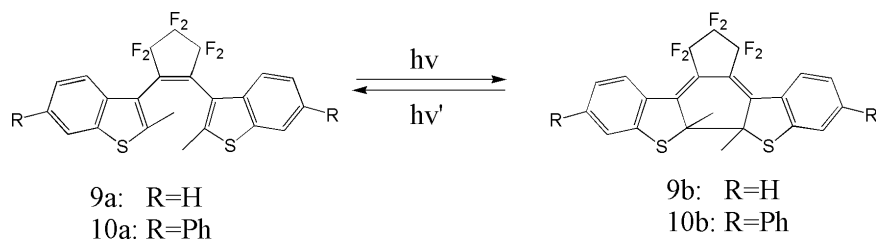
Scheme 12. Photochromism of diarylethenes synthesized by Uchida *et al.*⁷³

Table 2. Three bits eight states of the photochromic film composed of compounds 11–13 and the nondestructive readout wave numbers. (Reprinted with permission from Ref. 74, © 2005, Wiley-VCH)

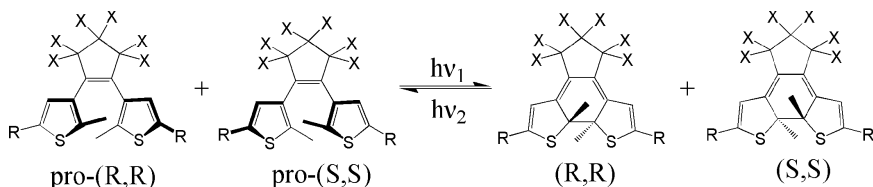
States	States of diarylethenes			Detectable IR wave numbers (cm ⁻¹)		
	11	12	13	1655	1549	1527
A	o	o	o	0	0	0
B	o	o	c	0	0	1
C	o	c	o	0	1	0
D	o	c	c	0	1	1
E	c	o	o	1	0	0
F	c	o	c	1	0	1
G	c	c	o	1	1	0
H	c	c	c	1	1	1

o — state in the open ring isomer; c — state in the closed ring isomer or the photostationary state; 0 — nondetectable; 1 — detectable.

data of eight states ($2^3 = 8$) can be carried out. To detect the eight states, the absorption at wave numbers at 1655, 1549, and 1527 cm⁻¹ was utilized (Table 2).

3.1.3. Optical rotation

Recording changes in optical rotation that originated in photochromic reactions is another alternative for reading information in a nondestructive

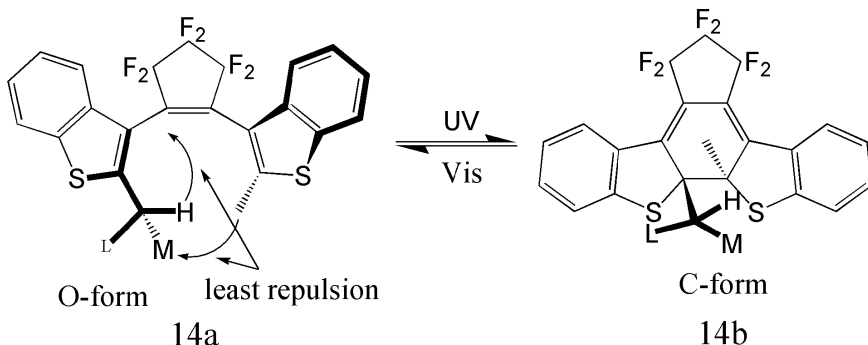


Scheme 13. The two stereoisomers generated by photocyclization reactions of diarylethenes.

manner, since the detection can be performed outside the photoactive spectral regions.⁷⁶ Diarylethenes are potentially applicable to this method because their photocyclization reactions generate two stereoisomers, albeit in a one-to-one ratio (Scheme 13). However, one criterion must be satisfied in order to use optical rotation as a detection technique: there must be stereoselectivity in the photochromic reactions to eliminate the production of a racemate and afford a recordable response.¹⁰ Various attempts have been carried out to enrich one of the enantiomers (or diastereomers).^{67,77–79}

Yokoyama *et al.*⁷⁸ synthesized 14, possessing a hydrogen atom, a methyl group, and a methoxymethoxyl (MOMO) group on the stereogenic carbon atom on C-2 of one of the benzothiophenes (Scheme 14). For the open ring of 14, the predominant conformational isomer is the following. Hydrogen faces the bulky hexafluorocyclopentene, two substituents (medium-sized, M; and largest, L) hang down in the rather wide space and the other benzothiophene would take the position close to M rather than to L because of steric repulsion. When the open ring isomer of 14 was irradiated with 313 nm light in hexane at room temperature, two diastereomer excess (de) was 87%. As the open ring form of 14 may take the helical structure, its optical rotation value is larger than that of the planar closed ring form possessing three asymmetric carbon atoms. Irradiated by light at 820 nm, where no isomer of 14 absorbs light, the optical rotation value can change repeatedly.

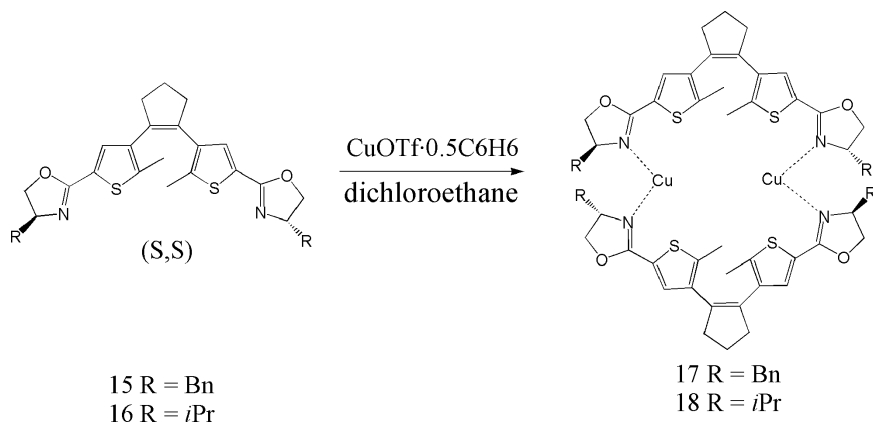
Branda *et al.*⁶⁷ prepared chiral bis-oxazoline photochromes 15 and 16 from 1,2-bis-(5-chloro-2-methyl-3-thienyl)cyclopentene (Scheme 15). Irradiation of the open isomer of 15 at 313 nm produced nearly the same amount of two diastereomeric isomers. In the presence of copper(I), ligand 15 generated complex 17 with a stereochemically pure binuclear double



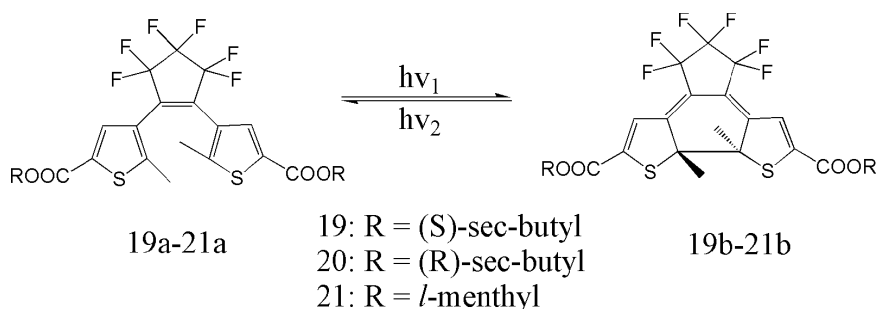
Scheme 14. H = hydrogen atom; M = methyl group; L = MOMO group. (Reprinted with permission from Ref. 78, © 2003, American Chemical Society)

helix. Under the 313 nm light irradiation, a major stereoisomeric product was formed with a diastereoselectivity of 98%. However, the diastereoselectivities were lower when the photocyclization reactions were conducted with the isopropyl ligand 16. This can be attributed to the formation of a less robust coordination compound. There are significant differences between the open and closed forms of photochromic coordination compounds $\text{Cu}_2(15)_2$ rotate light throughout the UV-Vis spectrum. Toggling between the open and closed forms by alternate irradiation at 313 nm and greater than 458 nm can regulate the angles of optical rotation at 450 nm and 475 nm, a spectral region where both forms of the photochromes are transparent. This detection method is noninvasive because of the lack of variation in the UV/Vis spectrum upon extended irradiation at 475 nm.

In practical applications, photochromic reactions often take place in solid matrices. In particular, a bulk amorphous state is favorable for processing and has various advantageous characteristics for practical usage, such as high dye density and high optical transparency. Yamaguchi *et al.*⁷⁹ synthesized three diarylethene derivatives, 19a, 20a, and 21a, which have two chiral substituents (Scheme 16). These molecules can undergo a diastereoselective photocyclization reaction in the bulk amorphous state. In the case of 19a, the diastereomeric excess was 25%. The amorphous film showed reversible circular dichroism (CD) spectral change upon alternate irradiation with 334 nm and >550 nm light.



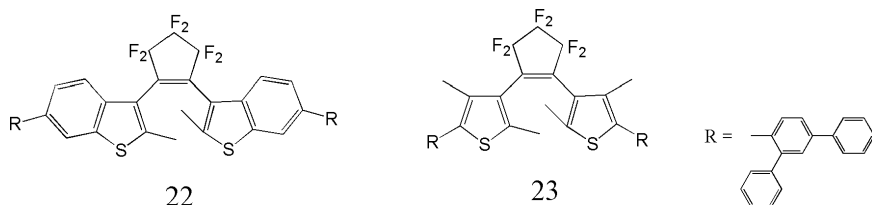
Scheme 15. Molecular structure of diarylethenes synthesized by Branda *et al.*⁶⁷



Scheme 16. Photoisomerization of diarylethenes 19–21.⁷⁹

3.1.4. Refractive index

The photocyclization from the open to the closed ring form of diarylethenes increases the electronic delocalization of the molecule as well as the polarizability of the electronic cloud of the photochromes. They are then able to change the refractive index of the medium in which they are incorporated.⁸⁰ However, the refractive index change of diarylethene-dispersed polymer films is relatively small, due to the low density of the photoactive molecules in the medium. To solve the problem, a convenient way is to make the photochromes form bulk



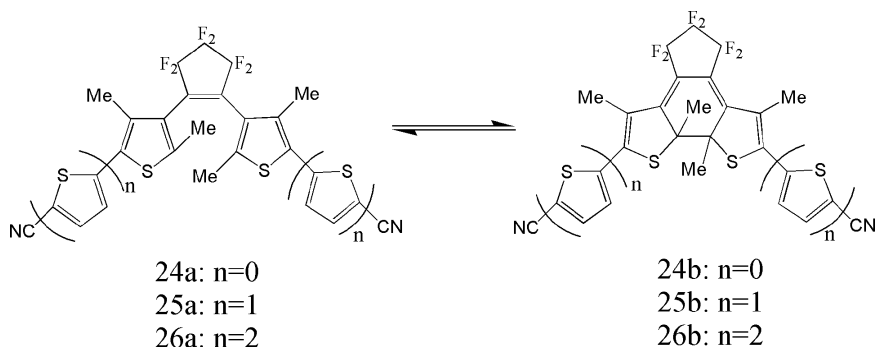
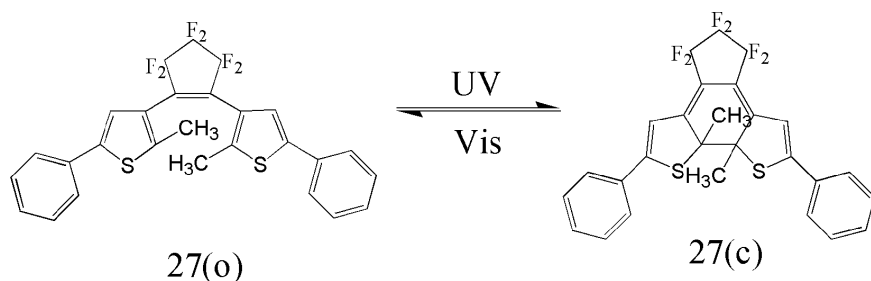
Scheme 17. Molecular structure of diarylethenes used by Kawai *et al.*⁸¹

amorphous solids by themselves. Kawai *et al.*,⁸¹ studied the optical properties of the amorphous films composed of diarylethenes 22, 23, and realized a large amplitude of refractive index modulation upon photoirradiation (Scheme 17). In particular, compound 23 exhibited a reversible refractive index change as large as 0.028 at 817 nm, where both forms of the photochrome are transparent. Using this compound, they also proposed and demonstrated novel readout methods for near-field optical recording.⁸² All these results demonstrated the possibility of realizing a photon mode rewritable disk based on photochrome 23 with nondestructive readout capability.

3.1.5. Gated reactivity

Gated reactivity is the property whereby irradiation with any given wavelength of light alone causes no color change, while a color change is induced when another external stimulus, such as additional photons of different wavelengths,^{83,84} a chemical,⁸⁵ or heat,⁸⁶ is present. Such threshold reactivity is very beneficial to memory technology.

Irie *et al.*⁸⁶ prepared diarylethenes having thiophene oligomers as the aryl groups (Scheme 18). They found that the ring opening quantum yields of these materials show temperature dependency. Especially for compound 26b, the yield increased by as many as 34 times when the temperature was raised from 25°C to 150°C. The conformational change of the oligothiophene groups by heating is considered to play an important role in the ring opening process. The large temperature dependency is useful for a nondestructive readout of the memory when the compounds are used for optical recording media. The recorded memory can be read many

Scheme 18. Photochromism of diarylethenes prepared by Irie *et al.*⁸⁶Scheme 19. Photochromism of diarylethenes used by Miyasaka *et al.*^{83,84}

times with weak laser light, which does not raise the media temperature. The memory can be erased with a high intensity laser, which can raise the media temperature to as high as 100–150°C.

Multiphoton gated reaction is another approach to erasable memory media with nondestructive readout capability. Miyasaka *et al.*,^{83,84} made a breakthrough in multiphoton gated photochromic reaction (Scheme 19). They excited 27c by a picosecond laser pulse to induce ring-opening reaction, and studied the dynamics and mechanism. The results indicated that the quantum yield from 27c to 27o was drastically enhanced by picosecond laser light exposure. They came to the conclusion that the excitation with the leading part of the picosecond laser pulse prepares the excited state, which is again excited by the trailing part of the pulse, resulting in the efficient reaction, as shown in Fig. 7.

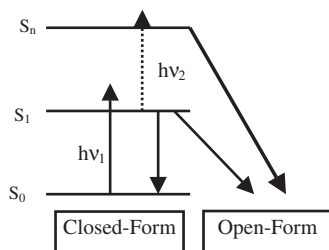


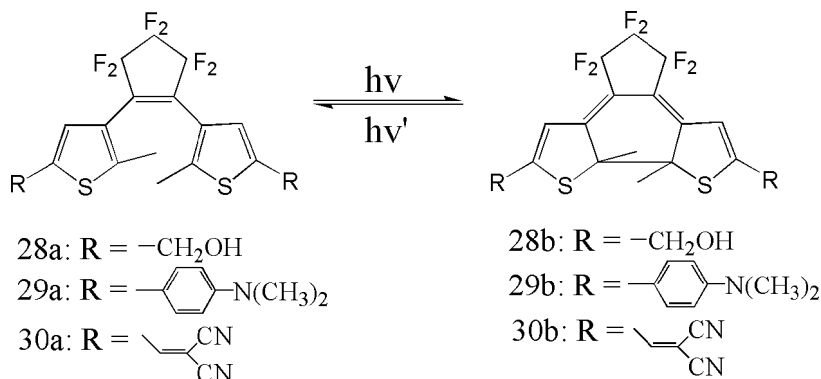
Fig. 7. Excitation of 27c by picosecond laser pulse.^{83,84}

3.2. Multiaddressable photochromism

Multiwavelength (or multifrequency) storage is a promising approach to increasing the recording density and data capacity. For such a storage method, multicomponent systems are desirable, where reversible multimode switching between more than two states can be realized. For example, in single wavelength storage the unrecorded and recorded dots are coded by (0 1), but in three-wavelength storage they are coded by eight states ($2^3 = 8$), namely (0 0 0), (0 0 1), (0 1 0), (1 0 0), (0 1 1), (1 0 1), (1 1 0), (1 1 1). Organic photochromes are especially suited to such systems because of the ease with which their structure can be synthetically modified, and the subsequent modulation of the absorption bands, and thus laser beams corresponding to the absorption of each material, will record data by photon-induced isomerization independently. Multicolor systems can be obtained by mixing photochromic compounds with different absorptions in polymer matrices or incorporating different photochromic units in one molecule.

3.2.1. Mixture of different photochromes

Pu and Zhang *et al.*⁸⁷ developed three-wavelength photon mode optical storage systems using photochromic diarylethene derivatives, 1,2-bis(2-methyl-5-hydroxy-methyl-thien-3-yl) perfluorocyclopentene (28a), 1,2-bis(2-methyl-5-(4-N,N-dimethyl-aminophenyl)-thien-3-yl) perfluorocyclopentene (29a), and 1,2-bis(2-methyl-5-(2,2'-dicyanovinyl)-thien-3-yl)perfluorocyclopentene (30a), which have different absorption bands of their closed ring isomers as the recording medium (Scheme 20).

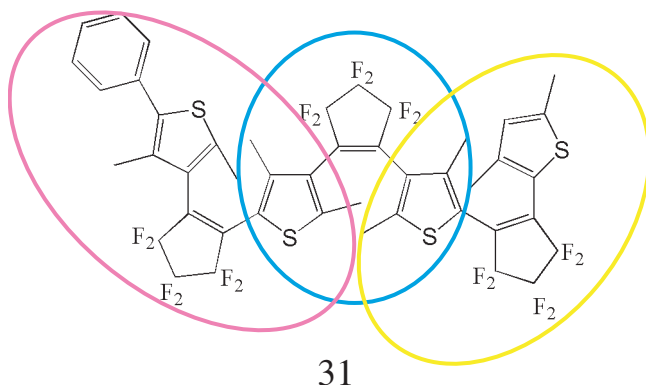


Scheme 20. Photochromism of diarylethenes used by Pu and Zhang *et al.*⁸⁷

Upon irradiation with 254 nm UV light, the colorless 28a turned red with a new absorption band between 420 and 620 nm, which can be assigned to the formation of 28b with the maximum absorption at 518 nm. Similarly, the colorless 29a and 30a turned blue and green upon irradiation with 365 and 397 nm UV light, respectively. The maxima absorption of their closed forms 29b, and 30b appeared at 650 and 742 nm, respectively. Using the mixture PMMA film containing 28b, 29b, and 30b as a recording medium, a single information dot was recorded by the three lasers at 532, 650, and 780 nm wavelength. In this process, the closed forms 28b, 29b, and 30b were regarded as unrecorded states, and the open forms 28a, 29a, and 30a as recorded states. The difference of reflectivity between the recorded and unrecorded areas was utilized as the readout signals. Experimental results indicated that the SNR was relatively high and there was no crosstalk existing in each of the diarylethenes although there was an overlap at 650 nm between 29b and 30b.

3.2.2. Multicolor in a one-molecule system

Another approach to multiaddressable systems is to incorporate different photochromic units in one molecule. The advantage of a one-molecule system over mixture systems is high image resolution arising from local homogeneity, constant color balance in a large area, and possible application to a multifrequency single molecule memory.^{8,88}



Scheme 21. Molecular structure of 31. The circle color is indicative of the closed ring isomer's color of each dithienylethene.⁸⁸

By incorporating three dithienylethenes with appropriate absorption bands, a fused trimer which undergoes full-color photochromism can be developed.⁸⁸ As shown in Scheme 21, the trimer has three dithienylethene moieties: bis(2-thienyl)ethane, (2-thienyl)(3-thienyl)ethane, and bis-(3-thienyl)ethane, with two thiophene rings in common. When 313 nm and 460 nm light were simultaneously irradiated, the colorless solution of 31 turned sky-blue. When the solution was irradiated with 313 nm and 633 nm light, the solution turned red–orange. The solution changed to yellow when it was irradiated with 313 nm and 578 nm light.

Photochromic polymers are desirable for optical data storage because they can be easily processed into large-area, optically homogeneous thin films. Developing photoresponsive polymers for use in multifrequency photochromic memories is more practical than doping several of the photoactive components in polymer matrices or relying on the challenge of obtaining multicomponent single crystals.⁸⁹ Branda *et al.* prepared a series of homo- and co-polymers containing different photochromic dithienylethene architectures by ring-opening metathesis polymerization techniques.⁸⁹ In the two- and three-component copolymers, each dithienylethene structure can be uniquely addressed, and thus a wide range of colors can be generated when the compounds are selectively photocyclized to their closed ring forms. For example, in the

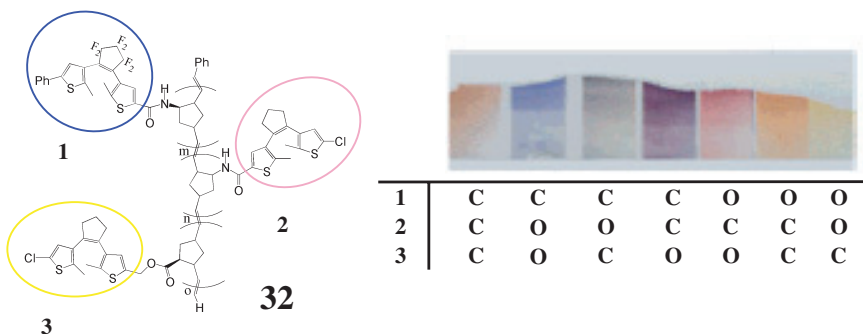


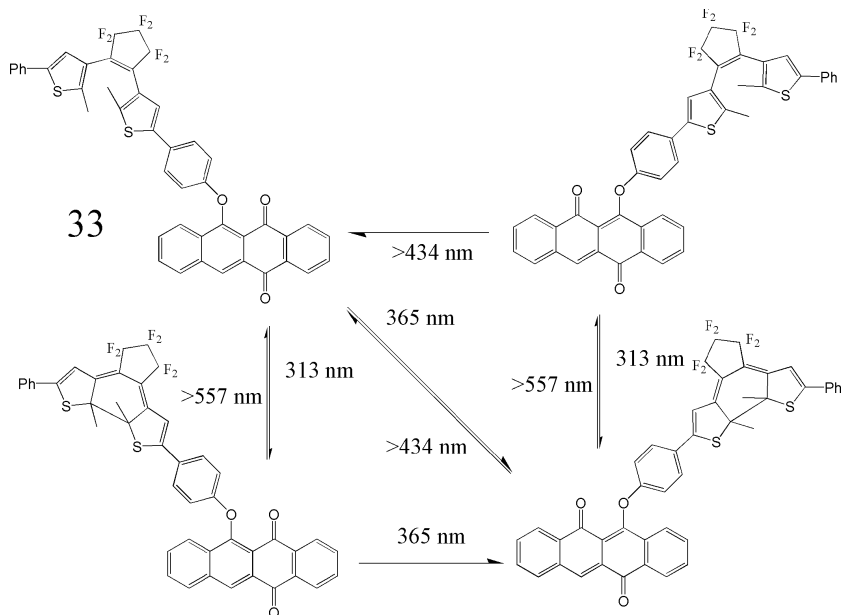
Fig. 8. Molecular structure of copolymer 32 and the colors generated by irradiating 32 with appropriate wavelength. The O and C labels describe the state of each photoactive structure (1–3); O refers to the open ring form of the dithienylethene backbone, and C to the closed ring form.⁸⁹

three-component copolymer 32, seven colors can be realized by appropriate light irradiation (Fig. 8).

Hybrid systems consisting of photochromic units of different kinds are another approach to multifrequency optical memories. An advantage of this method is the ease of selecting and designing photochromic moieties with different absorption bands. Phenoxynaphthacene-quinone (PNQ) is a kind of photochrome which can be interconverted between its *trans*- and *ana*-forms with a high level of thermal irreversibility and fatigue resistance. By incorporating the PNQ unit with dithienylethene moiety, an all-photon-mode multiaddressable photochromic system, 33, can be constructed (Scheme 22).⁹⁰ In this molecule, the absorption bands of both *trans*- and *ana*-isomers of PNQ reside in the narrow region (400–450 nm) where the open- and closed-ring isomers of the dithienylethene moiety do not absorb. The closed ring form of dithienylethene is transparent in this region and the open ring form has only a little overlap. By selectively irradiating the system with different wavelengths, four states can be realized.

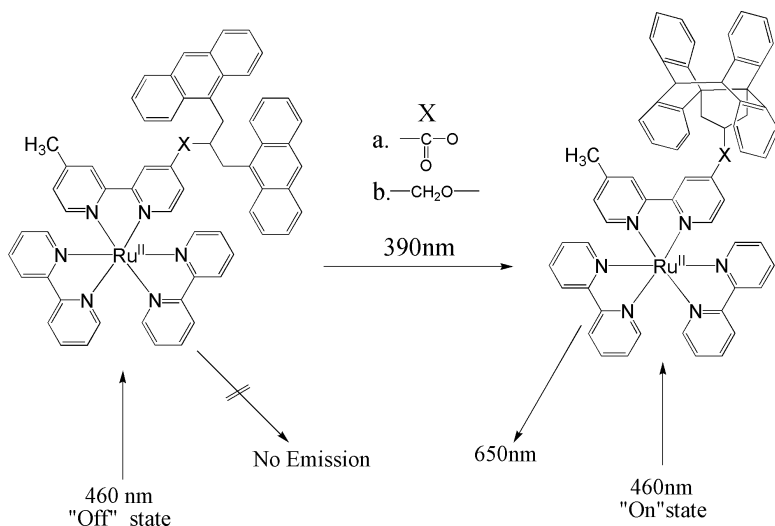
3.3. High SNR

Restricted by the low emission contrast of current photochromic systems, the films for optical recording often need a relatively large thickness to yield a sufficient optical difference for a readout of the stored information.



Scheme 22. Photochromism of multiaddressable photochromic system 33.⁸⁸

An approach to solving the problem is to employ photoswitchable luminescent molecular systems consisting of a highly fluorescent unit and a photochromic moiety. Castellano and Redmond *et al.*⁹¹ developed luminescent photoswitchable supramolecular systems to improve the luminescence efficiency and the SNR in optical storage. In this system, a Ru(II) chromophore with a luminescent metal-to-ligand charge transfer (MLCT) excited state is covalently attached to a photochromic dianthryl molecule that serves as a triplet energy transfer quencher in one of its photochromic states (Scheme 23). In the “off” state, the MLCT excited states of the Ru(II) luminophore are almost quantitatively quenched. In the “on” state, the dianthryl unit undergoes a UV-light-induced cycloaddition reaction, and can no longer quench the MLCT-based excited states of the luminophore through triplet energy transfer, resulting in a strong red emission following visible light excitation. Later, those authors demonstrated the near-field optical data record utilizing the compound.⁹² The areal data density is > 0.1 Gbit/inch² and the SNR is as high as 25:1.



Scheme 23. Chemical structure of the molecule synthesized by Castellano *et al.* (Reprinted with permission from Ref. 91, © 2002, American Chemical Society)

However, the above system was applied only in write-once-read-many (WORM) optical storage media. Enlightened by this thought, Song and Tian *et al.*⁹³ developed a new photochromic compound with high luminescence efficiency and high SNR for rewritable optical devices. In their strategy, a highly fluorescent chromophore naphthalimide (NA) dimmer was bridged by a dithienylethene. The photochemical reaction of dithienylethene can reversibly regulate the fluorescence emission of NA with very high contrast (85:1).

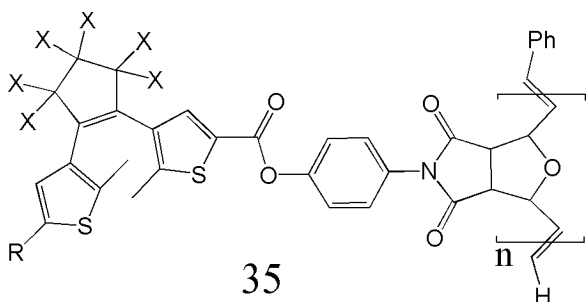
3.4. Photochromic polymers

For the sake of long term stability and environmental durability of storage devices, photochromic materials must be processed into large-area, high quality films. Although crystals of some photochromes show good properties, it is hard to prepare large size crystals or crystalline films. Dispersing the dye in a polymer matrix is by far the easiest strategy to prepare photochromic films.⁹⁴ However, the concentration of the doped photochromic

compounds must be kept low in order to preserve the optical homogeneity of the film.²⁰ By covalently bonding the photochromic unit to polymer chains, in the main chain or as a pendant, a high concentration of the active photochromic component can be realized, resulting in the amplification of the desired effect without crystallization, phase separation, or the formation of concentration gradients.⁹⁵ However, special attention should be paid to the fact that the polymer matrix must be appropriately flexible to accommodate the conformational requirements of the photoisomerization reaction.

In the case of diarylethenes, the ring-closing reaction can occur only from the antiparallel conformation of the open ring isomer. It is critical to have a polymeric architecture that is flexible enough to accommodate interconversion between the parallel and the productive antiparallel conformations; alternatively, a more rigid polymeric structure provided by the polymer backbone forces the diarylethene units into the antiparallel conformer.⁹⁴

Kim *et al.*⁹⁶ synthesized copolymers by copolymerizing an allylic dithienylethene with styrene and n-butylmethacrylate. The films prepared from these copolymers showed good photoconversion (approximately 70%) and large changes in the refractive index. The improved performance can be attributed to the presence of a bulky side chain in methacrylate copolymers which give a relatively large free volume.



Scheme 24. Dithienylene polymers prepared by Branda *et al.*^{97,98}

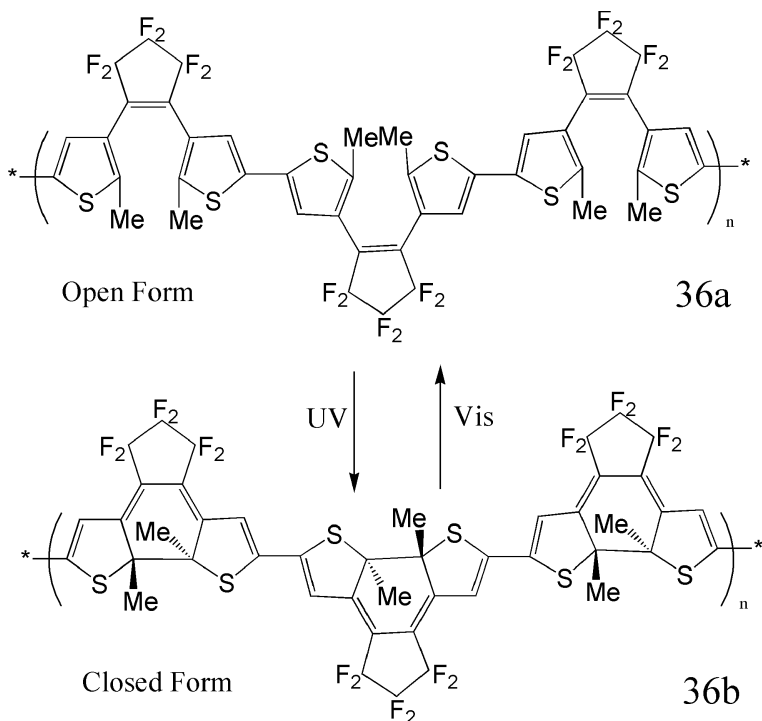
Homopolymers provide an advantage over copolymers, because they contain an even higher concentration of the photoactive component; however, the photochromism may be reduced to some extent, due to the increased densities. Branda *et al.*,^{97,98} prepared a family of dithienylethene polymers 35 from appropriate strained bicyclic olefins attached to the dithienylethene backbone (Scheme 24). The polymers are soluble in a wide range of common organic solvents, and the content of the dithienylethene component is as high as 63–69 wt%. The reversible photoisomerization reactions of these polymers are efficient both in solution and in the solid films. The low glass transition temperature (about -50°C) of these polymers illustrates that there is enough microscopic flexibility provided in the material at room temperature to accommodate the conformational requirements of the ring-closing reaction.⁹⁴

Several main chain photochromic polymers and copolymers also exhibit high cyclization quantum yields, partly due to enforcement of the antiparallel conformation. Zerbi *et al.*²⁰ developed the first example of a main chain photochromic polymer with dithienylethene as the photoactive unit (Scheme 25). The polymer shows a higher thermal stability than the monomer. The most impressive property of the polymer is the cyclization quantum yield, which was measured as up to 86%; while the opening quantum yield measured at ~ 430 nm at room temperature turns out to be very low — 0.15%.

4. Technologies

4.1. *Beating the diffraction limit — SIL and SNOM*

It is well known that data cannot be recorded with bit sizes too small to be imaged optically. This resolution limitation is imposed by the classical diffraction limit and is governed by the wavelength of illumination (λ) and the numerical aperture of the optical head (NA). The area of the diffraction-limited spot is then proportional to the square of these parameters, $A \sim (\lambda/\text{NA})^2$, and the resulting maximum areal density is simply the inverse of this area times the number of bits per spot b : $D \sim b(\text{NA}/\lambda)^2$.⁹⁹ This suggests that the resolution may be improved by simply decreasing λ or increasing NA. The differences in the capacity and



Scheme 25. The main chain photochromic polymer with dithienylene as the photoactive unit synthesized by Zerbi *et al.* (Reprinted with permission from Ref. 20, © 1999, Wiley-VCH)

data rate between the CD and DVD formats are a clear consequence of reducing the diffraction-limited spot size of the focus at the medium.

4.1.1. Solid immersion lens (SIL)

One solution to increase the effective resolution of the optical stylus, and permit sub-diffraction resolution, is to increase the refractive index of the optical head. The arrangement illustrated in Fig. 9 is called the solid immersion lens (SIL). There are three SIL configurations that are shown to give good performance for optical data storage. Kino and Mansfield described in 1990 the hemispherical configuration in Fig. 9(b) as a candidate for a solid immersion microscope¹⁰⁰ and later for use in optical data

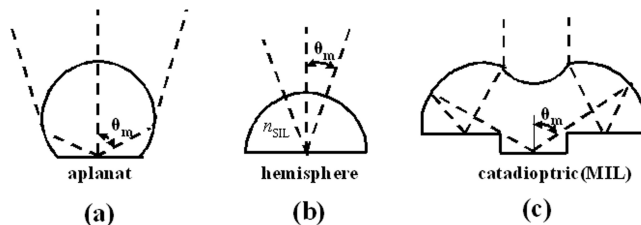


Fig. 9. Three configurations of SIL lenses: (a) aplanatic SIL, (b) hemispherical SIL, (c) catadioptric mirror immersion lens. The marginal ray angle θ_m is shown for each configuration. (Reprinted with permission from Ref. 104, © 2000, IEEE)

storage.¹⁰¹ With the hemisphere, light from the objective lens is focused on the flat surface. No refraction occurs at the curved interface. The spot size improvement over the objective lens focusing without the SIL is n .¹⁰¹ The second configuration is the aplanat, which is also called the truncated sphere, supersphere, or hyperhemisphere. The aplanat was discussed by Terris *et al.* in 1994.¹⁰² As shown in Fig. 9(a), the aplanat bends the light at the curved surface. The thickness of the aplanat is $r(1+1/n)$, where r is the radius of the curved surface. The SIL is positioned so that the vertex of the curved surface is located a distance rn from the focal point of the objective lens in air. Spot size improvement over the objective lens focusing in air is n^2 . The hemisphere and the aplanat are the only two configurations that yield high quality focused spots with simple spherical surfaces. A third configuration that uses an aspherical surface is the solid immersion mirror (SIM), introduced by Lee *et al.*,¹⁰³ as shown in Fig. 9(c). The SIM uses a highly divergent surface to distribute the light over a flat mirror and then focuses the light with an aspherical mirror. The attractive feature of the SIM is its simplicity, but a drawback is that n for molded optical components is not as high as bulk material used for hemispheres and aplanats. Therefore, the NA_{eff} (effective numerical aperture) for SIMs is typically lower than for hemispherical or aplanatic SILs. An interesting feature of the SIM is that the diverging surface creates a central obscuration in the light focused from the reflective surface. The obscuration blocks the central angular range of the cone, but it does not dramatically change the system's performance. In fact, the obscuration actually

narrows the central lobe of the focused spot slightly, at the cost of increased sidelobes. All surfaces are part of a single, molded glass component that uses collimated light as input. There is no need for an objective lens with the SIM.

SIL-based systems have found considerable interest in high resolution microscopy,^{100,105} and applications in data storage are on the increase.^{106–108} However, SIL-based storage systems have a number of limitations, such as the restriction on the flying height of the SIL lens in order to maintain sub-diffraction limited resolution and the associated problem of contamination in removable media. Guerra has proposed a neat solution to this,¹⁰⁹ where an on-disk SIL (for both land and grooves) facilitates the recording of data, and there are now no worries about flying the head above the media. Figure 10 schematically shows the calimetrics on the disk SIL.

4.1.2. *Scanning near-field optical microscopy (SNOM or NSOM)*

Nanometer-sized recording using evanescent light in an SNOM is expected to be one of the ultrahigh density recordings in the future.

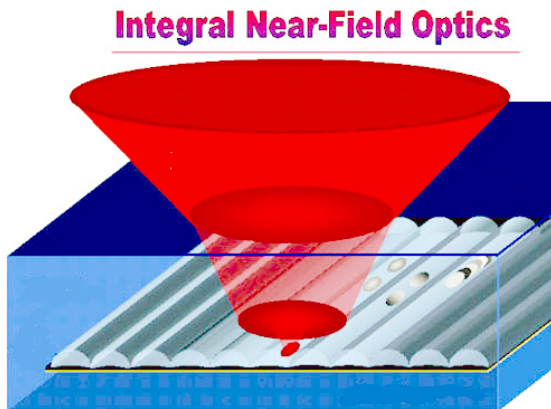


Fig. 10. Calimetrics SIL disk for high density optical recording beyond the diffraction limit. (Reprinted with permission from Ref. 110, © 2003, Springer Science and Business Media)

Early studies have shown the potential for data storage and retrieval using an SNOM.^{111,112} In contrast to conventional methods, SNOM allows us to overcome the diffraction limit due to the wave nature of light. An SNOM system uses a very small aperture through which the near-field evanescent wave can be imaged. The sample or probe (optical fiber through which the light travels) is then moved to scan the area of interest, and extremely sensitive detectors are used to form the image. The resolution of the image is that of the probe tip aperture, and a resolution of less than 50 nm is attainable. Some issues with SNOM have to be considered in order to achieve high resolutions. One is the tip-to-sample separation distance and how to control it. Also, a sensitive detection setup is required. The tip-to-sample separation has to be as small as possible, typically <10 nm because of the exponential decay with distance from the surface of the evanescent wave. Shear force feedback is the most commonly used method for tip-to-sample separations in SNOM applications.

The application of near-field optical addressing methods has been demonstrated for magneto-optical (MO), phase-change (PC) and photochromic memory media. The first near-field data storage using SNOM was demonstrated by Betzig *et al.* in MO materials.¹¹¹ The system used in the experiment is shown in Fig. 11. The aperture is formed from a pulled optical fiber that is coated with aluminum. All but the very end of the probe tip is coated, resulting in an aperture of ~ 50 nm in diameter. An Ar^+ laser beam is launched into the opposite end of the fiber to provide illumination for the aperture. The probe is brought into proximity with the sample by using piezoelectric transducers (PZTs). Transmitted light is collected by a microscope objective, and a polarization signal due to an MO media sample is detected with a polarizer. To obtain image data, the PZT raster scans across the sample. At each point in the scan matrix, the probe stops to integrate the signal in order to obtain an adequate SNR in the image. The dwell at each point is necessary because the transmission efficiency of the probe tip is only 10^{-6} – 10^{-5} , i.e. for each 1 mW input to the fiber, only 1–10 nW, respectively, is transmitted through the probe tip.

A result from Betzig's instrument is shown in Fig. 12. Figure 12(a) contains a crossed pattern of marks that are written with a far-field instrument

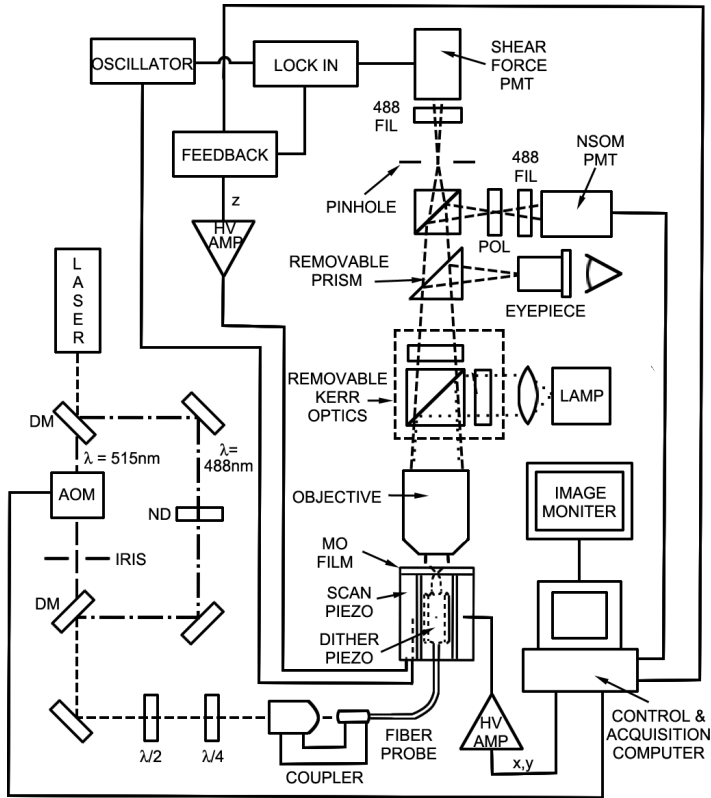


Fig. 11. Experimental configuration used by Betzig *et al.* to record and retrieve MO features with a pulled-fiber aperture probe. (Reprinted with permission from Ref. 111, © 1992, American Institute of Physics)

prior to scanning. Each mark is around $0.8\ \mu\text{m}$ in diameter. The resolution of MO features in the image is $\sim 60\ \text{nm}$. Figure 12(b) shows rectangles in which $\sim 100\text{-nm}$ -diameter MO marks are written into an “AT + T” pattern. The writing process involves pulsing the laser power launched into the probe as it dwells over a point in the scan matrix. The power transmitted during a pulse may be as high as $100\ \text{nW}$. A probe with a diameter of over $50\ \mu\text{m}$ can deliver $2.5\ \text{kJ}/\mu\text{m}^2$, which is sufficient to raise the temperature of the recording layers above the thermal threshold required to form marks.

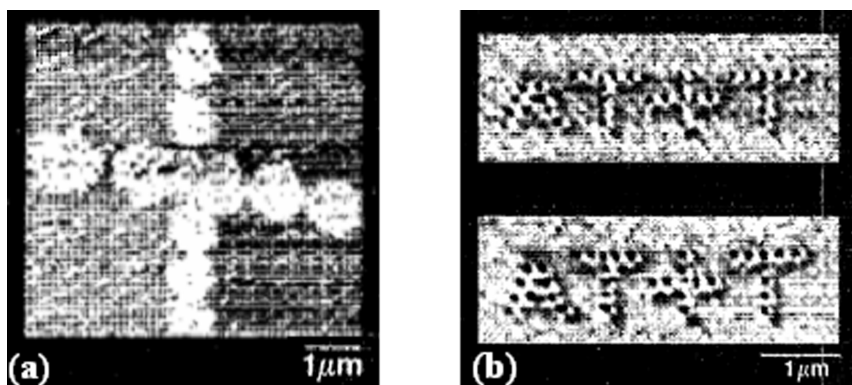


Fig. 12. Scanned image result from the system shown in Fig. 8: (a) a crossed pattern of marks that are recorded by a far-field device prior to scanning; (b) an “AT + T” pattern written with the near-field probe. (Reprinted with permission from Ref. 111, © 1992, American Institute of Physics)

Nanometer-sized PC recording using SNOM was also presented.¹¹³ In this experiment, the recording was performed with an SNOM using a 785-nm-wavelength semiconductor laser diode, shear force detection for gap control, and reflected light detection for observing the domains (reading). $\text{ZnS} \cdot \text{SiO}_2$ (20 nm)/ GeSbTe (30 nm)/ $\text{ZnS} \cdot \text{SiO}_2$ (150 nm)/polycarbonate substrate was used as the recording media. The writings were done at laser powers of 8.4–7.3 mW in the probe for pulse widths of 5 or 0.5 ms. As a result, a minimum recorded domain size of 60 nm in diameter could be obtained. This size showed a potential for achieving ultrahigh density PC-SNOM recording with about 170 Gb/in². The PC-SNOM reading was performed at the laser power of 0.2 mW, and a high speed readout such as 10 M or 100 Mbits/s was possible.

Both MO and PC memory are based on a heat mode recording method. In this method, the high laser spot intensities required result in slow data transfer rates, while thermal transfer from the nanometer-sized areas within the recording medium reduces the typically attainable maximum resolution. In principle, photochromic optical memories, which are based on a photon mode recording method, may have some advantages in these aspects. Several examples have already been given of near-field recording

using SNOM in photochromic thin films, such as diarylethene and azopolymer.^{92,114,115}

For near-field data storage using SNOM, a principal difficulty has to be overcome, i.e. how to deliver sufficient energy to the sample via a single tapered fiber, with an end aperture of the order of 50–100 nm, or less. Many efforts have been made to increase optical intensity throughput and resolution, of which using localized field enhancement effects where light is coupled to surface plasmon (SP) modes is believed to be a promising one.^{110,116,117} Another issue that has to be considered is the data transfer rate. At the present time, the recording speed of near-field optical recording using SNOM is still around $\mu\text{m/s}$, which is quite slow compared with the recording speed of a commercial digital versatile disk (DVD), which is higher than 3.5 m/s.¹¹⁸ Constructing aperture arrays provides a solution. Kurihara *et al.*,¹¹⁹ Minh *et al.*¹²⁰ and Kim *et al.*¹²¹ have proposed hybrid structures consisting of a vertical cavity surface emitting laser (VCSEL) and an aperture array for an optical near-field memory head, namely VCSEL/NSOM, which also has a relatively high optical throughput. Figure 13 shows such an array.

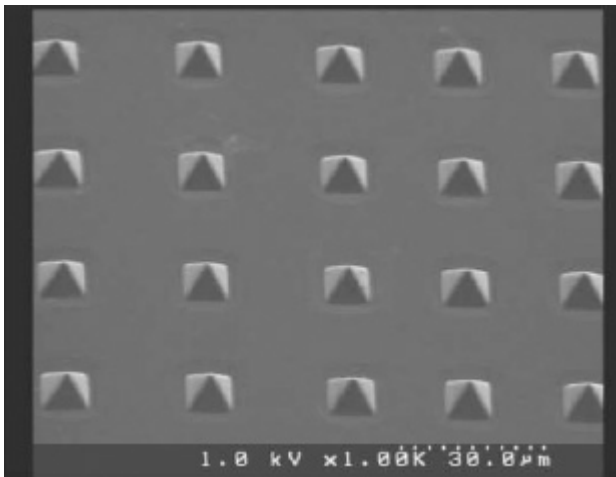


Fig. 13. SEM image of an aperture array. (Reprinted with permission from Ref. 120, © 2002, Elsevier)

4.2. 3D optical data storage

There have been vigorous efforts to develop three-dimensional optical storage in order to provide large increases in data density and media capacity. For 2D storage media which are written or read using monochromatic light of wavelength λ , diffraction normally limits the area data density to $\sim 1/\lambda^2 \text{ cm}^{-2}$,¹²² whereas the volumetric density that can be achieved in the diffraction limit would then scale with $1/\lambda^3$. The principal challenge to the development of 3D optical memory is to provide a means of writing and reading data without crosstalk between the multiple memory pages. Several approaches to 3D data storage have been explored. They can be distinguished by the method used to address the stored data. Some of the techniques simply extend the multiplayer nature of conventional optical storage already begun with the 2 layer 2 side DVD standard, while others take advantage of the 3D character of optics. The techniques described here are

- (1) Addressing a particular point, line, or plane in a medium by two-photon excitation.
- (2) Using a material with extremely narrow spectral sensitivities to address data.
- (3) Addressing data by the spacing and direction of interference fringes.

4.2.1. Two-photon volume information storage

It has long been known that chromophores may be excited, under sufficiently intense illumination, by simultaneous absorption of two-photons whose energy sum equals that of the excited state, even in the absence of an intermediate resonant state.¹²³ The two-photons can be of the same wavelength or different wavelengths, and neither of them can be absorbed by the storage media individually. A characteristic of two-photon absorption is its quadratic, or nonlinear, dependence on the incident light. For excitation that is linear in the intensity of the incident radiation, the same amount of energy is absorbed in each plane transverse to the optical axis regardless of distance from the focal plane, since nearly the same net photon flux crosses each plane. Thus linear excitation strongly contaminates

planes above and below the particular focal plane being addressed. However, for two-photon excitation, net excitation per distant plane falls off with the inverse of the square of the distance. Therefore information can be written in a particular focal plane without significantly contaminating adjacent planes beyond the Rayleigh range. This allows spatial resolution about the beam axis as well as radially, which circumvents out-of-focus absorption.⁶⁰

Rentzepis *et al.*³⁰ first demonstrated a bit-oriented 3D optical memory system using a photochromic spirobenzopyran. So far, besides photochromic materials,¹²⁴ two-photon optical data storage has been successfully employed in photorefractive crystals and polymers,^{53,55,56} photobleaching polymers,⁵⁴ and photopolymerizable materials.^{60,61} For materials used in two-photon data storage, a large two-photon absorption coefficient is preferred.

4.2.2. Holographic storage

4.2.2.1. Principle of operation

Holographic data storage, which was conceived decades ago, has recently made progress toward practicality with the appearance of lower cost enabling technologies, significant results from long standing research efforts, and progress in holographic recording materials.^{125,126} What makes holographic data storage attractive is its natural ability to read the stored information in parallel (therefore meeting the demand for fast access), its ability to perform associative recall at an incomparable speed, and the high storage density with theoretical limits around tens of terabits per cubic centimeter.^{125,126}

Figure 14 shows the principle of a holographic storage system. To store one bit of information holographically, one interferes with two plane waves, with one as the reference beam and the other as the object beam. The interference fringes are recorded inside the holographic medium as an index grating which serves as the memory bit of “1.” On the contrary, the lack of a grating indicates a bit “0.” When the memory is read by the original reference beam, the existence of a grating leads to a reconstructed object beam recalling the bit “1,” and the absence of a grating results in no reconstruction — in other words, a bit “0.” A set of 1’s and 0’s representing

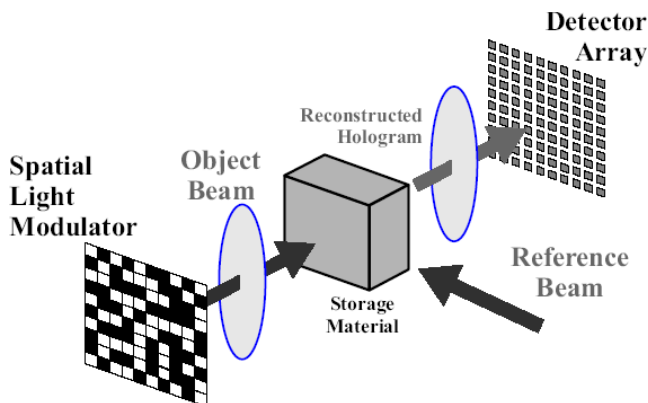


Fig. 14. Principle of a holographic data storage system. (Reprinted with permission from Ref. 99, © 2002, SPIE)

digitized information can be displayed on a two-dimensional spatial light modulator (SLM), e.g. a liquid crystal display, as bright and dark pixels, which are then converted to a set of plane waves by a lens. Using the language of Fourier optics, when the SLM is illuminated by a collimated laser beam and placed at the front focal plane of the Fourier-transforming lens, at the back focal plane of the lens, the Fourier transform of the image on the SLM is obtained. The laser beam carrying the Fourier transform of the image becomes the object beam in holography. When this information-carrying object beam is interfered with by a reference plane wave, and the interference pattern is in turn recorded by the holographic medium, it writes a page of digitized information. Alternatively, an analog image on the SLM can also be loaded and the same optical system can be used to record the Fourier hologram. This recording process can be repeated to write multiple pages of information, each associated with its own reference beam. The multiple exposure recording with different reference beams is known as multiplexing. When the difference between the reference beams is their incident angle, it is called angle multiplexing; and when the difference between the reference beams is their wavelength, it is called wavelength multiplexing. Other multiplexing methods, such as phase multiplexing, shift multiplexing, and peristrophic multiplexing, can

also be used in holographic storage. Once the holograms are recorded, they can be read out by using the corresponding reference beams and Fourier-transforming the diffracted object beams back into the image plane by using a lens. During the readout of one image with a specified reference beam (for instance, with a particular angle of incidence), the other images stored in the same volume of the recording medium will not cause significant crosstalk. This is guaranteed by the Bragg selectivity of the volume holography, which is one of the reasons for using a thick holographic recording medium.⁵²

4.2.2.2. Materials for holographic data storage

The ideal material for holographic storage should have the desired physical properties, such as a high optical quality, a proper thickness, a large dynamic range, and a high photosensitivity. The optical quality is related to the noise and in turn the bit error rate (BER). The thickness determines the angular selectivity (using angle multiplexing as an example). The dynamic range limits the number of holograms that can be stored in the same volume. And the photosensitivity is related to the energy needed to record the holograms, and therefore the kind of laser needed to record the holograms. Up to now, various kinds of materials have been used in holographic storage, such as photochromic materials, photocrosslinkable polymers,¹²⁷ photorefractive materials, and photopolymers — for which, currently, the most promising ones for volume holographic data storage are LiNbO_3 and photopolymers.⁵²

Photorefractive materials, such as LiNbO_3 crystals, are a kind of efficient media for the recording of volume dynamic holograms. In these media, information can be stored, retrieved, and erased by the illumination of light, in real time. The storage mechanism is quite similar to that introduced in Subsec. 2.3. Long term storage in photorefractive materials requires fixing of the recorded holograms to prevent partial erasure during repeated reading of the stored data.¹²⁸ The most commonly used fixing method is thermal fixing.¹²⁹ It can effectively stabilize the holograms against the volatility of the stored data in photorefractive crystals. The fixing procedure is based on the compensation of a photorefractive grating

by a pattern of light-insensitive charge species (protons in LiNbO_3 are known in some cases) at elevated temperature. Electrical fixing¹³⁰ is another approach to making the holograms not susceptible to optical erasure. However, such fixing techniques often require high voltages, ovens, or high power lasers, which are unfeasible from a system design point of view. An exciting approach currently under development is the use of gated photorefractives,¹³¹ in which two different laser wavelengths are used to excite charge out of two trap levels. The first light source excites the recording medium from its ground state to an intermediate energy state. Longer wavelength light then has sufficient energy to write the data hologram in the material by exciting these electrons from the intermediate state up into the conduction band. The spatially distributed charge eventually ends up in the lower trap, creating an interference pattern that is Bragg-matched to the long wavelength readout light but stored in trap levels too deep to be photoexcited.

4.2.3. *Persistent spectral hole burning*

Already in 1978, a high density storage device was proposed on the basis of permanent spectral hole burning as “frequency domain optical storage” (FDOS).^{132,133} In this method, the storage on the area (two dimensions) can be extended by the storage on the frequency axis as the third dimension, and the storage density can be raised to 10^{11} bits per cm^2 by the writing of typically 1000 spectral holes at each laser-focused spot. Besides, the storage density can be increased further by utilization of the electric field (Stark effect) as the fourth storage dimension and the combination with holographic methods.¹³⁴

The principle of spectral hole burning is represented schematically in Fig. 15. Guest molecules embedded in a solid matrix (crystals or amorphous solids such as polymers and glasses) have different environments, and therefore different local fields. This leads to a distribution of the absorption frequencies for the guest molecules, in which the various frequency packets are characterized by their homogenous line width, Γ_H . The envelope of all frequency packets observable in the experiment is the inhomogenous broadened absorption band of width Γ_I . At the liquid helium temperatures ($T \leq 4.2$ K), the homogenous line width Γ_H of zero

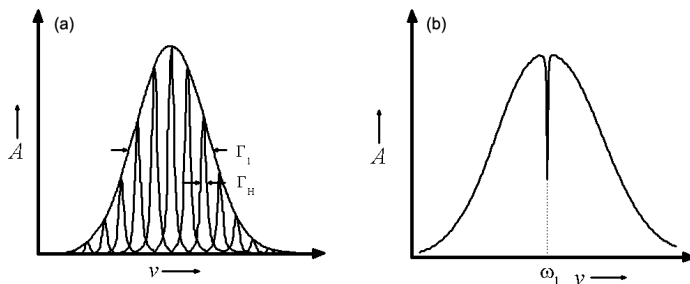


Fig. 15. (a) Absorption band before the burning. (b) After burning with the frequency ω_l (Figure (a) is reprinted with permission from Ref. 134, © 1992, Wiley-VCH)

phonon transition (pure electronic transition of molecules without the participation of the phonons of the surrounding solid) becomes very small (10^{-4} – 10^{-1} cm^{-1}), whereas the inhomogeneous line width Γ_I remains large (100–1000 cm^{-1}) and many (10^3 – 10^6) frequency packets are hidden beneath the inhomogeneous absorption band.

If a narrowed light source is held fixed at ω_l for a sufficient time period, the molecules that are resonant to the laser frequency are excited. The excited molecules undergo photoinduced transformations and the optical absorption at ω_l decreases over a narrow range. This decrease in absorption due to photoinduced transformations between the various ground states is called a “spectral hole.” In storage, the optical frequency or wavelength at which holes are burned is used to encode digital information where, for instance, the presence of a hole at a particular optical frequency may be used to encode a digital “1” and the absence of a hole a digital “0.” Thus, multiple bits can be stored in one laser focal volume, yielding areal densities several orders of magnitude higher than those for conventional optical storage.

5. Summary

Optical data storage is advancing rapidly as we move forward in the 21st century. The ever-increasing demand for high-density and fast-accessing-time data storage is pushing scientists and engineers to explore all possible approaches in both technique and storage media aspects. Where materials are concerned, photochromic materials are attracting significant attention

due to the advantages they provide over conventional heat mode recording media. Over the past few decades, storage media have undergone great developments and some of them have already met the basic requirements for optical storage media, such as thermal stability and fatigue resistance. However, to successfully place a photochrome in a high density, erasable memory medium, much more effort is still needed to rationally design materials fulfilling stricter requirements. For example, photochromes with switchable fluorescence, infrared, etc. have been synthesized for application to the nondestructive readout process. For long term stability and environmental durability, photochromic polymers that display excellent photochromic properties and can be processed into large-area, good-quality solid films have also been developed. But these achievements are just at the laboratory stage at the present time. When applied to practical use, they will meet with many problems, such as mismatching with commercial recording or reading equipment, and difficulty with large scale production due to the low conversion. From the technical point of view, the main goals are to overcome the diffraction limit in 2D storage and to take advantage of volumetric storage by adding the third dimension. By applying near-field recording which can avoid the diffraction limit to a great extent, the capacity of optical disks can be well beyond what is found in the current CD, DVD, and DVR (digital video recorder), which all use the mechanism of far-field recording. SIL and SNOM are two typical techniques in near-field optical recording. Adding a third dimension to 2D optical data storage is also an effective method to greatly increase the storage density. In this strategy, two-photon absorption volume storage addresses data by intersecting two laser beams, persistent spectral hole burning addresses data using materials with extremely narrow spectral sensitivities, and holographic storage addresses data by the spacing and direction of interference fringes. Looking to the future, the development of novel multiplexing techniques and construction of multi-addressable photochromic and/or multi-responsive molecular species to promote optical-coupled multi-mode recording, will open up new horizons and bring on new opportunities for optical data storage.

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CHAPTER 3

HIGH DENSITY ELECTRICAL DATA STORAGE

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As a promising approach to future large-capacity memories, electrical data storage has been receiving increased attention. Scanning probe microscopy-based recording technique has been demonstrated to be powerful for conducting data storage at nanometer scale or molecular scale. To improve the writing/reading speed, parallel recording techniques were further developed. In recent years, organic materials have been considered as promising recording media because of their low cost, simplicity, good stimuli-responsive properties and versatility in molecular design. To successfully implement organic materials into practical electrical recording, it still needs much more efforts to rationally design materials fulfilling more strict requirements including good film-forming property, stable reading-out, high on-off ratio, fast transition time, low power consumption, ease of fabrication etc. This chapter highlights the recent progress on electrical bistable materials and recording technologies for high-density electrical data storage, with emphasis on the motivation and the design of new materials and their recording mechanisms. The very recent multi-mode and spin-based recording techniques and related materials are also discussed.

1. Introduction

With the globalization of information technology, data storage has been becoming a big issue in this digital age.¹ In the past few decades we have witnessed the explosive increase of information storage density and the remarkable miniaturization of electronic devices. Such a trend continues

to demand new recording technologies and materials that combine high density, fast response time, long retention time and rewriting capability to overcome the intrinsic physical limitations on memory device components.² A vast amount of effort has been devoted to increasing the data density.

Electrical data storage, in contrast to magnetic and optical storage, offers many advantages; it has neither a superparamagnetic limit (unlike magnetic storage) nor a wavelength limit (unlike optical storage). In electrical data storage, the information is stored based on the high and low conductivity response to an applied voltage (electrical bistability). A number of possible models have been proposed to explain the switching mechanisms, including charge transfer,^{3,4} reoxidation,⁵ conformational change,^{6–8} etc. Table 1 summarizes the performance of the representative technologies. Among the various recording strategies, scanning probe microscopy (SPM) — such as scanning tunneling microscopy (STM),⁹ atomic force microscopy (AFM)¹⁰ and scanning near-field optical microscopy (SNOM)¹¹ — has proven to be a competitive technique for high density information storage. Since the 1990s, many scientists have been engaged in studying various materials for data recording using STM/AFM, and the ultimate data density has been demonstrated with atomic manipulation.¹² So it is a worthy effort to achieve high density data storage via tuning the local electrical characteristics of the recording media using a nanometer-sharp STM/AFM tip.

In this chapter, the latest progress in electroactive materials and recording technology will be reviewed. We will begin with the electrical

Table 1. Maximal density of current data storage technologies.

	Recording technology	Maximal data density
Optical storage	3D optical data storage ^{13,14}	~1000 Gbit/cm ³
	Holographic data storage ^{15,16}	~1000 Gbit/cm ³
	Near-field optics ^{17,18}	~170 Gbit/in ²
Magnetic storage	Perpendicular recording ^{19,20}	>230 Gbit/in ²
	Pattern media ^{21,22}	>250 Gbit/in ²
Electrical storage	STM/AFM ^{12,23,24}	>1000 Gbit/in ²
	Cross-bar technology ^{25,26}	~10 Gbit/cm ²

recording mechanism and related media. This will be followed by the current electrical recording technologies. Finally, we will give a comment on electrical data storage, and future research efforts on high density ($>10^9$ bit/in²) electrical data storage will also be discussed.

2. Electroactive Materials for Information Storage and Their Mechanisms

The materials for high density electrical storage should possess electrical bistability, i.e., they should have two distinguishable states under the threshold applied electric field. Furthermore, as ideal high density electrical recording media, they must possess several important parameters:

- (1) *Chemical stability*. It is easy to understand the importance of long-time stability of a recording medium under various conditions. If a molecule tends to decompose under elevated temperatures, it is not a good candidate for memory devices.
- (2) *Film-forming property*. Most of current memory devices are based on films, so the quality of films has important impact on the device performance.
- (3) *Storage capacity*. To meet the increasing demand for high density, the intrinsic property of material for recording should have potential for further scaling, desirably down to the nanometer or even molecular/atomic scale.
- (4) *Transition time*. A short transition time is intrinsically indicative of a fast writing.
- (5) *Retention ability*. The ability to remain the stored state is necessary for stable and secure recording.
- (6) *On-off ratio*. A high on-off ratio is crucial for the memory device to realize high-resolution and low-error-rate data storage.

In addition, low power consumption, ease of fabrication and competitive cost are important for application. Against this background, to design materials that have outstanding electrical properties and the combined characteristics mentioned above, and to explore their mechanisms for conductance transition under the action of an electrical field on this basis has been a key research

topic in high density electric data storage. In the following subsections, we will give a summary of different kinds of electroactive materials, especially organic materials, according to their differences and their mechanisms.

2.1. Inorganic materials

Since the observation of the switching process in thin films of metal oxides²⁷ and chalcogenide glass alloys,²⁸ they have been proposed as potential candidates for electrical data storage. In 1993, Sato *et al.*²⁹ demonstrated the use of STM in reversible recording and erasing of marks about 10 nm in size. The marks were written at ambient temperature and pressure on the surface of a composite medium consisting of a thin layer of vanadate glass deposited on vanadium bronze, $\beta\text{-Na}_x\text{V}_2\text{O}_5$. They obtained different-sized marks by applying voltage pulses of +4 V, 10 ms, 5 ms, 2 ms and 1 ms. The marks were erased by applying a reverse polarity pulse of -5 V and 10 ms. The reversible recording mechanism can be explained on the basis of sodium ion migration along the electric field. In 1995, Kado *et al.*³⁰ realized data storage on the surface of amorphous GeSb_2Te_4 film using AFM. A 300 nm Pt film was sputtered first on the surface of Si substrate, and then a 200 nm GeSb_2Te_4 thin film was sputtered as the recording medium. The Si_3Ni_4 tip was modified by deposited Cr 15 nm in thickness and Au 100 nm in thickness orderly, so that it was conductive. The marks were written by applying a voltage pulse of +3 V and 5 ms in contact mode. The size was 10 nm.

As storage media, inorganic materials are usually influenced by their crystal characteristics. The ion interactions in crystal make the recording area unidirectional and unsaturated. So it is difficult to control the size of marks and to make them less than 10 nm.

2.2. Organic materials

Compared with inorganic materials, organic materials have attracted more attention due to their several significant advantages: (1) rational design and fabrication, (2) ability to fine-tune electronic and structural properties, (3) easy characterization for mechanism study. The following are organic media-based on different recording mechanisms.

2.2.1. Charge transfer material for conductance transition

In 1973, Coleman *et al.*³¹ and Ferraris *et al.*³² reported the synthesis of a new, highly conducting complex, i.e. tetrathiofulvalene (TTF)-tetracyano-*p*-quinodimethane (TCNQ), at the same time. Since then, electron transfer organic conductors have been a focus of attention. Materials with charge transfer characteristics are among the most widely used in high density data storage. From the initial organic–inorganic complex materials to organic complexes until recent single-component organic materials, great progress has been made in improving their film-forming, thermal stability and characteristics for bistability.

2.2.1.1. Organic–inorganic complex materials

In the early stage, organic films for data recording based on charge transfer are mainly metal/tetracyano-*p*-quinodimethane (TCNQ) complexes^{33–35} represented by silver-tetracyanoquinodimethane (Ag-TCNQ) and copper-tetracyanoquinodimethane (Cu-TCNQ), in which metals are used as electron donors and organic molecules as electron acceptors. The change of electrical states is via charge transfer. The mutation from the high resistance state (“0”) to the low resistance state (“1”) happens under the abduction of the electrical field, along with color change. The low resistance state is still stable when the electrical field is removed, and can be erased by heating. The switching mechanism is shown in Fig. 1. So these materials provide a new kind of recording media for repeatable and reversible data storage.

To meet the requirements of the developments of electrical recording and also to provide important insights into this kind of thin film devices, a series of polynitrile π acceptors with similar structure to TCNQ have been designed and synthesized. Xue *et al.*³⁶ synthesized

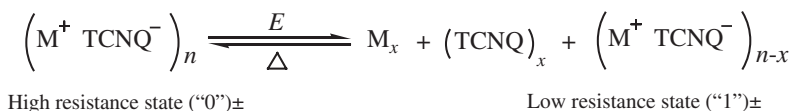
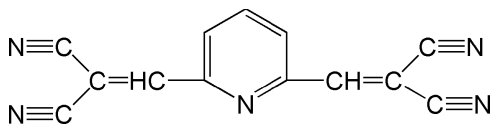
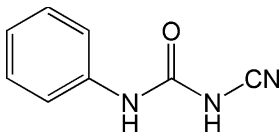


Fig. 1. Schematic diagram of the recording mechanism.

Scheme 1. Molecular structure of BDGP.³⁶

2,6-bis(2,2-bicyanovinyl)pyridine (BDGP), and prepared Ag-BDGP film on the Ag substrate by coevaporating equal moles of Ag and BDGP (see Scheme 1). Then, a Ag thin film of 100 nm thickness was deposited as a top electrode. Thus, the Ag-BDGP film sandwich like system Ag/Ag-BDGP/Ag was constructed. SEM, X-ray diffraction (XRD) patterns and the infrared transmission spectrum of the film showed that the charge transfer complex between BDGP and Ag had been formed in the film. I - V curves showed that the device was initially in a high resistance state of about $10^9 \Omega$. An abrupt switching occurred from the high resistance state to a low resistance state of $2.6 \times 10^2 \Omega$ at the threshold voltage of 5.01 V. The high- and low-resistance states can be seen as the “0” state and the “1” state, respectively. The ratio between the two states was about seven orders of magnitude. Once the device had been switched to the “1” state, it could remain in this state. When the device was heated at 80°C in the vacuum for about 1 h, it switched back to the “0” state. The bistable properties were stable and reproducible, indicating that Ag-BDGP is a promising material for storage and memory devices.

To promote the application of functional organic materials in memory devices and molecular electronics, it is also important to seek the desired and proper deposition methods for the thin films. Besides vacuum evaporation and chemical deposition in solution, the ionized cluster beam (ICB) deposition method is another effective method for preparing the films. Zhang *et al.*³⁷ designed a similar organic molecule, 3-phenyl-1-ureidonitrile (PUN, Scheme 2), and its complex films with silver were prepared by the ICB deposition method. The electrical bistability is found in the Ag-PUN complex thin films. When an external electric field is applied above a threshold of about $3.5 \times 10^7 \text{ V/m}$, the films can switch from a high resistance state to a low resistance state, and it can be switched back to the original state by heating the films at about 80°C .

Scheme 2. Molecular structure of PUN.³⁷

Yang's group, Scott and Bozano *et al.* have done several pioneering works in bistable memory devices using metal/organic hybrid active media,^{38–40} including metallic nanoparticles embedded within an organic film, metallic nanoparticle with donor molecules blended in an inert polymer matrix, etc. In all these devices, electrical bistability and nonvolatile memory were observed. In 2005, Yang *et al.*⁴¹ reported a memory device consisting of polyaniline nanofiber/gold nanoparticle composite film sandwiched between two electrodes. The active polymer layer is created by growing nanometer size gold particles within 30-nm-diameter polyaniline nanofibers using a redox reaction with chloroauric acid. The device exhibits bistable electrical behavior, and the ON and OFF states of the device with a ratio of 10^3 can be switched by external bias. Electrical pulse measurements show that the on–off transition time is less than 25 ns. The device possesses prolonged retention times of several days after they have been programmed. Write–read–erase cycle tests show that the device can be cycled many times with a readily distinguishable ON/OFF ratio around 20 maintained. Nanosecond conductance transition, X-ray photoelectron spectra and conductive atomic force microscope data all suggested that the switching mechanism is attributed to electric-field induced charge transfer from the polyaniline nanofibers to the gold nanoparticles. It should be noted that the diameters of the gold nanoparticles should be controlled below than 20 nm, otherwise, the device can be switched on only once, and the more metallic nature of the gold particles dominates the switching.

But, in most cases, such organic–metal compounds have their limitations. For example, metal is difficult to disperse well in organic material. Due to the action of the metal bond, the phenomenon of phase separation often happens, and the local property of a thin film is inhomogeneous. Such phase separation may prevent the device from having

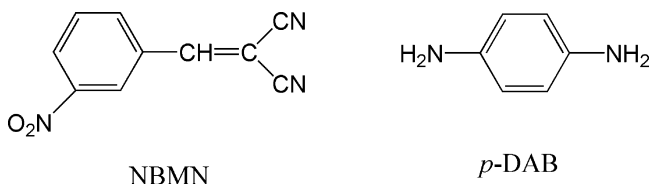
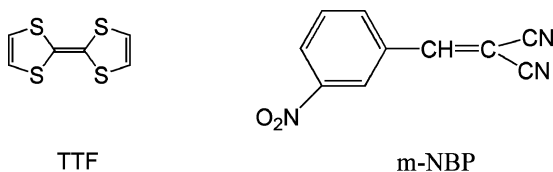
a stable long operating time. Furthermore, the sizes of recorded marks are different and it seems to be very difficult to reduce the sizes of marks.

2.2.1.2. Organic complexes

Compared with metal–organic complex films, all-organic films behave with good and uniform physical–chemical properties. Moreover, there exist close relations between the characteristics of the thin film and the structure of molecules. So the function of a film can be effectively controlled and the recording mechanism can be investigated via analyzing the change of molecular structure.

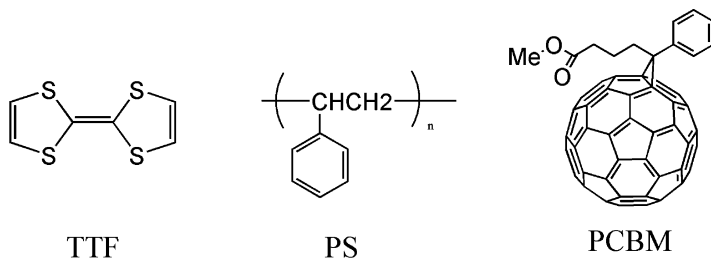
From the viewpoint of molecular design, the two components of the charge transfer complex should exhibit a strong difference in the ability to gain and lose electrons. The donor should have strong electron-pushing groups, while the acceptor should have strong electron-pulling groups. In order to facilitate the charge distribution and thus decrease the activation energy of the charge transfer, the molecule should possess conjugated structure. Furthermore, considering the film vacuum deposition, the two components should have nearly the same melting point and vapor pressure, and similar molecular conformation. With these thoughts in mind, in 1996, researchers from the Chinese Academy of Sciences and Peking University designed and synthesized the organic compounds *m*-nitrobenzole malonitrile (NBMN) and diamine benzene (DAB). They succeeded in writing recording marks with a diameter of 1.3 nm.⁴² In 2000, a remarkable result was achieved based on the same materials system, *m*-NBMN/*p*-DAB (Scheme 3).⁴³ The recording mechanism has been discussed. –CN and –NO₂ functional groups of *m*-NBMN are strong electron acceptors and –NH₂ of DAB is a strong electron donor. So, under an electrical field, charge transfer can happen and good bistability can be demonstrated.

Li *et al.*⁴⁴ studied a complex thin film of tetrathiofulvalene/*m*-nitrobenzylidene propanedinitrile (TTF/M-NBP) (Scheme 4) by a hot wall deposition method. Here, TTF was used as an electron donor, and *m*-NBP as an electron acceptor. The *I*–*V* characteristics of the Au/TTF/

Scheme 3. Structure of NBMN and *p*-DAB.⁴³Scheme 4. Molecular structure of TTF and m-NBP.⁴⁴

m-NBP/Au device were measured at room temperature. This showed that the film was initially in a state with a high resistance of about 10^8 – $10^9 \Omega$ (“0” state), and when the applied voltage was increased to 3.1 V, the film was abruptly switched to a low resistance of about $2.2 \times 10^3 \Omega$ (“1” state). The “1” state remained stable ever if the voltage was scanned in a wide range, and the film could be restored to its original “0” state when heated at 75 for 2 h in vacuum. On this basis, nanoscale data storage with the recording dots 1.2 nm in diameter was realized by applying voltage pulses between the STM tip and the substrate.

Besides thermal evaporation in high vacuum for the preparation of organic–composite film, introducing a charge donor and acceptor system into a polymer matrix by spin-coating method is another simple and effective approach. Yang *et al.*⁴⁵ reported on an electrical bistable device using organic composite thin films as the active layer. The films, which consisted of polystyrene (PS) as the matrix, methanofullerene 6,6-phenyl C_{61} -butyric acid methyl ester (PCBM) as the organic electron acceptor and tetrathiafulvalene (TTF) as the organic electron donor, were prepared by the spin-coating method. (The chemical structure of the materials is shown in Scheme 5.) Current–voltage results showed that the device could exhibit two states of different electrical conductivity at the same



Scheme 5. Chemical structure of the organic materials.⁴⁵

voltage. The on–off ratio was about three orders of magnitude, and the switching time between the two states was shorter than 100 ns. It was found that such electrical switching between the low and high conductivity states could be performed numerous times without any significant device degradation. Moreover, once the device was switched to either state, it remained in that state for a prolonged period of time. The write–read–erase cycles and the duration test demonstrated that the devices meet the basic requirements for binary information storage and have potential for operation as nonvolatile memory.

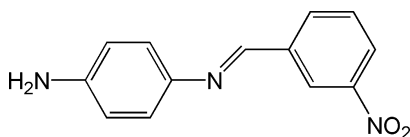
2.2.1.3. Single-component organic material

As the media of data storage, the materials are generally required to form high quality, uniform thin films. However, organic composite compounds do not easily meet this requirement, because different components in the films are difficult to monodisperse. In most cases, many defects exist in the film, which is unfavorable for the performance of a memory device. In this context, the organic molecule of N'(3-nitrobenzylidene)-p-phenylene-diamine (NBPDA) was synthesized, which includes an electron acceptor $-\text{NO}_2$ and an electron donor $-\text{NH}_2$ as shown in Scheme 6.⁴⁶ Due to the molecular interaction, large area orderly films can be obtained. By applying voltage pulse, high density data storage in the NBPDA system was demonstrated.

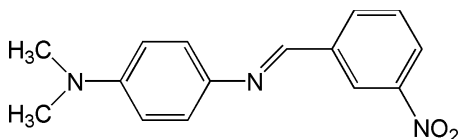
For application in potential recording devices, the recording media must be very stable under ambient conditions. But, for NBPDA, the $-\text{NH}_2$ is not stable enough for an ideal storage medium. To improve the thermal stability of the recording media, we designed and synthesized another new

organic material, *N,N'*-dimethyl-*N'*-(3-nitrobenzylidene)-*p*-phenylenediamine (DMNBPDA); see the molecular formula, Scheme 7. It is a molecule with a strong electron donor $-\text{N}(\text{CH}_3)_2$ and electron acceptor $-\text{NO}_2$. Also, it is more stable than NBPDA (the donor $-\text{NH}_2$ of NBPDA, which is sensitive to air, is protected by two $-\text{CH}_3$ groups, and the melting point of DMNBPDA is raised to 172°C , which is 26°C higher than that of NBPDA). Furthermore, $-\text{N}(\text{CH}_3)_2$ is a better electron donor than $-\text{NH}_2$, so charge transfer could occur more easily in the system of DMNBPDA than in that of NBPDA. By controlling the deposition rate, we prepared an ordered monolayer of DMNBPDA using vacuum vapor deposition, in which nanoscale data recording was successfully achieved by STM with a storage density of about 10^{13} bits/cm².^{3,47}

In general, charge transfer includes both the intra- and the intermolecular mode. According to our experience, electrical bistability based on intermolecular charge transfer is more stable than that based on the intramolecular mode, and thus is more favorable for electrical recording. Experimental and theoretical studies suggested that the efficiency of intermolecular charge transfer varies substantially in molecular assemblies with different packing modes.^{48–52} Our hope is that, by exploiting an ideal arrangement of the molecules resulting from strong intermolecular attraction, high quality thin films could be assembled, and efficient charge transfer for recording could be induced by an electric field. Recently, in



Scheme 6. Structure of NBPDA.⁴⁶



Scheme 7. Structure of DMNBPDA.⁴⁷

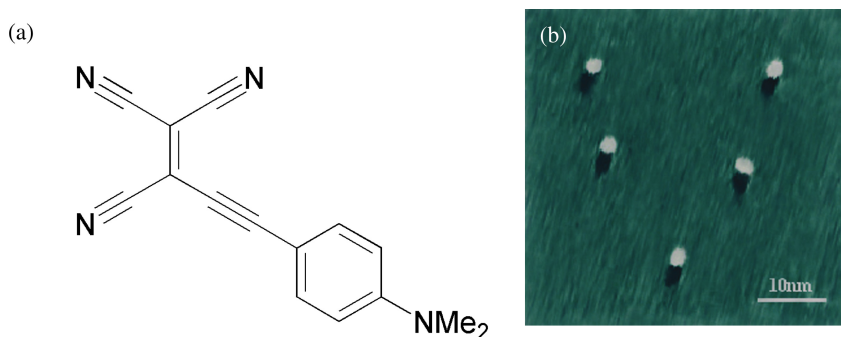


Fig. 2. (a) Molecular structure of TDMEE. (b) STM image of a nanoscale “v” pattern recorded on the TDMEE thin film by applying a pulse voltage of 2.64 V, 10 ms. STM was performed in constant height mode with set points of $V_{\text{bias}} = 0.34$ V and $I_{\text{ref}} = 0.06$ nA. The average diameter of the marks is about 2.1 nm. (Reprinted with permission from Ref. 4, © 2005, Wiley-VCH)

collaboration with Prof. F. Diederich in ETH-Hönggerberg, Zürich, Switzerland, we systematically studied the film-forming properties of a stable conjugated organic molecule TDMEE [Fig. 2(a)] with strong push–pull electron groups,^{53,54} and high quality crystalline thin films were prepared based on the self-assembly of TDMEE molecules by intermolecular π – π and donor–acceptor interactions using the vacuum deposition method. The molecules undergo π -stacking in the crystalline thin films, and the packing adopts regular alternate donor/acceptor stacks. By applying pulsed voltages between the STM tip and HOPG substrate, nanoscale data recording on these films was achieved [Fig. 2(b)]. The average size of the recorded dots is about 2.1 nm in diameter, corresponding to a potential storage density of about 10^{13} bits/cm². Further experimental and theoretical studies showed that the recording is based on an electric-field-induced intermolecular charge transfer mechanism which is strongly influenced by the ordered, antiparallel packing mode of the dipolar donor–acceptor molecules in the film.⁴ In detail, the TDMEE thin film is originally in a high resistance state, where electron conducting pathways do not exist. When a threshold voltage pulse is applied to the film, charge is transferred from the $-\text{N}(\text{CH}_3)_2$ residue of one molecule to the tricyanomonoethynylethene moiety of a neighbor

molecule. The charge transfer brings about an intermolecular electron conducting pathway, which ensures the conductance transition of the thin film from a high resistance to a low resistance state and forms a bright information dot.

To enhance the film-forming and electronic properties, some 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, Fig. 3(a)] has been designed and synthesized for STM-based data storage.⁵⁵ In a single CDHAB molecule, a hydroxyl group and a cyano group are included, which act not only as electron donor and acceptor groups, respectively, but also as hydrogen bonding recognition subunits. By molecular self-organization, CDHAB molecules have been 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 HOPG substrate [Fig. 3(b)]. An analysis

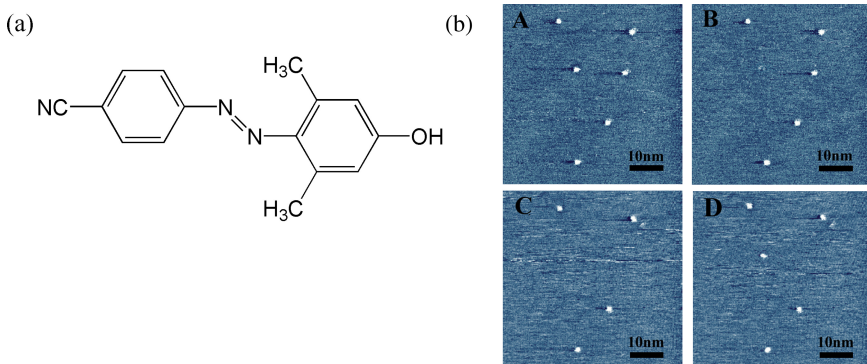
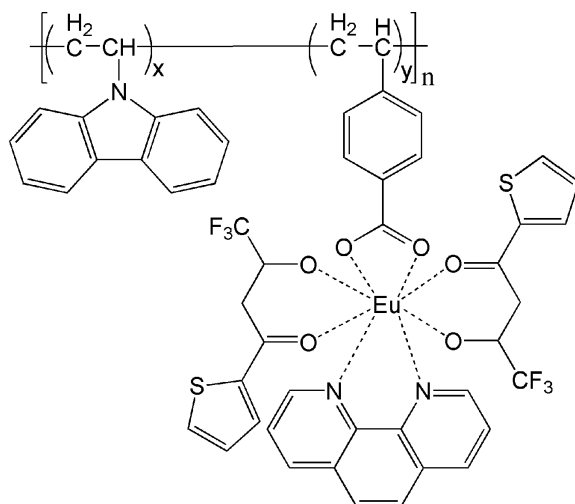


Fig. 3. (a) Molecular structure of CDHAB. (b) STM images of the CDHAB film during the information recording experiments. Tunneling conditions: $V_{\text{bias}} = 0.38 \text{ V}$, $I_{\text{ref}} = 0.28 \text{ nA}$, 0.2 Hz/image , constant current mode. (A) Recorded pattern (letter “y”): voltage pulses $+2.6 \text{ V}$, 3.0 ms ; area shown is $60 \text{ nm} \times 60 \text{ nm}$. (B, C) Patterns after erasing one and two marks, respectively: voltage pulses -2.2 V , 3.0 ms . (D) Pattern after rewriting one mark: voltage pulse $+2.6 \text{ V}$, 3.0 ms . (Reprinted with permission from Ref. 55, © 2006, Wiley-VCH)

of the mechanism suggests that the formation of the recording dots is due to a local change of the film's electrical properties, and reversible intermolecular charge transfer induced by electric fields is proposed as a possible reason for that change. This result shows that the STM-based memory with a self-assembled donor-acceptor compound in a crystalline thin film is a promising candidate for reversible nanometer scale data storage.

2.2.1.4. Polymer material

Due to their good scalability, mechanical strength, flexibility, and ease of processing, polymer materials have attracted considerable attention. In this context, polymer materials which have donor and acceptor groups in their structural units have been considered promising active electronic components for data storage and molecular electronic devices. As a typical example, Kang *et al.*² designed and synthesized a novel copolymer, poly[*N*-vinylcarbazole-*co*-Eu(vinylbenzoate)(2-thenoyltrifluoroacetone)₂ phenanthroline] (PKEu, Scheme 8), of which the carbazole group was used as an electron donor, and the Eu complex acted as an electron



Scheme 8. Molecular structure of the copolymer PKEu with the composition of $x/y = 0.987:0.013$.²

acceptor. Using this material as the active media, they constructed a metal–insulator–metal sandwich memory device. The electrical bistable behavior of PKEu was observed in the current density–voltage (J – V) characteristics of the device. The experimental result showed that J increases progressively with the applied voltage, and a sharp decrease in the current occurs at about 4 V, indicating the transition of the device from the high conductivity state (the “on” state) to a low conductivity state (the “off” state). This transition from the “on” state to the “off” state is equivalent to the “writing” process in a digital memory cell. On the other hand, the “off” state can be recovered with the application of a reverse voltage pulse (at about -2 V), which is equivalent to the erasing process of a digital memory cell. Furthermore, the device exhibits a high on–off current ratio (10^4), fast switching time (shorter than 20 μ s) and excellent reading stability (more than a million read cycles under ambient conditions, without any device encapsulation). All this indicates promise in the application of polymer materials in future electrical recording.

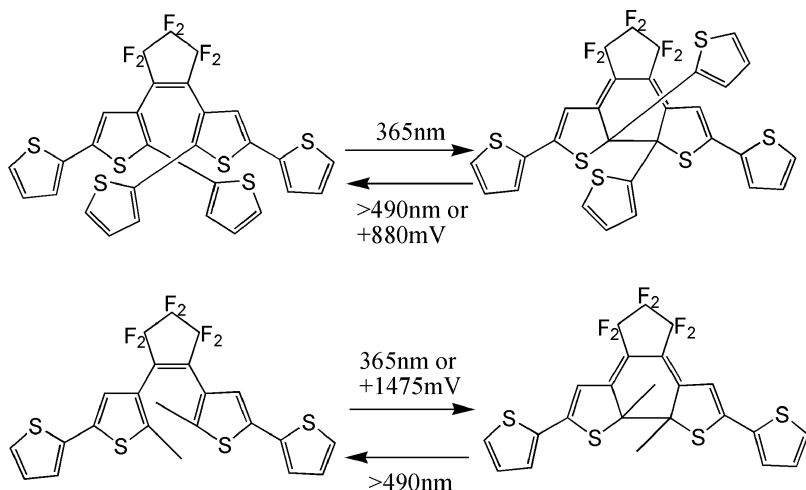
2.2.2. Conformational change for conductance transition

The conductivity of a molecule relates to its chemical structure and electronic structure. So, in some cases, the electrical properties of a molecule can be changed by varying its conformation. A typical example is from a work of Dulić *et al.*⁵⁶ In their experiments, a 1,2-bis[5'-(5''-acetylsulfanylthien-2''A-yl)-2'-methylthien-3'-yl] cyclopentene photochromic switch, which consists of a central switching unit, two thiophene rings on both sides of the switching unit, and two thiol groups, protected with acetyl groups, at the ends of the molecule, was connected to two gold electrodes. Under light irradiation, the conductivity and absorption of the molecule were measured. The experimental result showed that by exposing the molecule to the light of wavelength λ in the range $500 \text{ nm} < \lambda < 700 \text{ nm}$, the molecule switched from the closed form to the open form. Consequently, the covalent bonds in the central ring rearranged, and the conjugation throughout the molecule was turned off. Shown in electrical conductivity, a sharp increase in the resistance was observed. The resistance after switching was in the $\text{G}\Omega$ range, about three orders of magnitude larger than in

the initial value (closed state). Because of the change in quantum confinement, the energy levels of the molecule were also modified, resulting in a change in the absorption spectrum of the molecule. The authors also found that, for the molecule–gold system, the switching occurs only in one direction, namely from the closed to the open form, but the reverse process does not take place. They attributed that to the influence of the gold attached to the molecule; the gold could quench the first excited state of the open form of the molecule.

2.2.2.1. Diarylethene

It is known that diarylethene is a typical photochromic compound. Recent research by Branda *et al.*^{57,58} shows that some kinds of diarylethene are also electrochromic. They can be triggered by electrochemical or chemical oxidation; such electrochromism is contingent on whether the diarylethenes have the nonalkyl groups in bis(dithiophene) (Scheme 9). That is, for diarylethenes having nonalkyl groups attached to the carbons involved in forming the new single bond, their closed forms can return to open ring forms when electrochemically oxidized. For diarylethenes



Scheme 9. Isomerization of diarylethenes used by Branda *et al.*^{57,58}

having alkyl such as methyl groups in bis(dithiophene), the ring-closing reaction can also be triggered by the oxidation process. The above conclusions are obtained based on the fact that when the 2-methyl groups in bis(dithiophene) are replaced by aryl rings (thiophene or benzene, for example) the closed ring closed forms rapidly reopen when they are oxidized to their thermally unstable radical cations. It is also found that the absence of these methyl groups has little effect on the photochemical ring-closing and ring-opening reactions but does play a significant role in minimizing the electrochemical polymerization that is characteristic of thiophenes.

Tsujioka *et al.*⁵⁹ constructed an organic memory device using a bistable photochromic diarylethene as the active medium. The diarylethene is a nonsymmetrical bipolar molecule with a triphenylamine as electron donor and an oxadiazole as electron acceptor (Fig. 4). The function of the device is based on an isomerization reaction of the diarylethene molecule via its excited state caused by an electric carrier injection. It should be emphasized that the electric carrier injection and the excitation are via the encounter of the bistable molecule of a hole injected from the anode and an electron injected from the cathode (called electron mode recording), not on the photoexcitation (photon mode recording). The electron on the lowest unoccupied molecular orbital level and the hole on

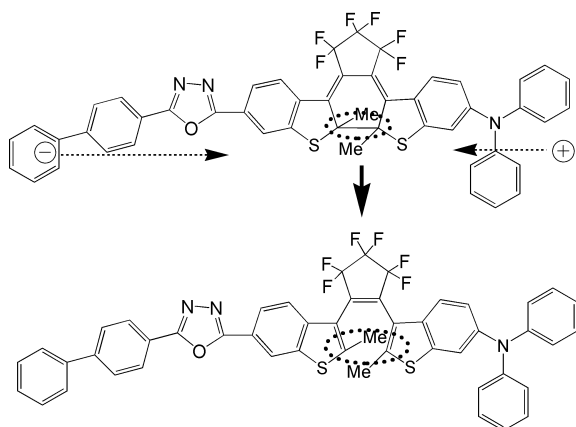


Fig. 4. Molecular structure of the bipolar diarylethene derivative used in the experiment.⁵⁹

the highest occupied molecular orbital level of the molecule produce an excited state identical to that produced by photoexcitation, so the molecule is transformed into another isomerization form. On this basis, reversible writing and nondestructive readout of information by the carrier injection were demonstrated.

2.2.2.2. Spiropyran and spirooxazine

The spirobenzopyran derivative is another typical photochromic compound that has been extensively investigated.^{60–65} It is stable in its closed ring isomeric form, with a colorless or pale yellow solution. Upon irradiation with UV light, the colorless closed ring form of SP converts to an intensely colored opened ring MC form due to the cleavage of the spiro-C–O bond. This process results in the extension of the π -conjugation system and leads to the appearance of a new absorption band with an optical absorption peak at 550–600 nm. The closed ring form of SP can be photochemically regenerated from its opened ring MC form by irradiation with visible light, and the characteristic color of the opened ring MC form disappears. Up to now, the main emphasis of the work reported has been on the photochemically induced open/closed ring isomerization process; much less attention has been paid to the electrochemical behavior. Recent research by Zhi *et al.*⁶⁶ showed that such photochemically induced isomerization can also be induced by the electrochemical mode by investigating the electrochemical behavior of the photochromic spiropyran derivative 1,3,3-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline) in dimethylformamide (DMF) solution. The absorption spectrum change in the potential range of -1.8 V to $+0.8$ V (vs. Ag quasi-reference electrode) indicated that the electrochromic reaction occurred, which is associated with a redox process of the nitro group. Further spectroelectrochemical measurements revealed that, as shown in Fig. 5 for the SP form, the absorption spectrum shows no peaks between 350 and 600 nm. When the potential was held at -1.3 V, a new absorption band centered at about 445 nm appeared and increased in intensity with increasing charge passed. The band is characteristic of the radical anion of nitrobenzene; when the applied potential was set at 0.8 V, a gradual decrease in the peak intensity at 445 nm and the appearance of a distinct

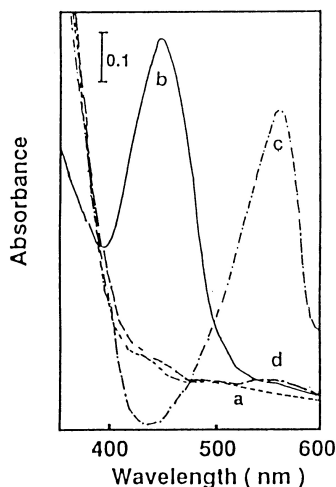


Fig. 5. Absorption spectral changes of SP-1 in DMF at -42°C : (a) measured after visible light irradiation of SP-1 for 15 min; (b) after reduction of solution in (a) at -1.3 V with a total charge of 1.2°C ; (c) after oxidation of reduced species in (b) at $+0.8\text{ V}$ with a total charge of 1.0°C ; (d) after solution in (c) was irradiated with visible light for 25 min. (Reprinted with permission from Ref. 66, © 1995, Elsevier)

peak at about 556 nm, which appears to be identical to that of the open ring isomer (MC) obtained on UV irradiation of SP, were clearly observed with increase of the charge passed. The result indicated that the open ring reaction was induced electrochemically. Also, the 556 nm absorption band can be bleached by visible light irradiation, and when the bleached species is again reduced by holding the electrode potential at 1.3 V, the absorption at 445 nm reappears. Hence it is suggested that the bleached species is the closed form isomer (SP), which can be electrochemically reduced to form the nitrobenzopyran radical anion. A similar process can be seen for the MC form. This suggests that a reversible open/closed ring process is involved in the redox reaction of the SP and MC forms of SP-1 in DMF, namely a nitrobenzopyran radical anion via reduction and an open-ring MC isomer via oxidation (Fig. 6). Such a combination of photochromism and electrochromism in a compound would endow SP-1 possible electrical-optical switching and dual mode memory applications.

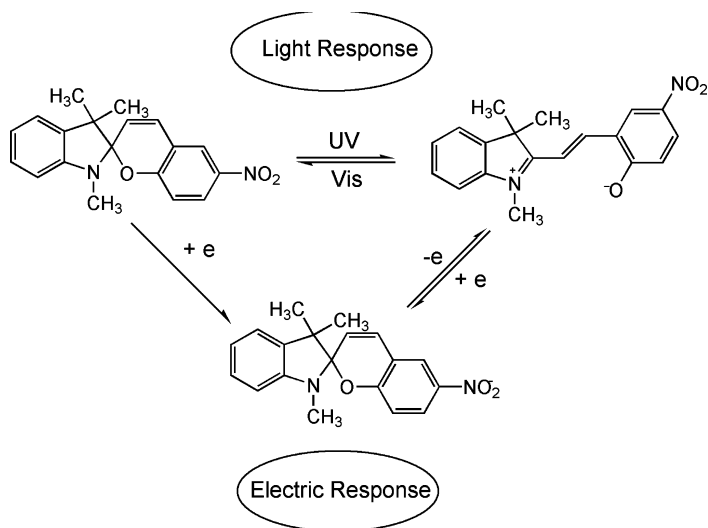


Fig. 6. Scheme for the photoelectrochemical operation of the conjugated SP-1 system.⁶⁶

	Sample No	R ₁	R ₂	R ₃
	SP6	NO ₂	—	—
	SP7	—	OCH ₃	—
	SP8	NO ₂	OCH ₃	—
	SP9		—	—
	SP10	NO ₂	—	Cl
	SP11	—	OCH ₃	Cl

Scheme 10. Spirocompounds.⁶⁷

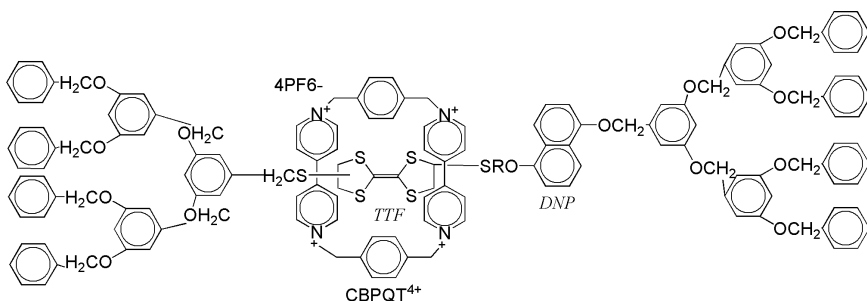
Ustamehametoğlu⁶⁷ investigated the electrochromic property of some spirocompounds (Scheme 10) and the matrix effect on the electrochromism using *in situ* spectrochemical measurements. By monitoring the conductivity and absorption spectra of the solutions before and after electrolysis, the electrochromism of these compounds were found, and the electrochromism capacity were shown to be dependent on particular molecular substitutions.

It was also found that PMMA could act as a matrix for spirocompounds. In the PMMA matrix, the rate of open/closed ring isomerization of the compounds can be manipulated by the concentration of the polymer.

2.2.2.3. Interlocked molecules

Rotaxanes are a family of interlocked molecules. The key structure of these molecules contains a π -electron-deficient macrocycle that is locked around a π -electron-rich component along the molecular “thread” with two bulky “stoppers.” Switchable rotaxanes are currently attracting considerable attention, due to their potential to perform relative intercomponent positional changes in response to external stimuli. Under external stimuli, the macrocycle can move between different π -electron-rich components, resulting in switching of the electronic configuration. This makes rotaxanes a promising candidate for electrical recording.⁶⁸ Gao *et al.*⁶⁹ prepared a rotaxane film on an ITO-based glass substrate using the LB technique. The chemical structure of the molecule (H1) is shown in Scheme 11. Using a two-terminal junction, a fast (60 ns) conductance-switching phenomenon with an on–off ratio of about 100 in the LB film was observed. The *I*–*V* characteristics of the H1 film show a reversible electrical bistability and a nonvolatile memory effect, and stable, reproducible nanorecording in the rotaxane film was demonstrated by STM.

But for H1 film, erasing of the marks showed some difficulties. Recently, erasable and rewritable nanorecording was further achieved on another rotaxane (H2, Scheme 11) film,⁷⁰ and the structural and conductance transition of H2 has been directly observed using STM at 77 K.⁷¹ It was proposed that the spacers in the molecules might be responsible for the difference in erasability. The only difference between H1 and H2 lies in the spacer between TTF and DNP. In H2, a rigid cyclohexyl spacer replaced the soft alkyl spacer $-(\text{CH}_2)_5-$ in H1, involving a larger steric hindrance compared to alkyl group. It is likely that two H2 molecules are packed less close than H1 molecules, and thus the intermolecular interaction of neighboring H2 molecules will not be as strong as that in H1 molecules. This makes the CBPQT⁴⁺ ring move back to the TTF from DNP sites relatively easier, and consequently the nanorecording in the H2 thin film are erasable.



H1 $R = -(CH_2)_5-$

H2 $R = -CH_2CH(CH_2CH_2)_2CHCH_2-$

Scheme 11. Rotaxanes H1 and H2.^{69,70}

Catenanes are another type of interlocked molecules and supramolecular complexes that have received much attention. Driven by external voltage, the mechanically interlocked molecules can undergo a reversible circumrotational motion of one of the rings through the cavity of the other ring upon oxidation and subsequent reduction. A solid state, electronically addressable, bistable [2] catenane-based molecular switching device was fabricated from a single monolayer of the [2] catenane anchored with phospholipid counterions and sandwiched between an *n*-type polycrystalline silicon bottom electrode and a metallic top electrode.⁷² The compound (Fig. 7(a)) consists of a tetracationic cyclophane that incorporates two bipyridinium units, interlocked with a crown ether containing a tetrathiafulvalene (TTF) unit and a 1,5-dioxynaphthalene ring system (NP) located on opposite sides of the crown ether. The device exhibits hysteretic (bistable) current/voltage characteristics. The switch is opened at +2 V, closed at -2V, and read at ~0.1 V, and maybe recycled many times under ambient conditions. A mechanochemical mechanism for the action of the switch is presented in Fig. 7. As illustrated, coconformer [A0] represents both the ground state structure of the [2] catenane and the switch-open state of the device. When the [2] catenane is oxidized (by applying a bias of -2 V), the TTF groups (green) are ionized and experience a Coulomb repulsion with the tetracationic cyclophane (blue), resulting in the circumrotation of the ring and the formation of coconformer [B+]. When the voltage

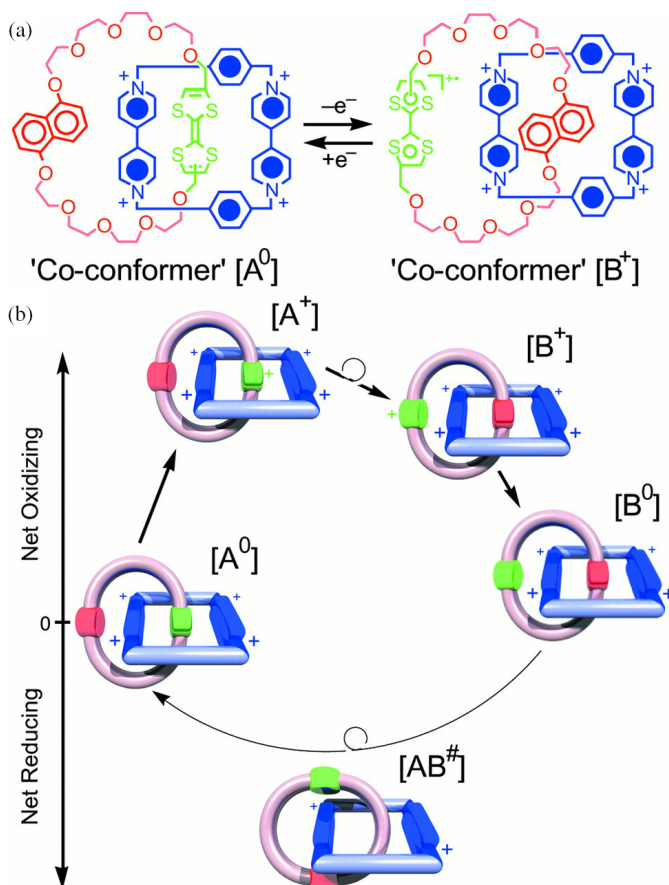


Fig. 7. (a) Molecular drawing of the bistable [2] catenane used in this work. The voltage-driven circumrotation of coconformer [A⁰] to coconformer [B⁺] is the basis of the device. (b) Proposed mechanochemical mechanism for the operation of the device. (Reprinted with permission from Ref. 72, © 2000, AAAS)

is reduced to a near-zero bias, coconformer [B⁰] is formed, and this represents the switch-closed state of the device. Partial reduction of the cyclophane (at an applied bias of +2 V) is necessary to regenerate coconformer [A⁰]. For simplicity of presentation, a 2e-reduction step is shown, but the actual number of electrons was not measured, and the reduced coconformer [AB[#]] is indicated with an unknown oxidation state. The

bistable devices exhibited robust operation under ambient conditions, and may, upon further engineering, be useful as memory devices.

2.2.3. *Conductance transition based on oxidation and reduction reaction*

Attaching the redox-active molecules to an electroactive surface such as a gold or silicon surface provides an attractive approach to molecule-based electrical recording. Driven by the external voltage, the molecules undergo oxidation and reduction reactions, and information is thus stored in the distinct oxidation states of the molecules. The reactions also result in change of the conductivity; the information can be read based on the difference of the conductivity. Such writing and reading of information in the molecules is accomplished electrically under ambient conditions, and multiple bits of information can be stored through the use of molecules or molecular arrays that afford a set of distinct oxidation states. The data density depends on the oxidation states that the molecules can afford. The more oxidation states they have, the higher the density that can be achieved. The availability of multiple, low potential oxidation, stable states could provide a potential means of storing more than one bit of information in a single storage location, with consumption of relatively little power.

Among the various redox-active molecules, porphyrinic molecules stand out, for the following reasons.⁷³ Firstly, porphyrins can provide three accessible oxidation states: the neutral state, monocation and dication. They can form stable radical cations and dications and undergo reversible electrochemistry, based on which, erasable electrical recording can be achieved. Secondly, since the information is stored in the different oxidation states and porphyrinic molecules can afford three distinct states, multiple bits of information storage can be realized on these molecules, thus providing a much higher storage density. Thirdly, the electrochemical potential of a porphyrin can be tuned over a large range (>0.5 V) by the choice of central metal and peripheral substituents. Several scientific issues should be taken into account for such electrically addressable molecule-based information storage. How is the rate of writing and reading information affected by the nature of the linker that attaches the redox-active molecule to the surface?

What molecular features (e.g. linker length and composition, nature of the redox-active unit, three-dimensional architecture) affect the retention of charge necessary for information storage? What is the maximum number of bits that can be stored in a molecular array? Do different oxidation states in a given molecule exhibit different charge retention properties?

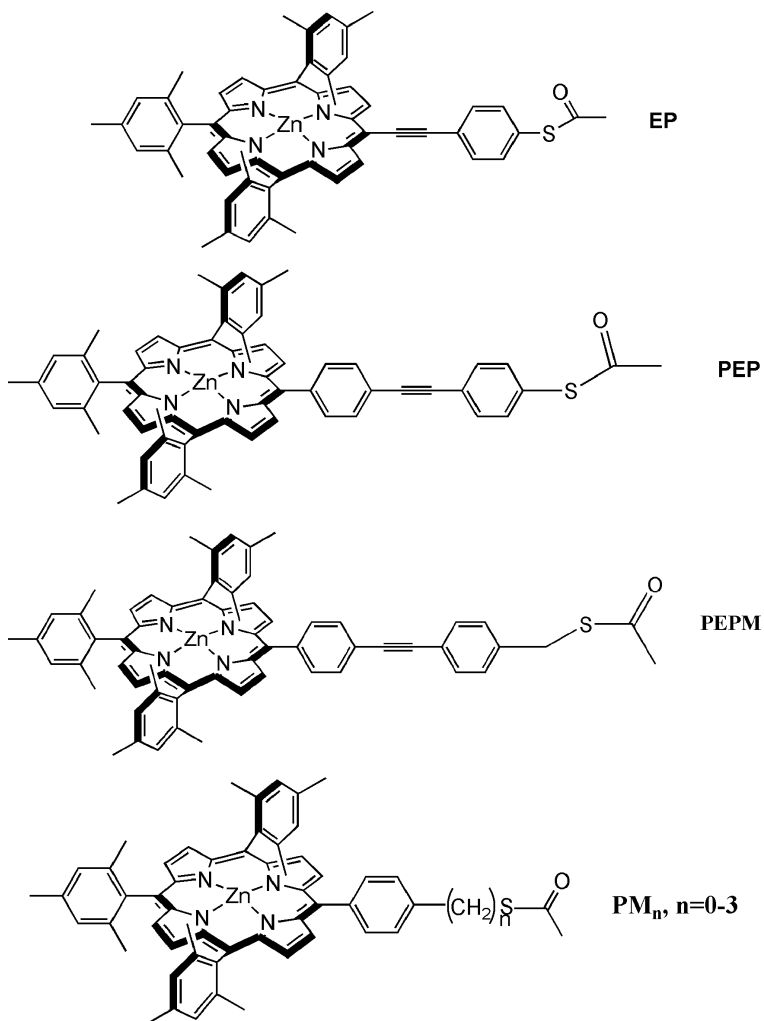
To address the above-mentioned fundamental scientific questions, Lindsey *et al.* have developed over 100 porphyrin-based molecules and examined the electrochemical behavior of the molecules self-assembled on gold via the thiol unit. The molecule family includes monomeric porphyrins,^{73,74} ferrocene porphyrins,⁷⁵ weakly coupled multimeric porphyrins,⁷⁶ tightly coupled multimeric porphyrins⁷⁷ and lanthanide triple deckers of porphyrins and phthalocyanines.⁷⁸ A number of molecules were prepared with linkers of different length and composition. The motivation for exploring different linkers was to investigate the effect of linker structure on the rates of writing and reading as well as the duration of charge storage (i.e. charge retention time). The emphasis on the multimeric systems and triple deckers was to achieve an increased number of oxidation states, thus increasing the information storage density.

Those authors' preliminary studies showed that SAMs of monomeric porphyrins retain charge for hundreds of seconds after disconnection of the applied potential, which is almost five orders of magnitude longer than that of the state-of-the-art DRAM elements. Charge retention times of porphyrin monomers bearing phenyl or alkylphenyl linkers can be altered ~10-fold via structural modification of the linker. The studies also showed that the nature of the linker plays a significant role in determining the charge retention characteristics of the porphyrins SAMs. The length of the linker is clearly important, with long linkers generally giving a longer $T_{1/2}$ (half-life for charge retention) time. The fact (Table 2) that the $T_{1/2}$ values for the "wire-linked" (conjugated linkers) porphyrin SAMs are significantly smaller than those for PMn SAMs [containing phenyl-(CH₂)_n linkers; see in Scheme 12] shows that the electronic properties of the linker have a strong influence on charge retention, which probably results from the greater electronic coupling of the latter between the Au surface and the porphyrin redox sites through the more conjugated linkers of the wire-linked molecules.^{79,80}

For electrical bistable media in memory devices, to achieve a stable read-out, the current ratio between the two states, i.e. the on-off ratio, is crucial.

Table 2. Charge retention half-lives for thiol-derived Zn porphyrins in SAMs.^{79,80}

Porphyrin	PEPM	PEP	EP	PM _{n0}	PM _{n1}	PM _{n2}	PM _{n3}
<i>T</i> _{1/2} /S	58	43	31	116	167	656	885



Scheme 12. Porphyrins for preparing SAMs with the designations EP (ethynylphenyl linker), PEP (phenylethynylphenyl linker), PEPM (phenylethylphenylmethyl linker) and PM_n (phenylalkyl linker).^{79,80}

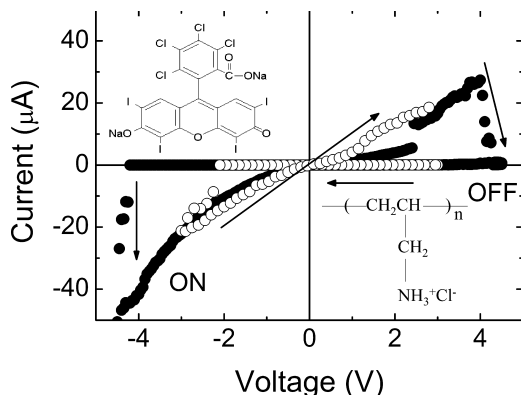


Fig. 8. I - V characteristics of devices based on spin-cast films of Rose Bengal for two sweep directions. Initial sweep voltages were ± 3.0 (open symbols) and ± 4.5 V (filled symbols). Arrows show the sweep direction of applied voltage. The molecular structure of Rose Bengal and PAH are shown in the second and fourth quadrants, respectively. (Reprinted with permission from Ref. 82, © 2003, American Institute of Physics)

The way to increase the ratio is to either increase the “on” state current or decrease the “off” state current. Aiming for a molecule with a very low conducting “off” state, Pal *et al.*^{81,82} chose Rose Bengal (Fig. 8), which has electron-acceptor groups all over the surface of the molecule, and fabricated memory devices based on spin-cast and layer-by-layer electrostatic self-assembled films of Rose Bengal. In these devices, a large electrical conductance switching with an on-off ratio of 10^5 in single layer sandwich structures at room temperature was observed. Such a high ratio in a single layer sandwich structure, as compared to contemporary switching devices, is due to low “off” state leakage current. In the absence of any donor group in Rose Bengal, the electron-withdrawing groups surrounding the molecule attract π -electron clouds are reduced, which largely affects conjugation in the molecules. The molecule behaves as an insulator, as represented by the very low “off” state leakage current. When a reverse bias is applied, the molecule receives an electron, which reduces the effects of the electron-accepting groups. Electron distribution in the benzene rings rearranges, resulting in overlapping electronic structure. The shape of the accessible molecular orbital extends over the entire molecule, and a conduction pathway opens up,

resulting in a high conducting “on” state. The molecule returns to its “off” state when the voltage sweeps to a suitable forward bias, which oxidizes the molecule by removing the extra electron previously added. It was also shown that by introducing the supramolecular matrix in conducting switching, the “on” and “off” state currents and thus the on–off ratio can be tuned by the resonance between the density of states and the electrode’s Fermi level. Furthermore, the devices suggested by Pal *et al.* exhibit a good repeating switching property, a stable readout, etc. indicating the important potential of redox-active molecules as electrical recording media.

3. High Density Electrical Recording Technologies and Their Recent Developments

The progress of high density information storage is related not only to the recording media, but also to the recording technology. They are the two sides of one thing. Here we will summarize the main electrical recording technology.

3.1. Scanning tunneling microscopy (STM)

In 1981, Binnig, Rohrer and their colleagues at the Zürich Research Laboratory of International Business Machines (IBM) developed a new kind of surface analytical instrument: the scanning tunneling microscope (STM).⁸³ The invention of the STM made it possible to observe the arrangement of individual atoms on material surfaces, and physical and chemical properties related to the behavior of surface electrons on a real surface. Furthermore, the STM can be used for atomic manipulation, surface modification, and nanofabrication. This ability makes it a highly effective tool in high density data storage.^{29,43,84}

The researchers at IBM¹² noticed that the probe would sometimes pick up an atom from a surface. They soon discovered that the single atom could be moved around when changing the voltage applied to the tip. They succeeded in writing their company name by positioning individual xenon atoms on a single crystal nickel (110) surface with atomic precision, and the corresponding density of storage reached

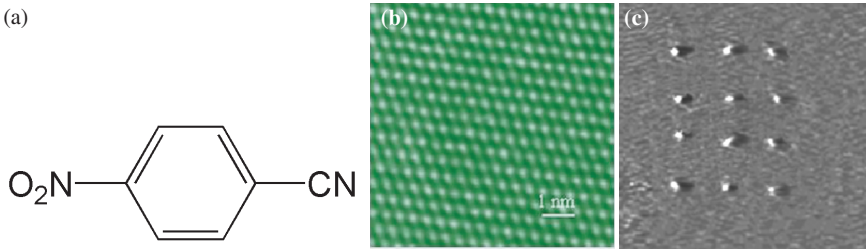


Fig. 9. Data storage on the surface of PNBN thin film. (a) Structure of PNBN; (b) orderly molecular structure of PNBN thin film (scanning condition: $V_{\text{bias}} = 0.1 \text{ V}$, $I_{\text{ref}} = 0.3 \text{ nA}$); (c) STM image of recorded marks on the surface of PNBN thin film (scanning condition: $V_{\text{bias}} = 0.4 \text{ V}$, $I_{\text{ref}} = 0.24 \text{ nA}$; scanning area: $24 \text{ nm} \times 24 \text{ nm}$). (Reprinted with permission from Ref. 23, © 2001, Wiley-VCH)

10^6 Gbit/in^2 . But the system was working at a low temperature (4 K) that was not easy to reach. The following research was conducted at room temperature, using STM to observe the change of the tunneling current of the sample surface to realize data storage. By applying a pulse voltage between the tip and the film, the local electronic characteristics of the film change from a high resistance (“0” state) to a low one (“1” state). According to the difference in the component of the film, the changes can be introduced by a different mechanism, which may be phase change, structure change or charge transfer. Now the smallest size of recording marks has reached 0.6 nm on PNBN thin film (Fig. 9).^{23,85}

3.2. Atomic force microscopy (AFM)

During the process of electrical recording, local conductance transition can be induced by applying voltage pulses to the recording media by STM. However, this method currently cannot be employed in large scale data storage. The main difficulty comes from the fact that the image by STM depends on the tunneling current between the tip and the sample surface. On one hand, this requires that the media be conductive and the distance between the tip and the sample be precisely controlled by a feedback system; on the other hand, the surface electronic

state is very sensitive, and is very prone to be damaged by the voltage pulses applied, so, in this case, it is very difficult to get a durable stable image. Taking this into account, to get a fine image by applying the voltage pulses via the conductive contact mode of AFM would be easier. In the contact mode of AFM, the tip makes contact with the sample surface, and the topography image can be achieved through the force between the tip and the sample surface; while the current image can be obtained through the contact current. In this condition, achieving the image does not require too much for the tip; furthermore, the topography image and the current image can be obtained simultaneously and independently, which would be favorable for elucidating the mechanism of the recording.

Researchers at the Canon Research Center realized nanometer scale data recording in polyimide LB films using an AFM combined with an STM.^{24,86} By applying a voltage pulse, an increase in conductance can be induced at any point in the LB film. The STM–AFM observation found that little surface modification had occurred by the voltage application, which showed that the conductance of the LB film changed without topography change.

3.3. Cross-bar nanocircuits

To perform memory and/or logic functions, Chen *et al.*²⁵ proposed and fabricated nanoscale molecular-electronic circuits comprising a molecular monolayer of rotaxane sandwiched between metal nanowires to form an 8×8 cross-bar, using the thermal nanoimprint method within a $1 \mu\text{m}^2$ area (as shown in Fig. 10). The resistance at each cross point of the cross-bar can be switched reversibly. Figure 11 shows the test configuration for the writing and reading modes of an 8×8 circuit. In order to write one bit at a cross point [e.g. (1, A) in Fig. 11], the corresponding row and column of the cross-bar were selected by applying a voltage pulse of amplitude V to the top nanowire [row A in Fig. 11] and grounding the bottom nanowire [column 1 in Fig. 11]. To prevent accidental writing of other bits, a voltage pulse of amplitude $V = V/2$ should be applied to all other rows and columns simultaneously. Thus, none of the

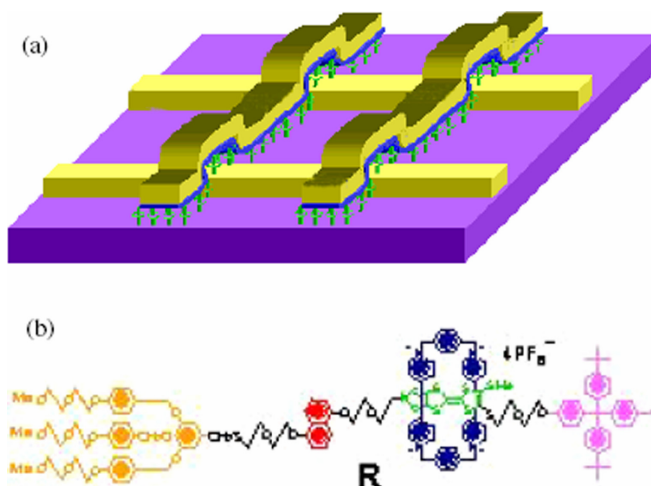


Fig. 10. (a) Schematic representation of the cross-bar circuit structure. A monolayer of the [2] rotaxane (green) is sandwiched between an array of Pt/Ti nanowires (gold, left–right) at the bottom and an array of Pt/Ti nanowires (gold, up–down) at the top. (b) Molecular structure of the bistable [2] rotaxane **R**. (Reprinted with permission from Ref. 25, © 2003, IOP Publishing Ltd.)

cross points at the intersections of rows (B–H) and columns (2–8) not selected for the write operation would have a bias voltage across them and they could not be written. To read the memory, a bias voltage $V = 0.5$ V was applied to the selected row, and all of the other rows and columns were grounded ($V = 0$). The resistance of the bit to be read could be determined uniquely by only measuring the current flowing to ground via the selected column. On such a cross circuit, rewritable, nonvolatile memory with a density of 6.4 Gbit cm^{-2} was successfully demonstrated. Moreover, by setting the resistance at specific cross points, two 4×4 subarrays of the crossbar were configured to be a nanoscale demultiplexer and multiplexer which were used to read memory bits in a third subarray.

According to Chen *et al.*, a crossbar has several advantages. First, the wire dimensions can be scaled continuously down to molecular sizes, while the number of wires in the cross-bar can be scaled up arbitrarily to

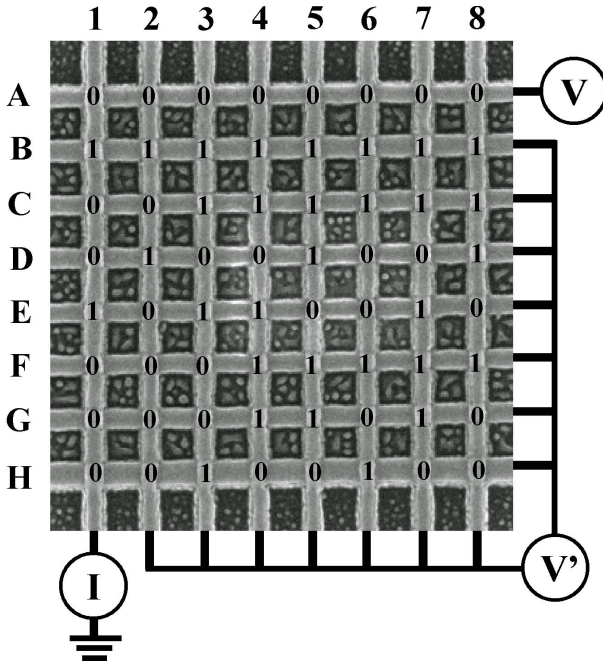


Fig. 11. The cross-bar as a 64-bit random access memory. The idea is “write” and “read” modes for the memory. To write a bit, V is increased in increments of 0.5 from 3.5 V until the bit is written or V reaches 7 V, while keeping $V = V/2$; to read a bit, $V = 0.5$, and $V = 0$. (Reprinted with permission from Ref. 25, © 2003, IOP Publishing Ltd.)

form large scale generic circuits that can be configured for memory and/or logic applications. Second, it requires only $2N$ communication wires to individually address 2^N nanowires with a demultiplexer,⁸⁷ which allows the nanocircuit to communicate efficiently with external circuits and systems, e.g. CMOS. Third, it is a reconfigurable architecture that can tolerate defective elements generated during the nanofabrication process.⁸⁸ Fourth, the simple physical structure of the cross-bar makes nanoscale fabrication feasible and potentially inexpensive.

In 2004, a 34×34 cross-bar circuit with a half-pitch of 50 nm (corresponding to a bit density of 10 Gbit/cm²) was effectively fabricated using a single-layer UV nanoimprint process.²⁶ Compared with the previous

thermal imprint method, UV nanoimprint could well eliminate the effect of high temperature and high pressure on devices in the thermal nanoimprint process.

4. New Emerging Techniques/Technologies for High Density Electrical Data Recording

4.1. Carbon-nanotube-based nonvolatile random access memory

Since being discovered by Sumio Iijma, nanometer-diameter single-walled carbon nanotubes (SWNTs) have been considered as attractive building blocks for molecular electronics because of their unique electronic, mechanical and chemical properties.⁸⁹ Depending on diameter and helicity, SWNTs behave as either one-dimensional metals or semiconductors,⁹⁰ which, by virtue of their great mechanical toughness and chemical inertness, represent ideal materials for creating reliable, high density input/output (I/O) wire arrays. A concept for molecular electronics exploiting carbon nanotubes as both molecular device elements and molecular wires for reading and writing information was developed by Leiber *et al.*⁹¹ Each device element is based on a suspended, crossed nanotube geometry that leads to bistable, electrostatically switchable on–off states (Fig. 12). The device elements are naturally addressable in large arrays by the carbon nanotube molecular wires making up the devices.

Qualitatively, bistability can be envisioned as arising from the interplay of the elastic energy, which produces a potential energy minimum at finite separation (when the upper nanotube is freely suspended), and the attractive van der Waals (vdW) energy, which creates a second energy minimum when the suspended SWNT is deflected into contact with the lower nanotube. These two minima correspond to well-defined “off” and “on” states, respectively, i.e. the separated upper-to-lower nanotube junction resistance will be very high, whereas the contact junction will be orders of magnitude lower. A device element could be switched between these well-defined “off” and “on” states by transiently charging the nanotubes to produce attractive or repulsive electrostatic forces.

These bistable and reversible nanotube device elements can be used to construct nonvolatile random access memory and logic function

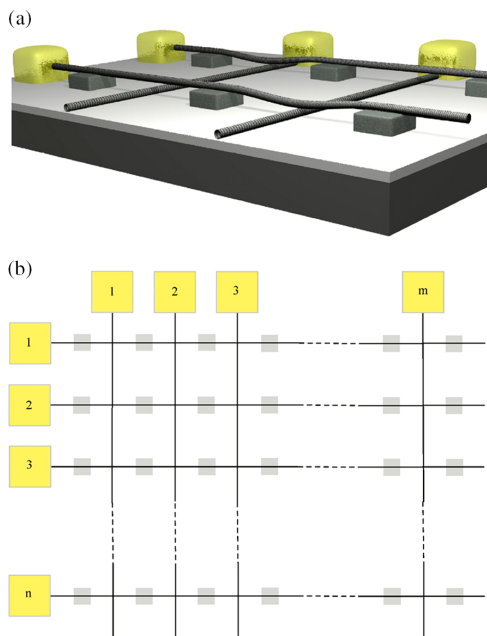


Fig. 12. Suspended nanotube device architecture. (a) Three-dimensional view of a suspended cross-bar array showing four junctions with two elements in the “on” (contact) state and two elements in the “off” (separated) state. (b) Top view of an n -by- m device array. (Reprinted with permission from Ref. 91, © 2000, AAAS)

tables. According to Leibel *et al.*, the potential of such a system lies in the following. First, it will be possible to achieve an integration level as high as 1×10^{12} elements per square centimeter. Second, the switching time for a 20 nm device, 10^{-11} s, suggests that on–off switching operations can be carried out at 100 GHz. Finally, the nonvolatile nature of the device is preferable from the standpoint of power consumption and corresponding heat dissipation as compared to dynamic RAM, which must be continually refreshed. All this is demonstrated by detailed calculations and by the experimental realization of a reversible, bistable nanotube-based bit.

On the other hand, to put forward integrated molecular electronics, there are several issues that must be addressed. The first one involves developing effective methods to separate metallic (M) tubes from semiconducting (S)

ones, because it is recognized that current SWNT samples consist of a random distribution of M and S tubes,⁹² and this might complicate device reading. Second, it will ultimately be important to create devices in parallel using individual SWNT. The last issue is how to assemble these memory bits and how to macroscopically address them.¹

4.2. Spin-based information storage (processing)

In conventional electronic devices, the storage and communication of information is based on the existence/absence and transport of electrical charge. With the relentless miniaturization of electronic devices and their ever-increasing integration, the advance may soon end due to fundamental physical and/or economic limitations. For this reason, investigators are trying to exploit the electron spin to create a remarkable new generation of spintronic devices which could be much smaller, consume less electricity, and be more powerful for certain types of computations than is possible with systems based on electron charge.⁹³ In spintronic devices, information is stored into spins as a particular spin orientation (up or down). And once the information is stored, it can be kept a relatively long time, which arises from the long coherence or relaxation property of spin. For the above-mentioned features, spintronic devices are particularly attractive for memory storage and quantum computing.^{94–96}

In the spintronic field, spin relaxation and spin transport are two fundamental research interests not only because of their being basic solid state physics issues, but also because of their demonstrated value as phenomena in electronic technology.^{97–102} Current spin-based electronic devices include giant magnetoresistive effect (GMR)-based devices,^{103,104} the spin valve (SV),¹⁰⁵ magnetic tunnel junction (MTJ),¹⁰⁶ magnetoresistive random access memory (MRAM),¹⁰⁷ etc. and most of them are based on ferromagnet materials. The disadvantages of such all-metal devices are that they do not amplify signals and will be difficult to integrate into the existing semiconductor microelectronics, while semiconductor-based spintronic devices could in principle overcome them.¹⁰⁸ To achieve semiconductor-based spintronic devices requires effective and efficient techniques for the electrical injection of strongly spin-polarized currents as well as electrical detection of such spin currents.

A long term and ambitious aim for spintronic devices is the application of electron and nuclear spins to quantum information processing and quantum computation. The spins of electrons and spin 1/2 nuclei provide a perfect candidate for quantum bits, as their Hilbert spaces are generally well-defined and their decoherence relatively slow.^{109–111} As for electrical recording and processing of quantum information, fast and coherent manipulation of local spins in electrical mode is required. Salis *et al.*¹¹² showed that spin coherence can be controlled in a specially designed $\text{Al}_x\text{Ga}_{1-x}$ quantum well, in which the Al concentration x is gradually varied across the structure. Application of an electric field leads to a displacement of the electron wave function within the quantum well, and because the electron g factor varies strongly with x , the spin splitting is changed. Using time-resolved optical techniques, they demonstrated gate-voltage-mediated control of coherent spin procession over a 13 GHz frequency range in a fixed magnetic field of 6 T.

4.3. Multimode coupled techniques for multiresponsive information storage

The recording and processing of information is based on the ability to control changes in a particular physical property of a material, such as the electrical, magnetic and optical response. In past decades, great progress has been made using different organic responsive media in nanoscale electrical data recording^{4,42,55,69} and in high density optical^{113–129}/magnetic^{130,131} information storage. However, most of these achievements are based on the single mode modulation of the recording materials. For practical application in high density data storage and also to enhance the multifunctionality of molecular devices, it is better to combine multiple physical channels (e.g. optical, electrical and magnetic multifunctionality) on a single device for recording and transmitting information.^{132–138} Furthermore, when two different physical channels are simultaneously involved, a new breadth of applications and even new fields of research often appear, such as optoelectronics, magnetooptics and spintronics.⁹⁴ As far as the recording medium is concerned, a molecule which can undergo different types of transformation, depending on the type of external

stimulus, can be expected for significant applications in multiple mode and complex information processing.^{66,139–140}

4.3.1. *SNOM–AFM coupled dual mode recording*

To overcome the diffraction limit of far-field optics, near-field optical technology has been developed. The application of SNOM for sub-100 nm recording has been demonstrated to be a good candidate for high density optical data storage.^{17,18,141} However, for SNOM, there exists a drawback of low light throughput, which involves a low data transfer rate and thus greatly limits its practical application. In this sense, STM/AFM which shows μs recording time gains a predominant advantage over SNOM,^{142–145} and the combination of merits of the probe recording technique and other data recording technologies has been a proposed issue in nanorecording. Kim *et al.*¹⁴⁶ presented a hybrid nanorecording system [the multifunctional probe recording (MPR) technique], which combines AFM recording and SNOM optical readout (see Fig. 13). In MPR, recording would be done with an AFM probe and optical reading with SNOM, all with a single, multifunctional probe. By using the MPR technique, the problem of the low recording speed of SNOM recording can be overcome. To demonstrate the feasibility of MPR, AFM recording and SNOM reading were carried out separately, where those authors made 50-nm-scale recording marks on gold films by applying 20- μs -long electric pulses to a conducting probe in AFM noncontact (NC) mode, and consequently used an SNOM to optically read them with 100 nm spatial resolution (see Fig. 14).

4.3.2. *TPE–STM coupled dual mode recording*

Recently, two-photon technology in 3D optical data storage has been widely used, owing to its ability to increase the dot density in a given material, where the excitation is only within a small region of the focus spot.^{13,14,147–149} In this method, the current optical memory density limit is overcome by introducing a Z-axis dimension to the recording process. Thus, the data are written not on the material surface (x – y space), but within the 3D volume of

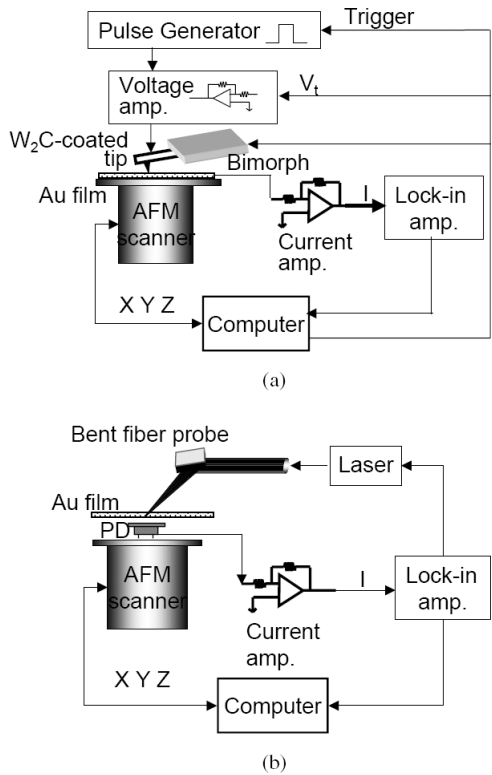


Fig. 13. Experimental layout of the multifunctional probe recording process; AFM recording part (a) and SNOM reading part (b).¹⁴⁶

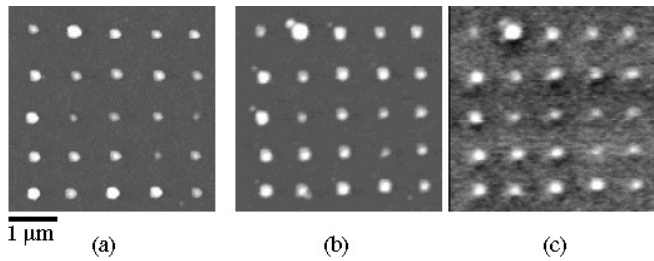
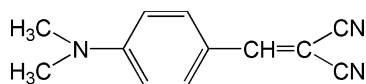


Fig. 14. AFM image (a), SNOM topography image (b) and SNOM optical transmission image (c) of recorded marks. The images are $4 \times 4 \mu\text{m}$ in size. The recording marks made by the AFM recording probe are perfectly reproduced by an SNOM reading probe. (Reprinted with permission from Ref. 146, © 2002, The Japan Society of Applied Physics)

the material. Systems that utilize multiple layer (or 3D) recording can achieve a recording density much higher than that in conventional 2D optical data storage devices. On the other hand, as we mentioned above, using STM, maximal areal density can be achieved. Based on the two points, in collaboration with Prof. A. D. Xia, we present a new strategy combining two-photon excitation (TPE) and scanning tunnel microscopy (STM) technologies for dual mode recording.¹⁵⁰ The recording medium is a stable organic molecule, 1,1-dicyano-2,2-(4-dimethylaminophenyl) ethylene (DDME), which is a conjugated system with a strong electron donor group, $-N(CH_3)_2$, and two electron acceptor groups, $-CN$. Its molecular structure is shown in Scheme 13. Based on our previous results,^{3,42,151–152} this molecule is a typical material possessing good electrical bistability, and can be used in nanoscale data recording by STM. Furthermore, this material shows intense absorption from 400 to 450 nm, which is very suitable for the recording wavelengths of blue laser (GaN) and femtosecond two-photon recording at 800 nm to increase the data density and readout resolution.^{153–155} Accordingly, nanoscale electrical data recording by STM and 3D optical information storage based on two-photon excitation have been achieved in the DDME thin films (Fig. 15). An analysis of the recording mechanism suggests that the optical- and electrical-responsive properties of the material could result from the same conformational change induced by light or electric field (Scheme 14), and therefore the data can be recorded and read optically and electrically. The specific ability to achieve multifunctional high density storage suggests that such a recording approach may have significant applications in novel recording technologies and multifunctional optoelectronic devices.

4.3.3. Magneto-optoelectronic trimode recording

In the context of the importance of multimode responsive molecules used for information processing and optoelectronic devices, Haddon and coworkers¹⁵⁶ reported that the electrical, optical and magnetic properties



Scheme 13. Molecular structure of DDME.¹⁵⁰

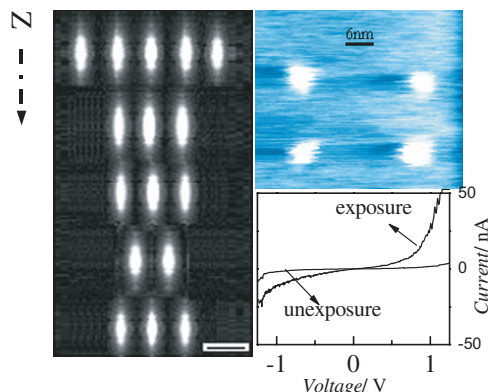
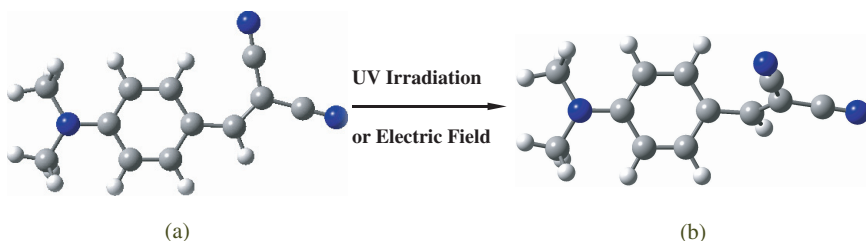


Fig. 15. Optical and electrical dual mode recording in DDME. On the left is five-layer optical storage, and on the upper right is nanoscale electrical recording.¹⁵⁰



Scheme 14. Recording mechanism of a DDME molecule by conformational change.¹⁵⁰

can be simultaneously switched between states in a phenalenyl-based neutral radical by thermal control of two neutral alkyl-substituted spiro-biphenalenyl radicals (see Fig. 16). By analysis of the bond length as a function of temperature, it is concluded that the location of the unpaired electrons were changed, and intradimer separation (indicative of molecular arrangement) varied from 3.2 Å to 3.3 Å with increasing the temperature, resulting the reduction of 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.

Although the compound simultaneously exhibits magneto-optoelectronic bistability, it has been pointed out by Miller¹⁵⁷ that such a compound is not

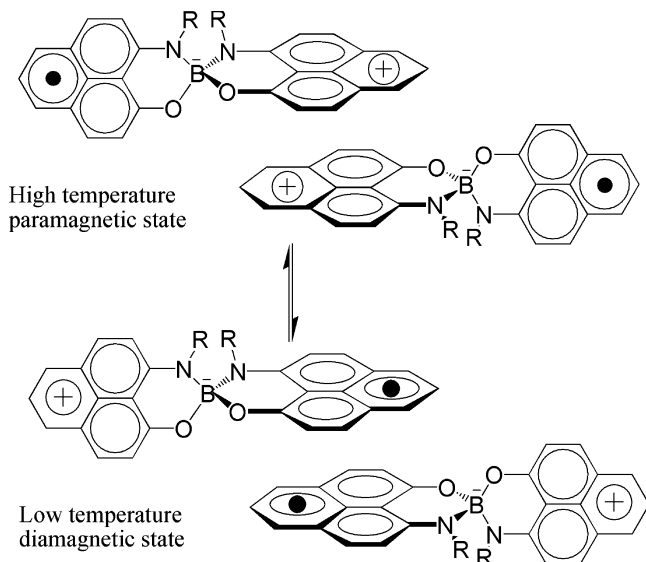


Fig. 16. Interconversion between the diamagnetic *p*-dimer (low temperature form) and the paramagnetic *p*-dimer (high temperature form) of ethyl radical 3.¹⁵⁶

a suitable candidate for next generation memory elements. Firstly, the three bistabilities are all based on thermal control, and such transformations limited by heat transfer rates are slow compared with electronically driven transformations. Secondly, the observed effects occur between 320 and 350 K; the temperature is too high to be considered for most practical applications. Thirdly, the absolute changes except for the conductivity change are too small, because there is often required an abrupt change of physical index for practical application. Even so, Haddon and coworkers have taken a big step with their demonstration that materials with three useful properties for future devices can be achieved.

5. Conclusion

In this chapter, we have reviewed the recent research on high density electrical information storage from the viewpoints of recording technologies and materials. SPM-based techniques represented by STM/AFM have been demonstrated to be powerful for conducting data storage on the nanometer

scale and/or molecular scale. However, limited by the slow writing/reading speed, this technique is still far from practical applications. To improve the speed, parallel recording techniques and crossbar nanocircuits were developed. Jumping from exploiting the charge property of electrons in conventional electrical information storage, a spin-based recording mechanism was proposed. Compared with conventional semiconductor devices, spin-based memory devices have the advantages of nonvolatility, high data processing speed, low electric power consumption and high integration densities. To overcome the shortages of electrical/optical storage and also to perform complex information processing, multiple physical channel techniques, such as the SNOM–AFM coupled recording technique and the STM–TPE coupled recording technique, were proposed. In such coupled techniques, the synergetic effect of different channels and characteristics in multifunctional recording media can be intensively exploited. As for recording media, organic materials, owing to their low cost, simplicity, good stimulus-responsive properties and versatility, have been proven to be promising candidates, and various kinds of organic recording media have been developed for electrical recording. Of particular interest are the systems capable of existing in more than two forms and that can be interconverted by more than one type of external stimulus. A molecule which can undergo different types of transformation, depending on the type of external stimulus, can be expected for significant applications in multiple mode and complex information processing. On the other hand, to promote their use in memory devices, further efforts should focus on the design and on developing materials and thin films which have better field-responsive properties, film-forming characteristics and fabrication compatibility. This imposes demands for a deep understanding of functional material design, the assembly technique, device fabrication and the recording mechanism. To achieve this broad interdisciplinary collaborations including chemists, physicists, materials scientists and electrical engineers will be required.

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CHAPTER 4

NANOSCALE DATA STORAGE

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This chapter reviews the development of nanoscale data storage, i.e., “nanostorage.” As a new storage system, the recording mechanisms of nanostorage may be completely different to those of the traditional devices. Currently, two types of materials are being studied for potential application in nanostorage. One is molecular electronic elements, including molecular wires, rectifiers, switches and transistors. The other approach employs nanostructured materials such as nanotubes, nanowires and nanoparticles. The challenges for nanostorage are not only the materials, ultrahigh data densities, fabrication costs, device operating temperatures and large scale integration, but also the development of the physical principles and models. There are already some breakthroughs in this field, but it is still unclear what kind of nanostorage systems can ultimately replace the current silicon-based transistors. A promising candidate may be a molecular-nanostructure hybrid device with sub-10 nm dimensions.

1. Introduction

In the previous chapters, the issues of ultrahigh density data storage have been reviewed from the viewpoints of magnetic, optical and electrical recording mechanisms, respectively. Although it has been proposed that silicon-based field effect transistors (FETs) could be scaled down to 10 nm, they will

face big challenges with leakage current, power consumption and random charge/fabrication fluctuations.¹ As predicted by Moore's law, fundamental change is needed in the way the present semiconductor-based electronic devices are fabricated by the year 2015, in order to maintain the current rate of increase in the circuit density (doubling every 18 months). In the last century, transition from one technology to another occurred several times in the information industry. For example, the mechanical relay was replaced by the vacuum tube, which was then substituted by the transistor. Subsequently, the transistor gave way to the current integrated circuit. For information storage in the future, we may need to develop nanoscale data storage devices with novel principles, materials, configurations and fabrication approaches.²

In recent years, many world's leading semiconductor companies and governments have been putting more and more funds into nanotechnology. According to a report by Nanomarkets Co.,³ by 2011, the market for nano-engineered information storage devices will be worth US\$65.7 billion. But analysis indicates that much of the present nanotechnology-related work on processing and logic is not likely to have a big commercial impact in a few years. Before nanotechnology have practical commercial application, conventional memory and disk systems will continue to exist, and major semiconductor suppliers will continue to hold the dominant position for a few decades. However, new companies may be created as the result of innovations in nanoengineered information storage devices and systems. Moreover, with the contribution of nanoengineered storage devices, pervasive, low cost and high capacity smart cards, sensors, mobile computers and communication devices will become commercially available. This will have a great impact on people's daily lives from the perspective of ultrahigh efficiency networks, mobile computing, and entertainment and communication devices.

Two approaches have been suggested and applied to fabricate nanoscale devices and systems, i.e., top-down miniaturization and bottom-up construction.^{4,5} For the top-down case, Feynman outlined in 1959: machines would make smaller machines, which would in turn be used to make even smaller machines, and so on.⁴ As an example, researchers have started to build devices at the single molecule level by using scanning tunneling microscope (STM)⁶⁻⁸ and other probe microscopy instruments.⁹ In contrast, Drexler suggested a bottom-up path in 1981, in which molecular machines would be constructed via the precise position and connection of

each molecular building unit in a designated location.⁵ For instance, it was proposed that monomolecular electronic devices may be possible with integration of wire, switch and/or storage units into a single molecule with memory and data storage functions.¹⁰

With these motivations, scientists from a variety of disciplines have been trying to fabricate suitable building blocks for such applications. Many prototypes of nanoscale devices have been demonstrated. Briefly, two kinds of building blocks have been investigated as active media for nanostorage. One is nanostructured materials such as nanotubes, nanowires and nanoparticles.^{11–16} The other is molecular electronic elements such as wires, polymers, dendrimers and biomolecules.^{17–22} Figure 1 shows a flow-chart reflecting a possible relationship between these different building blocks and nanostorage devices. Hopefully, the research may develop some effective and low cost ways to realize ultrahigh density data storage with dimensions down to sub-10-nm, which falls into the scale of a nanoparticle or a dendrimer molecule.

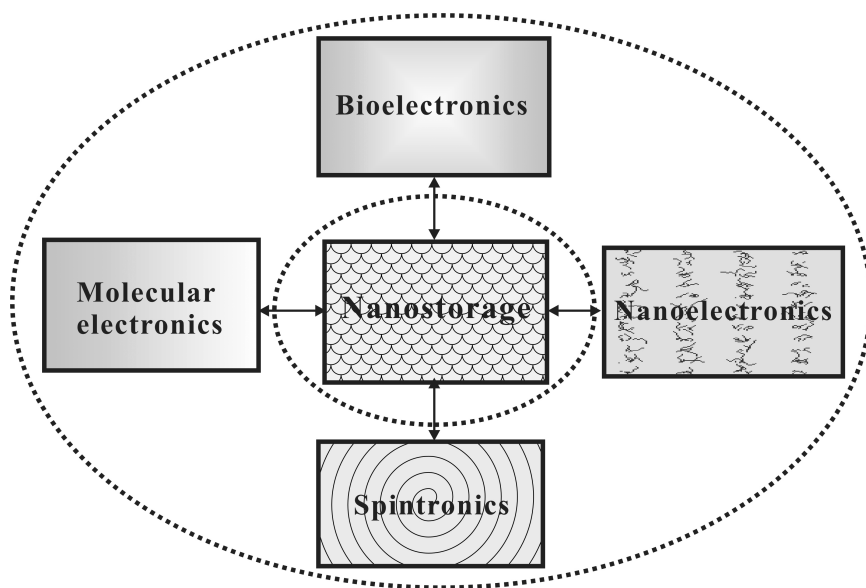


Fig. 1. Schematic diagram showing a possible correlation between nanostorage and various building blocks.

Doubtless that we need nanostorage devices in the “near” future, but it is still not quite clear how to get there.²³ What fabrication approaches and operating principles should be used to realize that effectively and inexpensively? The future nanostorage devices may not be limited to the configuration and the recording media/mechanism of the current devices. This chapter will mainly review the recent development of nanoscale data storage from the viewpoints of device fabrication and characterization. We first discuss the investigation of nanostorage devices on the basis of functional organic molecules. Then we focus on the memory devices based on dendrimers and biomolecules. Finally, other promising approaches and prospects are briefly discussed.

2. Molecular Electronics

Molecular electronics is one of the most promising nanostorage approaches, which has the potential to replace the current, semiconductor-based information devices.^{24,25} Weiss discovered in 1942 that charge transfer could happen in certain molecular complexes with electron donor and acceptor molecules.²⁶ Mulliken elucidated the quantum mechanics of these reactions 10 years later.^{27,28} In 1973, Ferraris and coworkers reported the preparation of a highly conductive organic complex between the electron donor tetrathiofulvalene (TTF) and the electron acceptor tetracyano-p-quinodimethane (TCNQ) with a TTF:TCNQ molar ratio of 1:1 (Fig. 2).²⁹ When highly purified TTF and TCNQ were codissolved in acetonitrile solvent, the 1:1 complex precipitated from the solution. Even when a large excess of TCNQ was used in the synthesis, only the 1:1 complex was obtained. Significantly, the UV spectrum of the complex in hexamethylphosphoramide solvent showed only the presence of the TTF radical and the TCNQ anion, while no absorption peak of neutral TCNQ was observed. The complex crystal has a layered structure with weak interactions between them. Such unique properties make the TTF–TCNQ complex an ideal example and impetus for studying highly conductive organic compounds with better structure than conducting complexes such as TTF^+Cl^- and M^+TCNQ^- .^{30,31}

Soon after the discovery of the TTF–TCNQ complex, Aviram and Ratner proposed a novel molecular rectifier based on a molecule with the

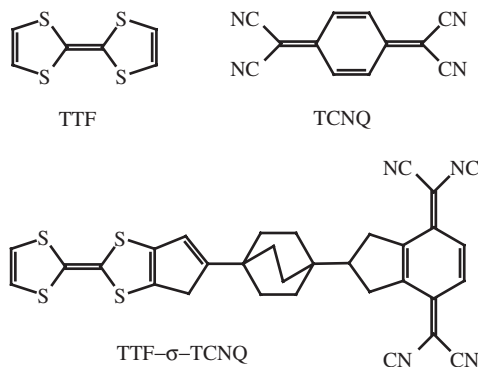


Fig. 2. Molecular structure of TTF, TCNQ and TTF-σ-TCNQ.

structure of donor-bridge-acceptor.³² As shown in Fig. 2, the molecule was designed based on TTF and TCNQ with a triple methylene bridge, i.e. TTF-σ-TCNQ. The bridge can effectively prevent interaction between the donor and the acceptor on the time scale of electronic motion to or from the electrodes in order for the device to function. They examined possible electrical rectification by looking at the current-voltage (I - V) characteristics of a single molecule connected with two metal electrodes. Both the sigma bridge and the two metal/molecule interfaces were treated as thin tunneling barriers. The shift of the device energy levels was then analyzed under forward and reverse bias voltages, respectively. The results suggested that it is possible to design molecules that have a larger threshold voltage for conduction in one direction than in the other direction at an appropriate device structure and bias voltage.

The true I - V performance of such molecular devices may be very complicated, due to other contributions to the current. These may include surface terms, direct passage due to inhomogeneous molecular layers, and direct electron tunneling between the electrodes. Several effects were neglected because of the calculation difficulty, including the direct energy transfer from donor to acceptor, electrode polarization and electron correlation. In fact, these effects are very complicated and difficult to understand and control even today, more than 30 years later. This is because it is technically very hard to unambiguously construct reliable and addressable single molecule-level metal-molecule-metal junctions,

to say nothing of their integration. As a result, the advance of molecular electronics is still far from practical application. However, researchers saw the promise of using single molecules as data storage media after the invention of the STM. Following the concept of TTF- σ -TCNQ, people have synthesized and investigated series of molecules with the structure of donor- σ -acceptor and donor- π -acceptor (Fig. 3).^{33–35}

Molecular electronic devices are classified in terms of molecular structure, device type, number of electrode terminals and state of the molecular media in Table 1. Two-terminal molecular junctions based on monolayers and single molecules are among the most important prototypes for nanostorage devices. In this chapter, we highlight how to construct addressable, reliable and nanoscale molecular junctions.

2.1. *Molecular junctions*

Previous studies of molecular electronics have been carried out using two-terminal device configurations, i.e. molecular junctions, where the electrical properties of the target molecules are characterized through current-voltage measurements. Various approaches have been proposed for the fabrication of molecular junctions, which can be classified as either solution-based or solid state junctions. As shown in Fig. 4, for the former case, the target molecules which are either vapor-deposited or self-assembled on a conducting electrode will be measured in electrolyte solution using a counter electrode. This method has the advantages of easy device fabrication and nondestructive characterization, and has therefore been widely used to study different molecular systems, with or without a third terminal. However, a serious disadvantage is that such molecular junctions cannot be used in practical applications, due to the problems of solvent effects, device integration and addressability.

In contrast, solid state molecular junctions have no such problems and thus have been intensively investigated. The fabrication methods are summarized in Table 2 from the aspects of junction size, addressability and temperature variability. The key findings are:

- (1) Although the fabrication of liquid metal droplet and crossed microwire junctions is simple, these microscale molecular junctions are neither stable nor addressable.

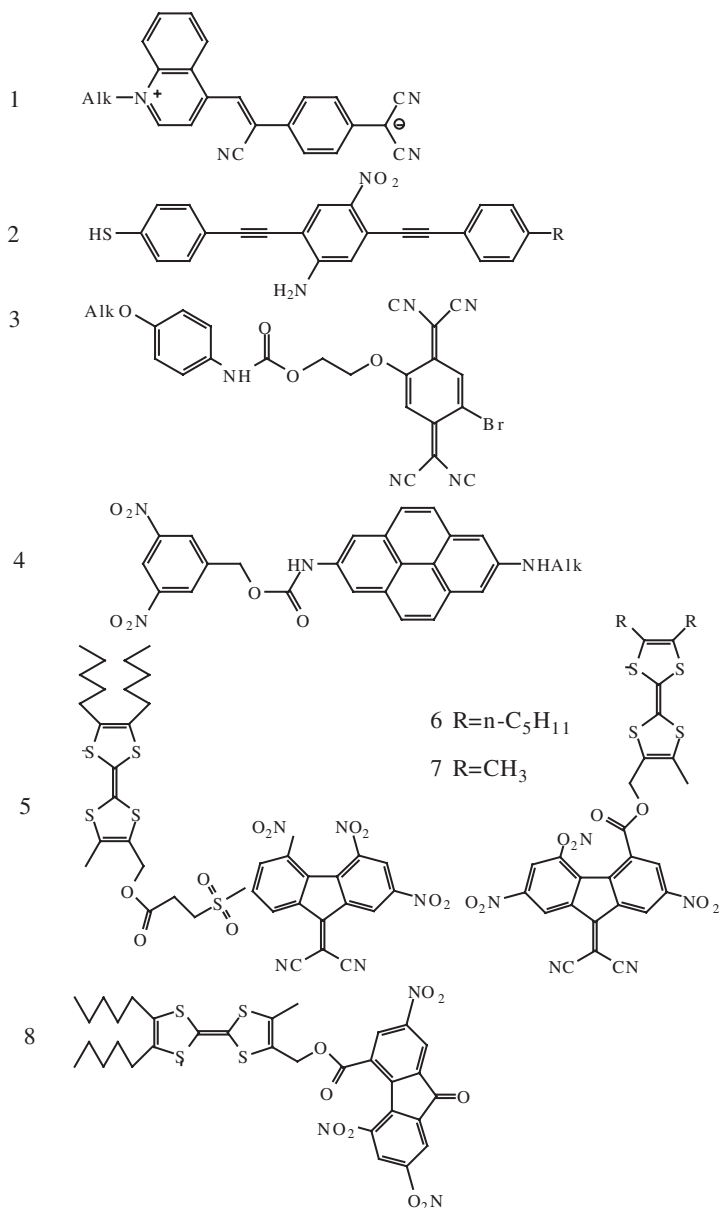


Fig. 3. Molecular compounds with donor- π -acceptor (1, 2) and donor- σ -acceptor (3–8) structures. Except for 2, all the molecules are designed with alkane chains for making Langmuir–Blodgett (LB) film.

Table 1. Classification of molecular electronics.

Material	Device type	Device terminal	Active media
Alkanethiols	Wires	Two-terminal devices	Gas
Alkanedithiols	Switches	Three-terminal devices	Solution
Conjugated molecules	Diodes	—	Thin film
Dendrimers	Transistors	—	Langmuir–Blodgett film
Polymers	Spintronics	—	Self-assembled monolayer
Metal–organic molecules	Cellular automaton	—	Pattern of molecule
Organic–inorganic hybrid molecules	Sensors	—	—
Biomolecules	—	—	—

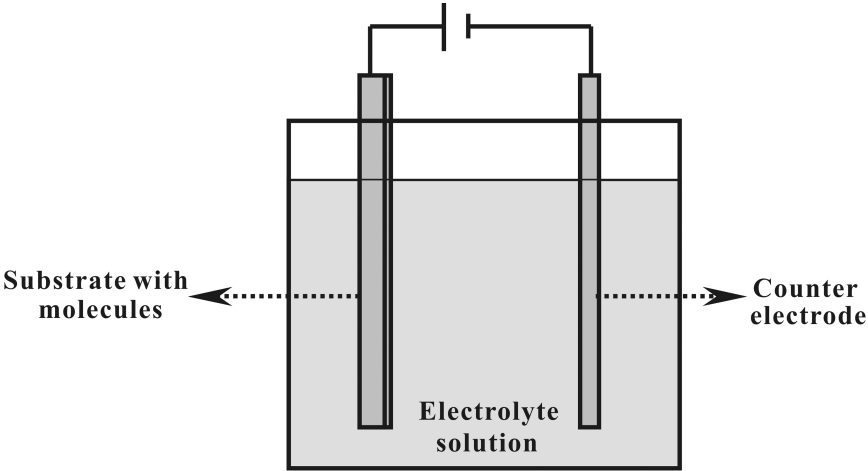


Fig. 4. Schematic cell structure of electrolyte-solution-based molecular junction.

Table 2. Fabrication approach and characteristics of various solid state molecular junctions. Here, “nano” is defined as a scale less than 10 nm.

Approach			Size (d)	Address	Var. T	Nano	References
Liquid metal droplet		Hg GaIn	50–200 μm	No	No	No	36–38 39,40
SPM tip	STM	STM tip	1~5 nm	No	No	Yes	41
		Nanodot coupled STM	1~5 nm	Yes	No	Yes	42
	CAFM	CAFM tip	5~50 nm	No	No	No	43
		Nanodot coupled CAFM	1~5 nm	Yes	No	Yes	44
Cross-bar	Magnetically controlled crossed wire		0.5–5 μm	No	No	No	45
	Lithography cross-bar		2–50 μm	Yes	Yes	No	46,47
	Stamp-printing cross-bar						48–50
	Crossed nanowire/tube		1~5 nm	Yes	Yes	Yes	51
Etched hole	Etched hole plus nanotubes		2~10 μm	Yes	Yes	No	52
	Nanopore		30~50 nm	Yes	Yes	No	53–55
Against nanowire	Electromigration		1~70 nm	Yes	Yes	Unknown	56,57
	Electrodeposited nanowire		1~50 nm	Yes	Yes	Unknown	58–63
	Mechanically breaking wire		1~50 nm	No	No	Unknown	64
Against nanoparticle	Nanoparticle bridge		1~5 nm	Yes	Yes	Yes	65

SPM = Scanning probe microscope

STM = Scanning tunneling microscope

CAFM = Conducting atomic force microscope

 d = Diameter

Var. T = Variable temperature

SAMs = Self-assembled monolayers.

- (2) The scanning probe microscope (SPM)-tip-based junctions will be useful in molecular scale data storage if the “addressing” issue can be solved.
- (3) The approaches of the cross-bar (both lithography and stamp-printing), nanopore and etched hole plus nanotube are applicable in characterizing the charge transport of molecular systems and probably have potential application in molecular devices with the scale between 0.1 and 10 μm .
- (4) The junctions based on electrodeposited nanowires and mechanically breaking wires are useful in characterizing nanoscale molecular systems. However, due to the “addressing” problem, it will be difficult to use these junctions in practical information devices.
- (5) Significantly, the junctions based on the crossed nanowire/tube and nanoparticle bridge can meet the requirements for nanostorage application from the viewpoints of device size, addressability and reliability. Therefore, we suggest that these technologies are worth further study.

We first discuss the development of SPM-tip-based molecular junctions, and then describe the cross-bar molecular junctions. Next, the approaches of the nanopore and etched hole are presented, which is followed by the discussion of breaking wire, electromigration/electrodeposited nanowire and nanoparticle bridge methods. Finally, the metal droplet method and the charge transport mechanisms are summarized.

2.1.1. *STM-tip-based molecular junctions*

One way to achieve nanoscale molecular junctions is to use STM-tip-assisted methods. STM cannot only image the surfaces of conducting or semiconducting materials with atomic resolution but also provide their electronic information via I - V measurements. There are two main device configurations for STM-tip-based molecular junctions (Fig. 5). One is tip-gap-molecule-substrate,⁴¹ the other is tip-gap-nanoparticle-molecule-substrate.⁴² The STM tip can be mechanically cut PtIr or Au wire or chemically etched tungsten wire. The substrate can be surfaces of single crystal metal or highly oriented pyrolytic graphite (HOPG). The molecular

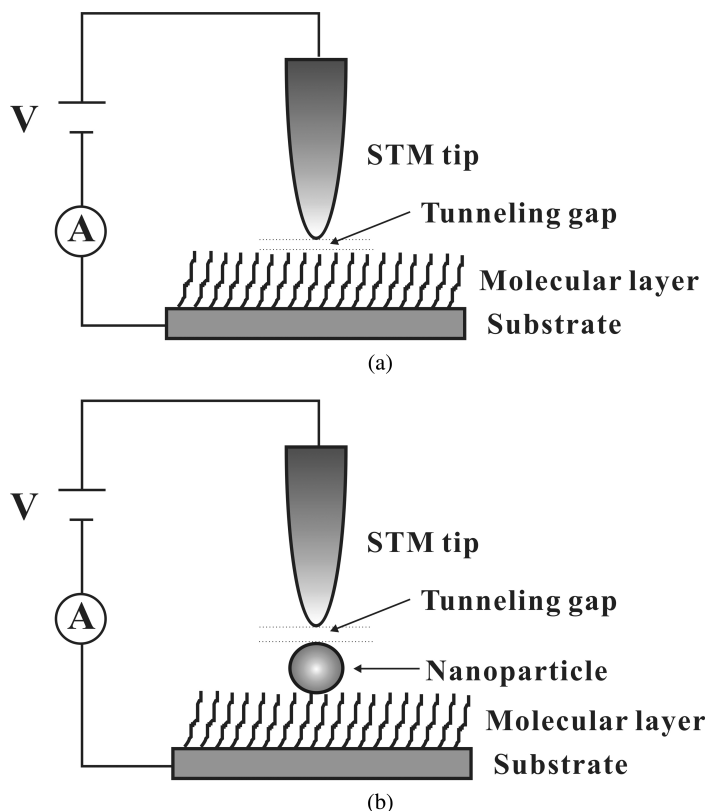


Fig. 5. Schematic structure of STM-tip-based molecular junctions (a) without (b) with coupled nanoparticle. Note that there exists a tunneling gap between the tip and the molecular layer or nanoparticle.

layer may be an SAMs, LB layer, or even a thin film. Obviously, it will be difficult to use organic thin films as the active medium in nanostorage due to the large roughness and poor uniformity.⁶⁶

To form a molecular junction, the molecule of interest can be self-assembled onto Au (111) surface via thiol–Au bonds, and the STM tip is then used to probe the electronic properties of the molecules. Single molecule-level junctions can be obtained with using a “nonconducting” molecular matrix technique, i.e. by inserting the molecule of interest into a relatively insulating molecular monolayer (e.g. dodecanethiol).⁴¹

However, owing to the thermal drift of the STM instrument, it is extremely difficult to measure the electrical properties of the same molecule for a long time. Therefore, such molecular junctions are not considered to be addressable and no data on I - V temperature dependence is available. Moreover, there exists a tunneling gap between the tip and the molecular layer. This tunneling gap can result in some nonmolecule-specific device performances such as electrical rectification.

Addressable single molecule junctions have been achieved using the nanoparticle coupled method, though there is no way to eliminate the tunneling gap between the tip and the particle. In this case, nanoscale metal clusters need to be covalently linked with dithiol-ended molecules. For example, Au clusters had been rigidly attached to a dithiolated molecular monolayer assembled on an Au (111) substrate.⁴² Moreover, a reliable approach to measure single molecule properties is to use the advantages of the nanoparticle coupled method and the insulating molecular matrix techniques.^{67,68} The nanoparticles and thus the dithiolated molecule of interest can be reproducibly addressed using a STM tip. But this does not guarantee the addressing and reproducibility of the junction, because the operation of the STM is extremely sensitive to the quality of the tip. If the STM tip adsorbs some contamination or even the molecule of interest, the measured electronic properties may be drastically affected and the consequent STM image might change a lot too. In an extreme case, if the tip is damaged by collision with the substrate, the target molecule will get lost. Obviously, such molecular junctions are not suitable for practical applications.

The STM has also been used to construct molecular break junctions. Tao and coworkers measured the conductance of single molecules using this method.^{69–71} Briefly, molecular junctions were created by repeatedly moving an Au STM tip into and out of contact with Au substrate in solution containing the target molecule (~ 1 mM). The breaking process was controlled by the feedback loop of the STM. Using this statistical method, the conductances of various molecular wires were calculated from histograms of the conductance curves. However, there are some problems associated with this approach. First, these break junctions are not addressable. Second, it is not known if double layer molecular junctions with the

structure of tip–SAM–gap–SAM–substrate were formed. This is because the experiments were conducted in solution with thiolated molecules, SAMs can form on the surfaces of both the substrate and the Au tip. Third, it is difficult to evaluate the effect of the chemical solvent on the device performance. Therefore, a modified STM-tip-based break junction method has been developed to deal with some of these issues.⁷² The main modifications were: (1) the molecular SAM was rinsed and blow-dried with nitrogen before any I – V measurements, while the molecule of interest was formed onto Au (111) surface from 1 mM ethanol solution; (2) the break junctions were measured under ultrahigh vacuum conditions; in this case, the solvent effect and the possibility of a double-layer junction can be excluded.

STM-tip-based atomic and molecular manipulation has been suggested for application in nanostorage too,^{73,74} but the problem of bit addressing still limits their potential applications.

2.1.2. CAFM-tip-based molecular junctions

Conducting atomic force microscopy (CAFM) is also used to study the electrical property of molecular wires. There are two approaches to achieve CAFM-tip-based molecular junctions (Fig. 6). One is to directly place the tip in contact with the molecular layer (e.g. SAM, LB or thin film) under a small load. Then the I – V data is collected at various applied forces and sites.⁴³ Unlike STM methods, there is no tunneling gap in the CAFM-tip-based molecular junctions, which may decrease the difficulty of analyzing the I – V data. The tradeoff is the big increase in the junction size as a result of the large radius of the CAFM tip (30–50 nm) as compared to that of the STM tip (a few angstroms). It was estimated that a CAFM-tip-based junction contains at least 50 molecules. Au nanoparticles were used to construct single molecule junctions with a combination of CAFM tip and molecular matrix techniques.⁴⁴ The junction size depends on both the nanoparticle diameter and the load of the CAFM tip. The molecular junctions based on the CAFM tip are unstable and difficult to be integrated with other devices. Moreover, it is impossible to investigate the temperature dependence of the molecular conductance using this approach, while temperature dependence data is critical for understanding the charge transport mechanism.

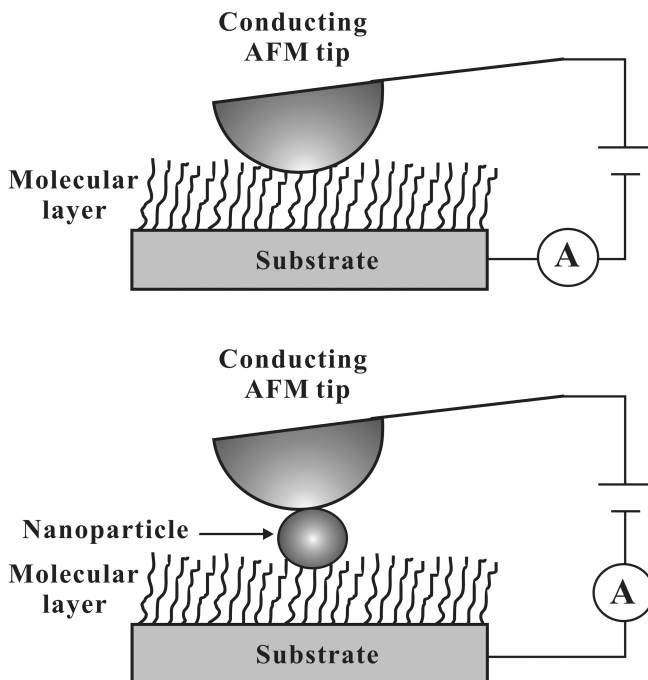


Fig. 6. Schematic representation of CAFM-tip-based molecular junctions without and with coupled nanoparticle, respectively. To form a molecular junction, a small force (~ 2 nN) has to be applied between the CAFM tip and the molecular layer/nanoparticle.

2.1.3. Cross-bar molecular junctions

Molecular junctions can be formed by two crossed metal wires; one wire is assembled with the target molecule. The electrical property of the molecules is investigated through I – V measurements under different conditions, such as variations in temperature, pressure and/or light irradiation. As demonstrated in Fig. 7, the cross-bar method may also be used to build a molecular junction array, which can be assembled and programmed to perform fast, powerful and reliable functions like data memory and communication with defect-tolerant characteristics.⁷⁵

As shown in Table 2, there are four approaches to making cross-bar junctions: magnetically controlled crossed wires, photolithography cross-bars, stamp-printing cross-bars and crossed nanowires/tubes. The simplest

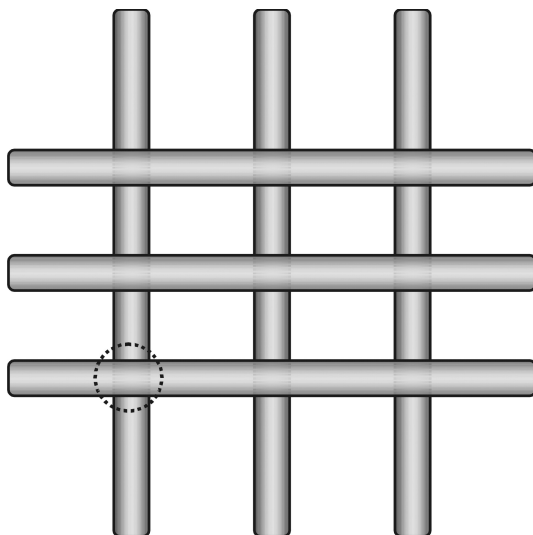


Fig. 7. Schematic representation of a 3×3 cross-bar junction array, with one outlined by the dashed circle.

junction is based on two crossed gold wires ($10\text{--}50\text{ }\mu\text{m}$ in diameter), with one of them modified with a SAMs of the target molecule.^{45,76,77} The wire spacing is controlled by Lorentz force: the d.c. current in one wire deflects it in a magnetic field. The deflection current is slowly increased to bring the wires into gentle contact and a junction is thus formed. Three different molecules have been tested using this method: 1,12-dodecanethiol (C12), oligo(phenylene ethynylene) (OPE) and oligo(phenylene vinylene) (OPV) (Fig. 8). The molecular conductance follows the trend of $\text{OPV} > \text{OPE} > \text{C12}$. However, these molecular junctions have some disadvantages in practical application, because they are neither addressable nor stable.

Addressable cross-bar junction arrays with an LB monolayer of **C20**, **DB** or **R** have been fabricated using the photolithographic technique (Fig. 8).^{46,47} The bottom electrode bars ($1\text{--}10\text{ }\mu\text{m}$ wide) and bonding pads ($>100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m}$) were formed by photolithography on silicon substrate with a thermal oxide layer (100 nm thick). The electrode surface was first cleaned using organic solvent and oxygen-reactive ion etching (RIE), and a molecular monolayer was then self-assembled onto it through the Au–thiol bond or LB technique. For the junction with an

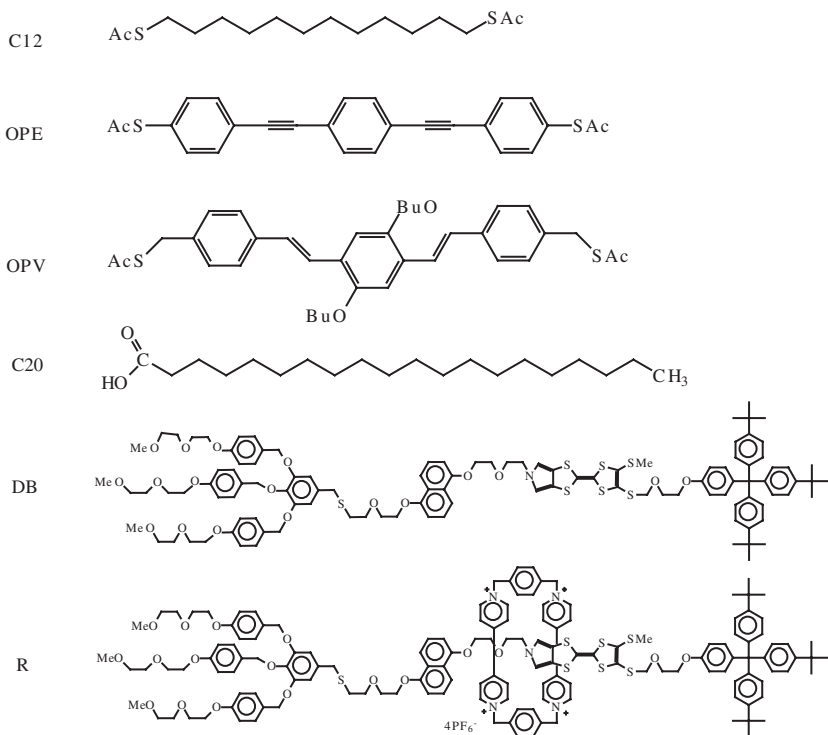


Fig. 8. Chemical structure of molecules studied using magnetically controlled crossed Au wires (C12, OPE and OPV) and photolithography cross-bar junctions (C20, DB and R).^{45–47}

LB layer, the bottom electrode can be a 100-nm-thick Al or Pt film.^{46,47} On the other hand, Au film with a 5-nm adhesion layer (Cr or Ti) is normally used in junctions with a self-assembled monolayer. To complete the fabrication, top electrode bars (5–20 μm wide) and bonding pads were evaporated through a shadow mask at the top of the molecular layer. To prevent metal filament formation, a 5-nm-thick Ti-reactive layer was deposited before the deposition of thick (50–100-nm-thick) Al, Pt or Au film.

The junctions were characterized through I – V measurements. Reversible electrical switching was observed from junctions with the structure: Al–LB monolayer of **R**–Ti–Al,⁴⁶ which was ascribed to an intrinsic property of the redox molecule **R**. It was later found that similar switching occurred in cross-bar junctions with nonredox-active molecules

(e.g. **C20**).⁴⁷ This suggests that the metal–molecule interface may play a significant role in such switching performance. On the other hand, there are some problems with this cross-bar method: (1) the deposition of the Ti-reactive layer may cause thermal damage to the organic monolayer; (2) the good-device-manufacturing rate is very low because of a pinhole-induced short circuit, especially if we consider the big size of the junction ($>5\ \mu\text{m}^2$); (3) it is difficult to decrease the junction size to a sub-10-nm dimension, due to limitations on scaling down the shadow mask.

An alternative way to fabricate the top electrode of the cross-bar junction is to use a solid state metal transfer technique. For instance, a poly(dimethylsiloxane) (PDMS) stamp-printing cross-bar method has been developed to make addressable molecular junctions with optoelectronic switching functions.⁴⁸ Figure 9 shows the fabrication procedure. Briefly, the cross-bar sample was made with the following steps:

- (1) The bottom Au electrode pattern was fabricated by photolithography. First, the Si (100) substrate, with 250-nm-thick SiO_2 on both sides,

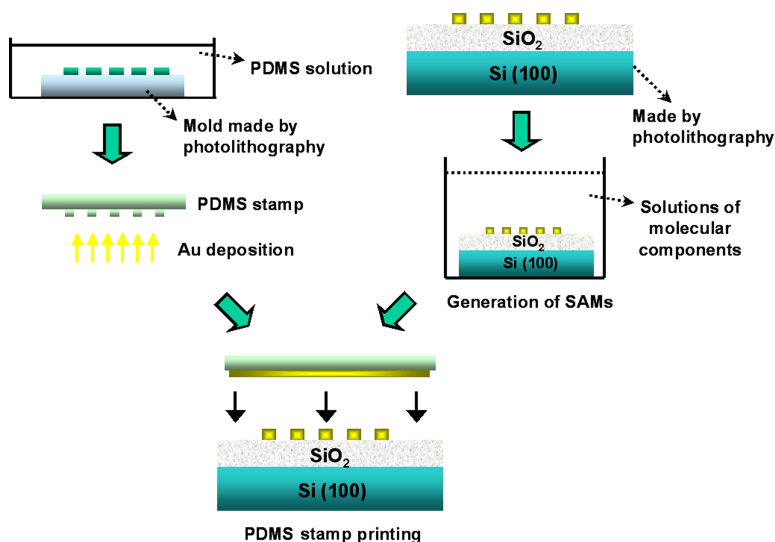


Fig. 9. Schematic diagrams for the fabrication procedure of molecular cross-bar junctions using PDMS stamp-printing technique.⁴⁸

was cleaned in a hot “piranha solution” (a 4:1 v/v mixture of concentrated H_2SO_4 and 30% H_2O_2) for 10 min, and this was followed by rinsing with deionized water, acetone and ethanol. *Caution: A piranha solution is a highly oxidizing solution that may react violently with organic materials.* Then, the gold pattern was defined on the substrate by photolithography and vacuum vapor deposition. The mask design and a scanning electron microscope (SEM) image of several junctions are shown in Fig. 10. The photolithography parameters are given in Table 3.

- (2) SAMs were formed on the gold bar surface by immersing the substrate in a 1 mM molecular solution in pure ethanol or tetrahydrofuran (THF) for 24 hr. The substrate was thoroughly washed in pure organic solvent and blow-dried just before stamp-printing. To reduce the number of monolayer defects, the SAMs of conjugated molecules were all made from a mixed solution with decanethiol in a molar ratio of 1 to 1.

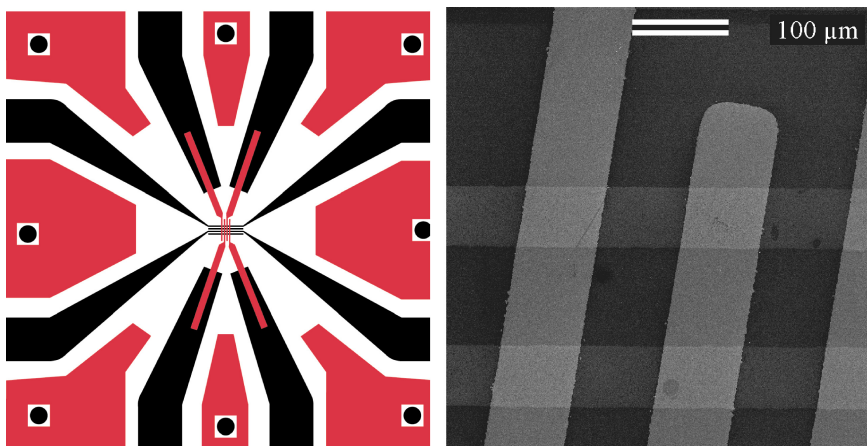


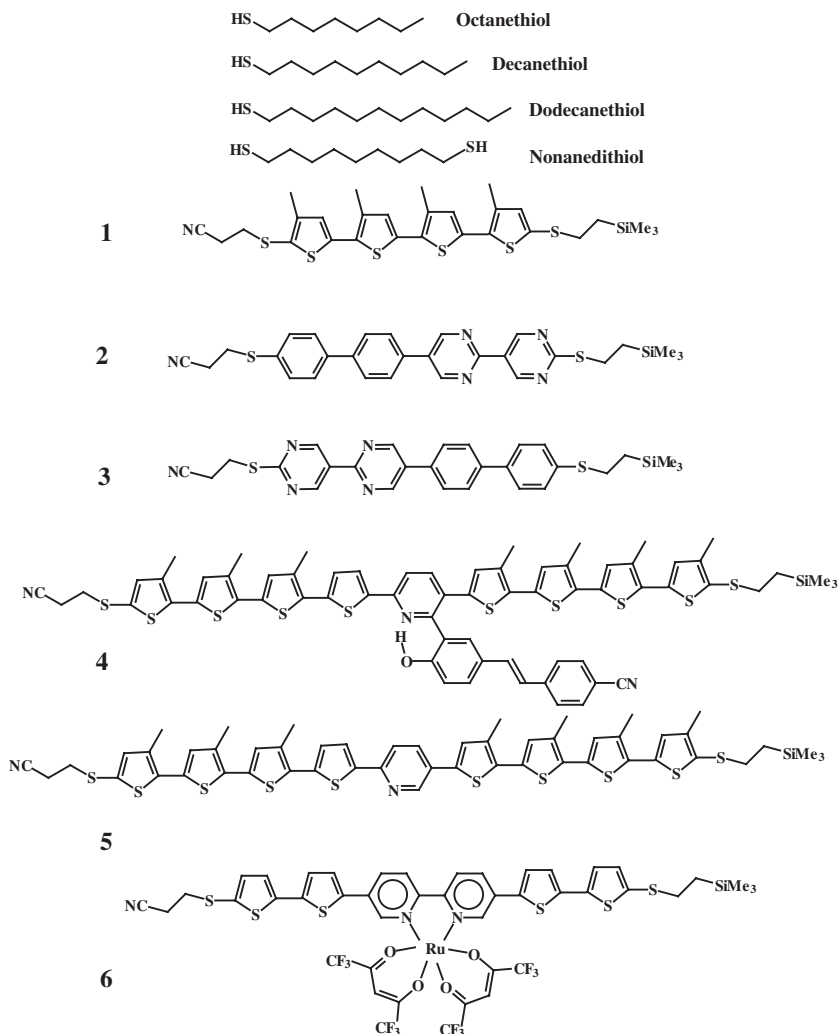
Fig. 10. Left: Schematic diagram of a mask design for a PDMS stamp-printing cross-bar experiment. The black color stands for the bottom electrode pattern defined using optical lithography, while the red color represents the top pattern printed by a PDMS stamp. Ohmic contacts between the printed Au bars and their bonding pads were ensured by a droplet of GaIn liquid metal through a sharp tungsten tip controlled by micrometer. Right: A SEM image showing several cross-bar junctions.⁴⁸

Table 3. Photolithography parameters for the fabrication of PDMS stamp-printing cross-bar junctions. Note that a temperature-increasing step is needed in the baking processes of negative photoresist.

Process	Photoresist patterns	
	For Au bars on Si (100) wafer	For PDMS mold
Photoresist	Positive resist S1813	Negative resist SU-8
Spin-coat	3.5 krpm, 60 s	3 krpm, 80 s
Soft-bake	115°C, 60 s	65°C, 120 s → 95°C, 300 s
Cooling	180 s	180 s
Exposure	60 s	85 s
Hard-bake	115°C, 180 s	65°C, 60 s → 95°C, 120 s
Cooling	180 s	180 s
Develop	45 s	90 s
Clean	Thoroughly rinse with deionized water flow and blow-dry with nitrogen	

- (3) The PDMS stamp was fabricated via casting and curing a prepolymer against a negative photoresist mold.⁷⁸
- (4) A 20 nm Au film was deposited onto the stamp (cooled by liquid nitrogen) using vacuum evaporation.
- (5) Under an optical microscope, the Au-coated stamp was brought into contact with the substrate Au bars in a perpendicular direction.
- (6) This stamp/substrate set was immediately loaded into a vacuum chamber and cooled down to 100 K for 10 min. After warming up, the stamp was carefully peeled off and the cross-bar junctions were obtained with good-device-manufacturing rate of 15%.
- (7) Lastly, the sample was wired and loaded into a vacuum chamber and the I - V characteristics were measured under different conditions.

Figure 11 shows the chemical structure of the molecular wires studied using the PDMS stamp-printing cross-bar approach. The molecules include not only alkanethiols (from C_8 to C_{12}) and alkanedithiols, but also conjugated wires with different chain lengths, molecular dipoles and/or metal cations. The I - V measurements were conducted under a high vacuum



condition and at temperatures from 95 to 300 K. Asymmetric I - V curves were observed for all the molecular junctions studied, which strongly depended on the temperature. The electrical performance of the cross-bar junctions was found to be extremely sensitive to optical illumination

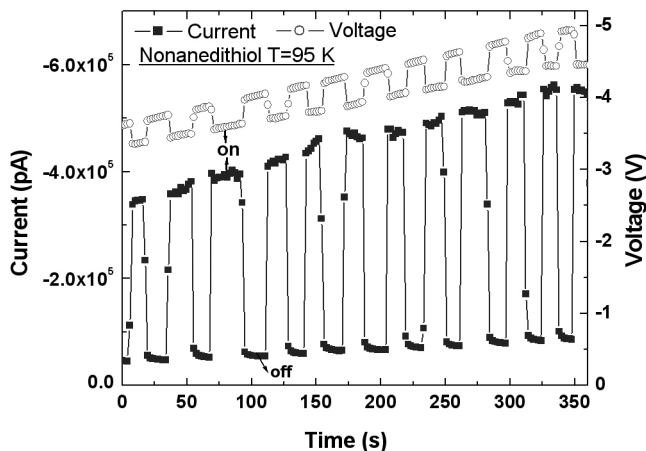


Fig. 12. Reversible optoelectronic switching of a 1,1-nonanedithiol cross-bar junction at the temperature of 95 K. The optical signal is fluorescent light with a wavelength of 400–700 nm.⁴⁸

despite wavelength variation (254–700 nm). Figure 12 shows the optoelectronic switching of a nonanedithiol junction under the stimulus of a fluorescent light signal. More interestingly, the conductance of the molecular junctions can be reversibly tuned by varying the light intensity,⁴⁸ which may make them serve as a prototype for optical gated molecular transistors. It is indicated that the switching is due to light-induced change of the tunneling parameters at the top PDMS-printed Au–molecule interface. The size of the molecular cross-bar junctions can be further scaled down to sub-50-nm using hard-stamp imprinting methods.^{79,80}

Cross-bar junctions comprising a LB monolayer of [2] rotaxanes **R** (Fig. 8) have been built using the nanoimprint lithography (NIL) technique, with device dimensions of 40 nm × 40 nm.⁴⁹ The imprint mold was fabricated into a 100-nm-thick SiO₂ layer grown on a silicon substrate by e-beam lithography (EBL) and fluorine-based reactive ion etching (RIE).⁸⁰ The oxide surface was patterned and etched to the form of 40-nm-wide nanowires connected by micrometer scale wires on each end to hundred-micrometer scale bonding pads. To make the bottom electrodes and bonding pads, 100-nm-thick PMMA (polymethylmethacrylate) film is spin-coated onto a silicon substrate with a 100 nm thermally grown oxide

layer. The mold and PMMA film are heated to 150–200°C, and then the mold is pressed against the PMMA substrate until the temperature drops below 105°C. After removal of the mold, oxygen RIE is used to etch the residual PMMA at the bottom of the trenches to expose the SiO₂ surface. Next, 10-nm-thick Pt nanowires (with a 5-nm-thick Ti adhesion layer) are fabricated using vapor deposition and lift-off techniques. A LB monolayer of **R** is then deposited over the entire substrate with the bottom electrodes, which is followed by a blanket evaporation of a 7.5 nm Ti protective layer onto the monolayer. Finally, the top perpendicular nanowire patterns (10 nm Pt/5 nm Ti) are prepared using the same imprint process. Electrical switching behavior was observed from the *I*–*V* measurements under ambient conditions, which has been proven to be independent of both the molecular structure and other molecule-specific properties.⁴⁷ Therefore, the switching may be related to the metal–molecule interfaces.

There are two problems with this imprint method. One is with the thermal deposition of the Ti protective layer. Though the Ti layer is very reactive with organic molecules, the thermally evaporated Ti clusters may still penetrate into the monolayer. This will consequently result in metallic filament formation owing to the defects and pinholes of the monolayer.⁴⁷ The other problem is with the imprint fabrication of the top electrode wires — the organic monolayer may suffer contaminations and/or damage in the procedures involving the PMMA spin-coating, the high temperature contact-imprinting, the oxygen RIE and the acetone lift-off.

To circumvent these problems, an improved imprint approach has been designed to fabricate molecular cross-bar junctions⁵⁰ (Fig. 13). First, a stack of 220 nm silicon nitride (Si₃N₄) films, 250 nm SiO₂ films and again 220 nm Si₃N₄ films are grown on a silicon wafer using low pressure CVD (chemical vapor deposition) and plasma enhanced CVD, respectively. A layer of imprint polymer is then spin-coated and patterned using an NIL hard-stamping mold. With this patterned polymer as a mask, CHF₃ RIE is used to etch down to the oxide layer and thus produce a patterned trench. The residual polymer and oxide are then stripped with acetone and etched to the bottom nitride layer with diluted HF acid, respectively. Note that underetching of the top nitride layer by about 400 nm is necessary to obtain a good device. The *I*–*V* curves of the 1-octadecanethiol SAMs show

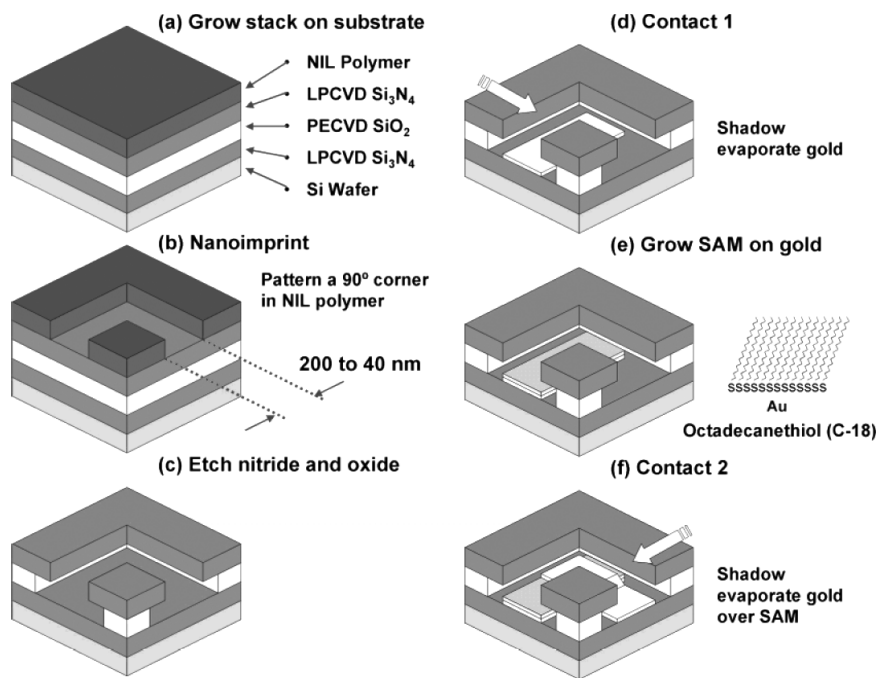


Fig. 13. Schematic fabrication process for a nanoimprint lithography cross-bar junction. (a) Initial stack on silicon substrate. (b) Nanoimprint lithography is used to make a pattern on the imprint polymer. (c) Form a trench using reactive ion etching and then use HF acid to selectively etch the SiO_2 . (d) Form the first electrode contact by shadow-mask deposition of Au in one trench. (e) Make an SAM of 1-octadecanethiol on the Au surface. (f) The second Au contact is deposited over the SAM down the other trench. (Reprinted with permission from Ref. 50, © 2003, American Chemical Society)

an electrical rectification with a value of about 2 at ± 0.8 V, which is claimed to be due to the extraordinarily different metal–molecule interfaces: one is a strong Au–thiol chemical bond and the other is weak physisorption. However, there is no temperature dependence I – V data for understanding the rectification mechanism.

One problem of this imprint method is that, although the substrate is cooled using a liquid nitrogen stage, the deposition of the top Au electrodes may induce thermal damage to the organic monolayer and consequently result in nanofilament formation and a junction short circuit.

This will lead not only to a very low good-device-manufacturing rate, but also to artificial effects in the devices.^{81,82} More critically, it will be very difficult to use this method to obtain cross-bar junctions with the dimension scale down to sub-10-nm.

The nanowire/nanotube cross-bar approach provides a promising way to fabricate addressable and reliable molecular junctions. It was demonstrated that molecular junctions can be made through a combination of carbon nanotube and shadow-mask-deposited Al electrodes (with a Ti adhesion layer).⁸³ But the microscale dimensions and the thermal deposition of the top electrode make this method unfavorable for application in nanostorage. Nanoscale molecular cross-bar junctions have been fabricated using the nanowire-assisted EBL technique.⁵¹ Briefly, large bonding pads and electrodes are first fabricated on SiO₂/Si substrate by photolithography. Then, EBL is carried out to write hundred-nanometer-scale electrodes with connection to the large ones. The next step is to self-assemble the target molecules onto the nanoelectrodes in solution. For the top electrodes, conductive nanowires with a diameter of 10–15 nm are spun onto the sample surface from a suspension of premade Pd nanowires in dichloroethane. Electrical switching and memory performances are observed in the cross-bar junctions with molecule 1, 2 and 3, respectively, while no similar behaviors are found in junctions with 4 or 5 (Fig. 14). It was suggested that the electron-retracting groups (i.e. nitro or pyridine) play a key role in the observed memory performance.

A concern is the electrical contact between the nanowire and the EBL-defined electrode with SAM. To eliminate the formation of double junctions, an AFM tip has been used to scratch the SAM off the electrode and expose the gold surface. However, it is doubtful if the loading force is big enough to scratch off molecules chemically bonded on Au surface. Even if there is no SAM between the nanowire and the scratched electrode, the contact is not guaranteed to be ohmic. Because the nanowires are spin-coated onto the substrate from solution, the interaction between the nanowire and the electrode is only weak physisorption. Another concern is how to make sure the nanowire suspension is free from undesired residues that may affect the good-junction-manufacturing rate and device performance to a great extent.

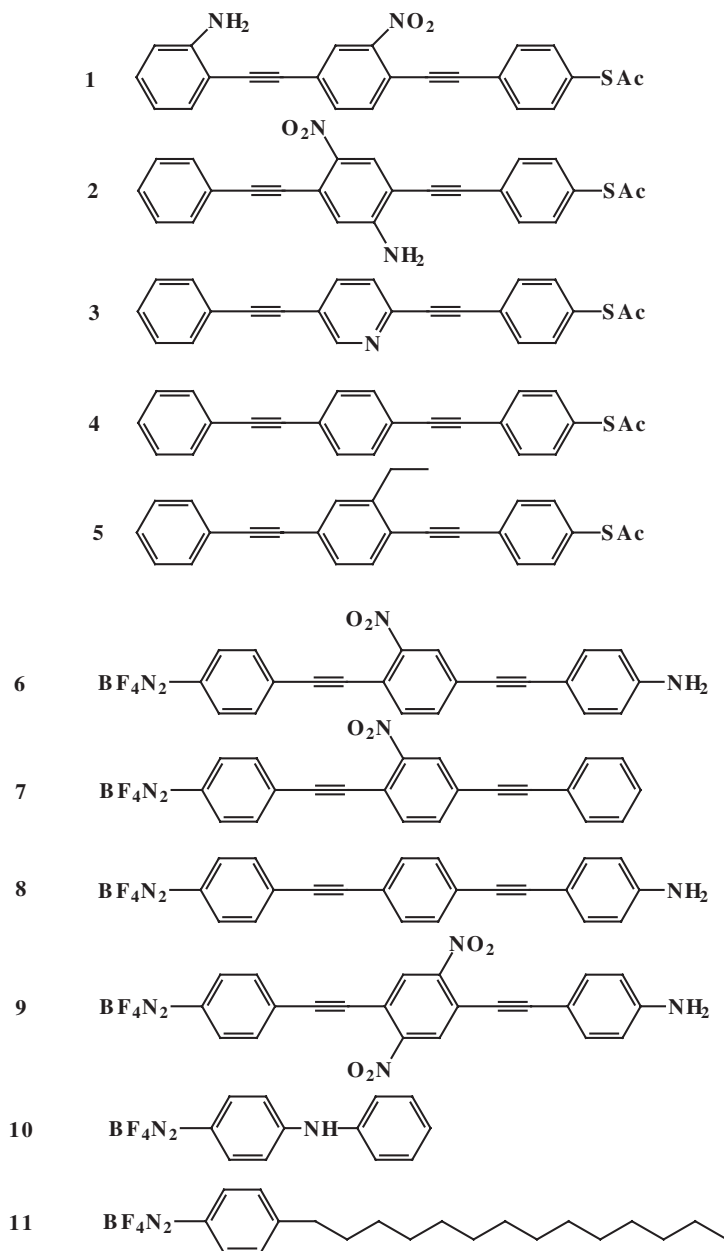


Fig. 14. Chemical structure of molecules tested using the approaches of crossed nanowires (1–5)⁵¹ and etching hole plus nanotubes (6–11).⁵²

Recently, an experiment revealed that no such electrical switching was observed in similar molecular junctions fabricated using a different method [Fig. 14 (6–11)].⁵² This observation clearly indicates that molecular junctions with a different size, electrode material and/or fabrication method may show tremendously different device performance. To make sure that all performances result from molecule-specific properties, rather than other factors, we need to examine the target molecule using different fabrication approaches. A single molecule-level junction is helpful in eliminating most nonmolecular factors. As shown in Fig. 15, this can be realized using a nanowire and/or nanotube crossbar configuration. The target molecule can be self-assembled onto a sub-10-nm Au wire connected with large bonding pads, and then another bare Au nanowire is perpendicularly placed on top. In this case, the junction may be so small that it contains just one or two molecules. Experimentally, it has been shown that addressable crossed nanowire/tube arrays can be successfully constructed using different methods.^{11,84–88} Theoretical simulations were performed to assess the prospective performance of a 16 Kbit crossed nanowire nanomemory system.⁸⁹ The results suggested that such a nanomemory system can operate at a density of no less than 10^{11} bits/cm². To solve the problem of double junctions, the molecule of interest can be controllably deposited on the desired locations of the nanowire/tube using techniques such as dip-pen nanolithography and the stamp-printing method.^{90,91}

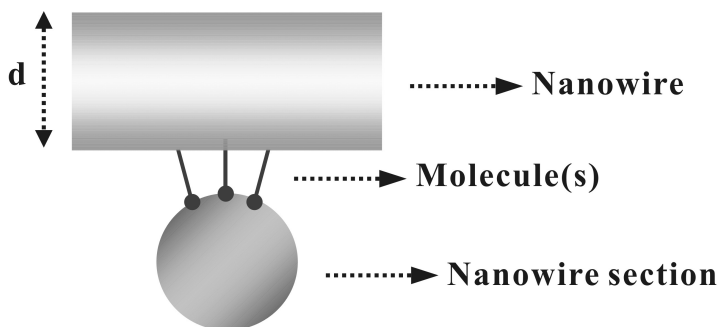


Fig. 15. Schematic diagram of a crossed nanowire molecular junction. The nanowire diameter (d) should be less than 10 nm.

2.1.4. Etching hole plus nanotube and nanopore molecular junctions

A silicon–molecule–nanotube approach has been developed as a testbed for fabrication of metal-free molecular junctions, i.e. the etching hole plus nanotube method.⁵² It is designed to circumvent the problems of thermal damage and metal filament formation in the monolayer induced by thermal deposition of the top electrodes. The junctions are fabricated on highly doped *n*-type Si(100) substrate ($< 0.005 \Omega$) with a 200 nm thermal oxide layer. First, Au bonding pads (200 nm thick, with a 20 nm Ti adhesion layer) are made on the substrate by photolithography. A second photolithography step is followed to form circular well patterns (5–20 μm in diameter) between the pads. The wells are then wet-etched down to the doped Si layer in a buffered oxide etch and this affords a H-passivated Si surface. A molecular monolayer is thereafter self-assembled in the well via a direct Si–arylcarbon bond.⁹² Figure 14 (6–11) shows the chemical structure of the molecules studied. A purified carbon nanotube mat is deposited from a suspension in chloroform onto the top of the well region to make an electrical connection to the neighboring Au pads. A 200 nm Au film is sputter-coated on the back side of the silicon substrate to serve as the bottom electrode. Finally, the device's *I*–*V* characteristics are collected at different temperatures in a cryostation.

Although this metal-free method can avoid thermal damage to the molecular monolayer and metal filament formation in the monolayer, there are some other problems with the junction. One question is about the electrical contacts between the Au pads and the carbon nanotubes. Are they ohmic or nonohmic contacts? What is the effect of these contacts on the electrical performance of the molecular junctions? The other problem is that the actual “effective” junction size is unknown owing to the uncertainty of the contacting area between the nanotube mat and the molecular monolayer. This is true especially if we take into consideration the comparison of the ultrathin monolayer with the roughness of the nanotube mat.

A nanopore approach can overcome these problems.⁵⁴ As shown in Fig. 16, arrays of 30–45-nm-diameter pores are opened in suspended SiN membrane deposited on a Si wafer using EBL and plasma etching.^{53–55,81} Gold film is evaporated from the bottom side to fill the bowl-shaped pores. Then, the sample is immediately immersed in millimolar molecular

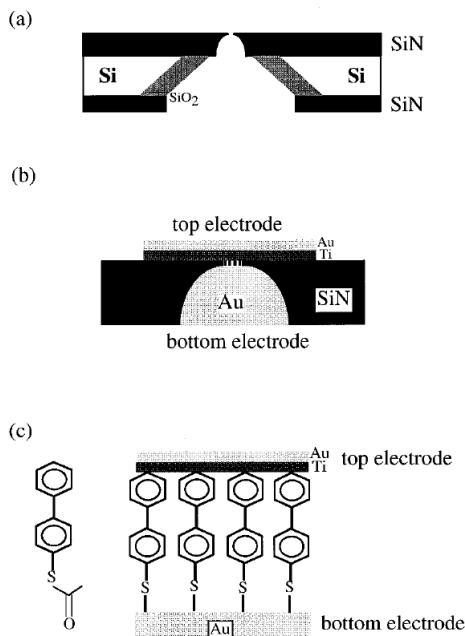


Fig. 16. Schematic diagrams of the fabrication process of a nanopore junction. (a) Cross-section of a nanopore (30 nm diameter) etched in suspended SiN membrane. (b) Molecular sandwich structure of Au-Ti-molecule-Au. (c) Chemical structure of 4-thioacetyl biphenyl and detailed structure of the junction. (Reprinted with permission from Ref. 53, © 1997, American Institute of Physics)

solution in pure ethanol for 24 hr under the protection of inert gas. After being thoroughly washed with ethanol and blown dry with nitrogen, the sample is transferred into a vacuum chamber to deposit the top electrode, which can be either a Ti/Au (4 nm/80 nm) bilayer⁵³ or a pure Au (200 nm) film.⁵⁵ Meanwhile, the sample has to be kept at liquid nitrogen temperature to minimize the thermal damage to the SAMs and prevent metal filament formation. Different molecules have been tested using this method, including 4-thioacetyl biphenyl (Fig. 16), 1-octanethiol, 1-decanethiol and 1-hexadecanethiol.^{53,55}

Molecule 2 in Fig. 14 has also been studied using the nanopore method, in which electrical switching and negative differential resistance behaviors are observed.⁸¹ However, it was later found that such

performances are probably due to the metal–molecule interfaces and/or metal nanofilament formation.⁸² This reminds that the device performance of a molecular junction strongly depends on the local environment, including the electrode–molecule interface, fabrication method, temperature, humidity, optical illumination and intermolecular interaction. Before these problems can be solved, it will be very difficult to discuss which, or what kind of, molecules are more suitable for practical application. Actually, it is for this reason that we limit this review to the issue of nanostorage device fabrication rather than to the molecular materials and devices mechanism.

2.1.5. *Mechanically breaking wire, electromigration-induced breaking wire and electrochemically deposited nanowire junctions*

Charge transport through the molecular junction of benzene-1,4,-dithiol has been investigated using the mechanically breaking wire approach in 1997.⁶⁴ The experiment is conducted at room temperature, with a notched micrometer scale gold wire immersed in 1 mM molecular solution in THF. The wire is glued onto a flexible substrate held by two mechanical supports. An atomically sharp tunneling gap can be established after the notched wire is fractured by a counter piezo element. The electrical measurements are conducted after the THF is evaporated under an argon atmosphere. Due to the thermal gradients induced by THF evaporation, the tunneling gap of the break junction will be disturbed. The tips have to be withdrawn and then carefully moved together to an onset of conductance before any I – V measurements (Fig. 17). This withdrawing/returning process can be repeated many times to test the reproducibility of the experiment. The break junction is neither stable nor addressable. As a result, it is impossible to measure the effects of temperature, pressure or optical illumination.

As shown in Fig. 18, there are some alternative ways to solve the above problems. One method is to fabricate molecular junctions by passing a large electrical current through a gold nanowire pattern defined by EBL. The current flow causes the electromigration of gold atoms and consequently the breakage of the nanowire at the narrowest site with a separation of about 1 nm.⁵⁶ This is known as the electromigration

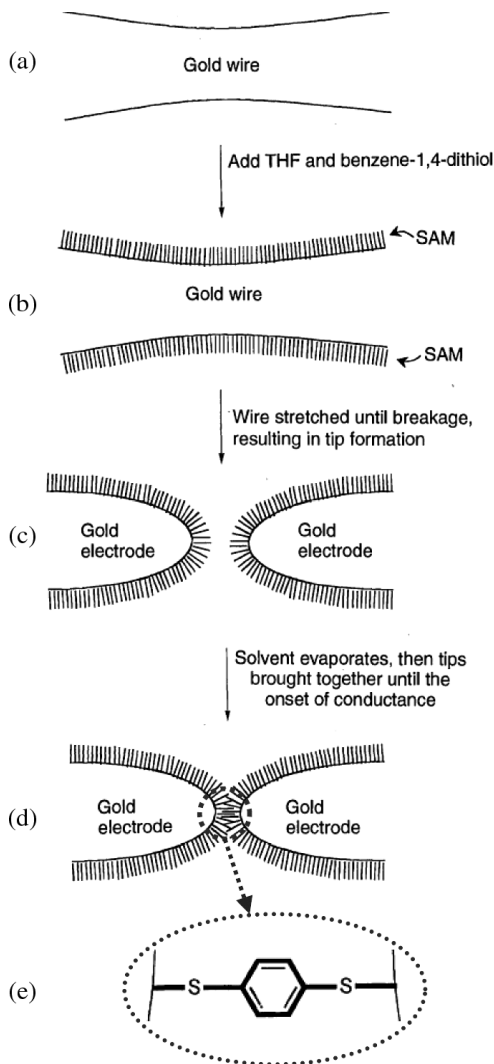


Fig. 17. Schematic process of break junction formation. (a) Thin Au wire with an etched neck. (b) SAMs formed on the wire surface after adding the molecular solution. (c) Mechanical breakage of the wire and SAMs formed onto the surfaces of the Au tips. (d) After evaporation of the THF, the tips are carefully brought together to the onset of conductance to collect I - V data. (e) A benzene-1,4-dithiol is schematically bridged between two gold electrodes. The processes (c) and (d) can be repeated many times to test the reproducibility of the experiment. (Reprinted with permission from Ref. 64, © 1997, AAAS)

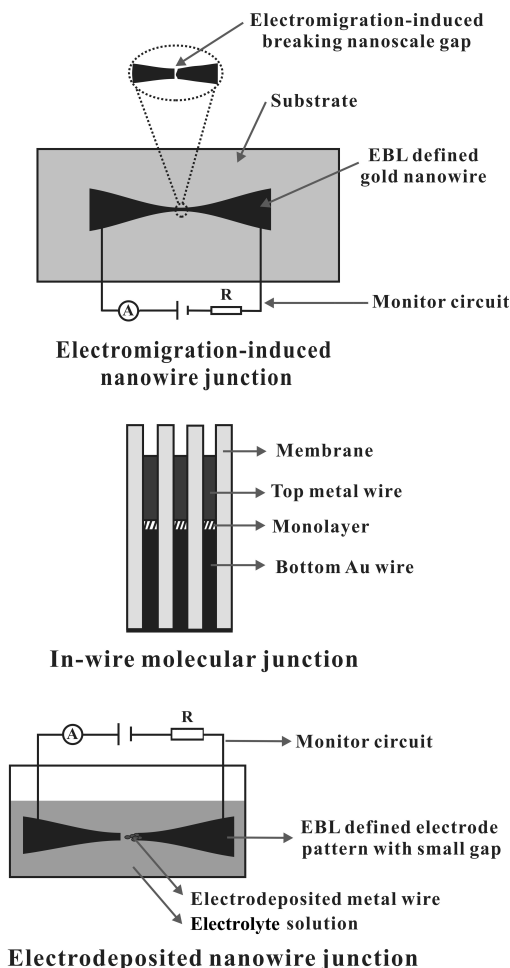


Fig. 18. Schematic setups for fabrication of nanowire molecular junctions. For the electromigration method, a gold wire pattern with a narrow neck is first defined by e-beam lithography and then a high current flow is used to induce a nanoscale gap (~ 1 nm) (no solution is needed in this step).⁵⁶ For the case of an in-wire junction, a polycarbonate membrane with 70-nm-diameter pores is employed as a template to grow the bottom half Au nanowire, the molecular monolayer and the top half nanowire, respectively. The nanowires are released by dissolving the membrane before I - V characterizations.⁵⁸ For an electrodeposited nanowire junction, a gold electrode pattern with a small gap (100 nm to 2 μ m) is first fabricated on a substrate. The gap is then decreased through electrochemical deposition of metal atoms on one of the electrodes in electrolyte solution. The gap distance is controlled by monitoring the junction resistance.^{59,60,62}

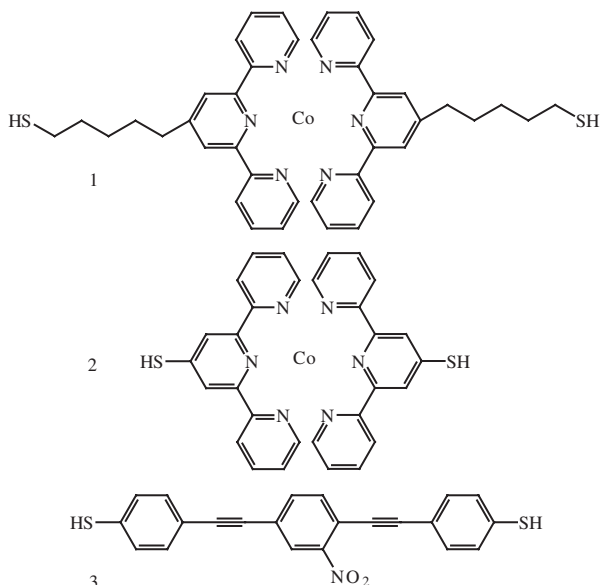


Fig. 19. Chemical structure of the molecules characterized using the electromigration nanowire junction approach.

breaking wire method. It has been used to measure the conductance of CdSe nanocrystals,⁵⁶ C₆₀,⁵⁷ C₇₀, and several other molecules shown in Fig. 19.^{93,94} The key issue for a successful experiment is to control the gold nanowire thickness to sub-20-nm. This can be realized by creating a 200-nm-wide PMMA resist bridge suspended 400 nm above the substrate at the neck part of the EBL-defined nanowire (indicated by the dashed circle in Fig. 18). EBL on a PMMA/P(MMA-MAA) bilayer resist is employed to produce a bridge through the undercutting effect, i.e. the different developing rates of the two kinds of resist layers. Then $\pm 15^\circ$ angle (with respect to substrate normal) evaporations are conducted to generate a gold nanowire with a thickness less than 20 nm. Finally, a thick metallic film is vapor deposited straight down through the bridge to make a good connection between the nanowire and the bonding pads. The advantage of this approach is that it does not use any organic solution in the process of the nanoscale gap formation, although the resist bridge fabrication and angle deposition make it complicated to some extent.

However, as a big challenge, the junction is difficult to scale down to sub-10-nm widths. Another challenge is the integration of individual junctions into functional systems.

The other method is to use electrochemical deposition to fabricate nanowire junctions. A pair of planar electrodes with a gap between 50 and 2000 nm is first made using EBL. Electrochemical deposition is then applied to shrink the gap to a sub-10-nm scale by applying a bias voltage between the electrodes in electrolyte solution. The gap distance is controlled through *in situ* monitoring of the resistance between the electrodes.⁶² The molecule of interest is then assembled into the nanoscale gap from molecular solution to measure the I - V characteristics. Different nanowire (such as Au, Cu and Pt) junctions can be made using this technique.⁵⁹⁻⁶³ It is simpler than the electromigration method, since no resist bridge and angle depositions are needed. As a tradeoff, the junction has to be fabricated in the presence of solvent, which may introduce some problems into the device performance.

The in-wire junction method has also been used to fabricate molecular junctions.^{58,95} A track etched polycarbonate membrane with nanopores (40–70 nm in diameter) is used as a template to make the junction. First, a 100-nm-thick Au film is vapor-deposited on one side of the membrane to serve as the cathode. Then, Au is plated at a constant potential into the nanopores from electroplating solution using a three-electrode electrochemical cell. The molecule of interest is self-assembled onto the surface of the Au nanowires inside the pores from 0.5–1.0 mM molecular solution in pure ethanol under an inert gas atmosphere for 24 hr. The monolayer is then capped with Pd or Ag seeding nanoparticles through electroless plating. Finally, the top portion of the pores is filled with the second half Au nanowires using electrochemical deposition again. The nanowires are released by dissolving the membrane. For I - V measurements, individual nanowires are positioned between EBL-defined electrode patterns using electrofluidic assembly.

Although molecular junctions can be made using this nondestructive in-wire electrodeposition method, there are some important issues that need to be addressed. First of all, as compared to the other two methods, it is not easy to assemble these nanowires on a large scale between the electrode patterns predefined by EBL. Second, the electrical contacts

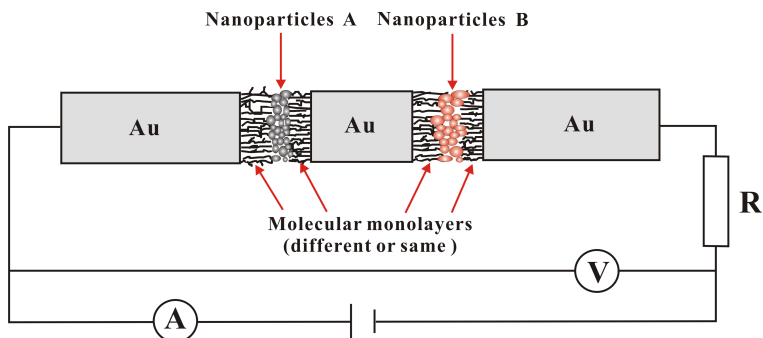


Fig. 20. Schematic setup of a nanoparticle-coupled multiple molecular junctions fabricated within a single nanowire.

between the nanowires and the EBL-defined electrodes are not well controlled. These wires just loosely reside on the electrode surface and they are not necessarily ohmic contacts. This may result in extra-high contacting resistance and consequently low power efficiency. Third, it is difficult to scale the junction dimensions down to sub-10-nm due to limitations imposed by the template pore size. Another big challenge is how to eliminate the contamination induced by the presence of electroplating solution during the nanowire preparation and electrofluidic assembly. Moreover, there is doubt about the monolayer quality, because it is difficult to thoroughly wash the molecular monolayer inside the pores.

However, hope emerges from these works. As shown in Fig. 20, if we can assure extra-clean solutions and solve the problems associated with the molecular assembly and electrode contact, then with utilizing a combination of techniques,^{96–99} we may develop nanoparticle-coupled multiple molecular junctions in a single nanowire. If this design can be experimentally realized, it might be an important step toward the generation of biomolecule–nanostructure hybrid nanostorage systems.

2.1.6. Nanoparticle-bridged molecular junctions

Conductance of single conjugated molecules has been measured using nanoparticle-bridged molecular junctions.⁶⁵ The basic concept of this method is schematically shown in Fig. 21 (top). Colloidal Au nanoparticles

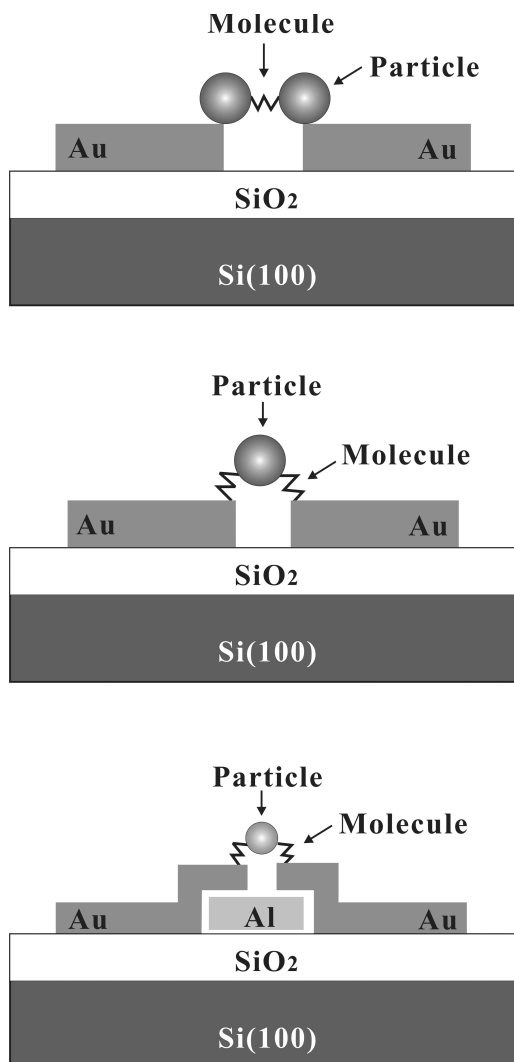


Fig. 21. Schemes of a nanoparticle-bridged molecular junction with the structure of (top) dimer and single particle (without (middle) or with (bottom) Al gate electrode). For particles with the diameter larger than 40 nm, the Au electrode pattern can be fabricated using e-beam lithography. Otherwise, the gap between the electrodes has to be further shrunk by electrodeposition or electromigration before electrostatic trapping a sub-10-nm scale nanoparticle. An aluminum film with a thin oxide layer can be used as the gate electrode in a three-terminal molecular electronic device. Note that extra interfaces (either electrode–particle or particle–molecule) are introduced into these molecular junctions.

with relatively large diameters (10–50 nm) are first prepared using a modified chemical method.¹⁰⁰ The next step is to synthesize dimers with the structure of two gold particles connected by a dithiolated molecule, which is realized by mixing a solution of the dithiolated molecule with the gold colloid but keeping the molecule: particle molar ratio below 1:10. The dimeric Au particles are then separated from other particles and oligomers by centrifugation. Then, electrostatic-trapping is performed by putting a drop of the dimer solution on EBL-defined Au electrode patterns with gaps of 40–50 nm, while an a.c. voltage of 0.8 V at 10 MHz is applied between the gaps. The samples are then cleaned with distilled water, organic solvents, and blow-dried in nitrogen before I – V measurements. The trapped colloid structure can be examined using SEM imaging after the electrical measurement. The molecular junctions made by this approach are nanoscale and addressable, but two new nanoparticle–electrode interfaces are introduced into the junction. These extra interfaces will inevitably affect the device performance and make it difficult to analyze. Moreover, there is a lack of clarity about the device stability because of the weak physisorption between the particle and the electrode. Similar junctions can be made by electrostatic-trapping a single nanoparticle in the gap of a nanowire pattern produced by the electromigration and electrodeposition methods.^{56,62} There are still four interfaces in these electrode–molecule–nanoparticle–molecule–electrode junctions (Fig. 21, middle and bottom), although the device stability can be greatly improved because the nanoparticle is strongly bonded to the electrode through dithiol linker molecules.

2.1.7. *Liquid-metal-droplet-based molecular junctions*

A simple low cost way to fabricate molecular junctions is the liquid metal droplet method, although the junctions are usually microscale, unstable and not addressable. Figure 22 shows the molecular junction with the structure of liquid metal tip (Hg or GaIn), molecular layer and base electrode on supporting substrate. A molecular junction is formed when the “tip” and the electrode are slowly moved together using a micro-manipulator. The active medium can be a molecular self-assembled or Langmuir–Blodgett monolayer,^{33,36,101} bilayer,^{37,38,102} or even a thin

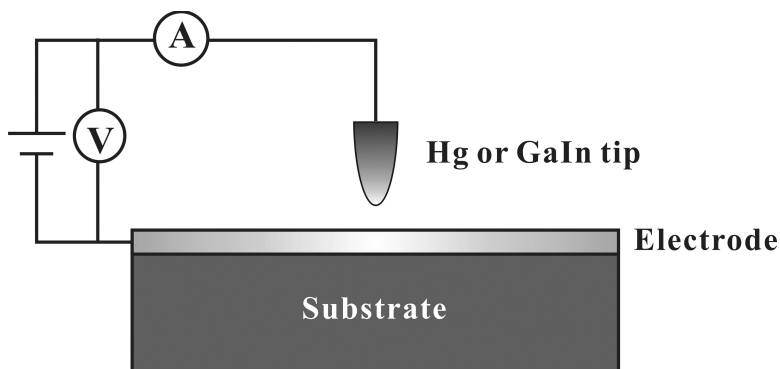


Fig. 22. Schematic setup of a liquid-metal-droplet-based molecular junction, in which the target molecule (not shown) is assembled onto the surface of the bottom electrode and/or the top tip. A bilayer junction is formed if both electrodes are covered with monolayers. The base electrode may use Au, Ag, doped Si with or without native oxides, or even a Hg droplet. In some experiments, the junctions are measured in solution. A junction is formed when the droplet and the electrode are brought into contact with each other through slowly moving either the droplet or the substrate using a micromanipulator. The bias direction could be switched back and forth for studying the charge transport mechanism.

film.³⁹ For bilayer junctions, the surfaces of both the tip and the electrode are covered with SAMs with the same or a different molecular structure. Multiple-layer junctions can be fabricated too. For example, an investigation of a gold nanoparticle array using a trilayer junction configuration, Hg–SAM–Au nanoclusters–SAM–Au, has recently been reported.¹⁰³ On the other hand, the base electrode may use a conductive material such as Au, Ag, Cu, ITO, doped Si, or even a Hg droplet.^{104,105} Electrical characterizations are usually conducted in the presence of solutions in ambient conditions, sometimes with the protection of Ar or N₂ gas. Table 4 summarizes typical results obtained on molecular junctions by various liquid metal droplet methods, while the chemical structure of the relevant molecules is shown in Fig. 23.

Most molecular electronic elements can be studied using this simple approach as long as they can form a large scale uniform layer on a conductive substrate. Earlier investigations have demonstrated that this method offers an effective way for fast screening of molecular building blocks preferable for nanostorage. For example, the molecular first oxidation

Table 4. Characteristics of molecular junctions based on the liquid metal droplet method.

Metal droplet	Device configuration	Active medium	Presence of solution	Junction area (10^{-3} cm^2)	Bias range (V)	References
Hg	Hg-SAM-SAM-Ag	Bilayer	Yes	4–7	± 1	37
	Hg-SAM-thin SiO_2 -p-Si	Monolayer	No	~ 2	± 0.8	36
	Hg-SAM-p-Si					
	Hg-SAM- SiO_2 -p-Si					
	Hg-SAM-SAM-Au	Bilayer	Yes	~ 2	± 1	38
	Hg-SAM-SAM-Hg	Bilayer	Yes	~ 0.5	−0.75 to 0.05	104,105
	Hg-SAM-Hg	Monolayer				
	Hg-SAM-SAM-Au	Bilayer	Yes	Not given	0.05 to 0.5	102
	Hg-SAM-SAM protected Au nanoclusters-SAM-Au	Trilayer	No	Not given	± 1.5	103
GaIn	Hg-SAM-LB-Au	Bilayer	Yes	2.5	± 1	33
	GaIn-organic film-Ag or Au, Cu, ITO	Molecular film	No	~ 0.1	± 10	40
	GaIn-organic film-SAM-Au					39

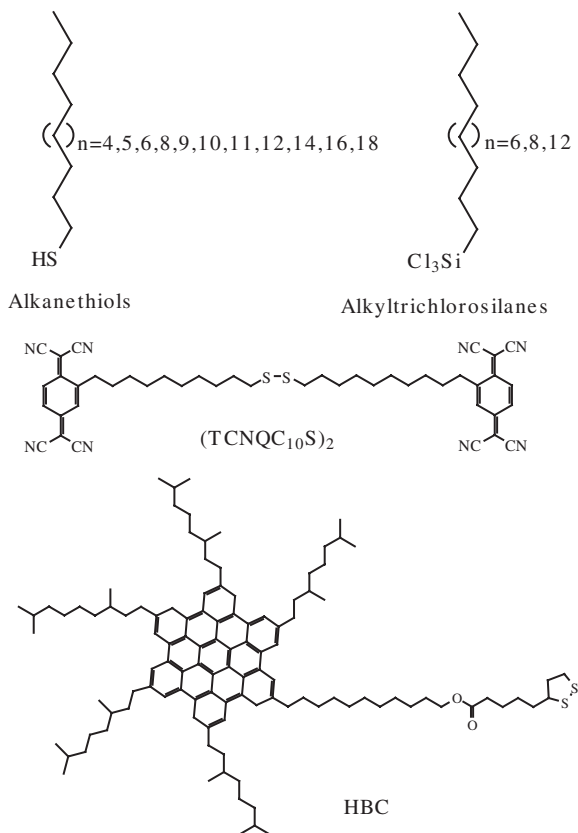


Fig. 23. Chemical structure of molecules investigated using the Hg-droplet-based junction approach.

potential was found to be directly proportional to the diode turn-on voltage after a series of polyarylamines were studied using the junction setup: GaIn–molecular film–Ag.⁴⁰ It was also indicated that the arylamine chemical structure plays a key role because it affects the film morphology, with larger, dendritic arylamines tending to produce smoother, more continuous films than those observed from smaller, more symmetric amines. Such dendritic arylamines may have potential for application in molecular electronic devices.

The interfaces between metal and dendritic arylamine molecular films were studied by measuring the I – V characteristics of single layer

organic diodes using a GaIn-droplet-based molecular configuration.³⁹ The investigation revealed that the diode turn-on voltage (V_t) is sensitive to the metal–arylamine interfacial electronic structure and can thus serve as a powerful tool for probing metal–molecule interface. Moreover, it was found that the junction performance strongly depends on the arylamine substituents, with the cyano ($-\text{CN}$) groups giving a higher V_t than the methoxy ($-\text{OCH}_3$) groups. When a monolayer of 1-decanethiol was self-assembled onto the Au anode, the diode V_t was abruptly increased. Data analysis suggests that there may exist an additional energy barrier in the diodes when the arylamine with $-\text{CN}$ groups was deposited on the SAM-Au anode. The conduction mechanism in these arylamine diodes is injection limited, which can be well described by the Richardson–Schottky (RS) thermionic emission model, because the plot of $\log(I)$ vs. the square root of the effective electric field ($E_{\text{eff}}^{1/2}$) shows a linear dependence over a large range of current and voltage. A similar conduction mechanism was observed in alkyl chain monolayer junctions with the structure Hg-SAM-p-Si ,³⁶ which confirms the effectiveness of the liquid metal droplet method. These results may promote future research efforts toward dendrimer-based nanostorage devices and systems, and this will be further discussed in the dendrimer section.

2.1.8. Charge transport mechanisms

Figure 24 shows a schematic molecular junction with the structure of two metal electrodes bridged by a “molecule”. The electrode–molecule interfaces may be a strong chemical bond (e.g. Au-S), a moderate charge transfer interaction (e.g. Au-CN) or a weak van der Waals contact. For different molecular structure and conjugation, the molecular properties may be very different. Taking these factors into account, the conductance of the molecular junction (G) can be expressed as¹⁷

$$G = T_L \cdot T_R \cdot T_M \cdot G_0,$$

where T_L and T_R are the electron transmission functions at the left and right electrode–molecule contacts, respectively, while, T_M is the transmission

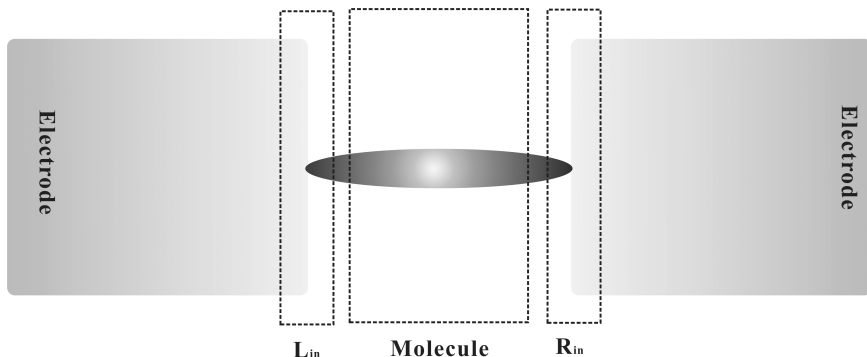


Fig. 24. Schematic diagram of a molecular junction in which the “molecule” is connected with two electrodes. As outlined by the dashed squares, serious consideration should be given not only to the molecule itself but also to the left (L_{in}) and the right (R_{in}) metal–molecule interfaces.

function related to the molecule itself and G_0 is the quantum conductance given by $G_0 = 2e^2/\hbar$ ($\sim 77.5 \mu\text{S}$).

The charge transport through a nanoscale molecular junction is usually treated as an electron tunneling process. Based on the temperature, bias voltage and molecular properties (like conjugation degree and molecule length), it may fall into several categories: coherent nonresonant tunneling (or classic tunneling),^{43,106–108} coherent resonant “super-exchange” tunneling^{109,110} and incoherent “diffusive” tunneling.^{111,112} It has been shown that incoherent tunneling is the dominant mechanism at high temperature, while coherent tunneling plays the main role at low temperature.^{113,114} Theoretical calculations predicted that the charge transport through the molecular junction may be sensitive to external optical fields,^{113,115,116} wire defects,¹¹² molecular vibrational excitation¹¹⁰ and electrode–molecule interfaces.¹¹² Some of these predictions have been confirmed by recent experimental results. For example, it has been demonstrated that the PDMS stamp-printing molecular junctions really respond to the stimulus of external optical signals with a different wavelength.⁴⁸

The Simmons equation, as a simple model for electron tunneling through a rectangular barrier in metal–insulator–metal junctions, is

widely used to analyze the experimental I - V curves.^{43,106} In the low bias voltage regime, the equation can be simplified to $J = J_0 \exp(-\beta d)$, with

$$\beta = \frac{2\alpha}{\hbar} (2m\phi)^{1/2},$$

where J is the current density, J_0 a constant, β the electronic decay parameter within the molecule, d the tunneling distance, α an adjustable parameter, m the electron mass, $\hbar$ Planck's constant and ϕ the barrier height. This simplification has been proven to be applicable in examining the effects of molecular conjugation and length on electronic transmission through molecular junctions.^{43,117} When the electrode-molecule interfacial effect needs to be considered, Fowler-Nordheim tunneling and Schottky-Richardson thermionic emission models are applicable in I - V data analysis for high bias voltage and high temperature regimes.^{20,118}

2.2. Three-terminal molecular devices

The next milestone, after the single molecule junction toward nanostorage, may be up to realize three-terminal molecular devices.²⁴ For the single molecule three-terminal device, there are two configurations (Fig. 25). The first one is a molecular junction coupled with one more terminal that is not limited to the gate electrode⁹³ and the electrolyte solution in the three-terminal electrochemical cell. This extra terminal can be a tip of STM or CAFM,¹¹⁹ an optical or laser beam^{48,113,115,120} or a nanoparticle with photoresponsive properties. The other form is more desirable and useful, whereby a three-branched molecule is connected with three electrodes through selective interaction between the specific branch and the designated electrode. This process can be realized by reactions of metal-sulfur and carboxyl reagent-Si with a combination of functional group protecting/deprotecting techniques.^{68,67} Obviously, there are still many challenges and a long way to go in the fabrication, integration and theoretical simulation of such three-terminal devices before practical application in nanostorage systems.

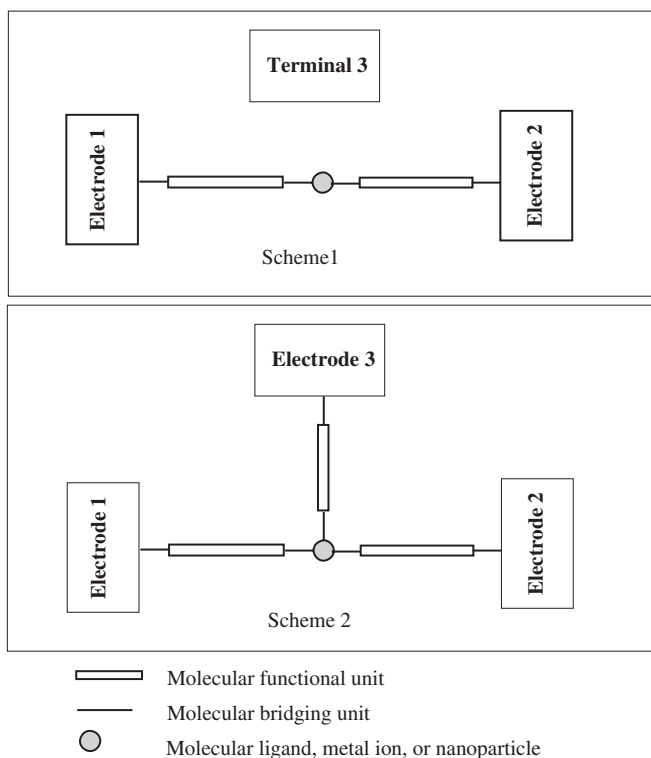


Fig. 25. Schemes of three-terminal molecular devices. In scheme 1, a single “molecular wire” is attached to two electrodes, in which the third terminal can be a tip of STM or CAFM, a coupled nanoparticle or a laser beam. In scheme 2, a branched “molecule” is connected with three electrodes through selective connection of each specific branch with the designated electrode.

2.3. Dendrimer-based memory devices

Dendrimers have become increasingly important in recent years because of their potential applications in information storage,^{121–123} electrical/optical switches,^{124–129} sensors,^{130–132} solar cells and light-emitting diodes.^{133–136} Dendrimers may be classified into two main types (Fig. 26). The advantages of dendrimers are related to their core/shell structure and nanoscale dimensions, and the presence of many functional sites and the controllability of these sites.¹³⁴ The electrical and/or optical properties of dendrimers

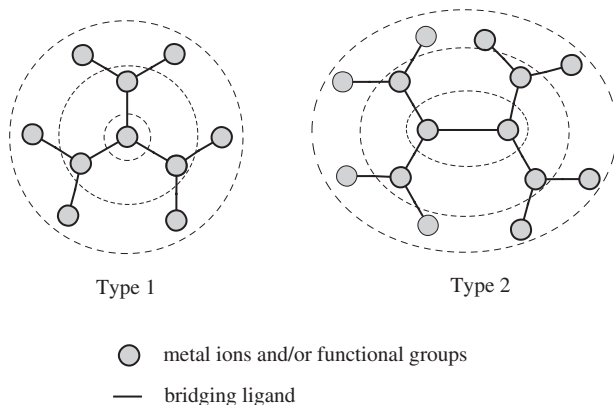


Figure 26. Schematic structures commonly used in dendrimers. The dashed circles outline the core/shell(s) structure.

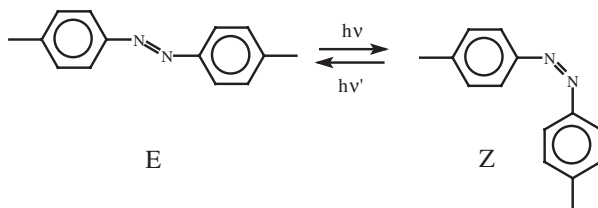


Fig. 27. Ultraviolet-light-induced reversible *cis/trans* isomerization of an azobenzene moiety.

can be thus tuned by (1) changing the core unit, (2) changing the chemical nature of the shell ligands and/or terminal groups, and (3) complexation with different nanoparticles and/or metal ions.^{137–140} Such capability makes dendrimers one of the most flexible candidates for building blocks in the bottom-up nanostorage system.

Ultraviolet light can induce reversible *cis/trans* isomerization reactions in compounds with an azobenzene moiety (Fig. 27). Various dendrimers containing such light-switchable units have been synthesized. As shown in Fig. 28, one choice is to use the azobenzene unit as the central linker (1),^{124,133} and the other approach is to place it in the periphery (2, 3).^{126,127,129} Redox-switchable dendrimers incorporating both electron

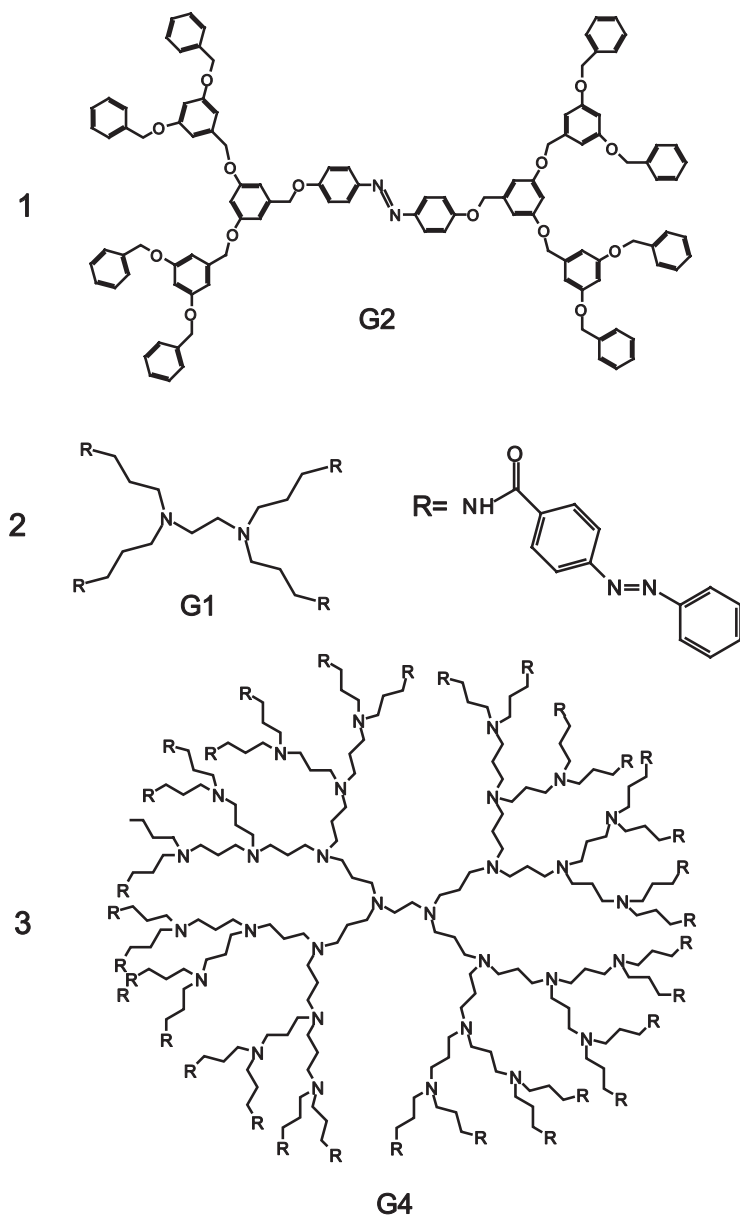


Fig. 28. Photoresponsive dendrimers with azobenzene as central linker (1) and periphery groups (2,3), respectively.^{124,129} Molecule 1 is the second generation dendrimer (G2), while 2 and 3 are the first (G1) and fourth (G4) generations, respectively.

donor and acceptor groups, such as TTF and cyanobiphenyl, have been studied.^{125,128} Other kinds of dendrimers complexed with metal ions (such as Sn^{2+} , Ru^{2+} , Fe^{2+} , Rh^{3+} , Ir^{3+} and Os^{2+})^{121,130,131,134,137,138} and/or nanoparticles^{139,140} have been reported too. Most of the dendrimers were investigated in the form of either molecular solutions^{124,129} or monolayers at the air–water interface.^{126,127} However, much of the interest in these dendrimers is to know if similar performance can be obtained in solid state single dendrimer devices. A critical step is to study the controlled assembly of dendrimers onto surfaces of different conducting substrates (such as Au, Ag, Pd and Pt).

Drop-casting, spin-coating or vapor deposition techniques can be used to prepare dendrimer thin films on various substrates. It has been shown that most dendrimer films are in the amorphous state and are composed of small, island-shaped domains due to their large, symmetric, globular, dense molecular structure.^{39,40,141} On the other hand, PDMS stamp-printing, solution adsorption and LB methods can be employed to fabricate multilayer or even monolayer dendrimers. However, there normally exists a large amount of patches/defects in the layer due to the effects of physical contact, solvent and/or layer transfer.¹⁴² This may result in high short circuit rates in the final devices. The traditional SAM approach, as used in small thiolated molecules, might be a good choice. A thiol-derivatized-alkyl linker can be added to the periphery of dendrimers. Moreover, to largely reduce the SAMs defects, an alkanethiol matrix is necessary for inserting individual dendrimer molecules into the monolayer. The methods for fabrication of solid state dendrimer layers are summarized in Table 5.

Table 5. Approaches to fabricate dendrimer layers.

Fabrication approach	Layer	For nanostorage	References
Drop-casting	Film to multilayer	No	140,143
Spin-coating	Film to multilayer	No	130,136
Vapor deposition	Film to multilayer	No	40,144
Stamp-printing	Multi- to mono-layer	Possible	145
Solution adsorption	Multi- to mono-layer	Possible	146
LB monolayer	Monolayer	Possible	126
SAMs	Monolayer	Very possible	122

Redox-active dendritic molecules are promising candidates for molecular scale charge storage. A series of zinc porphyrins have been investigated through electrochemical measurements, in which each porphyrin bears a S-acetylthiol-derivatized linker and can thus form an SAMs on Au electrodes.^{122,123} (Fig. 29). The gold microelectrode with a porphyrin SAMs was measured in a two-terminal electrochemical cell with dried and distilled CH_2Cl_2 containing 0.1 M electrolyte of Bu_4NPF_6 . Information was stored via removing electrons from the porphyrin units by applying a threshold bias voltage between the electrodes above the molecular oxidation potential. It was shown that multiple oxidation states (i.e. neutral, monocation and dication) of the porphyrins can be reversibly obtained. The charge retention time is hundreds of seconds. Similar redox-active information storage was observed in electrochemical experiments of dendritic molecules such as 4AA-PD and CN-4AA-PD^{39,40} (Fig. 29). The molecular layers were vapor-deposited on Au electrodes. Oxidation-induced color change was observed in the films, which were stable for more than three months in ambient conditions. However, a question is: What roles do the electrolyte and solvent play in such experiments?

To address this issue, the electrical performance of 4AA-PD thin films was studied in device configuration without organic solvent and electrolyte.¹⁴⁷ The shadow-mask-assisted cross-bar approach was used to construct junctions of Ag/4AA-PD/Ag, Ag/TPD/Ag, Ag/4AA-PD/TPD/Ag and Ag/4AA-PD/TPD/Ag. The films were vapor-deposited under a high vacuum condition and were immediately measured after removal from the chamber. It was shown that no such redox charge storage behavior exists in solid state devices of Ag/4AA-PD/Ag, Ag/TPD/Ag and Ag/4AA-PD/TPD/Ag in spite of the variation of layer thickness and metal material. However, irreversible electrical switching was observed for devices with the structure Ag/TPD/4AA-PD/TPD/Ag. Control experiments suggested that this is due to charge storage in the 4AA-PD molecular layer sandwiched by the TPD thin films. Since the oxidation potential of TPD is higher than that of 4AA-PD, an energy well may thus form in the sandwiched 4AA-PD film and where charges can be trapped.⁴⁰ This result may be applicable to design dendrimers with optimized core/shell structure for molecular scale charge storage.

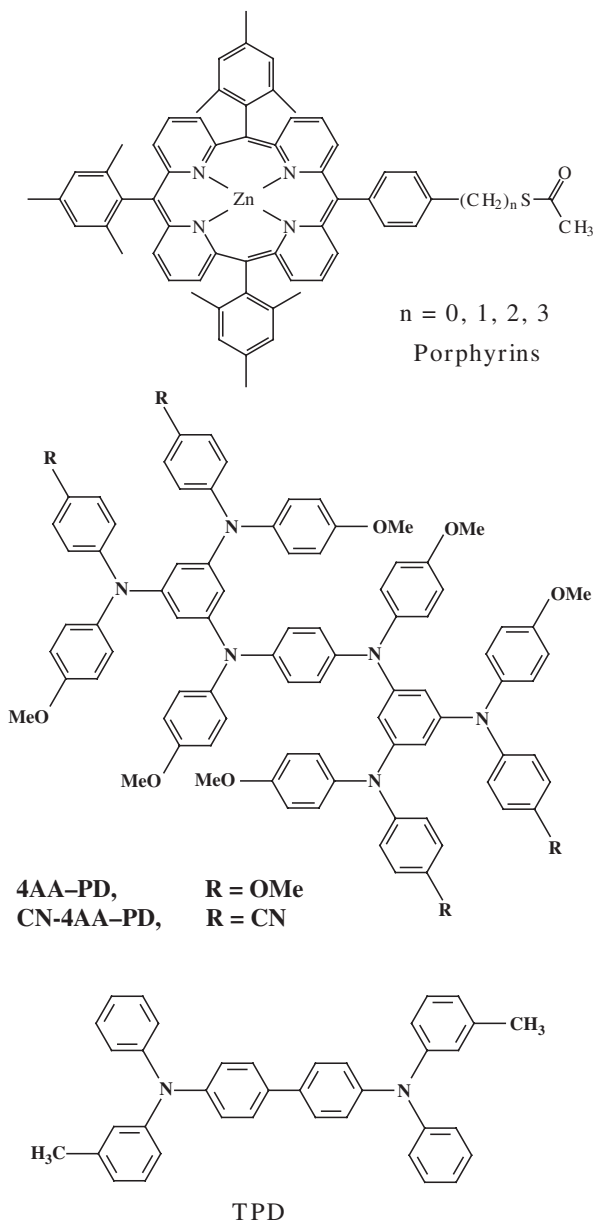


Fig. 29. Chemical structure of redox-active dendritic porphyrins 4AA-PD and CN-4AA-PD. The molecular structure of TPD is also shown, which is well known as a good hole transport material for organic light-emitting diodes.

3. Bioelectronics

The advance of nanostorage has a close relationship with the field of bioelectronics, because one main object of bioelectronics is to find effective ways to develop novel nanoscale devices, building blocks, principles, and technologies for ultrahigh density, low cost, intelligent information storage systems. The basic concept of bioelectronics is to address (electrically, optically and/or magnetically) a single biomaterial immobilized on substrate. The biomaterials may include proteins, DNA and enzymes,^{148,149} which can be treated as either an organic molecule or a nanomaterial. The assembly of these materials can be realized using the covalent bond (e.g. Au–thiol), affinity interaction (e.g. charge transfer) or hydrophilic–hydrophobic interaction. For example, Albert suggested in 1968 that charge transfer should be one of the most common and fundamental biological reactions and it may play a key role in biological regulation, defense and cancer.²²

Great advances have been made in biomaterial synthesis, layer assembly, fabrication of electrical contacts and tailoring of the biomaterial–electrode interfaces. Willner and coworkers reviewed the integration of layered biomaterials and conductive substrates for application in biosensors, bioelectronic arrays, logic gates and optical memories.^{148,150} They also reviewed the development of nanoparticle–biomolecule hybrid systems from the perspective of synthesis, properties and applications.¹⁵¹ DNA, as a chemically based molecular system, may be a key player in the bottom-up approach of nanotechnology owing to its features of about 2-nm-diameter, 4 nm helical repeat, and 50 nm persistence length.¹⁵² It was suggested that DNA can be used as conductive nanowires, branched nanoarchitectures, computers, nanomachines and sensors.^{153,154}

These studies were mostly focused on the synthesis, organization/immobilization, modification and simple characterization of the biomaterials,¹⁴⁸ although it was realized to controllably deposit molecules of interest at desired locations on the substrate using AFM-based dip-pen nanolithography⁹⁰ and/or the stamp-printing method.⁹¹ Electrical properties of single biomaterials were measured using CAFM or STM in combination with nanoparticles.¹⁵¹ As discussed in the previous sections, in

order to reproducibly address a single biomolecule and to further integrate it into a functional system, reliable methods still need to be established whereby sub-10-nm scale metal–molecule–metal junctions can be efficiently made. Moreover, the biomaterial–electrode interfaces need to be fully understood and carefully engineered. From the viewpoint of device fabrication and characterization, the molecular junction approaches are applicable to bioelectronics.²¹ More efforts are needed to address the development of hybrid nanoscale devices and information systems with combinations of molecules, biomaterials and nanostructures. It might be possible to realize semi-intelligent information storage systems through mimicking the human brain functions and structures.^{155,156} The first step is to build suitable neuron models by analyzing the biological neuron systems and their functions.¹⁵⁷ With such models and understanding, novel information devices and technologies may be available in the near future.

4. Nanoelectronics

Nanoparticles are also known as quantum dots, nanodots, nanocrystals or nanograins. Basically, they can be treated as a man-made “molecule.” A variety of nanoparticles have been fabricated by the methods of chemical reaction,¹⁵⁸ lithography,^{159,160} chemical vapor deposition (CVD),^{161,162} deposition plus annealing,^{163,164} molecular-beam epitaxy (MBE)¹⁶⁵ and anodization plus rapid thermal oxidation.¹⁶⁶ Nanoparticles, with sub-10-nm dimensions, are believed to be among the most promising materials for ultrahigh density memory devices.¹⁶⁷ For example, nanoparticles covered with insulating layers have been investigated for applications in non-volatile flash memory devices¹⁶⁸ and electrostatic data storage.^{9,169,170} The principle of the memory device is to inject a number of charges into a single nanoparticle or bundle of nanoparticles embedded in an insulator (i.e. write), store the injected charges (storage), and later sense the stored charges (i.e. read). The data erasing is realized by removing the stored charges using reversed electrical field and/or optical illumination. This charge injection–storage–erase process requires the nanoparticle to possess discrete energy levels where the charges can stay, which was confirmed by the electrical measurements of Au nanoparticles at the

temperature of 12 K.^{171–174} Semiconductor nanoparticles like Si, Ge, CdSe, InAs and Ga(In)As should be the most promising candidates to be examined for information storage.^{158,160,175–177}

Nanocrystalline silicon (nc-Si) has been studied for application in single electron memory devices.^{160,178,179} However, it was argued that nanodots of Ge,^{180,181} refractory metal (like TiN and W) and SiGe^{162,182} should be more suitable for nanomemory application owing to their band gap being smaller than that of silicon. Other kinds of information memory and processing systems were also investigated, including quantum-dot-based cellular automata,^{183,184} electron spin memory^{185,186} and the single electron parametron.¹⁸⁷

Although there are some breakthroughs regarding nanoparticle-based memory devices, major challenges still remain. The following issues need to be addressed:

- (1) Currently, most nanoparticle-based memory devices are made by photolithography or e-beam lithography. As a result, the device dimension is still too large to be used for nanostorage. Low cost fabrication approaches are needed to make a large array of sub-10-nm single nanoparticle devices.
- (2) The tunneling barrier is not well-defined. Effects of the materials, thickness and structure of the embedding insulating layer (or organic ligands) have to be examined in detail.
- (3) The device operating temperature is currently too low, and needs to be as close as possible to room temperature.
- (4) More effort is required with regard to controlling the size, shape, uniformity and assembly of nanoparticles.
- (5) Characterizing the electrical properties (e.g. I - V curves) of single nanoparticle devices in the presence of optical and/or magnetic fields.
- (6) Understanding (or even controlling) how the nanocrystal structure affects the device performance.

Nanotubes and nanowires are also being extensively investigated for application in various nanoscale devices.^{2,13,188} Besides the fact that they can be used to construct addressable molecular junction arrays,^{86,89} these nanostructures themselves can be used as information storage media.^{11,16}

For example, electrical switching has been reported for carbon nanotube Y-junctions.¹⁸⁹ A single nanowire superlattice with multiheterojunctions has also been synthesized and characterized.^{14,15} More effort is necessary to develop some low cost methods to controllably fabricate nanostorage device arrays.¹⁹⁰

5. Summary

The development of nanoscale data storage has been reviewed from the viewpoints of molecular device fabrication and the building blocks used. It has been shown that nanostorage should be sub-10-nm scale, addressable, durable, low cost, highly integrated, and compatible with bioelectronics and/or nanoelectronics. It seems quite possible to achieve applicable nanostorage devices using crossed nanowire/nanotube approaches in combination with the techniques of electrodeposition, self-assembly, nanoparticle assembly and bioelectronics. However, currently, it is still too early to conclude which approaches and building units will ultimately be used in the coming commercial nanostorage devices. As one of the most critical steps, more effort should be made to figure out some simple but applicable methods for fabrication of nanoscale devices. In the meantime, the current approaches can be used as testbeds to investigate various building blocks from the aspects of molecular synthesis, self-assembly, and effects of molecule–electrode interfaces, chemical structure, functional groups and/or the local environment on the device performance. Finally, some provocative questions will be arisen: What is next after the generation of nanostorage? How will it affect our daily life? One answer might be semi-intellectual memory systems with some characteristics of the human brain, which may be achieved someday using the novel technologies, equipments, materials and theories developed on the basis of nanostorage, molecular electronics, nanoelectronics and bioelectronics.

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