

Recent progress on switchable rotaxanes

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Switchable rotaxanes are currently attracting considerable attention from chemists, physicists and materials scientists because of their potential to perform relative inter-component positional changes in response to external stimuli and the potential applications in the fields such as molecular machines, molecular switches, molecular logic gates and memory devices. This *tutorial review* summarizes recent work on switchable rotaxanes and their potential applications.

1. Introduction

In the late 1980s and the early 1990s, with the development of supramolecular chemistry and with the better understanding of the processes of the host–guest molecular recognition, it has become possible to develop the so-called “template-directed” synthetic methodology for rotaxanes. From then on, the synthesis of a rotaxane has become quite routine and a large variety of these intriguing compounds of ever increasing regularity and complexity has been reported. Moreover, rotaxanes generally have some novel chemical and physical properties and, as a result, they have attracted more and more attention.

A rotaxane consists of one or more macrocycles encircling the rod portion of a dumbbell-like component. There are various species of rotaxanes, namely [2]rotaxane, [1]rotaxane, Janus rotaxane and polyrotaxane (Fig. 1). If properly designed, a shuttlable rotaxane can be switched between different co-conformational states when external energy (*e.g.*

chemical, electrochemical, photochemical, or entropical) is applied. The ability of these shuttlable rotaxanes to switch between alternative states has raised opportunities in the fabrication of molecular machines and molecular devices.

Although there are some reviews¹ and books² focusing on topics of rotaxanes, most of them are micro-reviews summarizing only the work of the authors and their co-workers. This tutorial review summarizes recent work on switchable rotaxanes and their potential applications since the year 2001.

2. Switchable rotaxanes

A [2]rotaxane is described as a molecular system in which a macrocycle (wheel) threads a linear subunit (dumbbell) with two bulky stoppers. If properly designed, two recognition sites for the macrocycle can be arranged within the dumbbell component. Moreover, the strengths of the non-covalent bonding interactions between two recognition sites with the ring component are quite different, and as a result, the ring component locates preferentially in the site that has stronger interactions with the ring (ground state in Fig. 2). In such a system, when a suitable external stimulus—either chemical or physical—is applied, the binding activity sequence of the two

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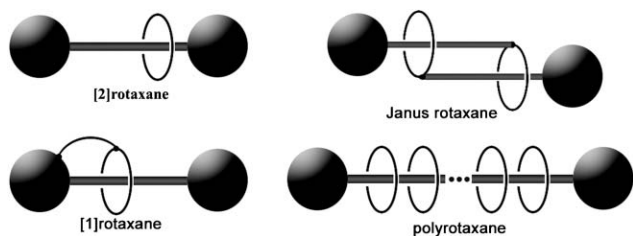


Fig. 1 The cartoon for rotaxane species.

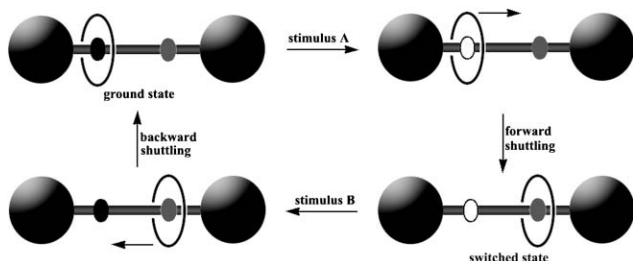


Fig. 2 The stimuli-triggered reversible shuttling motions in a [2]rotaxane.

recognition sites is altered, as a consequence, the ring component shuttles from the original recognition site to another (switched state in Fig. 2). In the ideal case, the properties of the two recognition sites can be shifted reversibly back to the original ones by another stimulus. Such a molecule constitutes a molecular shuttle.

It can be seen that the external stimulus employed to effect the switching motion of a rotaxane must be able to weaken the relative binding forces which stabilize the initial state. Thus, the type of stimulus used depends on the nature of the binding forces. A chemical (acid/base), an entropic stimulation, or a solvent change can drive a molecular machine based on

hydrogen-bonding; Chemicals (oxidant/reducer), electrochemical (redox) processes, or photochemical (photoinduced redox) processes can power a molecular machine relying on donor/acceptor interactions. A photoisomerization process can also induce relative spacial changes among the components and thus can drive a molecular shuttle.

Like a macroscopic machine displaying intercomponental relative position changes when applying power, a switchable rotaxane performs shuttling motion in response to external stimuli. From this point of view, a molecular shuttle is also deemed as a molecular machine, and the external stimuli are the driving forces or energy supplies of the machine system.

3. Driving forces of switchable rotaxanes

3.1 Chemical energy

The most obvious way of supplying a molecular machine system is to use some chemical reactions that release energy. Fig. 3 shows a chemically driven [2]rotaxane **R1** based on π -electron donor–acceptor interaction.³ In the neutral state, the macrocycle positions itself over the 1,4,5,8-naphthalene-tetracarboxylate diimide (NpI) unit for its better electron-withdrawing ability than the pyromellitic diimide (PmI) unit. However, since the pole–dipole interactions involving Li^+ ions and the oxygen atoms in the polyether loops of the macrocycle are stronger in the case of a PmI encircled unit, addition of Li^+ ions to the neutral bistable [2]rotaxane induces the macrocycle to move from the NpI to the PmI recognition site. Upon removing the Li^+ ions by adding [12]crown-4, the switched state is restored to the ground state.

Fig. 4 shows an acid/base driven [2]rotaxane **R2**.⁴ In CDCl_3 , the macrocycle encircles the pyridine unit because of the significant intercomponent hydrogen bonding between the amide groups of the macrocycle and the pyridine nitrogen atom of the rotaxane thread. However, with the protonation of the pyridine nitrogen atom by trifluoromethanesulfonic acid

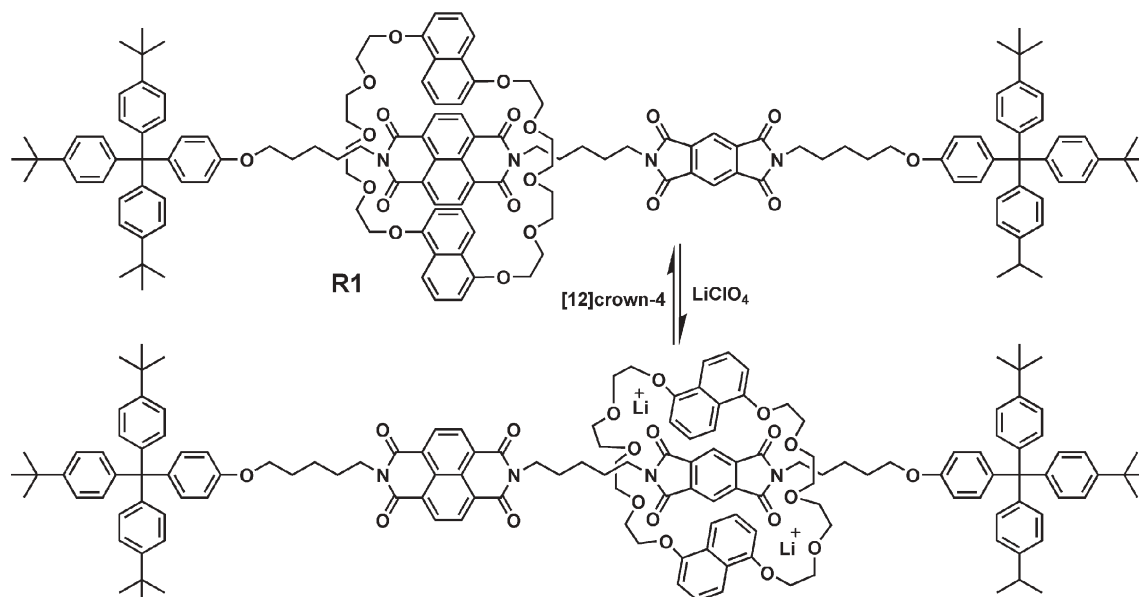


Fig. 3 Switchable molecular shuttle **R1** powered by Li^+ .

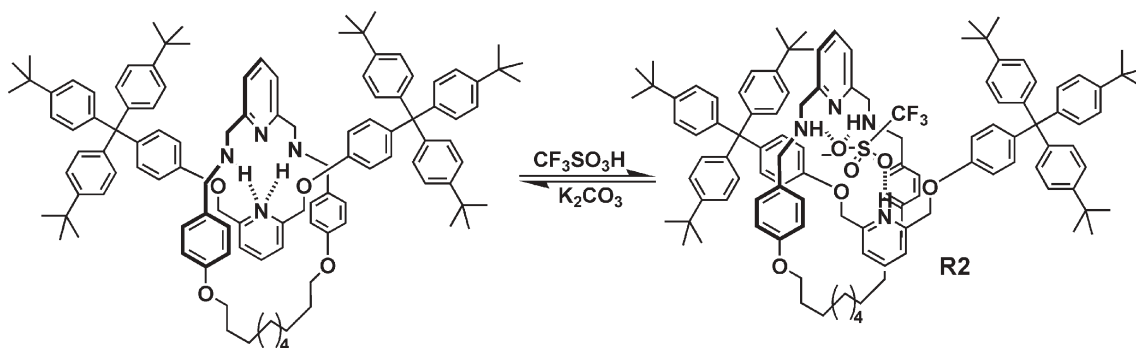


Fig. 4 The switching motion induced by acid/base in **R2**.

(TfOH), the intercomponent hydrogen-bonding interaction is disrupted and the macrocycle moves apart. The ground state can be restored by adding K_2CO_3 to remove the TfOH and the shuttling motion is thus reversible.

Like macroscopic internal combustion engines, the chemical driven molecular machine needs fresh reactants (fuel) at any step of its working cycle and produces waste products. For example, in **R1**, the forward motion is triggered by the Li^+ ions input, successive addition of [12]crown-4 returns the system to its original form, and the complexation reaction generates waste products. In **R2**, the alternant adding of TfOH and K_2CO_3 causes neutralization and by-products form too. It is obvious that the chemical driven molecular machine will be compromised by accumulated waste products, unless these wastes are expelled from the system.

3.2 Electrical energy

An electrical potential can be used to cause redox reactions. A molecular machine system based on π -electron donor–acceptor interaction can be induced a forward motion by oxidation of the electron donating group or reduction of the electron-acceptor unit. These redox reactions can be realized by an electrical potential and the backward reaction to the original state can be simply obtained by reversing the potential. One of the systems⁵ is the redox-controllable amphiphilic [2]rotaxane series based on the redox active TTF unit.

Fig. 5 shows a series of [2]rotaxanes **R3–R5**,⁶ containing succinamide and naphthalimide hydrogen-bonding stations for

a benzylic amide macrocycle. Electrochemical reduction and oxidation of the naphthalimide group alter its ability to form hydrogen bonds with the macrocycle to such a degree that redox processes can be used to switch the macrocycle between the two stations.

A bistable rotaxane **R6**,⁷ consisting of a 2,2'-bipyridine-containing thread and a ring incorporating both a bidentate chelate and a tridentate fragment, is shown in Fig. 6. Taking advantage of the fact that copper(I) prefers to form a 4-coordinate complex while copper(II) is apt to generate a 5-complex, the [2]rotaxane undergoes an electrochemically driven (oxidation of Cu^+ or reduction of Cu^{2+}) pirouetting motion of the ring around the axis which takes place on the millisecond timescale.

It is obvious that electrochemical inputs have advantages over chemical ones. An electrochemical stimulus can cause reversible switching processes by simply reversing the electrode couple to induce reversible redox reactions. No waste product is produced during the switching procedure. Besides, the supply of electrical potential can be switched on and off easily and rapidly. Furthermore, electronic devices can be easily fabricated with these electrochemically-triggered systems, directly without any signal transformation.

3.3 Solvent changes

Beside the different kinds of energy inputs described above, a simple solvent change can also be used to drive a molecular

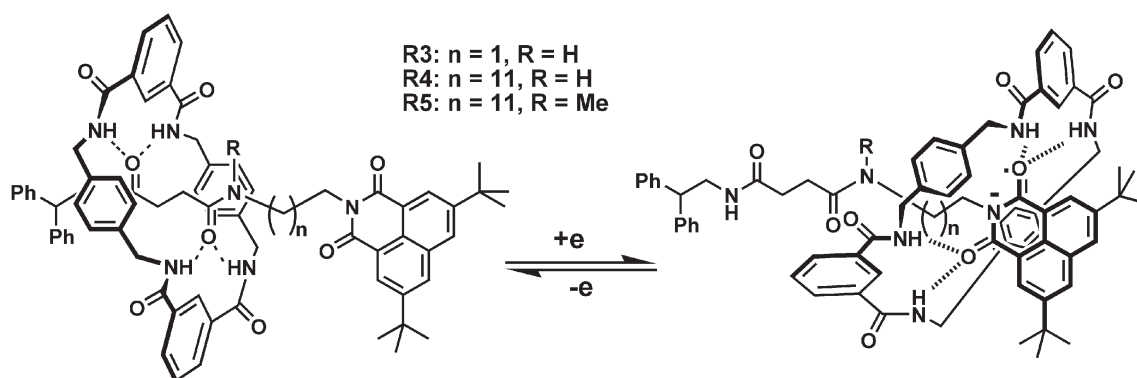


Fig. 5 The redox controllable shuttling movements in **R3–R5**.

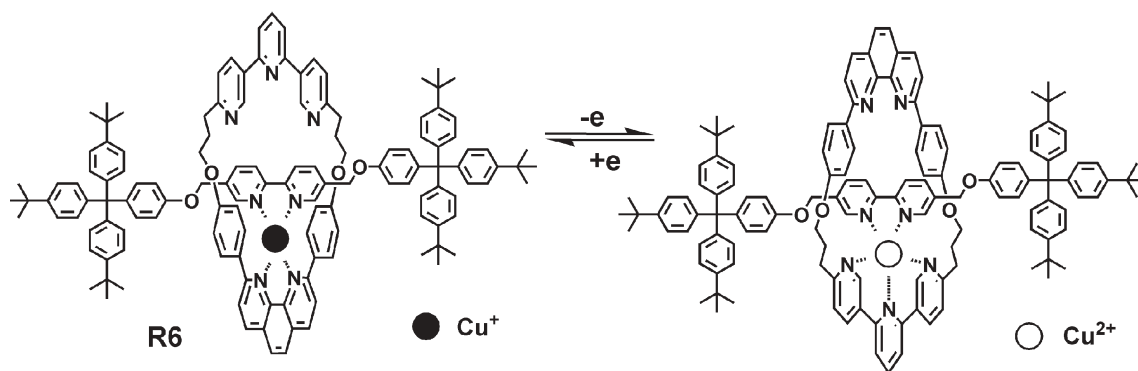


Fig. 6 The electrical driven pirouetting motion in **R6**

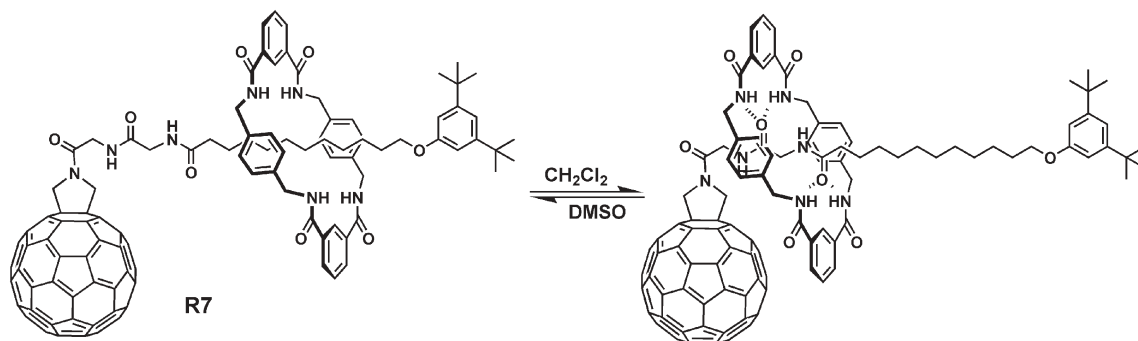


Fig. 7 The shuttling movements in **R7** can be driven by solvent changes.

machine. For example, [2]rotaxane **R7**,⁸ which can perform solvent-induced shuttling movements, is shown in Fig. 7.

Although a solvent change can drive a molecular shuttle, one solvent must be removed before the other is added to cause the switching motion. The need to carry out the solvent changing process brings difficulties in the design and fabrication of solid molecular devices.

3.4 Heat energy

The switching behavior of the ring component from one station to another rests with the free enthalpy change in the process, that is, $\Delta G = \Delta H - T\Delta S$. So, if the entropy change is big enough, the switching process of the ring component from one recognition site to another can be reversed by increasing or

lowering the temperature. Fig. 8 shows an entropy-driven [2]rotaxane **R8**.⁹ At 308 K, the macrocycle sites over the succinamide station, this being entropically favorable. However, when the temperature is lowered to 258 K, both of the amides units—one in fumaramide and the other in succinamide—form hydrogen bonds with the macrocycle because of the stronger hydrogen bonding ability of amide–amide than ester–amide, and the alkyl chain adopts a folded “S-shape”. The temperature dependent co-conformational changes are reversible and no any chemical reaction is involved.

A molecular shuttle that functions through reversible C–C bond formation has also been described.¹⁰ A Diels–Alder addition to a fumaramide in the presence of cyclopentadiene at 80 °C, results in the shuttling of the macrocycle from the

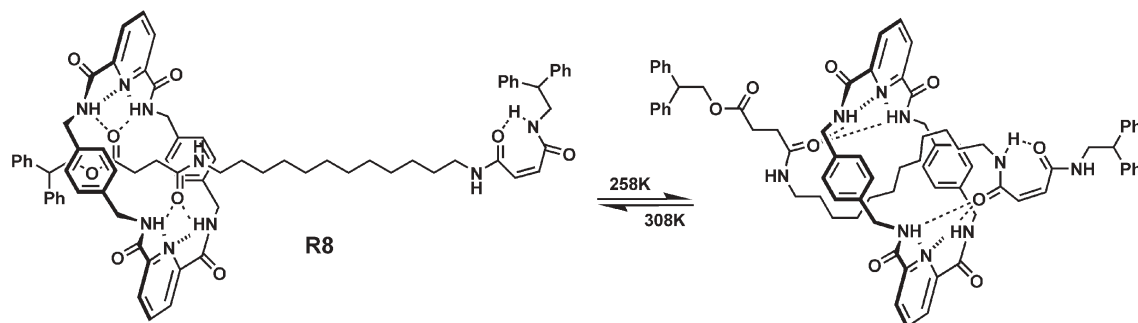


Fig. 8 The entropy driven folding motion in **R8**.

fumaramide unit to a succinic amide-ester station. The reverse process can be induced by raising the temperature to bring about a retro-Diels-Alder reaction.

Recently, we have demonstrated a thermo-driven molecular shuttle.¹¹ At room temperature, the cyclodextrin ring stays preferentially on an azobenzene station. Upon raising temperature, more cyclodextrin rings move to the adjacent biphenyl station. The reversible process can be obtained by lowering the temperature of the system. Like electrical power, heat energy is also a “clean” driving force because it does not produce any waste product.

3.5 Light energy

Light energy can also be used to power a molecular machine. For the hydrogen-bond assembled rotaxane **R4** (shown in Fig. 5),¹² the translation of the macrocycle between two stations took place after photoexcitation with a laser pulse. Before irradiation, the succinamide fits perfectly the binding sites of benzylic amide macrocycle and is held place by two sets of bifurcated H-bonds from the isophthalamide groups of the macrocycle to the two carbonyls of succinamide amide. After photolysis in the presence of an electron donor 1,4-diazabicyclo[2.2.2]octane (DABCO) at 355 nm, naphthalimide radical anion was generated and this station can bond strongly to the benzylic amide macrocycle. As a result, the macrocycle shuttled down the thread from its original position. After charge recombination (about 100 ms) the system returns to the ground state and can be pulsed again, providing with the same results. It should be noted that these submolecular motions are fast and fully reversible.

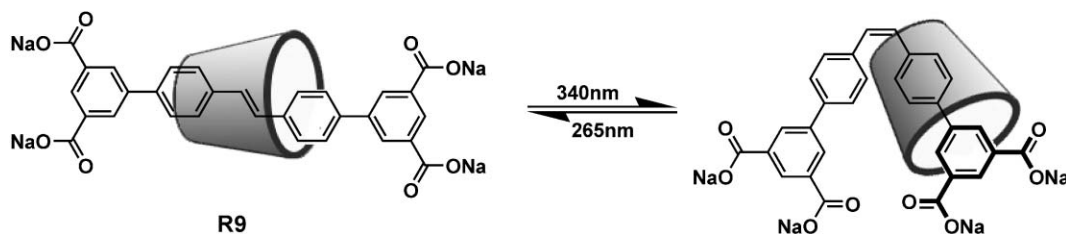


Fig. 9 The photoisomerization controllable shuttling motion for [2]rotaxane **R9**.

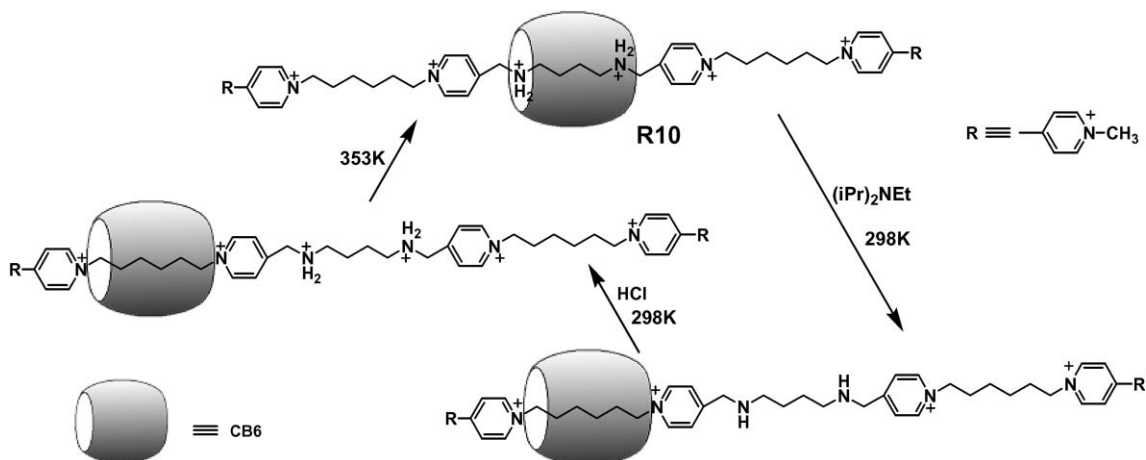


Fig. 10 The kinetic behavior of **R10**.

Beside the hydrogen-bonding changes, photoinduced isomerization of $-C=C-$ or $-N=N-$ double bonds from the *trans* to *cis* form can be used to drive a molecular machine. Fig. 9 shows a stilbene-based rotaxane **R9**,¹³ the alternant irradiation at 340 nm or 265 nm results in the *E/Z* isomerization of the stilbene unit, accompanied by the reversible shuttling motions of α -cyclodextrin. It is clear that light input is a clean resource, which produces no waste product during the photoisomerization-induced reversible shuttling process.

Another light driven molecular shuttle was **R8**,⁹ which can be also driven by heat. In CH_2Cl_2 , the irradiation at 312 nm results in the *cis* \rightarrow *trans* isomerization of the maleamide unit, the poor binding maleamide station is replaced with a group of stronger macrocycle-binding affinity (fumaramide) and the macrocycle shuttles away from the succinic amide ester site to the fumaramide station. The *trans* \rightarrow *cis* isomerization can be fulfilled by irradiation at 254 nm and the macrocycle shuttles reversibly back.

It can be seen that a light input can power a molecular machine and that no waste product forms during the operation. Compared with the other inputs, besides its cleanness, photochemical input has some other advantages:

- ◆ laser can be switched on and off easily and rapidly.
- ◆ laser beam can work in a small space.
- ◆ the excitation with photons can lead to a fast response.

3.6 Multi-energy inputs

Cucurbiturils have different affinity towards dicationic ammonium guest molecules, which can be used to develop chemical-driven molecular switches.¹⁴ In most cases, these molecular

switches operate under thermodynamic control and the switched state reverts to its ground state once the external stimulus is removed. Fig. 12 presents a kinetically controlled switchable [2]rotaxane **R10**.¹⁵ The switching of the molecular bead from one site to the other was driven by pH value, but the reverse process requires a change in pH plus a thermal activation. **R10** behaves as a kinetically controlled molecular switch—the new state induced by an external stimulus can be “locked in” after removal of the stimulus.

A series of bistable [2]rotaxanes based on the photochemical and thermal interconversion of fumaramide and maleamide groups were also reported.¹⁶ Irradiation at 254 nm of these rotaxanes produces the corresponding *cis*-maleamide rotaxanes, considerably reducing the binding strength between the macrocycle and the thread, and the macrocycle shuttles to the succinamide unit. The back-shuttling motion can be accomplished by raising the temperature from 298 K to 393 K to introduce the *cis* to *trans* maleamide recovering.

Another example of multi-forces driving a [2]rotaxane system is one which powered by light and chemicals.¹⁷ In CH_2Cl_2 , the benzylic amide macrocycle resides on the fumaramide unit, but upon irradiation at 312 nm the fumaramide isomerizes and the macrocycle moves to the glycyglycine unit. The original state can be restored by treatment with piperidine.

4 Co-conformational identification

Besides the kind of energy supplied to make a molecular machine work, the monitoring of the co-conformation of each state is of great importance for the sake of controlling its operation and to readout the different states. Generally, the stimulus-triggered relative positional changes were spectroscopically characterized in solution and some other spectra such as absorption spectrum, NMR spectrum, cyclic voltammetry, circular dichroism spectrum and fluorescence spectrum, were also often used.

4.1 UV-visible absorption spectrum

Co-conformational changes occur in every step of the working cycle in a molecular machine and a change in the conjugated

structure within the machine system might be involved during the switching process and, as a result, different absorptions with respect to the different translational states would originate. In the [2]rotaxane **R11** shown in Fig. 11,¹⁸ the forward shuttling motion of the tetracationic macrocycle results from the photolysis of the diarylcycloheptatriene unit at 360 nm. In the original state, the diarylcycloheptatriene moiety has a maximum absorption at 380 nm, but after the photolysis a new absorption at around 580 nm is obtained because of the generated tropylium ion.

In the Li^+ driven [2]rotaxane **R1**,³ the co-conformational change can be monitored by the absorption spectral changes. Upon addition of Li^+ ions, the CT band ($\lambda_{\text{max}} = 490 \text{ nm}$, $\epsilon = 850 \text{ M}^{-1}\text{cm}^{-1}$) corresponding to the macrocycle–NpI interaction is replaced by a CT band ($\lambda_{\text{max}} = 460 \text{ nm}$, $\epsilon = 550 \text{ M}^{-1}\text{cm}^{-1}$) characteristic of the “ Li^+ -ion-assisted” macrocycle–PmI interaction.

4.2 NMR spectra

In every working step of the molecular machine, the co-conformational motions are accompanied by inter-component relative displacements. As a result, the micro-environments around these components change, which may be monitored through nuclear magnetic resonance (NMR) techniques. Although the NMR spectra have limitations in some cases (NMR is unavailable in those systems containing radicals or paramagnetic compounds), with the development of high-field NMR spectrometers and the 2D NMR techniques, NMR spectrometry is one of the most important approaches to investigate the co-conformation of molecular machine systems.

4.3 Cyclic voltammetry

The cyclic voltammogram is usually used to identify the co-conformations in an electrochemically-triggered molecular machine system, whose operation relies on the oxidation or reduction of a redox couple. These redox processes can be easily reflected by the redox signals on the CV curve, especially for those metallo-rotaxane examples.

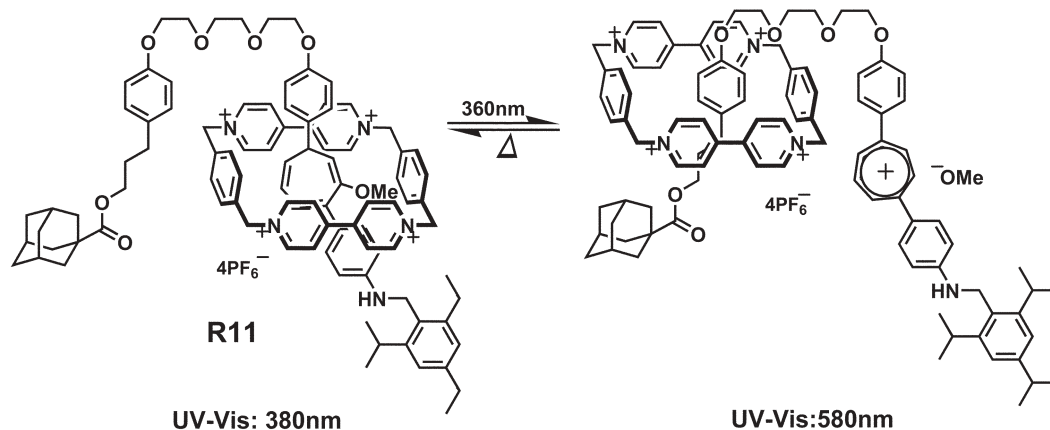


Fig. 11 A new absorption band at 580 nm appears when **R11** is excited to its switched state by light.

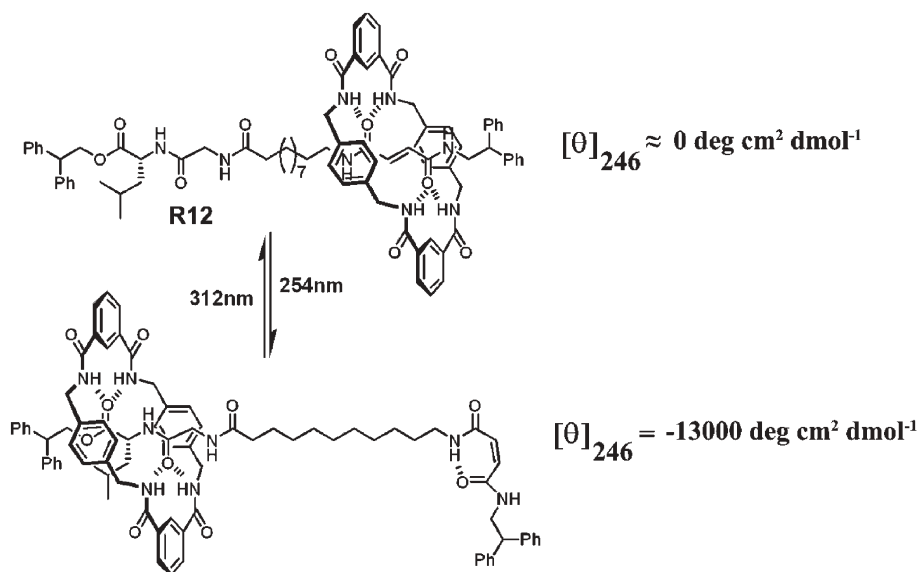


Fig. 12 The ICD spectra used to identify the shuttling motion in **R12**.

4.4 Induced circular dichroism spectrum

Circular dichroism spectra have been widely used to interpret the absolute conformation of chiral compounds. When an achiral guest chromophore is located in a chiral host, the guest becomes optically active and induced circular dichroism (ICD) signals originate.

In a molecular shuttle consisting of a chiral station, once the macrocycle moves apart from or close to the chiral “station”, the ICD signals could be influenced. Fig. 12 shows an example of this kind of shuttle.¹⁹ In the initial state of **R12**, the macrocycle resides over the fumaramide portion of the thread and the asymmetric center is not close enough to any aromatic rings to influence their ICD spectrum. Upon photoisomerization of the olefin station, the ring moves to the glycy-L-leucine unit, locking the molecule in the co-conformation where aromatic rings are held in a well-expressed chiral environment.

In a molecular machine comprising a chiral ring component, such as a cyclodextrin or calixarene, the movement of the macrocycle from one chromophore to another would result in changes in ICD spectra of these chromophores. Fig. 13 shows a light-driven [2]rotaxane **R13**.²⁰ Before the irradiation, the α -cyclodextrin is far from the naphthalimide unit and has little effect on this group, and ICD spectrum shows a weak negative Cotton effect at 431 nm. After photoisomerization, the α -cyclodextrin ring moves close to the naphthalimide unit and thus a strong decrease in the ICD signal at around 430 nm originates.

4.5 Fluorescence spectra

One of the most important applications of switchable rotaxanes is to construct molecular devices that can process and store information. The principle for designing such a

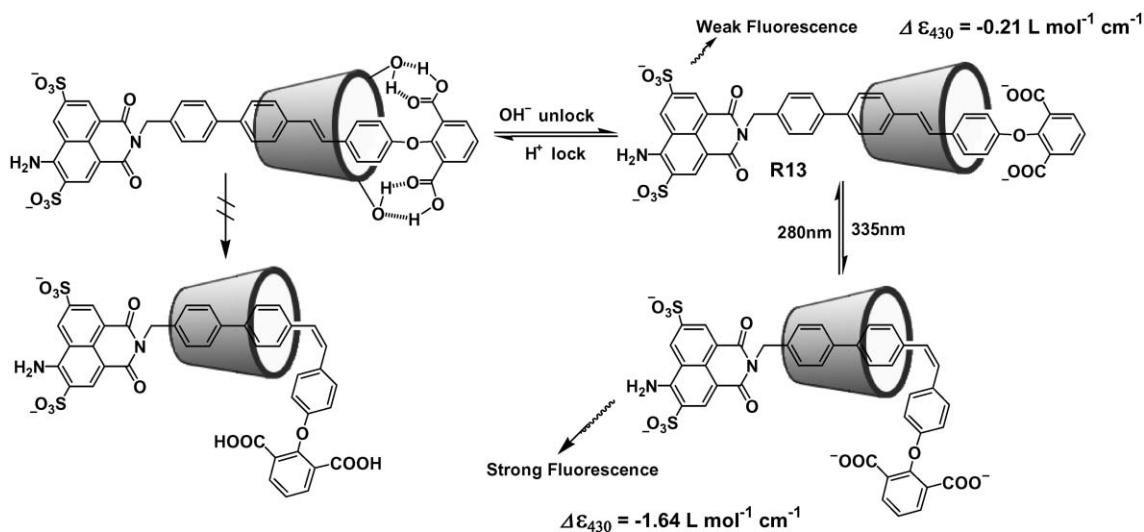


Fig. 13 The light-driven “lockable” molecular shuttle **R13** is fully reversible with a fluorescent output and can also be monitored by the ICD spectra.

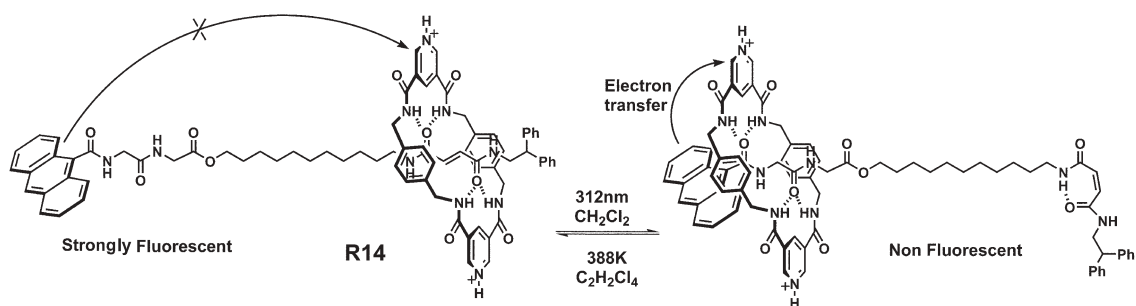


Fig. 14 The light-driven shuttling motion and the shuttling-induced fluorescence quenching in [2]rotaxane **R14**.

molecular device is that, the molecule shuttle switches from a ground state to another switched state with an output signal in response to an input and the switched state can be reverted reversibly back to the ground state when another input is applied. From this point of view, a driving force of a molecular shuttle acts as the input and the spectral signals used to identify the co-conformations serve as the outputs.

In summarizing the driving forces and the monitoring methods of switchable [2]rotaxanes, it can be found that an optical device, based on a light driven molecular machine with a fluorescent output, will be characterized by:

- fast response.
- low-cost because the detection of photons can be easily carried out in a small space.
- highly sensitive output signal and furthermore, one which can be remotely detected thus allowing non-contact readout to be achieved.

However, little attention has been focused on this kind of optical interlocked molecular system despite that a large number of molecular machine systems have been set up for more than a decade. These facts became our impetus to build up light-driven molecular machines with fluorescence outputs.

In 2004, we built up a “lockable” light-driven molecular shuttle **R13**,²¹ as shown in Fig. 13. In a basic environment, the cyclodextrin ring resides over the stilbene unit and far away from the ANS fluorophore. Upon irradiation at 335 nm the photoisomerization of the stilbene unit is induced, and the cyclodextrin ring is forced to shuttle to the biphenyl unit and becomes close to ANS. The rigidity and the displacement in the solvent environment as well as the shielding from molecular oxygen quenching of the cyclodextrin ring to the

methylene and the fluorescent stopper results in an increase in the fluorescence intensity of the fluorophore by 63%. The backward isomerization can be reversibly obtained by irradiation at 280 nm and the fluorescence decreases to the original level.

It should be noted that the switching process can be disabled in the acid form by the hydrogen bonds between the isophthalic acid and the hydroxy group on the cyclodextrin. It should also be emphasized that **R13** can serve as a molecular switch and the photons can be explored in this system for both causing the translational changes (input) and monitoring the different co-conformational states (output). It is a superior system to any others for neatness and convenience.

Fig. 14 shows the light-driven molecular shuttle **R14** using a fluorescence signal.¹⁷ The photo-induced large positional change of the macrocycle from the fumaramide station to the glycylglycine station results in the fluorescence quenching of the anthracene by the pyridinium unit. Such a photo-driven system exhibits a 200 : 1 on-off fluorescent intensity ratio between the two translational states.

Another optical switchable [2]rotaxane **R15** is shown in Fig. 15.²² The cyclodextrin unit can be driven from the azobenzene unit to the biphenyl group by light irradiation at 360 nm with a decrease of the fluorescent intensity of ANS at 520 nm and an increase of NS at 395 nm. The backward process can be obtained reversibly by irradiation at 430 nm and the fluorescence intensities of the two stoppers are recovered.

More recently, a molecular shuttle driven by solvent changes with a fluorescent output was also reported.²³ The photo-induced large positional change of the macrocycle results in the

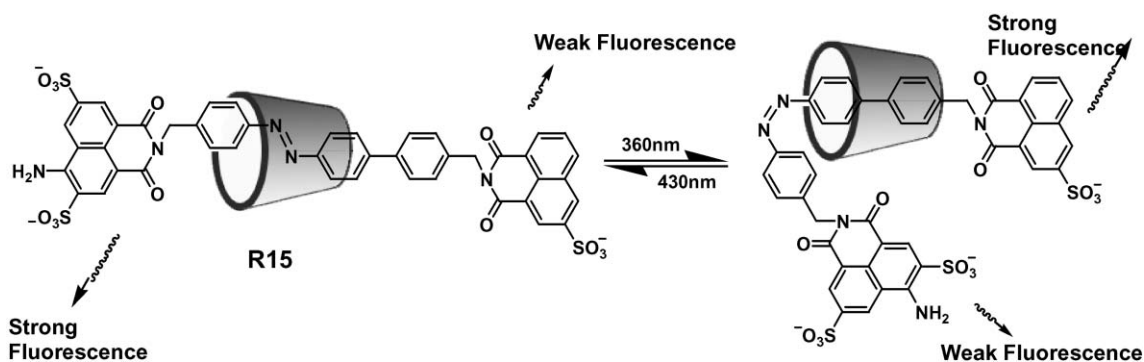


Fig. 15 The optical switchable [2]rotaxane **R15** with two fluorescent addresses.

fluorescence quenching of the anthracene stopper by the nitrobenzene unit in the macrocycle and the photo-induced system exhibits a 15 : 1 on-off fluorescent intensity ratio between the two translational states.

A pyrene and perylene bisimide containing [2]rotaxane, in which a pyridine-based macrocycle can be shuttled between co-conformations, was synthesized.²⁴ The protonated pyridine macrocycle can act as a switcher for the energy transfer from the pyrene to the perylene moiety and its light-induced shuttling elicits a fluorescence response.

5. Applications of switchable rotaxanes

5.1 Molecular machines

A switchable [2]rotaxane is deemed as a “molecular machine” because it applies an external power to display changes of inter-component relative position. There is no doubt that these molecular shuttles are clever enough to move on command in bulky solutions. However, a solution consists of a large number of incoherent molecules. Before we harness useful functions out of the beautiful molecular motion, it is necessary to organize these shuttling molecules in order that they can behave coherently. In the context of this urge, much effort has been paid to deposit these beautiful molecules onto a surface or an inter-surface to obtain assemblies in good order.

5.1.1 Self-assembling monolayers on electrodes. Bistable interlocked molecules can be easily deposited on a gold surface in the form of a self-assembling monolayer (SAM) by making use of the affinity of the thiol group for gold. A [3]rotaxane containing a disulfide linkage was prepared²⁵ and adsorbed on a gold electrode to obtain a self-assembling monolayer as a [2]rotaxane structure. The rotation of the ring from a tetra-coordinated to a penta-coordinated complex can be reversibly triggered by electrochemical redox reactions of the Cu(I)/Cu(II) ions in solution. However, the rotation of the ring is too slow to be detectable in the form of SAM, which might be due to the confinement on the surface.

Bistable [2]rotaxane species that consist of a π -acceptor tetracationic ring (CBPQT⁴⁺) and two π -donor stations (TTF and DNP) can be induced by electrochemical redox switching process in solutions. A [2]rotaxane of this kind was terminated by a five-membered disulfide ring (R16 in Fig. 16) and a self-assembling monolayer was immobilized on gold surface.²⁶ The translational isomerization in this SAM from the ground state

(the CBPQT⁴⁺ ring encircling the TTF unit) to the switched state (the macrocycle residing on the DNP group) can be achieved by oxidizing the TTF unit to cationic radical, and the backward relaxation process can be obtained not only by electrochemical reduction, but also by thermal neutralization of the TTF cationic radical.

Molecular dynamic simulations of such self-assembling monolayers were also reported recently.²⁷ The optimal packing density and the thickness were calculated. It seems that the surface tension at optimal density of the ground state co-conformer (GSCC) is less than the one of the metastable-state (MSCC), which means the water contact angle for the GSCC is larger than that for the MSCC. This prediction is confirmed by Langmuir–Blodgett film experiments.

5.1.2 Langmuir–Blodgett films on interfaces. The Langmuir–Blodgett film (LB film) technique affords the opportunities to make molecules in order, especially for those molecules which have different tails of different hydrophobic ability. A Langmuir monolayer of bistable amphiphilic [2]rotaxane was prepared by spreading the diluted [2]rotaxane solution in chloroform on the water surface. After the solvent was evaporated, a monolayer was formed on the surface.²⁸ Transferring the Langmuir monolayers onto a silica substrate results in the formation of LB films, which exist in a conformation with the tetraarylmethane stoppers sticking out towards the air and the [2]rotaxane backbones laying tilted at an acute angle to the silica surface. The consistency of the molecular conformation raises opportunities for electronic device fabrication.

To further examine the shuttling motion in the form of LB film, a Langmuir monolayer of a bistable amphiphilic [2]rotaxane was deposited on the water surface,²⁹ and triggered by external stimulus. Both of the Langmuir monolayers of the start state and the triggered state were transferred *in situ* as LB film to substrates. The X-ray photoelectron spectroscopy (XPS) studies revealed that shuttling motion occurs among the LB film.

Besides X-ray photoelectron spectroscopy, surface-sensitive synchrotron X-ray reflectometry (XR) can also be used for the structural investigation of the above redox-controlled switching process in the LB layer at the air/water interface.³⁰ It should be noted that XR can provide direct detailed information about monolayer organization.

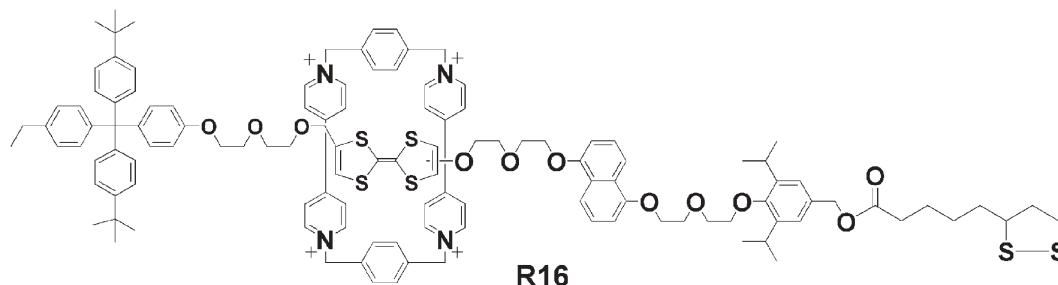


Fig. 16 The chemical structure of R16, which has a five-membered disulfide ring functionalized terminal, used to react with gold electrode.

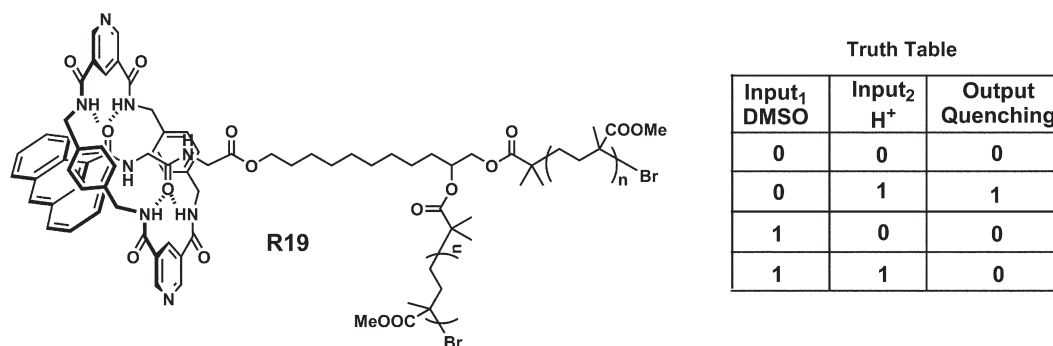


Fig. 20 “INHIBIT” logic function displayed on the polymer film of rotaxane **R19**.

ring is threaded onto the electron-donating phenyldiimino unit. The tetracationic ring can be electrically reduced and shuttles apart from the π -donating group to the gold surface. As a result, a fast electron transfer rate with $K = 1100 \text{ s}^{-1}$ is found. The relaxation process to the initial state can be carried out by reversibly oxidizing the reduced cyclophane and a slow electron transfer rate with $K = 80 \text{ s}^{-1}$ is obtained.

5.3 Molecular transistor

A single molecular transistor devices based on a bistable [2]rotaxane **R18** was fabricated, as shown in Fig. 19.³⁴ Using the Si gate electrode a 30 nm-thick SiO₂ film was grown. On the top of the SiO₂ 14 pairs of Pt electrodes were arranged and then a drop of dilute **R18** solution was placed onto the device, after dried, bonded with wired, mounted on carrier and finally broken by a voltage, those broken junctions containing one molecule were collected and I–V measurements were carried out. The behavior of such devices is that of a single-electron transistor.

5.4 Molecular logic gates

When a single-molecular switch can be fabricated, it will allow opportunities for isolated switch devices to be arranged in a complex form (*e.g.* two-dimensional crossbar architecture) to obtain useful functions such as logic and memory circuits.³⁵

The [2]rotaxane species based on the hydrogen binding can be induced to shuttling motion when the hydrogen bonds are destroyed by a polar solvent. The large relative translational movement of the ring component with respect to the dumbbell unit can be used to create switches with high fluorescent on/off intensity ratio by intercomponent electron transfer. In order to create solid-state devices, a polymer [2]rotaxane **R19** that contains about 10% of this kind of solvent sensitive molecular shuttle was prepared and coated on a quartz slide, as shown in Fig. 20.²³ In the polymer film, the movement of the macrocycle from the glycolglycine unit to the alkyl chain can be induced by a DMSO vapor. Furthermore, the fluorescence of the anthracene is quenched once the pyridine unit on the ring is protonated by an acid vapor, and the fluorescence is recovered when the protonated pyridine macrocycle shuttles to the alkyl

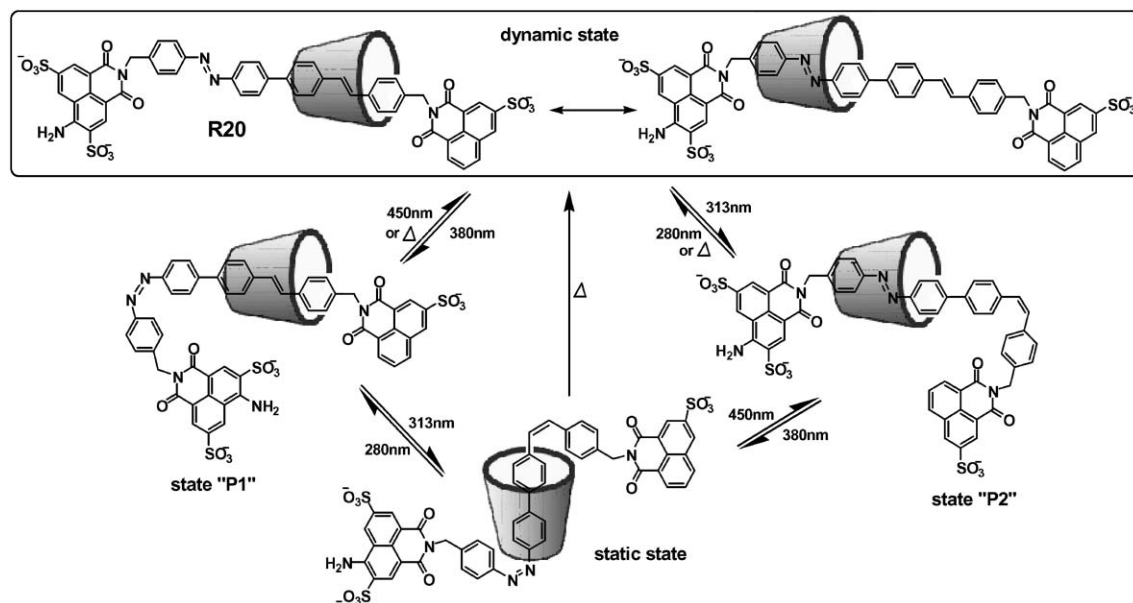


Fig. 21 The interconversion network of **R20** between the four states.

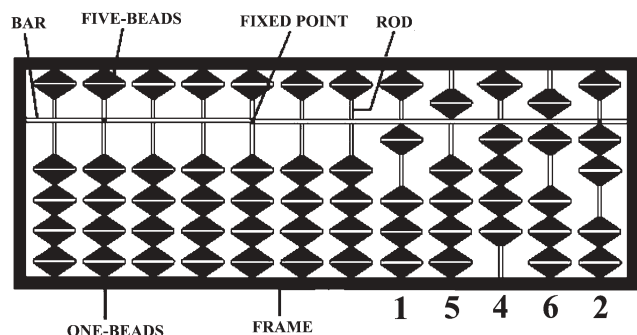


Fig. 22 The structure of a Chinese abacus and its expression of the digit “15462”.

chain. Accordingly, the fluorescent output of the polymer film to the different combination of the two inputs (DMSO and CF_3COOH) corresponds to an “INHIBIT” logic gate.

In 2005, we set up a complicated molecular shuttle **R20**, as shown in Fig. 21.³⁶ In state **P1**, the photoisomerization of azobenzene unit drives the cyclodextrin ring close to NS stopper, and the fluorescent intensity of NS at 395 nm increases. The same situation occurs in state **P2**, the cyclodextrin ring approaches to the ANS unit and the fluorescent intensity at 520 nm increases. All these interconversions are reversible. The relations between the light inputs (313 nm and 380 nm) and the outputs (absorption and fluorescence changes) indicate that this [2]rotaxane system is an all-optical half-adder logic gate.

Fig. 22 shows the structure of a “Chinese Abacus” and its expression for the digit “15462”. It is amazing that this ordinary ancient tool can do complicated arithmetical calculations quickly and precisely, not in the shade of the modern calculator at all, just with the different positions of the abacus beads. The abacus came into use several thousand years ago and is still used now among Chinese accountants.

From this point of view, it is possible for a switchable rotaxane to carry out arithmetic because of its abacus-like structure.

Recently, a complicated [3]rotaxane **R21** (Fig. 23) was synthesized to simulate the abacus system.³⁷ The $E \rightarrow Z$ photoisomerization of azobenzene results in the shuttling of the two macrocycles close to the NS stopper accompanied by the an increase in the fluorescent intensity at 395 nm and a decrease in the fluorescent intensity at 520 nm. The $E \rightarrow Z$ photoisomerization of stilbene shifts the two rings close to the ANS stopper, and the fluorescent intensity at 395 nm decreases, at the same time the fluorescent intensity at 520 nm increases. These isomerizations are reversible. It can be seen that the photo-induced shuttling motions of two macrocycles of the [3]rotaxane are analogous to the movements of the beads of an abacus when carrying out “+2” or “-2” arithmetical calculations. It should be noted that the results of the calculations in this [3]rotaxane can be “read” from the fluorescent changes.

5.5 Memory devices

The ability of an interlocked molecular assembly that can be switched between two different co-conformations offers the possibility for storing information by encoding the two different states into binary digits. This is most appealing since every molecule is a storing unit and high-density mass data storing would be possible. In 2003, three kinds of [2]rotaxanes were grown as thin films on graphite or mica.³⁸ Using the tip of an atomic force microscope, the ring component can be reorganized and a series of regular dots are formed by increasing the load force. These dots could encode data, and such a film could store up to 100 Gbits of data per square inch.

More recently, a rotaxane film on an ITO-coated glass substrate was prepared using LB deposition technique.³⁹ Owing to the reversible electrochemical switching ability of the CBPQT⁴⁺ on **R22** (Fig. 24), the rotaxane thin film exhibits

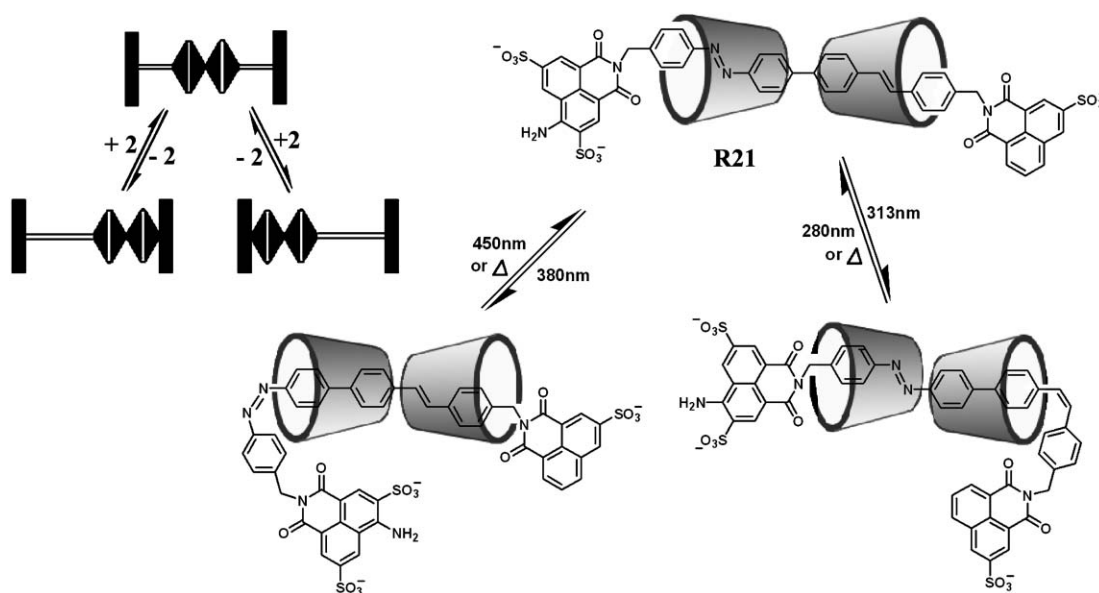


Fig. 23 The photoisomerization-induced shuttling motions in [3]rotaxane **R21**.

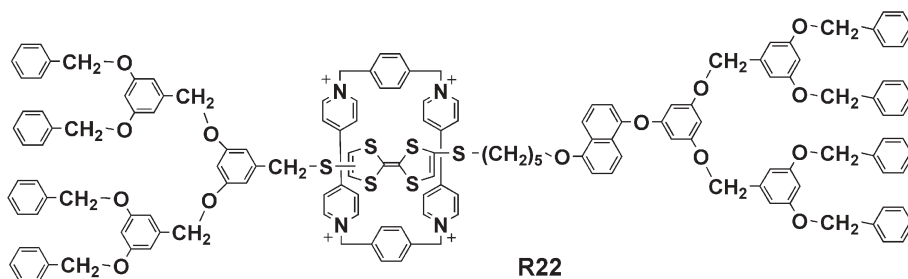


Fig. 24 The switchable [2]rotaxane **R22** used for nanorecording.

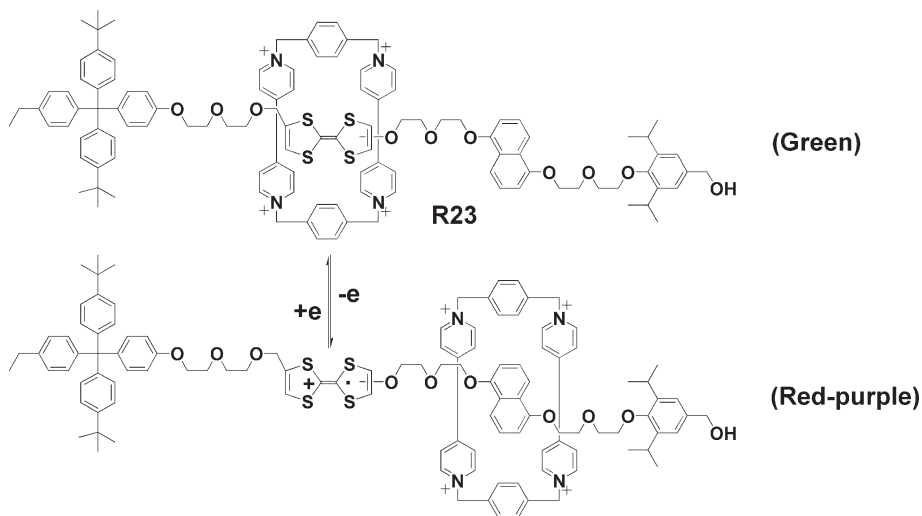


Fig. 25 Capping **R23** within polymeric electrolyte to build up an electrochromic device.

a reversible conductance switching and nonvolatile memory effect with an on/off ratio of about 100 on the basis of STM nanorecording.

5.6 Electrochromic devices

Electrochemical redox reaction can also take place in polymeric electrolyte. Taking advantages of this fact, a solid-state electrochromic device was fabricated by immobilizing the bistable [2]rotaxane **R23** within a solid polymeric electrolyte, and three electrodes—working, counter and reference electrodes—were arranged.⁴⁰ The color of the [2]rotaxane in the ground state (the ring encircles the TTF unit) is green. When an oxidizing potential of +1 V is applied on the working electrode, the rotaxane is changed into a switched state (the ring resides on the DNP unit) and the color of the device changes to red-purple, as shown in Fig. 25. Once the electrical potential is removed, the metastable state is relaxed back to the ground state and the green color recovers.

6. Conclusion and perspective

The molecular shuttle, a switchable rotaxane, has potential applications in the areas shown above, and far more than these. For example, by making use of the stimuli-triggered shuttling motion in a switchable rotaxane, a transporting carrier that could be used for drug delivery systems, molecular

elevators,⁴¹ artificial molecular-level muscle as well as a macroscopic transporter by synthetic molecular machines.⁴² Today, it is inspiring that more and more scientists enter this research field. However, we still walk not far away from the beginning and most of the beautiful functions of switchable rotaxanes can only be obtained in solutions. Many molecular devices were thus fabricated, especially those devices that can compute and store information—switches, logic gates and storage mentioned above. Once these devices can come into practical use, a molecular-level chemical computer might be fabricated, and a revolution in computers would be initiated.

One important approach for the fabrication of a molecular device is to use electrons as the input and output, that is, set up by sandwiching a molecular shuttle LB film between an electrode couple to obtain a molecular switch tunnel junction that can be electrically switched between high- and low-conductive states. However, the performance of a LB film based molecular device depends greatly on properties of the interfaces within the device, and the stability of a LB film is also a problem. It seems that using a molecular shuttle doped in conductive polymer matrix to replace the LB film in the construction of a molecular device is a promising strategy.

Another promising strategy to computing and memory devices, which is what we try to exhibit, is based on the switchable rotaxanes that use photons as input and output. Such a device has advantages over other systems for its convenience and low-cost. However, there are improvements

needed to be carried out. One is to improve the fluorescence intensity ratio between “on” and “off” states. Another is to find switchable rotaxanes that can perform beautiful motions in the solid state the same as in solution. It can be foreseen that, in the near future, switchable rotaxanes will find practical applications in scientific areas and new concepts originated from this area will instill into our daily life. Like the ancient Chinese philosopher Confucius said: *a journey of a thousand miles begins with a single step*.

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