Functional molecular transport junctions based on nanogap structures

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FUNCTIONAL MOLECULAR
TRANSPORT JUNCTIONS BASED ON
NANOGAP STRUCTURES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

The use of individual molecules as functional components in electronic circuits offers the great opportunity to improve and revolutionize electronic systems. With the rapid achievement of nanofabrication, molecular electronic devices have been realized based on the investigation of electron properties of molecules. However, the study to build molecular architectures with electronic functions still leaves us a lot of room for improvement and optimization. Hence, this dissertation focuses on the exploration of hybridized electronic systems with judiciously designed molecules and metal nanostructures, to undertake advanced and complex functions.

Herein, the newly-developed on-wire lithography (OWL) is employed to fabricate nanogaps as nanoelectrode pairs for the formation of molecular transport junctions (MTJs), the most essential structures in molecular electronics. In order to obtain more complex nanodevices with advanced functions, rationally designed or selected molecules are utilized to functionalize the nanogap structure, while several external stimulations are also introduced to modulate the device performance.

Firstly, photo-modulable MTJs are developed via OWL-generated nanogaps functionalized by rationally designed and synthesized complexes with the photochromic dithienylethene unit(s) bearing the electro-active ruthenium fragments. A reversible and repeatable bi-state conductive switching upon alternate irradiation of UV and visible light is distinctly observed. Then, more external stimulations are introduced and orthogonally modulated MTJs are further achieved. The addressable and stepwise control of molecular isomerization is repeatedly and reversibly completed with a judicious use of

the orthogonal optical and electrochemical. Through the rational design, these photo-/electro-cooperative nanodevices can be applied as resettable electronic logic gates for Boolean computing.

Besides chemically synthesized organometallic complexes, natural biomolecules are also used to functionalize nanogap structures. A programmable controllable and reproducible memristive behavior is achieved by natural ferritin-based MTJs, which can be applied for nonvolatile memory. Additionally, the rapid development of biotechnology provides us another option to improve the device function or performance. By tuning the amount of iron inside an engineered ferritin, the ON/OFF ratio of conductance switching of such protein-based nanodevices is modulated accordingly, suggesting that protein molecules can be tailored using biotechnology to suit the specific requirements of molecular devices. These works provide direct proof that natural biomolecules as a parallel choice of chemically synthesized complex can be used to fabricate functional nanodevices.

In conclusion, we develop advanced molecular nanodevices based on the feasible platform of precise nanogap structures fabricated by OWL, under various external controls. Both the synthetic chemistry and natural biosystem have been demonstrated to present enormous resources that fulfill the requirement of molecular devices. With chemical or biological modification of molecular architectures, the function and performance can be obviously improved. Therefore, after optimizing fabrication and operative conditions, such functional MTJs show promising applications in multifunctional nanocircuits.

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Chapter 1 Introduction

This chapter firstly introduces the fundamental background of molecular electronics, followed by the part regarding to the electro-active properties of individual functional molecules. Next, the state-of-the-art of particularly interesting at nanofabrication of physical structures to provide the solid platform to investigate electronic behavior at molecular level and to explore functional molecular devices was reviewed. Moreover, the chemical enabled nanofabrication technique for device development used in this thesis was introduced. Lastly, the research motivation and objectives, as well as the organization of the thesis are presented.

1.1 Molecular Electronics and Molecular Transport Junctions

Molecular electronics,^[1] based on incorporating molecules into electronic circuits, provides us a possibility to further minimize the size of functional component in microelectronic circuit and challenge Moore's Law.^[2] Electronic properties of molecules, such as polarity, delocalization, and charge density, are all determined by the chemical structures and given molecular microenvironments,^[3-5] making molecular electronics that is conceptually different from conventional solid state semiconductor electronics. Therefore, rationally designed molecules are used in such electronic applications (details in Section 1.2) as diodes,^[6, 7] switches,^[8, 9] transistors,^[10, 11] dielectrics,^[12, 13] which are the basis to construct complex functions as logic computing, photovoltaics, sensors, and memories.^[14, 15]

For electronic applications, molecular structures show four major advantages: 1) The size scale of molecules is from a few Å to around 100 nm, suiting to fabricate

functional electronic elements in nanoscale; 2) By choice and design of molecular composition and geometry with synthetic chemistry, the electronic, optical, and structural properties will be tailored to tune molecular transport and binding; 3) Multiple stable geometric structures or isomers of synthesized molecules show distinct electronic properties, which are sensitive to external optical, electrical, and magnetic stimulations; 4) Various electronic behavior, for example switching and sensing capabilities, can be achieved via intermolecular recognition.^[16, 17]

Scheme 1.1. Schematic molecular junction spanning metal electrodes. (Reprinted with permission from reference [2])

Molecular transport junctions (MTJs) are essential structures for developing the field of molecular electronics, as the format of metal-molecule(s)-metal (Scheme 1.1). These simple structures, based on nanofabrication and molecular self-assembly, are basic elements in functional nanocircuits and provide feasible investigation platform for experimental measurement and theoretical modeling of molecular functions.^[18, 19] Four types of molecular-electronic junctions (Scheme 1.2) are represented with examples of molecular structures as follows: a) A linear chain (such as molecules in section 1.2.1); (b) A donor-bridge-acceptor (DBA) molecule (such as molecules in Section 1.2.2); (c) A

molecular quantum dot system (such as molecules in Section 1.2.3); (d) A molecule with multiple functional groups (such as molecules in Section 1.2.4-1.2.6).^[16]

Scheme 1.2. Examples of molecular transport junctions with depicted molecular orbitals (top); electronic energy levels (middle); representative molecular structures (bottom). (Reprinted with permission from reference [16])

Several techniques have been developed to form such MTJs, which will be reviewed in detail in Section 1.3. All of these techniques can be classified as sequential approaches and one-step methods.^[20] In the former one, the molecules are first covalently attached to one electrode and then another electrical contact is introduced to the single molecule or molecular layers (Section 1.3.1 to 1.3.3). Alternatively, the latter one is directly assembly of molecules within predefined nanogap with a pair of nanoelectrodes (Section 1.3.4 to 1.3.6).^[21] Although impressive advances in measuring the molecular conductance have been achieved, the question of how to reliably and repeatedly fabricate appropriate platform capable of manipulation of molecules in nanoscale, which is also favorable to be integrated into electronic circuit as functional components, remains open.

1.2 Electronic Effects of Functional Molecules

1.2.1 Tunneling Barrier

Figure 1.1. (a) I - V characteristics of Al/molecules/Hg at 20°C (Full curves: Al electrode positive biased; dashed curves: Al electrode negative biased.), inset: table of assembled molecules (Reprinted with permission from reference [13]); (b) Plots of current density as a function of the bias voltage between the Hg and Ag electrodes for different molecular junctions (Reprinted with permission from reference [23]).

One of major goal in molecular electronics is the measurement of charge transport in single molecules or molecular monolayers in order to determine their conductance. The early work goes back to the report about the conductivity of fatty acid salts in 1970s, experimentally providing us an original concept of molecular insulating layer.^[13] The tunneling theory has been firstly demonstrated by quantitative proof, as that the tunneling conductance shows the exponential dependence on the thickness of molecular layer, which is shown as I - V characteristics in Figure 1.1a. With the development of

nanofabrication and scanning probe microscopes, many reliable methods can be used to measure the conductance of linear molecules, and molecular monolayer.^[22, 23] Apart from thickness of tunneling layer that is approximately equal to molecular length, the electronic structures also decide the conductance of MTJs. As presented in Figure 1.1b, the organic molecules with π -conjugation exhibit distinctly higher current density than liner carbon chains. As a result, even the simplest organic molecules as alkane, hold the ability to be employed as tunneling barrier and control the whole conductivity of MTJs.

1.2.2 Rectification

Figure 1.2. Rectification through the monolayer of functional molecules with sandwich structures between Al electrodes (Reprinted with permission from reference [7]).

Following the first theoretical prediction of molecular diodes in 1974,^[6] a lot of experimental efforts have been made to verify such devices with unipolar electronic properties. As proposed in the Aviram-Ratner (AR) ansatz, asymmetrical conductance was observed when electron flow through the single molecule with DBA structures, as illustrated in Scheme 1.2b, which was described as unimolecular rectification. DBA molecules as mentioned above are made of units as electron donor (D), insulating

saturated bridge (B), and electron acceptor (A). Since the excited zwitterionic state of D^+-B-A^- exhibits more electron accessibility than the opposite D^--B-A^+ , rectification of current is observed in such molecular diodes. After more than 20 years, this ansatz has been experimentally verified in the configuration, as shown in Figure 1.2. The electrical properties of $C_{16}H_{33}Q-3CNQ$ monolayer were measured with the help of liquid metal contact (in section 1.3.2), and an obvious rectified I - V response was observed, providing a guiding example to design traditional electronic devices by synthesized organic molecules.

1.2.3 Coulomb Blockade

Figure 1.3. (a) Chemical structures and (b) electrochemical properties of Co-based molecular quantum system; (c) electrical performance of the single-molecule transistor (Reprinted with permission from reference [11]).

Besides of DBA type molecules, as shown in Scheme 1.2c, molecular quantum dots are also a model system to explore the quantum effect in the charge transport in MTJs. Meanwhile, since their energy level is simpler than DBA, such kind of complex is more favorable to investigate the interaction of electrode and molecules. In the molecular quantum dot, as shown in Figure 1.3a, the metal atom (Co here) dominates the electron transport in MTJs. It is well known that only low energy is enough to change the charge state of Co from 2^+ to 3^+ . In 2^+ state, there is no sufficient energy to support the electron tunneling to the metal atom, causing coulomb blockade. However, once gate voltage reaches the threshold for transition of Co charge state to 3^+ , the electron tunneling can be achieved and therefore such MTJs present signature behavior of transistors, resulting a single-molecule transistors.^[11] Additionally, in these MTJs, the length of the insulating layer is another key factor that mediate coupling between electrode and molecular quantum, enabling the electronic properties such as the coulomb blockade discussed here. Based on similar mechanism, other molecular transistors have been also fabricated by designed function complex, such as divanadium molecules,^[10] C_{60} ,^[24] and so forth.

1.2.4 Electro-Active Switching

As presented in last section, molecules may undergo isomerization causing the variation of molecular conformation or electronic structure under external stimulation, such as the electrical field introduced before.^[11] In most cases, different molecular isomers have been demonstrated to dominate different charge transport mechanism in MTJs. In electronic devices, electricity is a naturally driven force to trigger molecular isomerization. For instance, a negative differential resistance (NDR) with large on/off ratio was observed in MTJs based on the functional molecules with a nitroamine redox

center (Figure 1.4a).^[25] Such large on/off ratio was owing to the reduction process of electro-active molecules in solid state by increasing voltage. The electro-reduced molecules provided more charge carriers to support high current flow. Apart from NDR, such net reducing and oxidizing processes also caused hysteretic I - V characteristics. A stable bi-conductivity of [2]catenane were achieved by alternately applying set and reset voltage.^[9] The repeatable operation of this on/off switching exhibited promising potential in memory applications. Furthermore, based on the crossbar structure, the array of such MTJs with the electro-driven switching has been demonstrated to carry out logic computing.^[26] Therefore, such molecular switching presents opportunities in the construction of electro-active device with advanced functions.

Figure 1.4. (a) Scheme and I - V characteristics of large NDR effect based on electro-active MTJs (Reprinted with permission from reference [25]); (b) Scheme of electro-switching of bistable [2]catenane and electrical response under cycled operation (Reprinted with permission from reference [9]).

1.2.5 Photochromic Switching

Figure 1.5. Schematic photochromic molecular switch between two gold electrodes in closed state and open state and the corresponding I - V responses (Reprinted with permission from reference [8]).

Following electro-triggered switching, other designed MTJs can also be optically functionalized, based on the rapid development of synthetic chemistry in field of photochromic organic complex. Promising candidates, such as dithienylethene family,^[27] and azobenzenes family,^[28] are synthesized for photo-switching, owing to their properties of photo-isomerization. Azobenzene is a fundamental molecular motor, capable of transducing light into structural switching about the $\text{N}=\text{N}$ double bond between *cis* and *trans* isomers. These photoreactions have been thoroughly investigated, even at single molecule level in solid state by scanning tunneling spectroscopy (STM).^[29] In addition to the *cis-trans* isomerization, upon alternate irradiation of UV and visible light, the molecular electronic structures of DTEs undergo interchange between π -conjugated closed state and non-conjugated open state. As is shown in Figure 1.5, when closed DTE

molecules were integrated to a pair of gold nanoelectrodes with covalent bonds of Au-S, a sharp I - V response could be observed with high conductance,^[8] as molecular π -conjugation facilitates charge transport. However, after a certain time of visible light illumination, the conductivity of such MTJs decreased dramatically, which corresponded to the structural rearrangement to non-conjugation. In this initial design, due to strong electronic coupling between the DTE unit and Au electrode, only one-way switching from closed state to open state can be observed. In this thesis (Chapter II), we will address this problem and design multi-functional molecules to achieve reversible molecular isomerization.

1.2.6 Bio-Conductor

Electron transfer through proteins, a fundamental element of many biochemical reactions,^[30] inspires us to explore functional molecules besides of chemically synthesized complex. In order to study their electronic properties, many attempts were made to integrate proteins into solid-state junctions.^[31, 32] Solid-state protein monolayer junctions have been fabricated by many representative types of proteins with maintaining their native conformation, and high-yield electrical transport has been achieved on these junctions (Figure 1.6).^[33] As a result, the proteins with the physiological function of charge transfer provide more efficient electron transport than a protein such as BSA without such function. This BSA monolayer still exhibited higher efficiency of electron transport than a monolayer of saturated organic carbon chains. The remarkable current densities were measured, indicating that proteins are not insulators, especially redox proteins should be viewed as active electronic materials.^[34] Meanwhile, double strand

1.3.1 Scanning Probe

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from single molecule, some shorter space molecules were employed to dilute the density of target molecules on the surface (Figure 1.7a). Then, the other electrical contact is easily achieved by conductive STM or AFM tip. The further design of STM break junction (Figure 1.7b) may avoid the prior formation of SAM. By comparing the retraced position of Au tip and measured conductance, the resistance of single molecule in the solution is addressed. One problem of STM is that the formation of molecular junctions must rely on the parameter of conductance, which is also the result needed to measure. The control system of AFM may avoid this problem and therefore, after metal coating of AFM tip, a conductive AFM provides an alternate approach (Figure 1.7c) of STM. However, although these scanning probe microscopes present feasibility and universality in the investigation of the mechanism of charge transport in MTJs, the complex equipment limit their application in the fabrication of nanodevices that is favorable be integrated into electronic circuits.

Figure 1.7. (a) Scheme of MTJs formed by STM (Reprinted with permission from reference [22]); (b) A typical experiment of STM break-junction (Reprinted with permission from reference [37]); (c) Scheme of MTJs formed by conductive AFM (Reprinted with permission from reference [38]).

1.3.2 Liquid-Metal Drop

An experimentally simple system with the help of liquid metal as one electrode is developed to measure electron transport across molecular thin films (Figure 1.8), which is inspired by the commonly used liquid mercury electrodes in electrochemistry. Through this method, one can easily bring a metallic electrode as the second contact onto the SAM that is previously modified onto the first electrode surface without the help of complex equipment. Besides of mercury, the alloy of gallium and indium, was also introduced as top electrode with a cone-shape owing to its superficial layer of Ga_2O_3 .^[40] These methods provide convenient platforms to format electrical contacts of MTJs, but the quality of SAM on the substrate is also a key factor in the measurement of molecular conductance to affect the analysis of results.

Figure 1.8. Schematic illustration of MTJs with liquid metal as top electrode (Reprinted with permission from reference [23]).

1.3.3 Sandwich Structures

A major challenge to form MTJs with sequential methods is to avoid the destroying of SAMs during the metal deposition of a top electrode. Additionally, the electrical shorts in SAMs were often observed, which limited contact areas of such molecular junctions. A modification of such metal-molecules-metal structure was further improved as is illustrated in Figure 1.9. This technique involved the immobilization of the SAM in the holes patterned by photoresist with photolithography. Before deposition of a metal top electrode, a layer of conductive polymer was previously coated to avoid directly exposure of SAM during the vapor deposition process.^[3] The yield of this method is closed to 100%, but similar as other sequential techniques introduced in the previous sections, it is hard to obtain MTJs with symmetry electrical interfaces. Moreover, other useful sandwich structures were also fabricated based on Si nanopore^[25] and crossing Au wires.^[41]

Figure 1.9. Processing steps of a large-area sandwich structure molecular junctions (Reprinted with permission from reference [3]).

1.3.4 Mechanical/Electrical Break Junction

Figure 1.10. (a) A schematic of the mechanical break junctions (Reprinted with permission from reference [8]); (b) Representative conductance trace obtained during a nanowire breaking procedure and the SEM before and after gap generation (Reprinted with permission from reference [43]).

The fabrication of predefined nanogap structure to load functional molecules and to form MTJs provides us another parallel option. If the dimension of electrode pairs of a gap can be minimized to nanoscale, such molecular nano-structures will show promising applications as functional elements to build functional nanocircuits. The initial design of this concept is break junction, in the structure of which the nanogap was generated from a single metal wire cleaved by controllable mechanically bending^[42] or electromigration^[10] (Figure 1.10). In the former approach, a notched gold wire was immobilized onto a flexible substrate. Then, an adjustable nanogap is generated by bending the substrate via piezo elements (Figure 1.10a). Whereas, in the latter method, gold atoms of nanoscale wires electrically migrated owing to the large current flow when applying a certain voltage and therefore cause the breakage of the nanowire to form a nanogap (Figure

1.10b). However, in neither of above methods, the geometry of the electrodes and the number of molecules cannot be precisely controlled, causing the low yield of work devices.

1.3.5 Self-Aligned Lithography

Figure 1.11. (a)-(d) The illustrated nanogap fabrication with self-aligned lithography; (e)-(g) SEM image of generated nanogaps. (Reprinted with permission from reference [44])

In the further improvement of nanogap fabrication, chemical reaction is introduced to design and guide the formation of controllable nanostructures. In a technique, called self-aligned lithography (Figure 1.11),^[44] two metal layers of Pt and Al were sequentially deposited onto the substrate, and here the Pt layer was employed as first electrode. After the oxidation of an Al₂O₃ layer on the Al surface that overhung the Pt layer, the second Pt electrode was deposited next to Al₂O₃/Al/Pt layers. With wet etching, a nanogap could be generated between two Pt electrodes, the size of which was determined by the thickness of the aluminum oxide layer. In this approach, the geometry of the electrodes can be precisely controlled. However, lower yields of devices will be

caused by the defects and irregularities in the lateral surface of the gap. Meanwhile, the thickness of Al_2O_3 cannot be quantitatively controlled, affecting the accuracy of gap size.

1.3.5 Single-Walled Carbon Nanotube Cutting

In another strategy for nanogap fabrication, single-walled carbon nanotube (SWCNT) was selected to replace the traditional gold nanowire as the electrodes.^[45] The surface of carbon-based gap can be carboxylated to anchor the target molecules, which provide a parallel option for Au-S bond. In this method, SWCNTs were selectively etched by oxygen plasma with the template of E-beam lithography-patterned polymethylmethacrylate (PMMA).^[45] Defined by the resolution of E-beam lithography, the size of nanogap can be controlled to less than 10 nm, as shown in Figure 1.12. However, based on the processes, this method must fabricate nanogap case by case, and therefore it is hard to controllably incorporate with other functional components to build more complex nanodevices. Therefore, the fabrication techniques with high-throughput are needed to be developed.

Figure 1.12. (a) and (b) Precise cutting of SWCNTs under PMMA patterns with oxygen plasma; (c)-(d) Characterization of the SWCNT and obtained nanogap. (Reprinted with permission from reference [45])

1.4 On-Wire Lithography and the Application in Molecular Electronics

1.4.1 Introduction of On-Wire Lithography

On-wire lithography (OWL), a chemistry-based nanofabrication technique, is a high-throughput method used to prepare nanogaps with feature size control down to molecular dimensions (~ 1 nm).^[46-49] This method relies on the template-directed synthesis of nanowires in an anodized aluminum oxide (AAO) membrane by the electrochemical deposition of desired metal materials, such as Ag, Au, Pt, Ni, and so forth. The gap size is precisely controlled by the thickness of a thin sacrificial layer, normally the Ni layer, which is selectively etched to create the gap. The structure is held together by a thin coat of silica (~ 50 nm) on one face of the wire, which is introduced prior to wet etching. This novel lithographic process allows one to generate designed gap structures on nanowire templates, which is remarkably controllable, high-yielding, and easy to implement. Furthermore, it does not require sophisticated and expensive instrumentation and facilities, and it also allows manipulation of an important class of structures that cannot be easily manipulated with conventional lithographic tools.

1.4.2 Fabrication of Nanogap Structures with On-Wire Lithography

The standard procedures of OWL are illustrated in Figure 1.13,^[50] and the detail processes are as followings: (i) A silver backing is evaporated onto an AAO template as working electrode during electrochemical deposition of metal segments; (ii) A sacrificial silver layer is electrochemically deposited to ensure a solid connection to the evaporated silver backing; (iii) Multi-segment nanowires are grown by electrochemical deposition with electrolyte containing corresponding metal ions; (iv) The silver backing and alumina template are sequentially dissolved by wet chemistry and then the nanorods are dispersed

onto glass slides; (v) SiO_2 is used as a backing material that is deposited onto one-half of each nanorod by vapor deposition; (vi) The nanorods are sonicated off the surface of glass slides; (vii) The sacrificial segments are then etched to form nanogaps, the size of which are depended on the thickness of such sacrificial metallic layers. The obtained metal nanogap structures can be distinctly observed as the sizes of them were precisely tailored (Figure 1.14).

Figure 1.13. On-wire lithography protocol, (Reprinted with permission from reference [50]) and SEM images of multisegment metallic Au-Ni nanowires before (left) and after (right) coating one side with 50 nm of silica and subsequent wet-chemical etching of the Ni segments. (Reprinted with permission from reference [46])

1.4.3 Applications of On-Wire Lithography-Fabricated Nanogap Structures

Figure 1.14. (a-c) Confocal Raman microscopy images of gapped nanowire structures functionalized with probe dye molecules; (d-e) SEM images of designed nanodisk arrays. (Reprinted with permission from reference [51])

OWL has been used to build high-throughput devices for the research field including nano-optics,^[48, 51-58] nano-mechanics,^[59] biosensing,^[60-62] synthesis^[63, 64] and molecular electronics^[65-68] that is also the topic in this thesis and will be discussed in detail in the next section. Such technique allows us to fabricate unique and tunable one-dimensional noble-metal nanostructures that facilitate light harvesting and energy transfer.^[48, 51-58] Rational designs with nanometer precision, as shown in Figure 1.14, lead us to explore plasmon coupling and electromagnetic enhancement that are the basis

of the well-known analytical tool, surface-enhanced Raman spectroscopy (SERS). Therefore, such SERS-active nanostructures enabled the development of sensitive spectroscopic detection systems with the high enhancement factor up to $\sim 10^8$, especially for the biomolecules, including DNA (Figure 1.15a), proteins, certain small molecule analytes and so forth.^[60-62] Based on the further improvement of such bio-hybridized nanostructures, a novel and highly sensitive encoding system (Figure 1.15b) for both chemical and physical covert labeling was developed.^[60] Importantly, in principle, any chemical or biological species may be attached with conventional metal-ligand-binding chemistry to the OWL structures for the applications listed above.

Figure 1.15. (a) An OWL-gap electrical device, with etrapped target molecules in the Raman hot spots as sensitive DNA sensors (Reprinted with permission from reference [69]); (b) Nanodisks code (5-disk-pair) with optical readout (Reprinted with permission from reference [60]).

1.4.3 New Testbeds for Molecular Electronics

Figure 1.16. (a) SEM image and (b) TEM image of wires with 3.2 ± 0.4 nm gaps fabricated by OWL; (c) SEM image of a device prepared with an OWL-fabricated wire with a ~ 3 nm gap; (d) a diagram of OPE-1 molecules spanning the ~ 3 nm gap; (e) Representative I - V response for ~ 3 nm OWL-fabricated gaps before (black curve) and after being modified with OPE-1 (upper red curve) or other shorter molecules (bottom colorful curves), such as OPE-2. (Reprinted with permission from reference [65])

In studies of molecular electronics, nanoelectrodes with nanogaps small and suitable enough to accommodate “molecular wires” can be rapidly constructed by OWL. (Figure 1.16a-c) As is illustrated in Figure 1.16d, OWL-generated nanogaps served as a new testbed to construct MTJs through the assembly of thiolated molecular wires across a gap formed between two Au nanoelectrodes.^[65] The distinct electrical response for the effective junctions of molecules (e.g. OPE-1 in Figure 1.16d) with suitable length by

covalent Au-S bonds was observed (Figure 1.16e), suggesting the high conductance of such conjugated organic molecular wires. Meanwhile, the approach allows one to easily study the electrical properties of molecules in different condition, and can be looked as a novel testbed to identify mechanism of electron transport.^[65] Additionally, when the asymmetry OPE-2 was incorporated, a rectification behavior was observed, owing to different contacts between the molecule and two electrodes. Indeed, from a molecular electronics point of view, OWL-fabricated structures offer an investigation platform of remarkable simplicity, stability, and scalability.

Figure 1.17. (a) SEM image and (b) EDS line scan of multisegmented nanowires (Pt-Ni-Au) after OWL; (c) and (d) Representative I - V response for a ~ 3 nm OWL-fabricated heterometallic (Pt-Au) nanogap device modified with OPE with theoretical fitted I - V curve (red curve), inset: a sketch and SEM image of the device. (Reprinted with permission from reference [66])

Furthermore, the process of OWL is extremely flexible with respect to the type of materials one can use as nanoelectrodes. Any commonly-used metallic material that can

be deposited in an electrochemical experiment is a candidate of electrode material. Hence, heterometallic nanogaps with tunable gap dimensions can be chemically synthesized to be used for fabricating MTJs. For example, the 3 nm gap combined with two sides of Au and Pt nanorods was produced (Figure 1.17a and b), in which the different metallic interfaces were available for chemical modification on opposite ends of the gap.^[66] A nano-diode that showed electrical rectification (Figure 1.17c) as a result of different molecule-electrode couplings at the interfaces causing the asymmetric voltage drop (Figure 1.17d) was demonstrated. Therefore, OWL provides a promising potential platform to create a wide variety of electronic nanodevices with diverse advanced functions.

Figure 1.18. (a) Scheme of click chemistry within the nanogaps; (b) Representative Raman spectrum taken for the different reaction steps; (c) and (d) Representative I - V response curves for the multistep click reactions within OWL-fabricated gaps before and after the final click reaction step (5 nm: two-step; 7 nm: three-step). (Reprinted with permission from reference [67])

Additionally, this OWL-generated nanostructure shows inherent Raman enhancement as previously discussed, and thereby SERS may be employed to spectroscopically characterize the molecular assembly processes within the gaps. Apart from simple Au-S bonds, other chemical processes are also helpful to form junction with nanogap structures, such as click chemistry in Figure 1.18a.^[67] Such chemical assembly process was demonstrated to be monitored as Raman spectra (Figure 1.18b) and the nanogaps could also be tailored to fit different reaction cycles and to form successful junctions (Figure 1.18c and d). Therefore, one of the major challenges in molecular electronics has been overcome, as the achievement of spectroscopy tracking the assembly processes of MTJs, providing the possibility to spectroscopically discover the mechanism of electron transport in MTJs.

1.5 Research Motivation and Objectives

The use of individual molecules as the functional component in electronic circuits offers the great opportunity to improve and revolutionize electronic systems, which holds substantial promising application in the fields including IT, environment, medicine, and energy. The nature of charge transport in the molecular architectures has been gradually understood via theoretical and experimental investigation, as well as the rapid advancement in the field of nanofabrication provides us possibilities to manipulate molecules in nanoscale. This has been demonstrated by the realization of molecular resistors, rectifiers, switches, transistors and so forth, based on the formation of functional MTJ utilizing the various techniques from scanning probe microscopes to nanofabrication, as presented in the previous sections, which is summarized as a roadmap in Figure 1.19.

Figure 1.19. Roadmap of functional MTJs development.

However, the study in the combination of these two research fields, building molecular architectures with electronic functions, still leaves us a lot of room for improvement and optimization. Hence, an in-depth study on development of hybridized systems of judiciously designed molecules and metal nanostructures toward electronic devices with advanced functions are required in my PhD study. The objectives of this work are summarized as below:

- To fabricate a feasible and universal metal nanostructures as investigation platform to provide a suitable nanoelectrode pair for the incorporation of functional molecules;

- To design and synthesize multi-functional molecules capable of co-modulation of light, electricity, or electrochemistry, aiming to obtain advanced nanodevices with multi-addressable control by external stimuli;
- To extend key components from synthetic chemistry to natural biosystem and thereby to employ the specific functions of protein in physiological or biochemical processes to explore biomolecule-based electronic device;
- To tune and improve the device performance by bioengineering following the achievement of bio-nanodevice, which allows us to circumvent the complex chemical synthesis.

1.6 Organization of the Thesis

This thesis is divided into seven chapters. Chapter 1 provides a solid introduction into the field of functional molecular nanodevice, starting with the fundamental concept of molecular electronics and then address on MTJs that are the essential structures to understand the fundamental phenomenon of charge transport at molecular level. Subsequently, electro-active properties of individual molecules and potential application as the elements in electronic circuits were presented, with the state-of-the-art of development in nanofabrication of physical structures to incorporate such functional molecules, and finally the newly developed testbed for molecular electronics, OWL-generated nanogap, was addressed. Due to the special advantages in device fabrication, OWL has been selected to generate nanoelectrode pairs for exploration of molecular nanodevices with advanced functions. The processes of the fabrication and measurement of nanogap devices are fully described in Chapter 2, including the preparation of nanogaps, the fabrication of blank nanogap devices, the assembly of functional molecules,

and the electrical measurement of device performance. As demonstrated in the previous reports, through the modification of the interfaces between functional molecules and electrodes, molecular diodes were achieved based on such nanostructures. As is well known, external stimuli, such as light, mechanical force, magnetic field, electrical field and electrochemical potential, are commonly used to control the molecular conformation or structures that determine the molecular conductivity, and thus they are all naturally driven forces to modulate the electronic behaviors of molecular devices. Therefore, in Chapter 3, light irradiation is firstly employed as inputs to tune device performance and a photo-controllable nanoswitch based on the rational chemical modification of photochromic complex is developed. In the following Chapter 4, inspired by synergies between such external stimuli, such as the giant magnetoresistance effect and photoelectric cooperation, more controls are introduced to synergistically modulate designed molecules, and multi-addressable MTJs are fabricated. The functionality and complexity of previous molecular device is further improved to achieve Boolean computing with orthogonal and stepwise modulation of photo-/electro-stimuli. The successful application of chemically designed complexes in nanodevice fabrication has been proved in the previous chapters, while use of biomolecules as functional elements also represents an attractive strategy to circumvent complex processes of chemical synthesis, since biomacromolecules, such as DNA and proteins, always perform specific functions in all physiological or biochemical processes. Consequently, in Chapter 5, a nanogap device is functionalized by a kind of natural protein, ferritin, and repeatable memristive switching is observed under cyclic electrical scanning, revealing the promising application of natural biomolecules in the exploration of electronic device.

Although the diversity of these natural molecules is vast, tailoring their structures to fit the variable and complex requirements is still achievable by leveraging on the rapidly developing bioengineering field. Based on the ferritin-nanogap device in Chapter 5, the obtained memristive behavior is further improved via structural modification of the functional protein by bioengineering in Chapter 6. Hence, it is demonstrated that bioengineering will provide an alternative approach of synthetic chemistry to tune electronic performance via structural modification of biomolecules. Finally, the thesis closes with conclusions and future perspectives for this project as addressed in Chapter 7.

Chapter 2 Experimental Procedures and Techniques

2.1 Preparation of OWL-Generated Nanogap

As fully discussed in Chapter 1 (Section 1.4), OWL is a powerful technique to provide nanoelectrode pairs as electrical contacts for functional molecules with precisely gap size control. The whole process of nanogap device fabrication is illustrated in Scheme 2.1. In this thesis, the Au nanoelectrode pairs were used, and thus the Au-Ni-Au multi-segment nanowires were firstly synthesized by electrochemically deposition using an anodic aluminum oxide (AAO) porous membrane (Whatman, Anodisc 0.02 μm pores, 47 mm outer diameter) as a template. AAO membranes were evaporated with 200 nm of Ag metal on the reverse, and then placed in an electrochemical cell, which contained a Pt counter electrode and an Ag/AgCl reference electrode. In all experiments, commercially available 1025 Silver (Ag) and Nickel Sulfamate RTU (Ni) and Orotemp 24RTU (Au) electroplating solutions (Technic Inc.) were used for electrochemical deposition (EC epsilon, BASi). Ag was deposited as an initial electrical contact layer under DC current at -800 mV (vs. Ag/AgCl), nickel was plated at -850 mV, while gold was plated at -950 mV. We tune the thickness of nickel layer by controlling the charge (10 mC for 1 nm) during the electrochemical deposition of nickel. The silver backing and AAO template were sequentially dissolved by 4:1:1 solution and 3 M NaOH and then the Au-Ni-Au nanowires were dispersed onto glass slides. Plasma enhanced chemical vapor deposition (PECVD) was used to deposit ~ 50 nm silica on the wire surface. The metal nanowires with half coating of SiO_2 were re-suspended by sonication in ethanol. After etching the sacrificial layer of Ni by 1 M HCl for 3 hours, a nanogap with precisely size control was

generated for the assembly of functional molecules within. In this thesis, 3 nm, 5 nm, and 12 nm gaps were synthesized corresponding to bimetallic DTE complex, trimetallic DTE complex, and ferritin, respectively. It should be noted that the gaps for bioengineered ferritin were slightly adjusted by controlling the charge (~ 120 mC), according to the actual size of the various iron loaded ferritin molecules. SEM (JEOL JSM-7600F SEM, Tokyo, Japan) was employed to observe the morphology of the nanodevices and measure the size of the nanogap, the images of which are presented in the following chapters accordingly.

Scheme 2.1. Illustrated fabrication processes of nanogap device.

2.2 Fabrication of Nanogap Device

In order to measure the electronic properties of such molecular device, the two ends of a single nanowire should be contacted with outer electrodes, which will also make such nanogap devices as real applicable elements in electronic circuits. Two powerful and commonly-used nanofabrication techniques, photolithography and electron beam lithography (EBL), were employed to achieve such target, as shown in Figure 2.1.

Figure 2.1. Schematic processes of (a) photolithography and (b) e-beam lithography for device fabrication. Inset: SEM image of nanogap devices connected with outer microelectrode.

First, microelectrodes were formed following the standard procedures of photolithography by three steps. 1) Si wafers with 600 nm SiO_2 layer were cleaned via sonication in acetone and ethanol for 30 min, rinsed with ethanol and dried with N_2 , and then placed in an oven (95 °C) for 5 min after spin coating with a photoresist (AZ 1518 Photoresist) at 500 rpm for 5s and 4500 rpm for 45 s. 2) The resist was subsequently patterned using a mask aligner (SUSS MJB4 Mask Aligner) with a proper photomask for microelectrodes and developed with AZ 300 MIF. 3) Cr (5 nm) and Au (50 nm) were thermally evaporated onto the patterned wafer and the wafer was immersed in acetone for liftoff.

Subsequently, a suspension of gold nanorods with OWL-fabricated nanogaps was deposited on a chip containing prefabricated Au microelectrodes. EBL was employed to define an inner electrode pattern that connects the nanorods with the microelectrodes. A resist layer of PMMA was prepared by the following procedure: 950 PMMA C7 was spin-coated at 500 rpm (10 second) and 3000 rpm (45 second) followed by baking at

180 °C for 4 min. EBL was carried out using a SEM (JEOL JSM-6360 SEM, Tokyo, Japan), equipped with the Raith SEM lithography kits (Raith ELPHY Quantum, Dortmund, Germany) at 30 kV acceleration voltage and 40 pA beam current. Cr (5 nm) and Au (400 nm) were then thermally evaporated onto the e-beam resist-coated substrate after it had been developed with 1:3 (v/v) MIBK/IPA solution for 30 s, and then rinsed with IPA. Finally, the two ends of the nanorod were connected with the microelectrodes. These nanogap devices (Figure 2.1) were ready for assembly of functional molecules, and electrical measurement.

2.3 Assembly of Functional Molecules within Nanogaps

2.3.1 Assembly of Organometallic Complexes

Chemical reaction may provide an efficient approach to obtain stable connection between functional molecules and nanoelectrodes by covalent bond. The most commonly-used strategy is modified target molecules with thiol ends as anchor group to form the Au-S bond when incorporated within gold electrode pairs, as illustrated in Scheme 2.2a. Therefore, the organometallic molecules used in this thesis (Chapter 3 and 4) were thiolated at the two terminals of molecular wire. However, thiol groups can be mildly oxidized in the air to form disulfides and affect the yield of junctions. Consequently, acetylation was employed to protect free thiol in the chemical synthesis. The assembly details of thiolated functional molecules are presented as the followings. The fabricated nanogap devices were cleaned by oxygen plasma for 1 min to remove organic contamination on the wafer surface, followed by cleaning in ethanol and drying with N₂. The wafer was then immersed in the 5ml degassed 50 μ M tetrahydrofuran (THF) solution of functional organometallic molecules. NH₄OH (28% of NH₃, 5 μ L) was added

dropwise for deprotection of the thiol, as mentioned above. During the assembly process, the sample was kept in the dark for 24 hours under N_2 atmosphere. Finally, the wafer with nanogap devices was removed from the solution and rinsed with THF and ethanol, and then blown dry with N_2 .

Scheme 2.2 Assembly of functional (a) organometallic complex and (b) protein.

2.3.2 Assembly of Biomacromolecules

The thiolation of DNA sequences is a very developed technique that is commercial already, and thus the same Au-S strategy can also be work, whereas, the site directed modification of protein is still a challenge in molecular biology. However, protein always contains a terminal with amine group while the gold surface is easily modified by a layer of small molecules with carboxyl group, which exhibit little tunnelling barrier. With the help of catalysts, amide bond will be formed between gold substrate and protein molecules, and therefore the target protein is immobilized as shown in Scheme 2.2b. The detail processes of protein (ferritin in the Chapter 5 and 6 of this thesis) assembly are described as the followings. After oxygen plasma cleaning, the wafer with nanogap devices was then immersed in a solution of 1 mM 3-mercaptopropionic acid (MPA) for 2 hours and rinsed thrice with water. Then, it was

sequentially immersed in a deaerated 100 mM HEPES solution containing 2 mM 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and 5 mM *N*-hydroxysuccinimide (NHS) for 1 h followed by a PBS solution containing horse spleen ferritin or apoferritin (5 μ M) for 3 h. Finally, the nanogap electrode was removed from the solution and rinsed with PBS and water, and then blown dry with N₂.

Additionally, for the direct assembly of thiolated DNA molecules, the chip was incubated in a 10 mM Tris-HCl buffer (pH 8.0) containing 1 μ M HS-dsDNA (hybridization by 5'-SH-AAA TAT TAC CCT TAC CCT TAC CCT TAC CCT TAT AAA-3' and 5'-SH-TTT ATA AGG GTA AGG GTA AGG GTA AGG GTA ATA TTT-3', purchased from Invitrogen, in Chapter 7), 1 mM Tris (2-carboxyethyl) phosphine hydrochloride (TCEP), 1 mM Ethylenediaminetetraacetic acid (EDTA), and 1 M NaCl for 12 h. Here, TCEP is used to avoid the formation of S-S bond between DNA molecules. Finally, the Raman probe molecules were incorporated into the dsDNA-functionalized nanogap devices by immersing the chip into 50 μ M ethanol solution of Methylene Blue (MB) for 20 min. After being washed with ethanol and 10 mM pH 7.4 Tris-HCl buffer, the devices were ready for measurement.

2.4 Electrical Measurements of Device Performance

The electronic performance, such as current-voltage characteristics and current-time curves, of the nanogap devices were obtained using a semiconductor parameter analyzer (Keithley 4200-SCS) for application of potentials and measurement of currents, combined with a micromanipulative probe station (Janis, Closed cycle cryogenic probe station) for connecting the microelectrodes, as shown in Figure 2.2. In typical

experiments, the measurements were conducted under vacuum (5×10^{-5} torr) to eliminate the influence of humidity and oxygen.

Figure 2.2. Experimental configuration of the electrical measurement of nanodevices.

During electrical measurement, external stimuli were applied in some following chapters. UV-vis irradiation was performed with a 150 W xenon lamp with single wavelength light filters (365 nm for 30 min and 700 nm for 2 h in Chapter 3 and 4). All electrochemical stimuli (Chapter 4) were performed using an electrochemical analyzer, model 832C (CH Instruments). Electrolysis for organometallic complex were carried at 0.45 V (10 min) for oxidation and -0.05 V (10 min) for reduction in CH_2Cl_2 with a three-electrode system consisting of the gold nanoelectrode as working electrode, a platinum wire counter electrode, and a homemade Ag/AgCl reference electrode.

Chapter 3 Photo-Modulable Molecular Transport Junctions

Based on Organometallic Molecular Wires

In this chapter, light irradiation is firstly introduced to tune molecular behaviors in on-wire lithography-fabricated nanogaps and photo-modulable molecular transport junctions are developed by a rationally designed complex with a dithienylethene unit bearing two ruthenium fragments. A reversible and repeatable bi-state conductive switching upon alternate irradiation of UV and visible light can be distinctly observed. Theoretical calculations further suggest that bi-directional isomerization is due to the ruthenium moieties that modulate judiciously the electronic coupling between the photochromic part and the metal electrodes, and that the differences in electronic structure between the two isomers (open and closed states) are responsible for conductivity switching.

3.1 Introduction

Building molecular function into molecular transport junctions (MTJs) to exploit advanced nanodevices with promising applications is both a formidable challenge and an opportunity that, if realized, could have a revolutionary impact on molecular electronics.^[5, 14, 70, 71] Several functional MTJs, such as diodes,^[6] transistors,^[72] and switches,^[73] have been made to show promising application in fields from information technology to nano-bio interface. Integrating photo-switchable molecules,^[28, 29, 74] such as dithienylethylene (DTE), stilbenes, and azobenzenes, into nanodevices is receiving increasing attention.^[75-80] For example, for DTE molecules in solution,^[27, 81-84] the photo-switching is induced by structure cyclization from a cross-conjugated open state to a π -conjugated closed state under ultraviolet (UV) light, while the reverse process is triggered by visible region irradiation.^[27, 81-84] Nevertheless, in the solid state devices, the covalent connection between metal electrodes and DTE molecules may cause just one-way switching from closed to open state, due to the strong electronic coupling formed in such a configuration in MTJs,^[8, 85] thus affecting molecular functionality in photochromic isomerization.

In order to solve this problem, we designed and synthesized a novel and longer photochromic molecule, compound **I**, by covalently bonding two ruthenium fragments $[\text{HS-C}_6\text{H}_4\text{-C}\equiv\text{C}(\text{dppe})_2\text{Ru}]^+$ (dppe=1,2-bis(diphenylphosphino)ethane) on either ends of a DTE unit. The ruthenium complexes are expected to achieve an efficient coupling along the entire conjugated path,^[86-90] while decreasing the strong electronic coupling between the gold electrodes and the DTE groups observed with direct connections. Besides, such fragments are known to maintain the photoisomerization properties of DTEs, characterized by two open (*o*) and closed (*c*) states, in order to ensure electronic

switching between the π -conjugated and non-conjugated states.^[91] In addition, their intrinsic low oxidation potential close to the Fermi level of gold should favour highest occupied molecular orbital (HOMO) mediated-tunneling.^[92, 93]

In this context, we combine the advantages of photo-isomerization of DTE molecules and MTJs fabrication based on OWL-produced nanogaps to explore a photo-controllable reversible switching nanodevice with two-state conductance. Importantly, we found that the organometallic strategy with the DTE molecule **1** leads to a proper modulation of the strong electronic coupling between the gold electrodes and the DTE groups, solving the problem of one-way switching from closed to open state,^[8, 85] without the use of gold nanoparticles for example.^[94-96] In addition, theoretical calculations were performed in order to assess the geometries of both closed and open forms of **1** and understand the geometric reorganization upon irradiation, as well as the transmittance process through the molecule when incorporated between gold electrodes.

3.2 Materials and Methods

3.2.1 Synthesis of Bimetallic DTE Complex

The diethynyl-substituted dithienylethene,^[97] $\text{AcS-}p\text{-C}_6\text{H}_4\text{-C}\equiv\text{CH}$,^[98] and the ruthenium precursor, $[(\text{dppe})_2\text{RuCl}](\text{OTf})$,^[99] were prepared as previously reported. The reactions were achieved under an inert atmosphere in the dark, using Schlenk techniques, as illustrated in Scheme 3.1. Solvents were freshly distilled under argon using standard procedures.

Scheme 3.1. Synthetic route of synthesis of the molecular switch **1**.

***trans*-[(dppe)₂(Cl)Ru=C=CH-*p*-C₆H₄-SAc](OTf).** In a Schlenk tube, [(dppe)₂RuCl](OTf) (1.863 g, 1.75 mmol) and AcS-*p*-C₆H₄-C≡CH (363 mg, 2.06 mmol) were pumped for 30 minutes. Then, well degassed dichloromethane (100 mL) was transferred onto the solids. The solution was stirred for 24 hours at room temperature and then evaporated. The residue was dissolved in dichloromethane (30 mL) and further slow addition of pentane (70 mL) led to a light green precipitate. After filtration, the residue was washed with ether (2 × 50 mL) to yield to 2.05 g of a light green solid (95% yield).

***trans*-[AcS-*p*-C₆H₄-C≡C-(dppe)₂Ru-C≡C-(DTE)-C≡C-Ru(dppe)₂-C≡C-*p*-C₆H₄-SAc] (1o).** In a Schlenk tube, the synthesized precursor (368 mg, 0.29 mmol), NaPF₆ (98 mg, 0.58 mmol), and the diethynyl-substituted dithienylethene compound

$\text{HC}\equiv\text{C}-(\text{DTE})-\text{C}\equiv\text{CH}$ (60 mg, 0.15 mmol) were pumped for 30 min. Then, dichloromethane (20 mL) mixed together with triethylamine (0.39 mL, 2.92 mmol) was saturated with argon and transferred into the Schlenk tube. More triethylamine (0.39 mL, 2.92 mmol) was further added. The mixture was stirred for five days in the dark, and then the solvent was evaporated. The residue was solved in dichloromethane (15 mL), washed with degassed water (3×15 mL), and the solvent was evaporated. The residue was dissolved in dichloromethane (15 mL) and further slow addition of pentane (60 mL) led to a light green precipitate. The product was further purified via filtration on small alumina plugs (elution with dichloromethane) to obtain 220 mg of compound as a greyish solid (59% yield).

1o was then dissolved in the degassed tetrahydrofuran (THF) as 50 μM solution in the dark. This THF solution of **1o** was irradiated with 365 nm UV light for 30 min to ensure that all the **1o** switched to **1c**, which was ready to functionalize the 3 nm gap device. It should be noted that the more rigid closed state molecules were preferred to the unfavorable molecular conformation of the open state molecules (less linear and rigid) to form active MTJs, the detail of which will be discussed later.

3.2.2 Characterization of Bimetallic DTE Complex

High resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest) on a ZabSpecTOF (LSIMS at 4 kV) spectrometer. UV-vis irradiations were performed in toluene with a LS series Light Source of ABET technologies, Inc (150 W xenon lamp), equipped with single wavelength light filters "350FS 10-25" and "750FS 40-25". UV-vis-NIR spectra were recorded with a Cary 5000 apparatus.

3.2.3 Theoretical Computation

Density functional theory (DFT) calculations were performed with the Amsterdam Density Functional package (ADF 2010.02)^[100] on slightly simplified models of **1o** and **1c** (i.e., phenyl groups replaced by hydrogen atoms). The geometries were fully optimized without constraints (C_1 symmetry). Due to the size of the molecules and resulting computational limits, frequency analyses were not performed but the convergence criteria were nonetheless stricter than usual (energy 0.0005 ua, displacement 0.005 Å). Geometry optimizations were performed on **1c** by imposing the S-S distance to be that of the relaxed **1o**, and on **1o** by imposing the S-S distance to be that of the relaxed **1c**.

Electron correlation was treated using the local density approximation (LDA) with the Vosko-Wilk-Nusair parametrization.^[101] The non-local corrections (GGA) of Becke and Perdew were added to the exchange and correlation energies, respectively.^[102, 103] The analytical gradient method implemented by Verluise and Ziegler was additionally used.^[104] The standard ADF TZP basis was set, i.e., triple- ξ STO basis set for the valence core augmented with a 3d polarisation function for C, P was used. Orbitals up to 1s, 2p, and 4p were kept frozen for C, P, and Ru, respectively. In order to evaluate the steric hindrance due to phenyl groups of the dppe ligands, non-optimized structures were built on the basis of the optimized simplified structures.

We used the ATK2008.10 package^[105, 106] to compute the Non-Equilibrium Green function of the device with DFT Hamiltonian at the GGA.revPBE level.^[107, 108] We used the SIESTA^[109, 110] scheme with SZP numerical orbital basis set for valence electrons of gold atoms and DZP for valence electrons of molecular atoms, a (9,9,100) Monkhorst-

Pack k-sampling, and a 300Ry mesh cut-off. Five layers of gold were included on each side of the molecule in the scattering region to soften the transition of the electrostatic potential from the bulk to the (111) chemisorbed gold surface. The Au-S bond distance between the molecule and gold is about 2.42 Å in the chosen on-top configuration. The MPSH states are projected on the molecular part connected to the two gold layers.

3.3 Results and Discussion

3.3.1 Characterization of Bimetallic DTE Complex in Solution

The targeted binuclear compound **1** was readily obtained from the reaction between the diethynyl-substituted dithienylethene and the vinylidene complex $[\text{Cl}(\text{dppe})_2\text{Ru}=\text{C}=\text{CH}-p\text{-C}_6\text{H}_4\text{-SAc}](\text{OTf})$ in the presence of a base and of a non-coordinating salt, as previously described in Scheme 3.1. The complexes were fully characterized (Figure 3.1) and **1** shows very similar characteristics to those of the previously reported analogue complex, $[\text{Cl}-(\text{dppe})_2\text{Ru}-\text{C}\equiv\text{C}-(\text{C}_{15}\text{S}_2\text{F}_6\text{H}_6)-\text{C}\equiv\text{C}-\text{Ru}(\text{dppe})_2-\text{Cl}]$.^[91]

It is to be noted that dithienylethenes can adopt two conformations, with the two thiophene rings in mirror symmetry (parallel conformation) and in the *pseudo*-C₂ symmetry (anti-parallel conformation), and that the photocyclization reaction can only proceed from the anti-parallel conformation. Importantly, as expected on the basis of ¹H and ³¹P NMR characterizations (Figure 3.1) and previously demonstrated by theoretical calculations for the analogue complex,^[91] only the antiparallel isomer is formed due to steric hindrance.

Figure 3.1. (a) ^1H NMR and (b) ^{31}P NMR spectrum of **1o** in CDCl_3 . ^{31}P NMR (81 MHz, CD_2Cl_2 , 297 K): $\delta = 53.6$ (s, PPh_2). ^1H NMR (200 MHz, CDCl_3 , 297 K): $\delta = 7.69\text{--}6.83$ (m, 88 H, Ph), 6.27 (s, 2 H, H_{DTE}), 2.62 (m, 16 H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.44 (s, 6 H, COCH_3), 1.82 (s, 6 H, CH_3_{DTE}). ^{13}C NMR (125.8 MHz, CD_2Cl_2 , 297 K, δ (ppm)): 194.95 ($\text{C}=\text{O}$), 140.65 (quint., Ru-C, $^2J_{(\text{P,C})} = 15$ Hz), 136.93 and 136.61 (m, *ipso*- C_6H_5), 135.86 (DTE), 134.34 and 133.83 (m, *o*- C_6H_5), 133.90 (*m*- C_6H_4 -*p*- SCOCH_3), 131.58 (DTE), 130.40 (*o*- C_6H_4 - SCOCH_3), 129.62 (*p*- C_6H_4 -*p*- SCOCH_3), 128.94 and 128.64 (*p*- C_6H_5), 127.12 (*m*- C_6H_5), 124.14 (DTE), 124.03 (DTE), 121.44 (*ipso*- C_6H_4 - SCOCH_3), 117.23 (Ru-C $\equiv$ C-Ph), 107.26 (Ru-C $\equiv$ C-DTE), 31.39 (m, $|^1\text{JPC} + ^3\text{JPC}| = 23$ Hz, CH_2), 29.83 (COCH_3), 14.38 (CH_3_{DTE}). IR (KBr): $\nu = 1704\text{ cm}^{-1}$ ($\text{C}=\text{O}$), 2050 cm^{-1} ($\text{C}\equiv\text{C}$). HR-MS FAB+ (m/z): 2560.3948 ($[\text{M}^+]$, calcd: 2560.3901). Elemental analysis (%) for $\text{C}_{143}\text{H}_{118}\text{F}_6\text{O}_2\text{P}_8\text{Ru}_2\text{S}_4 \cdot 2\text{CH}_2\text{Cl}_2$: C 63.78, H 4.50, S 4.70 (calcd: C 63.73, H 4.43, S 4.59). Data for **1c**: ^{31}P NMR (121 MHz, C_6D_6 , 297 K): $\delta = 52.8$ (s, PPh_2). ^1H NMR (300 MHz, C_6D_6 , 297 K): $\delta = 7.78\text{--}6.88$ (m, 88 H, Ph), 5.71 (s, 2 H, ArH), 2.63 (s, 6 H, ArCH_3), 2.43 (m, 16 H, $\text{PCH}_2\text{CH}_2\text{P}$), 1.89 (s, 6 H, COCH_3). IR (KBr): $\nu = 2016\text{ cm}^{-1}$ ($\text{C}\equiv\text{C}$).

Figure 3.2 (a) UV-Vis absorption spectra of **1o** and **1c** in toluene. ($[1] \approx 10^{-5} \text{ mol}\cdot\text{L}^{-1}$); (b) Plots of $[1\text{o}]$ vs time upon 365 nm (blue) and $[1\text{c}]$ vs time upon 700 nm irradiation (red). Inset: Plots of $\ln([1])$ vs time.

Therefore, as highlighted in Figure 3.2a, isomerization studies in toluene unambiguously show that the photochromic conversion process upon irradiation of **1o** to the very stable **1c** complex is fully reversible in UV-vis cells ($[c] \approx 10^{-5} \text{ mol}\cdot\text{L}^{-1}$). More specifically, the colourless complex **1o** displays an absorption at $\lambda_{\text{max}} = 359 \text{ nm}$ ($\varepsilon = 84000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). The transition associated with this excitation occurs between the HOMO, π (DTE) and π/d $[\text{AcS-}p\text{-C}_6\text{H}_4\text{-C}_2\text{-Ru-C}_2]$ in character, and the lowest unoccupied molecular orbital (LUMO) which is the corresponding π^* of the DTE, where the LUMO, in particular, possesses two lobes on the methylated carbon atoms that can overlap upon rotation to lead to a ring closure (see below).^[91] Upon irradiation with UV light ($\sim 350 \text{ nm}$), this band vanishes, while a broad absorption assigned to the deep green closed isomer **1c** appears at $\lambda_{\text{max}} = 713 \text{ nm}$ ($\varepsilon = 45000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). This absorption corresponds mainly to a HOMO ($\text{Ru}_{\text{d}}/\pi\text{-C}_2\text{DTE}_{\pi}$) $\rightarrow$ LUMO ($\text{Ru}_{\text{d}}/\pi\text{-C}_2\text{DTE}_{\pi^*}$) transition which removes bonding electrons between the two methylated carbon atoms. It was previously shown that the broadness of the band is due the overlapping absorptions of different rotamers of **1c** in solution with various orientations of the metallic units with

respect to the DTE plane.^[91] This **1c**-containing solution can be further bleached back to a colourless solution of **1o** under visible light (~700 nm) via ring opening, with quantitative recovering of the initial spectra. As shown in Figure 3.2b, the reaction rate of the UV-triggered isomerized process of **1** in solution is apparently higher than that of the visible light-triggered process, which is consistent with the behaviors of their parent complex.^[91] Complete conversions in both directions were further confirmed with ³¹P and ¹H NMR studies, with characteristic resonance shifts of the eight equivalent phosphorus atoms, and of the thiophene and methyl group protons (Figure 3.3).

Figure 3.3. Selected ³¹P and ¹H NMR signals in C₆D₆ of **1o** (up) and of **1c** (bottom) after excitation at $\lambda = 350$ nm in the NMR tube. The initial spectra were recovered after bleaching at $\lambda = 750$ nm.

3.3.2 Theoretical Studies of Molecular Structures

3.3.2.1 Calculated Conformations of **1o** and **1c**

In order to better predict the behaviour of the device, theoretical studies of molecular conformations and electronic structures were performed. The geometry optimization of simplified structures (Phenyl groups of the dppe were replaced by hydrogen atoms to reduce computational cost) of **1o** and **1c** in vacuum reveal different three-dimensional geometrical arrangements (Figure 3.4), due to the modification of the

DTE structure.^[111] The **1o** skeleton presents an angle of roughly 135° between the two acetylide branches (projected straight lines) with a distance of $33.1 \text{ \AA}$ between the terminal sulfur atoms. The **1c** conformation is slightly more spread out with a distance of $34.2 \text{ \AA}$ between the two anchor atoms and an angle of 158° between the two conjugated chains. Considering the S-S axis as reference, the two molecules can be included in cylinders of same circumference (*ca.* $15.2 \text{ \AA}$). When comparing the change in geometry between **1c** and **1o**, a shortening of $1 \text{ \AA}$ of the sulfur-sulfur distance is observed in **1o**. It is attributed to a change in direction of the acetylide chain axis which is almost collinear in the closed form. The adaptability of **1o** is remarkable since a constraint of only 0.03 eV is needed to keep the same molecular length as that of **1c** (S-S distance of $34.2 \text{ \AA}$). This suggests that the structural changes between **1c** and **1o** within nanogaps can occur without detachment of the molecule from the electrode.

Figure 3.4. Calculated molecular conformations of **1o** (left) and **1c** (right) viewed in three different orientations

3.3.2.2 Calculated Electronic Structures of **1o** and **1c**

The electronic structures of the simplified **1o** and **1c** adducts are given in Figure 3.5. The closed form **1c** is less stable than **1o** by 0.26 eV. The electronic structure of **1c** (that has one more double bond than **1o**) displays an additional MO in the HOMO-LUMO gap (i.e., the new HOMO) which has bonding character between the two carbon atoms of the newly formed bond. Important for conduction, this orbital is also delocalized over the conjugated carbon skeleton, including the ruthenium centers. From the above calculated results of both molecular conformations and electronic structures, it is shown that the conformational isomerization between **1o** and **1c** can be achieved even when covalently immobilized within the nanogaps. Meanwhile, the different molecular orbital arrangement of **1c** and **1o** anticipates a conductive switching of **1**-based MTJs, suggesting that such a DTE molecule would be a promising candidate for fabrication of photo-modulable MTJs.

Figure 3.5. Molecular orbital diagrams of **1o** (left) and **1c** (right). The contour values used for the MO representation are ± 0.03 (e/borh) $^{1/2}$.

3.3.3 Photo-Modulable MTJs Based on Bimetallic DTE Complex-Functionalized Nanogap

3.3.3.1 Fabrication of **1c**-Based Nanogap Devices

Experimentally, $\sim 5\ \mu\text{m}$ Au wire structures with $\sim 3\ \text{nm}$ gaps, (which are consistent with the length of **1**) were synthesized and cast onto a silicon substrate (containing a 600 nm SiO_2 layer) with patterned gold microelectrodes. Then, the wires were connected to the microelectrodes by e-beam lithography and subsequent thermal deposition of chromium and gold. Scanning electron microscopy (SEM) revealed that the two ends of an Au nanowire were connected to two separate microelectrodes (Figure 3.6a), with the gap on the wire around 3 nm (Figure 3.6b) as expected.

Figure 3.6. (a) SEM image of a device fabricated with an OWL-generated nanowire; (b) SEM image of $\sim 3\text{nm}$ gap in the nanowire.

The unmodified nanogap device was immersed in a 5 ml tetrahydrofuran (THF) solution of dithiol terminated **1c** (after deprotection of thiol, by eliminating the acetyl group with 5 μL of 28% ammonia) for 24 h. Through the formation of Au–S bonds between the two sides of the nanogap and **1c**, the molecules can be immobilized into the nanogap, as depicted in Scheme 3.2. As the gold nanorod is of 300 nm in diameter, the

accessible surface is thus roughly of $7 \times 10^4 \text{ nm}^2$ if the surface is considered as planar (minimum surface). The molecules have a diameter of 1.5 nm (Figure 3.4), if grafted perpendicularly to the electrode surface, thus roughly of 2.25 nm^2 in surface. Therefore, a maximum number of $\sim 3 \times 10^4$ molecules could be ideally assembled in the junction. The covalent bonds will ensure a strong electronic coupling between **1c** and the electrodes^[65, 67] to achieve the photo-controllable conductance switching due to the photochromic properties of **1c** (Scheme 3.2).^[86-90]

Scheme 3.2. Illustration of a prepared **1c**-based nanogap device and the molecular isomerization upon light irradiation.

3.3.3.2 Photo-Controllable Performance of **1c**-Based Nanogap Devices

Two-terminal I - V characterization of the $\sim 3 \text{ nm}$ gap devices was conducted under a vacuum of 5×10^{-5} Torr at room temperature in the dark both before and after **1c** assembly. The blank nanogap devices showed no conductance within the noise limit of the measurement ($<1 \text{ pA}$). However, when the $\sim 3 \text{ nm}$ gap was loaded with a **1c** monolayer, the devices exhibited an obvious I - V response (black curve in Figure 3.7) at low bias ($\leq 1 \text{ V}$). The observed symmetry of the curves indicates that the **1c** molecules were covalently bound to each of the gold electrodes on opposite sides of the gap. If the molecules were bound only to one contact, the I - V curves would display asymmetry due

to different injection barriers.^[65] This I - V characteristic explicitly suggests a successful fabrication of **1c**-based transport junctions.

Figure 3.7. Representative I - V characteristics of ~ 3 nm OWL-generated gap devices loaded with **1c** molecules, as measured in the dark under vacuum (black curve: initial device; red curve: device after 700 nm irradiation for 2.5 h; blue curve: device after subsequent 365 nm irradiation for 30 min).

More interestingly, the I - V curves of **1c**-functionalized nanogap devices exhibited light-triggered switching (Figure 3.7). After the device was irradiated with visible light at a wavelength of 700 nm for 150 min, the current decreased by about an order of magnitude, as shown in Figure 3.7 (red curve), thus indicating that the device is switched from high conductance (ON state) to low conductance (OFF state). Light at 365 nm was then employed to irradiate the device for 30 min. It can be observed that the current surged back (blue curve in Figure 3.7), suggesting the reverse switching of the device to the low-resistive ON state. Though the conductivity of the device after switching was a

somewhat lower than in the initial state, the **1c**-based devices have a high potential as light-triggered switches under different excitations. This bi-directional transformation is consistent with the photochromic properties of molecule **1** in solution.

Figure 3.8. Selective I - V characteristics for different ~ 3 nm gap devices loaded with **1c** (measured in vacuum and dark).

The yield for working devices is 22% (21 out of 94 devices with $I > 1$ nA on a single chip with an area of $1\text{ cm} \times 1\text{ cm}$, some representative I - V curves are presented in Figure 3.8). In addition, it should be mentioned that the magnitude of the current under 1 V bias obtained from different **1c**-based devices varied in the range from 300 μA to 10 nA (Figure 3.8). This disparity is presumably mainly due to the different number of **1c** molecules that are actually incorporated into the nanogap via chemical bonds with the

gold surface at each side. The roughness and morphology of the gold surface, and the ± 0.2 nm gap size variation, may be among the reasons that cause these variations.^[65]

Figure 3.9. Temperature dependent I - V curves of **1c**-modified ~ 3 nm nanogap device.

Note that the temperature-dependent I - V measurement was also performed in a large temperature range (20K-300K) (Figure 3.9) and just less than twofold variation was observed, eliminating the influence of thermal effects on the device conductivity, and confirming the stability of the high conductance state in the dark (vide infra). Therefore, the photo-controllable structural rearrangement of **1** definitely affects the conductivity of the device, since the π -conjugation pattern in the closed form facilitates the electron transport along the molecule wire.^[65]

3.3.3.3 Performance of **1o**-Based Nanogap Devices

It is worth noting that we also employed **1o** to substitute **1c** for device fabrications with same gap size and that these **1o**-based devices showed very low conductivity and no

photochromic behaviour as **1c**-based devices (<10 pA, 1 V bias, Figure 3.10), suggesting that the MTJs cannot be achieved with **1o** molecules. The failure could be ascribed to the conformation of **1o**, as discussed in the theoretical studies, which is less linear and rigid than **1c**, and hence less favourable to form a connection on the two opposite nanoelectrodes. Although these mono-grafted **1o** molecules may experience the photo-isomerization under UV light, we still cannot measure the conductivity change of the devices that is dominated by the disconnection at one side of nanogap. Note that, based on the calculated **1o** conformation, double bonding onto the same side of the gap could be proposed but the steric hindrance due to the phenyl groups would disfavour it if molecules lie down on the surface. In addition, for **1o** molecules connected to both nanoelectrodes, there is no energy level suitable to support high conductivity of the device (see the following theoretical calculations).

Figure 3.10. Representative I - V characteristics of blank (black curve) and different **1o**-fabricated (red curves) ~3 nm nanogap devices.

3.3.4 Theoretical Transmission Spectra of Bimetallic DTE Complex-Based Nanodevices at ON/OFF States

Figure 3.11. Transmission spectra (in log scale) of the closed and open isomers around the Fermi level of the electrodes which are set to zero for convenience. The black line corresponds to the calculation at equilibrium and the red line in non-equilibrium to observe the bias effect. The red dashed line delimits the transmission window at 0 K showing the part of the transmission spectra which must be integrated to obtain the current at 0.6 V. The HOMO transmission peaks discussed in the text are highlighted in blue.

Furthermore, in order to analyze these experimental current characteristics of the devices, we have calculated the transmission spectra of both the closed and open structures (as obtained in the gas-phase geometry with the constraint of matching the interelectrode gap size) when incorporating them in a gold nanojunction. Current flowing through the junction is obtained by integration of this spectrum in the bias transmission window, according to the Landauer formula.^[105, 111] Transmissions at both equilibrium (zero bias) and under a bias of 0.6 V were calculated in order to take into

account the polarization effects arising from the electric field.^[106] Transmissions for each isomer are separately reported in Figure 3.11. The spectrum of the closed isomer **1c** exhibits an intense peak of transmission near the Fermi level thus allowing for high conductivity. The applied bias induces a shift of this peak, keeping it at the limit of the transmission window and hence restricting the possibility of this isomer to theoretically achieve high conductivity.^[112] On the other hand, the open isomer **1o** exhibits a small peak collapsing under bias. The theoretical closed/open current ratio at 0.6 V is around 40 which is consistent with the one order of magnitude observed experimentally (Figure 3.7 and 3.8), taking into account the high number of molecules in experimental nanojunctions as against our single-molecule calculations.

Figure 3.12. MPSH state identified as the HOMO orbital for the closed and open isomers. The first row corresponds to the calculations at equilibrium and the second to the non-equilibrium calculations showing the polarization effects.

By computing the molecular projected self-consistent Hamiltonian (MPSH) spectrum, we can associate each transmission peak of the spectra with a molecular state.^[105, 106] Formally, the MPSH states can be described as an electronic reorganization

of the isolated isomers upon substitution of the terminal hydrogen atoms by the gold electrodes. Relevant MPSH states are reported in Figure 3.12. In comparison to the gas-phase calculations, we clearly identify the HOMO as the orbital aligned near the Fermi level for both isomers.

The intense peak observed for the closed isomer **1c** is driven by the good delocalization of the MPSH HOMO on the entire photochromic core between the ruthenium linkers, which are crucial to ensure a smooth transmission pathway. However, this orbital shows a moderate weight on the linkers and the gold surface, leading to a valuable reduction of hybridization with the metal, which helps to avoid the quenching of the photochromic switch^[113] in order to maintain photoreversibility. Thus, it is the ruthenium moieties that judiciously adjust the electronic coupling between the photochromic part and the metal electrodes. Under bias, the photochromic part remains unchanged while a polarization of the linker towards the positive side takes place. The final shape rationalizes the conserved intensity of the peak under bias and points to its pinning to the lower (positive) Fermi level. In contrast, the HOMO of the open isomer **1o** in the junction has a small weight on the central photochromic part; this breaks the delocalization and gives rise to a weak transmission peak near the Fermi level. Under bias, the orbital is completely changed and gets strongly polarized leading to the collapse of the weak transmission peak.

3.3.5 Repeatable Operation of Bimetallic DTE Complex-Based Photo-Modulable Switches

Finally, we have demonstrated that such a **1c**-functionalized nanodevice can be used as a photo-modulable switch, for which reversibility, repeatability, and stability

upon irradiation during ON/OFF cycles are all key characteristics. The ON/OFF cycle test conducted under 1 V bias is shown in Figure 3.13. The repeatable wave-shape current response is generated by alternate irradiation of light with wavelengths at 700 nm and 365 nm, reflecting the reversible conductive switching of the device between ON and OFF. It is clearly observed that upon 700 nm irradiation, the conductance of the device gradually decreases following the isomerization from **1c** to **1o**, while upon 365 nm irradiation, the conductance is progressively enhanced due to the recovery of the **1c** arrangement.

Figure 3.13. Current response of an **1c**-based nanogap device at -1 V under alternate irradiation of light at 700 nm and 365 nm for ON/OFF cycle test (the black range represents the state of the device in the dark)

The conductivity of nanodevice is dominated by the amount ratio between **1c** and **1o** bridging the nanogap and therefore the dynamics of **1** isomerization can be studied through the conductance change of the devices. The switching dynamics can be reflected by the conductance change of nanodevices upon different light irradiation, as shown in

Figure 3.14a. The ratio of the isomerized reaction constants (slopes of $\ln(G)$ vs time in Figure 3.14b) k_{365} to k_{700} is about 3, which it is consistent with the behaviors of **1** (Figure 3.2b) in solution, showing a much faster isomerization under UV irradiation than under visible light. However, the kinetics of molecular isomerization is uncomparable due to the distinctly different condition and microenvironment of the photochromic molecules in these two system, such as the medium (vacuum, organic solvent), molecular state (up to thousands of immobilized in a nanogap, 1 μM free in solution), and even the light path (penetration into a nanogap, direct irradiation). In addition, in order to test whether the conductive switching is really photo-related, we also measured the device in dark for 1 h, and found no notable resistive change (Figure 3.13, black range). The reversible light-triggered conductive switching can be repeatedly operated for several cycles, maintaining a stable bi-state of system.

Figure 3.14 (a) Conductance (G) of an **1c**-based nanogap device under alternate irradiation of light at 365 nm (blue) and 700 nm (red) for one ON/OFF cycle; (b) Plots of $\ln(G)$ vs time upon 365 nm (blue) and 700 nm (red) irradiation. The slopes of the fitting lines reflect the reaction constant of the isomerization between **1o** and **1c** and vice versa.

Nevertheless, a progressive loss of reversibility is observed in the course of such a cycling experiment (Figure 3.13), as often observed.^[75-80] This can be the result of the stochastic behaviour of thiols on gold leading to the desorption of molecules from the substrates,^[114, 115] that is increased by the slight additional constraint upon opening. One has also to consider the effect of UV irradiation, causing the decomposition of the molecules,^[116] and the ductility of gold in the reorganization process occurring upon opening.^[117-119] The reorganizations that follow bond breaking with the surface or the gold wire pulling (Such gold wire pulling also modifies the conductivity.) might be unfavourable for re-anchoring and/or for reclosure respectively. We could also observe that, in comparison to single-molecule studies on a related molecule,^[76] the irradiation time required to reach the photostationary state is longer. This is reasonable, since the nanogap can contain thousands of molecules, and the number of those isomerised molecules is a function of exposure time.^[120] Finally, it is also worth noting that the observed closed/open ratio about one order of magnitude is consistent with the theoretical calculation of not only molecule **1** in gold nanogap here, but also relative molecules in previous reports,^[121-123] which is also comparable with conductance change observed in single-molecule switches on other DTE molecules.^[77, 79, 124]

3.4 Conclusion

In summary, we have demonstrated a photo-controllable MTJ nanodevice based on the association of a ruthenium-based organometallic molecular wire including a DTE unit and an OWL-generated nanogap. The obtained devices perform bi-directional conductive switching upon irradiation with UV and visible light. The theoretical calculations performed on **1** reveal (i) that the ruthenium acetylide moieties decrease

judiciously the electronic coupling of the DTE fragment with the metal electrodes in its open form, allowing the system to close upon irradiation, and (ii) that the delocalization of the HOMO of the closed isomer lying near the Fermi level of the junction is high enough to lead to a good conductivity. The switching in conductivity is explained by a weak delocalization in the photochromic part in addition to the polarization of the HOMO level of the open form lying near the Fermi level. Therefore, such a photo-controllable device not only shows a potential application in functional nanocircuits, but also provides a promising platform to clarify the nature of charge transport across single molecules.

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Chapter 4 Orthogonally Modulated Molecular Transport

Junctions for Resettable Electronic Logic Gates

In the preceding chapter, based on the photo-controllable nano-switches fabricated via on-wire lithography-generated nanogaps functionalized with dithienylethene units bearing organometallic ruthenium fragments, more external stimulation were introduced to improve the functionality and complexity of nanodevice in this chapter and the orthogonally modulated molecular transport junctions were further achieved after the optimization of the device configuration. The addressable and stepwise control of molecular isomerization can be repeatedly and reversibly completed with a judicious use of the orthogonal optical and electrochemical stimuli to reach the controllable switching of conductivity between two distinct states. Through the rational design, these photo-/electro-cooperative nanodevices can be applied as resettable electronic logic gates for Boolean computing, such as a two-input OR and a three-input AND-OR.

4.1 Introduction

Since the first molecular rectifier proposed in 1974,^[6] functional devices developed with individual molecules as functional components have exhibited promising applications in fabrication of computing nanocircuits. Their advantages lie in synthetic tailorability, chemically controllable assembly, scalable size, and so forth.^[16] As an essential structure in molecular electronics, MTJs have been used to investigate electronic conduction through functional molecules.^[18, 19, 125] As a result, many electro-active properties, such as rectification,^[7, 40, 66] negative differential resistance,^[25, 126] and coulomb blockade,^[11] have been uncovered, indicative of their promising applications in functional electronic devices. Additionally, external stimuli, such as light,^[75, 77, 79, 80, 96] mechanical force,^[127, 128] magnetic field,^[129, 130] electrical field^[9, 131, 132] and electrochemical potential,^[133-137] were introduced to modulate the molecular conductivity and thus to tune properties of functional molecular devices, thereby significantly driving their development. As attested by the giant magnetoresistance effect^[138, 139] and photoelectric cooperation,^[140, 141] a better synergy between such external stimuli and corresponding fabrication of multi-addressable MTJs may further efficiently advance the field of molecular electronics. Therefore, herein, we will take the advantages of synergetic modulation by multiple external controls, to explore multi-modulable molecular devices, which have not been addressed so far.

In this respect, chemical tailoring of functional molecules with multi-addressable properties will serve as an effective approach to fabricate such molecular devices. In order to address this issue, a new family of organometallic compounds were designed and synthesized, which combines an ideal dithienylethene (DTE) photochromic unit^[27, 142]

and a unique electroactive carbon-rich ruthenium complex,^[88, 89, 143-145] targeting multifunctional switching properties addressable with photon and/or electrons.^[91, 146-148] In the previous chapter, we showed that the bimetallic compound **1** bearing two ruthenium fragments $[\text{AcS}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}(\text{dppe})_2\text{Ru}]^+$ (dppe = 1,2-bis(diphenylphosphino)ethane) on either ends of a DTE unit (Scheme 3.1) exhibits the reversible photo-controllable switching of conductivity when placed within a pair of gold nanoelectrodes fabricated by OWL.^[46-48] In such a molecular wire, the DTE unit undergoes photo-isomerization between a π -conjugated closed state (**c**) and a non-conjugated open state (**o**), and thus dominates the conductive state of the nanodevice, while the ruthenium moieties properly modulate electronic coupling between this DTE moiety and Au electrodes to avoid one-way switching.^[8] In addition to this photochromic property, such a ruthenium/DTE association can also perform electrochemical cyclization of the DTE unit in solution at low potential,^[91] in contrast to organic systems.^[149, 150] Therefore, since it has been successfully demonstrated that molecular conductance can be respectively tuned by light irradiation^[75, 77, 79, 80, 96] or electrochemical potential,^[133-137] we were strongly motivated in the association of these two stimuli in a single electronic device to achieve orthogonally modulated MTJs.

In this context, we develop for the first time the photo and electro commutation of MTJs based on OWL-generated nanogaps modified with two Ru/DTE complexes. First, the reversible and repeatable conductivity switching can be achieved upon orthogonal optical and/or electrochemical triggering of the molecular isomerization of **1o**, thanks to the remarkably low potential for electrochemical cyclization allowing the maintenance of stable thiol linking bonds at electrode interface. Then, a new longer trimetallic complex

with two DTE units is designed toward a multi-addressable system and to further improve device complexity. It results in the fact that the corresponding device can achieve an original stepwise control of conductance requiring both stimuli. Finally, with a judicious choice of photo-/electro-inputs, OR and AND-OR Boolean computing are achieved within the orthogonally modulated MTJs.

4.2 Materials and Methods

4.2.1 Synthesis of Multifunctional Organometallic Complexes

The synthesis of the binuclear compound **1o** was described in Chapter 3, and that of the new trinuclear compound **2oo** is also achieved under an inert atmosphere in the dark, using the Schlenk techniques, as illustrated in Scheme 4.1. Solvents were freshly distilled under argon using standard procedures, while the precursors $\text{H}-\text{C}\equiv\text{C}-$ $(\text{C}_{15}\text{S}_2\text{F}_6\text{H}_6)-\text{C}\equiv\text{C}-\text{Ru}(\text{dppe})_2-\text{C}\equiv\text{C}-(\text{C}_{15}\text{S}_2\text{F}_6\text{H}_6)-\text{C}\equiv\text{C}-\text{H}$ (**3**) and $[(\text{dppe})_2\text{Ru}=\text{C}=\text{CHC}_6\text{H}_4\text{SAc}](\text{OTf})$ (**4**) were prepared as previously reported.^[146]

Scheme 4.1. Synthetic route of **2oo** synthesis.

trans-[AcS-*p*-C₆H₄-C≡C-(dppe)₂Ru-C≡C-(C₁₅S₂F₆H₈)-C≡C-Ru(dppe)₂-C≡C-(C₁₅S₂F₆H₈)-C≡C-Ru(dppe)₂-C≡C-*p*-C₆H₄-SAc] (**200**). In one schlenk tube, complex **3** (32 mg, 0.02 mmol) was dried under vacuum for 30 minutes before addition of dichloromethane (20 mL) and triethylamine (4.0 mL, 0.37 mmol). The solution was cannula-transferred into a second schlenk tube containing the metal vinylidene **4** (54 mg, 0.04 mmol) and NaPF₆ (12 mg, 0.07 mmol), also previously dried under vacuum for 30 minutes. The reaction mixture was stirred at room temperature for 5 days. Then, the reaction mixture was washed with water (3 × 15 mL). The remaining solvent was removed under reduced pressure. The residue was taken up in dichloromethane (10 mL), and pentane (30 mL) was slowly added leading to the formation of a light brown precipitate that was washed with further pentane (2 × 15 mL) to obtain **200** (60 mg, 81 %).

10 and **200** were then respectively dissolved in the degassed THF as 50 μM solution in the dark. These THF solutions of functional molecules were irradiated with 365 nm UV light for 30 min to ensure that all the open state molecules switched to closed state, which were ready to functionalize the 3 nm or 5 nm gap device, respectively. It should be noted that the more rigid closed state molecules were preferred to the unfavorable molecular conformation of the open state molecules (less linear and rigid) to form active MTJs as previously demonstrated in Figure 3.10.

4.2.2 Characterization of Multifunctional Organometallic Complexes

High resolution mass spectra (HRMS) were recorded in Rennes at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest) on a ZabSpecTOF (LSIMS at 4 kV) spectrometer. UV-vis irradiations were performed in toluene with a LS series Light

Source of ABET technologies, Inc (150 W xenon lamp), equipped with single wavelength light filters “350FS 10-25” and “750FS 40-25”. UV-vis-NIR spectra were recorded with a Cary 5000 apparatus. Electrochemical studies were carried out under argon using an Autolab PGSTAT 30 potentiostat (CH_2Cl_2 , 0.2 M Bu_4NPF_6). The working electrode was a Pt disk and ferrocene the internal reference.

4.3 Results and Discussion

4.3.1 Optically and Electrochemically Co-Modulated MTJs.

4.3.1.1 Electrochemical Isomerization of **1**

Figure 4.1. (a) CV of **1o** in CH_2Cl_2 (0.2 M Bu_4NPF_6) before (red line) and after irradiation at 350 nm leading to **1c** (blue line), scan rate $0.1 \text{ V}\cdot\text{s}^{-1}$; (b) Schematic electrochemical processes of **1o**.

The binuclear compound **1** can achieve photo-triggered isomerization both in solution and in solid-state nanodevices. As previously demonstrated, reversible photochromic processes are achieved upon irradiation with UV light for ring closure and visible light for ring opening in solution (Figure 3.2). A typical cyclic voltammogram (CV) of **1o** is also shown on Figure 4.1a. It presents a partially reversible wave at $E_{\text{pa}} =$

480 mV *vs* Ag/AgCl composed of two slightly separated one-electron oxidations for the two electronically independent metal fragments leading to $\mathbf{1o}^{2+}$. During the reverse cathodic scan, two new waves appear at less positive potentials and are ascribed to the $\mathbf{1c}^+/\mathbf{1c}$ and $\mathbf{1c}^{2+}/\mathbf{1c}^+$ processes involving the closed isomer electrochemically generated due to radical coupling as observed with its parent complex (Figure 4.1b).^[91] Logically, identical waves are obtained after photolysis ($\lambda = 350$ nm) of $\mathbf{1o}$, i.e. at $E^\circ_{c1} = 16$ mV and $E^\circ_{c2} = 144$ mV, along with the vanishing of the wave at ca. 480 mV. Therefore complex $\mathbf{1}$ is an ideal candidate to explore photo-/electro-switchable MTJs when incorporated into a pair of nanoelectrodes, as illustrated in Scheme 4.2, which is also strongly supported by the theoretical calculations of molecular geometric reorganization and transmittance process through the molecule in Chapter 3.

Scheme 4.2. Illustrated molecular isomerization of $\mathbf{1}$ under external controls (light irradiation and electrolysis).

4.3.1.2 Photo-/Electrochemical Modulation of $\mathbf{1c}$ -Based Nanogap Devices

OWL-generated gap-based nanodevices have been demonstrated as a unique testbed for molecular electronics.^[65-67] In order to apply optical and electrochemical

stimuli to functional molecules, the nanogap devices are further incorporated with one fluidic cell to achieve an electrochemical environment for device modulation, as shown in Scheme 4.3. Electrochemical processes were carried out using the gold nanorod one side of nanogap as the working electrode with the diameter of ~ 300 nm, a Pt wire as counter electrode, and a homemade AgCl coated Ag wire as reference electrode (Scheme 4.3).

Scheme 4.3. Diagram of the functionalized nanogap devices. (Inset: SEM image of a device fabricated by OWL-generated nanowire.)

In a typical experiment, complex **1c** was covalently bonded onto the two sides of OWL-generated ~ 3 nm gaps (Figure 4.2, inset) after deprotection of the thiol, to ensure the accurate electronic coupling between the molecule and electrodes.^[65, 67] As expected, a photo-triggered conductive switching from low resistance state (LRS, Figure 4.2 black

curve) to high resistance state is observed (HRS, Figure 4.2, red curve) upon 700 nm irradiation, leading to the photochemical isomerization of π -conjugated **1c** to non-conjugated **1o**. The reverse process switches back the device to LRS via the photochemical closure upon UV light irradiation (365 nm) (Figure 4.2, blue curve).

Figure 4.2. *I-V* characteristics of ~ 3 nm gap devices loaded with **1c** obtained in the dark under vacuum. Black curve: initial **1c**-device. Red curve: after 700 nm irradiation of **1c**-device for 2 h to **1o**-device. Green curve: after subsequent electrolysis of **1o** at 450 mV vs Ag/AgCl for 10 min followed by -50 mV for 10 min in CH_2Cl_2 to return to **1c**-device. Blue curve: after 365 nm irradiation of **1o**-device for 30 min to obtain the **1c**-device. (Inset: SEM image of a ~ 3 nm gap.)

Subsequently, the electrochemical cyclisation was also attempted with a device loaded with **1o** molecules by applying a positive potential of 450 mV vs Ag/AgCl followed by a slightly negative potential (-50 mV), in CH_2Cl_2 solution. For enabling comparison with photochemical processes, electrical measurements were then carried out

in vacuum after removing CH_2Cl_2 , in order to eliminate the influence of the solvent on the device conductivity and to only obtain information on molecular resistance (Figure 4.3). Thus, as attested by the resultant switching to the high conduction state (Figure 4.2, green curve), the electrochemical ring closure was successfully realized.

Figure 4.3. Representative *I-V* characteristics of **1c**-functionalized ~3 nm OWL-generated gap devices (a) in CH_2Cl_2 solution or (b) in Vacuum.

By analogy with what occurs in solution, after applying a potential of 450 mV, it is anticipated that **1o** within the nanogap is oxidized to **1o**²⁺. Then, **1o**²⁺ undergoes radical coupling to form more stable isomer **1c**²⁺, which is further reduced to **1c** by the slightly negative potential (-50 mV) applied subsequently. Importantly, due to the unique electronic structure of the ruthenium fragment, this electrochemical cyclisation in the nanogap can be achieved at a low potential, avoiding the breakage of the Au-S bond, which is not possible in the case of pure organic DTE (> 1 V potential is needed to perform ring closure).^[149, 150] Moreover, this electrochemically obtained LRS state could

be switched back to the initial HRS state (open state) upon visible light irradiation as described above.

4.3.2 MTJs-Based Resettable Electronic Logic Gates.

Scheme 4.4. 1-based logic gate: **1** isomerization within nanogap devices under different inputs (UV irradiation and electrolysis). Reset: visible light irradiation.

Based on its unique orthogonally modulable property, the **1**-functionalized MTJs can be viewed as an electronic logic gate (Scheme 4.4). The LRS **1c**-based device is first set to HRS (**1o**) by irradiation of 700 nm light. Then, the UV light irradiation and electrochemical stimulus are employed as inputs. The presence and absence of each input is respectively defined as “1” and “0”. The outputs (“1” for LRS and “0” for HRS) can be recorded from conductance change, as the ratio between that of the modulated devices and that of previous HRS devices is about an order of magnitude at 0.6 V.

Figure 4.4. (a) Conductance changes with different input combinations; (b) The electronic symbol and a truth table of the OR logic gate.

As shown in Figure 4.4a, except in the case of absence of both inputs (0, 0) which leaves the device in HRS (output = 0), the present of either (0,1 or 1,0) or both inputs (1,1) could all trigger the molecular arrangement from the open state to the π -conjugated closed state, resulting in the enhancement of device conductivity to LRS (output = 1). Hence, the Boolean computing of OR (Figure 4.4b) has been achieved with the **1c**-functionalized nanodevices. In addition, a distinct advantage of such functional MTJs as logic gates is the resetability. Upon irradiation under visible light (700 nm), this nanodevice can be reset from LRS (1) to HRS (0).

Thus, to illustrate the feasibility of these resettable MTJs as operative electronic devices, the reversibility and repeatability under the two different external stimuli have been investigated. As shown in Figure 4.5, the two distinct states of the device conductivity can be clearly observed after different cycles. The reversible photo- and electro-triggered resistive switching can be repeatedly operated for several cycles and it maintains a bi-state system, indicating the potential application of such a device in resettable electronic logic gates. As previously demonstrated by us in last chapter and others,^[75, 77, 79, 80, 96] a progressively reduced reversibility in the course of a cycling test using the photochemical stimuli was observed (Figure 4.5a). As the conductance of the

devices showed no obvious change but rather just regular fluctuations with several electrochemical modulations (Figure 4.5b, green dots), it can be concluded that UV irradiation is responsible for decomposition of some molecules and of the subsequent conductance drop (Figure 4.5a, blue dots), rather than desorption of molecules from the gold surface due to stochastic behavior of thiols^[114, 115] or mechanical breaking of bonds upon isomerization as previously proposed. Consequently, the electrochemical control appears to be more reliable in maintaining a stable conductance. Another possible reason for the reduced reversibility, especially comparing to the initial device state, is that some molecules are connected in the nanogap with some constraints due to the roughness of the gap or interactions with other molecules. The first opening process can reduce these constraints and thus further re-closing is not favorable.

Figure 4.5. Endurance performance: current response of a **1c**-based nanodevice under alternate modulation of visible light irradiation (700 nm for 2 h). (a) UV irradiation: 365 nm for 30 min; (b) Electrochemical stimuli: oxidation at 450 mV and reduction at -50 mV for 10 min.

Nevertheless, herein, an OR logic gate has been developed by the orthogonally modulated MTJs. In contrast to other logic gates based on chemical systems,^[151, 152] such

molecular nanodevices exhibit unique advantages of resettablity.^[153, 154] Additionally, comparing to other outputs, such as nonlinear optical signals arisen from the similar complex,^[148] direct electronic outputs will be more convenient for nanocircuits construction.

4.3.3 Stepwise Isomerization of Longer Trimetallic DTE Complex.

4.3.3.1 Characterization of **2**

Figure 4.6. (a) ^1H NMR and (b) ^{31}P NMR spectrum of **200** in C_6D_6 . ^1H NMR (500 MHz, C_6D_6 , 297 K) δ : 7.73-6.92 (m, 128 H, $\text{C}_6\text{H}_5 + \text{C}_6\text{H}_4$ -*p*- SCOCH_3), 6.83 (s, 2 H, H_{DTE}), 6.74 (s, 2 H, H_{DTE}), 2.47 (m, 24 H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.00 (s, 12 H, CH_3_{DTE}) 1.92 (s, 6 H, COCH_3). ^{31}P NMR (121 MHz, C_6D_6 , 297 K) δ : 53.5 (s, $\text{dppe}_{\text{remote}}$), 53.4 (s, $\text{dppe}_{\text{central}}$). IR (KBr): $\nu = 1702\text{ cm}^{-1}$ ($\text{C}=\text{O}$), 2052 cm^{-1} ($\text{C}\equiv\text{C}$). HR-MS FAB^+ 3872.5555 (m/z): ($[\text{M}]^+$, calcd 3872.5623). Analysis for $\text{C}_{214}\text{H}_{174}\text{F}_{12}\text{O}_2\text{P}_{12}\text{Ru}_3\text{S}_6$: C 66.69, H 4.43 (Calcd: C 66.37, H 4.53). Data for **2cc**: ^1H NMR (500 MHz, CD_3Cl_3 , 297 K) δ : 7.36-6.91 (m, 124 H $\text{C}_6\text{H}_5 + o\text{-C}_6\text{H}_4$ -*p*- SCOCH_3), 6.81 (d, $^3J_{\text{HH}} = 6.0\text{Hz}$, 4H, *m*- C_6H_4 -*p*- SCOCH_3), 6.34 (s, 2 H, H_{DTE}), 6.24 (s, 2 H, H_{DTE}), 2.59 (m, 24 H, $\text{PCH}_2\text{CH}_2\text{P}$), 2.42 (s, 6 H, COCH_3), 1.82 (s, 6 H, CH_3_{DTE}), 1.81 (s, 6 H, CH_3_{DTE}). ^{31}P NMR (121 MHz, CDCl_3 , 297 K) δ : 53.0 (s, $\text{dppe}_{\text{remote}}$), 52.4 (s, $\text{dppe}_{\text{central}}$).

In order to explore more advanced functions toward multi-addressable light and electro-triggered multifunctional objects and to increase device complexity, the new trinuclear compound **2** was designed, as is depicted in Scheme 4.1. It was readily achieved using the similar synthetic pathway to that used for the previously reported analogue complex without the protected linking functions.^[146] **2** was fully characterized (Figure 4.6) and shows characteristics similar to those of the latter.

Figure 4.7. (a) Absorption spectra and spectral changes upon 350 nm irradiation of **2oo** (50 μ M in toluene). The process is fully reversible upon irradiation of **2cc** at 750 nm. (b) Selected ^{31}P NMR (left) and ^1H NMR (right) signals in C_6D_6 of **2oo** and of **2cc** after excitation at $\lambda = 350$ nm in the NMR tube. Initial spectra were recovered after bleaching at $\lambda = 750$ nm.

In particular, isomerization studies unambiguously show that the photochromic conversion of **2oo** to the very stable **2cc** complex upon irradiation is complete and fully reversible (Figure 4.7a), which were further confirmed with ^{31}P and ^1H NMR studies (Figure 4.7b). More specifically, the colorless complex **2oo** displays an absorption at $\lambda_{\text{max}} = 357$ nm, and upon irradiation with UV light (350 nm), this band vanishes while a broad absorption assigned to the deep green closed isomer **2cc** appears at $\lambda_{\text{max}} = 733$ nm.

This solution can be further bleached back to the colorless solution of **2oo** under visible light (750 nm) via ring opening. During light irradiation, the intermediate **2co** is just transitorily formed and cannot be isolated, as already demonstrated with the related complex.^[146]

4.3.3.2 Stepwise Ring Closure of **2**

A typical CV of **2oo** is shown in Figure 4.8a that presents a similar wave to that of **1o** at $E_{pa} = 500$ mV vs Ag/AgCl composed of three slightly separated one-electron oxidation for the three electronically independent metal fragments leading to **2oo**³⁺. During the reverse cathodic scan, two new waves appear at less positive potentials and are ascribed to the **2oc**⁺/**2oc** and **2oc**²⁺/**2oc**⁺ processes for the open-closed isomer electrochemically generated (Figure 4.8b), since only one radical coupling could be obtained with oxidation of three Ru centers.^[146] The cyclic voltammogram of **2cc** is obtained after photolysis ($\lambda = 350$ nm) of **2oo**, and presents four systems at $E^{\circ}_{c1} = 94$ mV, $E^{\circ}_{c2} = 210$ mV, $E^{\circ}_{c3} = 330$ mV and $E^{\circ}_{c4} = 500$ mV.

Figure 4.8. (a) CV of **2oo** in CH₂Cl₂ (0.2 M Bu₄NPF₆) before (red line) and after irradiation at 350 nm leading to **2cc** (blue line), scan rate 0.1 V·s⁻¹; (b) Schematic electrochemical processes of **2oo**.

Thus, as illustrated in Scheme 4.5, **2oo** displays the same unique properties as those of its parent compound without the linking functions, and is thereby a multi-addressable light and electro-triggered multifunctional object for integration in nanogaps. Of particular interest is the stepwise ring closure: after electrochemical oxidation followed by reduction to the neutral state, a single ring closure leads to **2oc**, and further full closure to **2cc** can thus be accomplished electrochemically or with UV light.^[146]

Scheme 4.5. Illustrated molecular isomerization of **2** under external controls (light irradiation and electrolysis).

4.3.4 Multi-Addressable MTJs for Advanced Boolean Computing.

4.3.4.1 Multi-Addressable and Stepwise Control of **2cc**-Based MTJs

Complex **2cc** was further assembled into OWL-generated ~ 5 nm gap devices (Figure 4.9, inset), under the same condition as those used for **1c** immobilization. The gap size here was tailored to be consistent with the length of **2cc** that was estimated to c.a. 49 Å using molecular model based on the bimetallic parent complex.^[91] As shown in Figure 4.9, a characteristic I - V response has been observed with the symmetric black

curve, which represented the successful formation of **2cc**-based transport junctions. As observed with **1c**-based device, the conductivity of the **2cc**-based nanodevices decreased after irradiating with 700 nm visible light (Figure 4.9, red curve), corresponding to the molecular isomerization from the fully π -conjugated **2cc** (LRS) to the non-conjugated **2oo** (HRS). Then, molecule **2** can also undergo the fully reverse photo-isomerization upon UV irradiation, and directly interchange from **2oo** to **2cc** through the transitory **2co**. The device is then tuned back from HRS to LRS (Figure 4.9, blue curve).

Figure 4.9. I - V characteristics of a ~ 5 nm gap devices loaded with **2cc** under vacuum. Black curve: initial **2cc**-device. Red curve: after 700 nm irradiation of **2cc** for 2 h to **2oo**-device. Half green curve: the resulting **2co**-device after one step of electrolysis of the **2oo**-device at 450 mV vs Ag/AgCl for 10 min followed by -50 mV for 10 min in CH_2Cl_2 . Green Curve: after two cycles of such electrolysis of **2oo** to achieve the **2cc**-device. Purple curve: one electrolysis cycle of **2oo** followed by 365 nm irradiation for 30 min to achieve the **2cc**-device. Blue curve: 365 nm irradiation of **2oo** for 30 min to **2cc**-device. (Inset: SEM image of ~ 5 nm gap.)

More interestingly, further application of the electrochemical stimuli defined as E_1 (sequentially applying 450 mV for oxidation of the organometallic ruthenium moieties, and -50 mV for reduction of the complex to the neutral state) to the **2oo**-based nanodevice, to perform DTE ring closure as for **1o**-based devices, led to no significant change in the conductance of the device. Only a slight increase could be observed as shown by the half green curve in Figure 4.9. This expected fact is attributed to a single DTE electrochemical cyclisation of **2oo** to **2co**, since only one ring closure is obtained via one radical coupling in the triply oxidized molecule **2oo**³⁺ to provide **2co**³⁺ before reduction, as stated above.^[146] Thus, in this case, the non-conjugated open DTE unit dominates the resistance of the whole molecule and the device is maintained in the HRS state. Starting from this **2co** state, the conductivity jumps to the LRS when the device is further exposed to 365 nm UV irradiation (Figure 4.9, purple curve), as expected, leading to the **2cc**-based nanodevice. Significantly, when the **2co**-device is further submitted to another electrochemical cycle (also sequentially applying 450 mV, and -50 mV), defined as E_2 , under the same conditions as the first (Figure 4.9, green curve), the LRS is also reached. These results indicated that two DTE units are fully closed and that the π -conjugated **2cc** is also formed within the nanogap in both cases. Thus, in addition to the one step UV irradiation, the full molecular isomerization of **2oo** to **2cc** in the nanogap can be also achieved by stepwise and orthogonal electrochemical and photo stimulations or via a two-step electrochemical process, most likely via two stepwise radical couplings of the two DTE units. It should be noted that owing to the unique gap structure of this nanodevice, the two opposite nanorods of the gap can both be employed as working

electrodes for electrolysis, and therefore the later step can be achieved using the same or the opposite nanoelectrodes.

4.3.4.2 2-Based MTJs as 3-Terminal Logic Gate

As discussed with **1c**, **2cc**-functionalized MTJs can also be designed for Boolean operation (Scheme 4.6). Upon 700 nm light irradiation, the **2cc**-functionalized device is set to the **200**-based HRS. Electrochemical modulation and UV irradiation for ring closures can be employed as inputs.

Scheme 4.6. 2-based logic gate (a) without or (b) with UV irradiation: **2**

isomerization within nanogap devices under different inputs (UV irradiation and electrolysis). Reset: visible light irradiation.

First, without introduction of 365 nm UV light irradiation (UV: 0), the presence and absence of each of the electrochemical input step (E1 and E2) were defined as “1” and “0”. Only the presence of both inputs (1,1) could cause the two stepwise ring closure to form π -conjugated pattern of **2cc**, promoting the electron transport (output = 1); while in absence of both (0,0) or either inputs (1,0 or 0,1), the device conductivity remain as HRS (output = 0) (Figure 4.10a). These results suggest that an electronic AND gate has

been achieved with only stepwise electrochemical modulations. It is worth noting that although the device remained in HRS with the inputs of (0,0), (0,1) or (1,0), the molecular structure is not the same in all cases. By one step electrochemical modulation, **2oo** likely completed a single ring closure to form **2co**. As discussed above, in this case, only slight conductance enhancement was observed and the device remained in HRS. On the other hand, when the UV irradiation as the third terminal input (UV: 1) was used, **2oo** could undergo the photo-isomerization to **2cc** by closure of two DTE units simultaneously, and therefore the device were directly tuned from HRS to LRS (Figure 4.10a), irrespective of any electrochemical stimuli being applied. Hence, a more complicated three-terminal logic gate has been developed combining the sequential Boolean computing AND and OR. (Figure 4.10b)

Figure 4.10. (a) Conductance changes with different input combinations. (b) The electronic symbol and a truth table of the AND-OR logic gate.

Then, this functionalized three-terminal logic gate is also resettable with the help of 700 nm irradiation. Therefore, as shown in the Figure 4.11, both photo- and electro-triggered conductive switching could be repeatedly operated. Note that the progressive reduced reversibility in Figure 4.11a also suggests that UV irradiation may cause

decomposition of some functional molecules with time. In contrast, the stepwise electrochemical modulations clearly exhibit reversibility in Figure 4.11b. This fact highlights the pertinence of our electrochemically driven Ruthenium/DTE nanodevices. Note that owing to the sensitivity of UV irradiation, the stability of such logic devices is not yet competitive to conventional semiconductor devices. However, this first proof of concept of MTJs-based logic devices will push forward the development of such multifunctional molecular devices.

Figure 4.11. Endurance performance: current response of a **2cc**-based nanodevice under alternate modulation of visible light irradiation (700 nm for 2 h) and (c) UV irradiation (365 nm for 30 min) or (d) two successive electrochemical cycles (oxidation at 450 mV and reduction at -50 mV for 10 min). The current values were recorded at 0.6 V bias in vacuum.

4.3.5 Yield of Operative Devices with Orthogonal Modulation

It is worth noting that the yield of operative devices was around 21% (18/86 on a single chip of 1 cm $\times$ 1cm, Table 4.1) for **1c**- functionalized devices and 17% (13/77 on a

single chip of 1 cm $\times$ 1cm, Table 4.2) for **2cc**-functionalized devices. For different operative devices, a disparity in conductivity can be observed (current range: $\sim 10^{-5}$ to $\sim 10^{-9}$ A, at 1 V bias). This disparity should be mainly ascribed to the different number of functional molecules that actually span the nanogaps from one to the other, which may be due to the ± 0.2 nm gap size variation, and the uncontrollable roughness and morphology of the gold surface.^[65, 67]

Table 4.1 Performance of **1c**-based Nanodevices.

Device	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1c initial	57.9 μ A	22.1 μ A	16.7 μ A	11.6 μ A	8.93 μ A	5.78 μ A	5.12 μ A	2.63 μ A	2.01 μ A	1.76 μ A	0.83 μ A	0.39 μ A	79.2 nA	28.4 nA	10.2 nA	7.71 nA	1.85 nA	0.82 nA
1o Vis	2.17 μ A	1.79 μ A	0.58 μ A	0.49 μ A	0.60 μ A	0.37 μ A	0.67 μ A	0.14 μ A	0.32 μ A	93.6 nA	30.1 nA	24.7 nA	4.77 nA	3.48 nA	1.92 nA	0.52 nA	176 pA	90 pA
1c E	44.4 μ A	20.5 μ A	14.0 μ A	10.8 μ A	6.68 μ A	5.03 μ A	4.55 μ A	2.02 μ A	1.72 μ A	1.47 μ A	0.69 μ A	0.29 μ A	71.3 nA	22.6 nA	8.70 nA	7.44 nA	1.50 nA	0.54 nA
1c UV	35.9 μ A	18.7 μ A	12.3 μ A	9.12 μ A	6.11 μ A	3.78 μ A	3.61 μ A	1.57 μ A	1.59 μ A	1.29 μ A	0.54 μ A	0.26 μ A	60.5 nA	18.4 nA	5.69 nA	5.95 nA	1.28 nA	0.49 nA

[a] Current values were recorded at 0.6 V.

Table 4.2 Performance of **2cc**-based Nanodevices.

Device	1	2	3	4	5	6	7	8	9	10	11	12	13
2cc initial	20.8 μ A	12.2 μ A	9.07 μ A	6.31 μ A	4.39 μ A	2.52 μ A	1.34 μ A	0.51 μ A	0.37 μ A	117.6 nA	30.2 nA	8.48 nA	1.13 nA
2oo Vis	0.93 μ A	0.54 μ A	0.51 μ A	0.19 μ A	0.47 μ A	84.8 nA	90.4 nA	27.2 nA	15.6 nA	9.88 nA	4.97 nA	1.93 nA	0.21 nA
2co E ₁	1.12 μ A	0.72 μ A	0.58 μ A	0.28 μ A	0.49 μ A	107.8 nA	110.1 nA	30.9 nA	16.6 nA	11.3 nA	5.04 nA	1.90 nA	0.22 nA
2cc E ₁ +E ₂	18.5 μ A	10.6 μ A	8.92 μ A	4.94 μ A	3.61 μ A	2.15 μ A	1.22 μ A	0.39 μ A	0.32 μ A	110.4 nA	22.1 nA	6.29 nA	0.85 nA
2cc E ₁ +UV	16.1 μ A	9.33 μ A	7.02 μ A	4.50 μ A	3.07 μ A	1.89 μ A	1.07 μ A	0.32 μ A	0.26 μ A	100.9 nA	16.9 nA	5.98 nA	0.69 nA
2cc UV	13.8 μ A	7.14 μ A	5.99 μ A	3.47 μ A	2.54 μ A	1.66 μ A	0.90 μ A	0.27 μ A	0.21 μ A	89.7 nA	13.2 nA	5.13 nA	0.44 nA

[a] Current values were recorded at 0.6 V.

As estimated on the diameter of molecules, up to $\sim 3 \times 10^4$ molecules can be ideally assembled in the junction (see Section 3.3.3.1 in previous chapter for detail),

which is according to the four orders of magnitude range of the measured currents. As similar conductivity disparity can be found in the other reported molecular junctions based on the OWL-generated nanogap,^[65-67] and considering the different size and resistance of single functional molecules, all these highly agreed with each other. In addition, the lowest observed current magnitude is at $\sim$ nA level that corresponds to the junction with only few molecules loaded, which is comparable to the results of single-molecule studies in previous reports on shorter DTE containing molecules.^[77, 142]

Besides the conductivity disparity, the current ratios between “1” and “0” states of different devices exhibit a slight fluctuation (Table 4.1 and 4.2). However, these ratios are all located in the range of 10 to 20 times, which are consistent with theoretical (see last chapter) or experimental^[77, 142] closed/open current ratios of single DTE derivatives, taking into account the high number of molecules loaded in the nanogaps. Such random fluctuation may be ascribed to slightly different orientations and conformations of functional molecules within each working device with variable roughness affecting the efficiency of the switching events.

Note that the logic nanodevices presented here show a longer switching time comparing the traditional semiconductor systems, especially during photo-stimulation. This issue should be significantly improved through quantity control of assembled functional molecules within the junction since molecular number also determines the photostationary switching time upon light irradiation,^[120] and amelioration of the device design for the irradiation procedure. Therefore, there is a lot of room for improvements in the optimization of device fabrication and functional molecule assembly to fit the potential application of complex logic computing in future studies.

4.4 Conclusion

In summary, we have demonstrated the achievement of multi-modulated MTJs based on the association of original ruthenium/DTE complexes and OWL-fabricated nanogaps with suitable gap sizes. The devices represent the very first molecular nanodevices that perform bi-state switchable conductivity by judicious control of the orthogonal light irradiation and electrochemical stimuli. The successive structural rearrangement of the incorporated molecules, i.e. the photo-triggered reversible isomerization and especially the low potential electro-triggered metal-promoted electrochemical cyclisation, are all based on rational molecular design that allows stable Au-S bond connection between the functional molecules and two nanoelectrodes. Remarkably, the unique electronic structure of the longer molecule combining two DTE units offered the achievement of stepwise modulation. Therefore, depending on the properties of orthogonal modulation, these multi-addressable MTJs-based nanodevices can be designed to achieve Boolean computing, such as the presented OR operator and the 3-input device AND-OR logic operation. Importantly, these organometallic molecular wire-based logic gates can be simply reset by introduction of visible light, ensuring the cycled set-reset operation. The proof-of-concept of logic gate demonstrated here provides a solid platform for development of multifunctional molecular devices after optimizing fabrication and operative conditions.

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Chapter 5 Protein-Based Molecular Transport Junctions as Memristive Nanodevices

Besides newly designed organometallic complexes from chemical synthesis, natural biomacromolecules are also promising candidates as functional elements to fabricate nanodevices. In this chapter, natural ferritin molecules from horse spleen were chemically immobilized within nanogaps fabricated by on-wire lithography. A controllable and reproducible memristive behavior can be observed during electrical measurement of such protein-based molecular transport junctions. Through a series of control experiments, it was suggested that programmable resistive switches were due to the electrochemical processes in the active centre of ferritin. In addition, we demonstrated that such ferritin-based nanodevices with reversible resistance can be used for nonvolatile memory based on write-read-erase cycle tests. This work provides direct proof that proteins could be used to fabricate functional nanodevices.

5.1 Introduction

Memristors (short for memory resistors), the fourth fundamental two-terminal circuit element following the resistor, the capacitor, and the inductor,^[155, 156] have attracted intensive attention owing to their potential applications in nanoelectronic memories, computer logic, neuromorphic computer architectures, and so on.^[157-160] Williams et al. were the first to demonstrate a solid-state memristive device based on a titanium dioxide thin film, which was inserted between two Pt electrodes.^[156] Thus far, various materials, such as metal oxides^[161-164] or chalcogenides,^[165] amorphous silicon^[166-169] or carbon,^[170] and polymer-nanoparticle composite materials^[171] have been demonstrated to exhibit memristive phenomena. Many activities in life exhibit memory behavior and substantial research has focused on biomolecules serving as computing elements,^[172-174] hence, natural biomaterials may have potential to be exploited as electronic memristors. Some types of proteins, especially redox proteins, have been shown to act as electronic materials when inserted between electrodes to achieve solid-state electron transport junctions.^[33, 34, 175] In this work, we demonstrate protein-based bipolar memristive nanodevices in which proteins are embedded into the nanogaps.

Herein, we present the exploitation of ferritin to fabricate protein-based nanodevices using OWL-fabricated nanogaps. Ferritin was chosen as a model system in this experiment for a variety of reasons. First, ferritin is the main intracellular iron storage protein^[176, 177] with a nearly spherical shell (diameter: ~12 nm) and an active center of hydrous ferric oxide (Fe(III)O·OH) mineral core. It has often been used as a template for nanoparticle synthesis^[178, 179] and for electrochemical analysis due to the reversible electrochemical redox chemistry of Fe(III)/Fe(II).^[180-183] Second, ferritin

exhibits high stability and can withstand a pH range of 2.0 to 12.0 as well as high temperatures up to 80 °C,^[178, 184] thus it is a desirable, natural biomaterial for fabricating electronic devices. Third, the conductivity of Ferritin have been measured by conductive AFM (c-AFM), indicating the application of this protein in electronics.^[185] Finally, the mechanism of iron uptake and release *in vivo* shows biological “memory” storage,^[176, 177] which provides a potential target to develop biomolecule-based memristors. Therefore, in this context, we incorporated natural ferritin into OWL-generated nanogaps, resulting in reproducible memristive behavior.

5.2 Materials and Methods

5.2.1 Ferritin

Scheme 5.1. Protein structure of ferritin

Ferritin and apoferritin from horse spleen were purchased from Sigma – Aldrich. Ferritin (~450 kDa), the iron storage protein that plays a key role in iron metabolism *in vivo*, consists of 24 subunits as a globular shell (Scheme 5.1) and ~ 4500 iron (Fe^{3+}) crystallized with phosphate and hydroxide ions as the mineral complex inside. Ferritin without the inorganic core is named as apoferritin, which exhibits ferroxidase activity to

mediate iron release and uptake.^[176, 177] In this chapter, the 5 μM PBS solution (pH 7.4) of horse spleen ferritin or apoferritin were used to functionalized 12 nm gaps devices, which were pre-modified by MPA, with the catalysis of EDC and NHS.

5.3 Results and Discussion

5.3.1 Ferritin-Based MTJs

5.3.1.1 Ferritin-Functionalized Nanogap

In a typical experiment, $\sim 5\ \mu\text{m}$ long gold wire structures (diameter $\sim 300\ \text{nm}$) with $\sim 12\ \text{nm}$ nanogaps were cast onto a silicon substrate (with a 600 nm SiO_2 layer), which was patterned with gold microelectrodes using photolithography and thermal evaporation. Then, the wires were connected to the electrodes by e-beam lithography and subsequent chromium and gold thermal deposition, as shown in Figure 5.1a and b. The size of ferritin ($\sim 12\ \text{nm}$ in outer diameter) was appropriate to span the $\sim 12\ \text{nm}$ nanogap defined by the OWL process.

Figure 5.1. (a) and (b) SEM images of a device prepared with an OWL-fabricated nanowire with a $\sim 12\ \text{nm}$ gap.

The obtained nanogap device was functionalized with chemical immobilization of ferritin molecules through the following two steps (Scheme 5.2): (1) two gap sides were covalently modified with MPA via Au-S bond; and (2) the MPA-modified nanogap device was immersed in a PBS solution (pH 7.4) containing 2.5 mg/mL ferritin or apoferritin from horse spleen under the catalysis of EDC and NHS. Through these two steps, amide bonds were formed between ferritin and MPA with the activation of EDC.^[186] The covalent bonding between the ferritin molecules and the electrode surfaces ensures a strong electronic coupling between proteins and electrodes, as the Au – S bond in the previous chapters. Through these efforts, we anticipated that ferritin-based nanodevices developed from OWL-generated nanogaps could be fabricated for electrical testing.

Scheme 5.2. Diagram of ferritin molecules spanning the ~12 nm gap and the reaction scheme of chemical immobilization of ferritin onto gap sides.

5.3.1.2 Memristive Behaviors of Ferritin-Based Nanodevices

Two terminal I - V characteristics of the ~ 12 nm gap devices were conducted under a vacuum of 5×10^{-5} Torr at room temperature both before and after ferritin immobilization. The empty nanogap or MPA-modified nanogap device exhibited no conductance within the noise limit of the measurement (black curve of Figure 5.2, <10 pA). However, the nanogap devices loaded with ferritin molecules showed an obvious I - V response (Figure 5.2), suggesting immobilization of the protein molecules within the nanogap via covalent bonding to each of the gold electrodes on opposite sides of the gap. The I - V response strongly suggested the successful fabrication of ferritin-based transport junctions.

Figure 5.2. Representative I - V characteristics of ~ 12 nm OWL-generated gaps before (black curve) and after immobilization of ferritin (colorful curves, scan for five times under vacuum)

Significantly, the I - V curves of the ferritin nanodevices exhibited reversibly programmable resistance switching. When the potential was applied higher than ~ 0.7 V (V_{set}), current abruptly increased, suggesting a change of the device from high resistance (OFF state) to low resistance (ON state). The device remained stable in this high conductivity state until the potential fell to around -0.8 V (V_{reset}). Once the voltage was lower than V_{reset} , the current decreased immediately, and the ON state was accordingly changed back to OFF state with high resistance. Such cyclic switches can persist, maintaining a stable bi-state of conductivity. The observed I - V response is similar to the bipolar memristive behavior of devices made by titanium dioxide thin films reported by Williams et al.^[156]

Figure 5.3. The I - V characteristics for four different 12-nm gap devices loaded with ferritin (measured in vacuum).

It is noted that for different ferritin devices, the magnitude of current measured may be different, ranging from 800 nA to 1 mA under 1 V bias in ON state and 350 nA to 750 μ A under -1 V bias in OFF state (Figure 5.3). As discussed in the last two chapters, this difference is presumably ascribed to the number of ferritin molecules that actually span the nanogap and chemically connected with the each gap-side because the roughness and morphology of the gold electrode surface is non uniform. Although different devices showed variable current magnitudes, they all performed the similar bipolar memristive behavior.

Remarkably, the conductivity of such ferritin-based nanogap devices is evidently higher than the conductivity of ferritin molecule measured by conductive c-AFM.^[185] There are two reasons for such high current magnitude. One is due to the contact area of the bridged molecules. The current magnitude of the devices is strongly depending on the number of ferritin molecules that actually bridge the nanogap. The contact area of nanogap devices is much higher than the configuration of c-AFM. Maximally, the ~ 12 nm nanogaps could host about 700 protein molecules (estimated by the size of the ferritin, 12 nm, and the diameter of the nanowires, about 300 nm), whereas in c-AFM measurement, normally, there would be single or few molecules bridged between the AFM-tip and substrate.

Another one is the effective covalent bonding of molecules to both electrode sides. In the nanogap devices, the connection between proteins and two electrodes is Au-S covalent bonds, which can facilitate electronic coupling between molecules and electrodes.^[65] While for c-AFM measurement, the contact between tip and protein normally is non-covalent bridge, which leads to high contact resistance. If we

immobilized the protein into nanogap whose size is larger than 12 nm (Figure 5.4a), it exhibited no conductance within the noise limit of the measurement, similar to that of the empty nanogap devices (Figure 5.4b).

Figure 5.4. (a) SEM images of a device prepared with a ~ 14 nm gap; (b) The I - V characteristics for 14 nm gap devices loaded with ferritin (measured in vacuum).

5.3.2 Memristive Mechanism of Ferritin-Based MTJs

5.3.2.1 High Conductivity of Ferritin-Based MTJs

It is known that a stable ferric-oxyhydroxy-phosphate complex core, the active center of ferritin, is the key factor of electron transfer within electrochemical devices in solution.^[180-183] Our hypothesis is that the mechanism to have such bipolar memristive behavior is related to the redox complex core of ferritin. To test the hypothesis, a series of control experiments were performed. When we measured the I - V response of ~ 12 nanogap devices loaded with apoferritin (from horse spleen), which had similar structures to ferritin but lacked the active center, no resistance switching was observed (black curve of Figure 5.5a and 5.5b). The magnitude of current was at the level of 10 pA, which was much lower than that of ferritin-based devices. However, when we reconstituted the iron-core active center in apoferritin by incubating the apoferritin-based devices into

H₃PO₄ aqueous solution (pH 7.4) containing 1 mM FeCl₂ for 24 hours, switchable resistance with much higher current was clearly observed (Figure 5.5b). It is well known that apoferritin can perform as the ferroxidase to facilitate the Fe(II) oxidation and Fe(III) depositon, which ensures the reconstitution of the active center of ferritin.^[179, 187, 188] These results strongly demonstrate that the ferric-oxyhydroxy-phosphate complex core of ferritin plays a crucial role in the memristive behavior of ferritin as an electronic material.

Figure 5.5. (a) Representative I - V characteristics of ~ 12 nm OWL-generated gaps before (red curve) and after immobilization of apoferritin (black curve); (b) Representative I - V characteristics of apoferritin-modified OWL-generated gaps before (black curve) and after reconstitution of iron core inside apoferritin (colorful curves, scanned for five times under vacuum).

It is known that this complex core contains several thousands of Fe (III). Meanwhile, in the core, there are several hundreds of inorganic phosphates, which cause the ferritin iron core to form some disordered regions,^[176] which may facilitate the electron transport. Thus, the active center of ferritin can be regarded as naturally doped

hydrous ferric oxides that can ensure the efficient electron transport through ferritin molecules, which is consistent with the reported conductivity of ferritin tested by c-AFM^[185] Apart from the mechanism of conductivity, the next question is how the iron complex core contributes to the switchable resistance of ferritin-based nanodevices.

5.3.2.2 Memristive Switching of Ferritin-Based MTJs

Both the forward and reverse bias traces cross zero current at zero voltage (Figure 5.2), indicating that bipolar memristive behavior of the device is not related to a capacitive effect.^[9] Redox processes of solid electrochemistry in metal oxides or ionic conductors were reported to be one of the possible mechanisms for memristive behavior.^[157, 162, 165] Based on these and the structure of the ferric core, we propose the following mechanism for the memristive behavior for ferritin-based nanodevices. After applying bias to the ferritin device, the solid-state electrochemical reaction would occur in the ferric-oxyhydroxy-phosphate complex core and part of Fe(III) would be reduced to Fe(II) due to the process of net reduction when the current was flowing through the molecules.^[9] The mechanism of iron release *in vivo* suggests that monoatomic Fe(II) has more freedom than Fe(III).^[177, 187] Hence, the Fe(II) drifted more easily when bias was applied, and thereby more disorder regions could be formed in ferritin iron core. The conductivity of ferritin molecules would abruptly increase once more Fe(III) was reduced to Fe(II) under bias leading the formation of more disordered regions, which could facilitate the electron transfer within the mineral core. Whereas the opposite bias was applied, the net oxidization occurred and the mineral core was converted to the original state. This can explain the hysteretic I - V characteristics of ferritin-based nanogap devices. In the solid-state transport nanojunctions, the reduction/oxidation of the molecule and the

neutralization of the reduced/oxidized molecule are both owing to the current flow, but the neutralization is slower than the redox process due to the thicker tunneling barrier.^[9] In this case, the molecule spends a relatively large amount of time in its redox form, therefore current flowing through the ferritin-based device can be looked as a process of “net reducing and oxidizing”.

Figure 5.6. The I - V characteristic for 12-nm gap device loaded with (a) ferritin and (b) apoferritin before (solid line) and after (dash line) added with iron ion (measured in air).

It is noted that the devices cycled reproducibly only if they were switched to ON state at voltage greater than the V_{set} (~ 0.7 V) and changed back to OFF state at voltage less than the V_{reset} (~ -0.8 V), implying that both oxidation and reduction are critical for device switching. Furthermore, the same devices in ambient condition were measured to further confirm this. We found that the value of set voltage increased and the ratio of ON/OFF lowered (Figure 5.6), suggesting that less Fe(II) was produced because oxygen can inhibit the reduction from Fe(III) to Fe(II). Finally, temperature dependent measurement of the ferritin-based device (Figure 5.7) showed that the hysteretic behavior of I - V curves become inconspicuous with decreasing temperature, indicating that the

overall cycling of the switches has at least one thermally activated component. One reason is that the cryogenic conditions limit the drift of monoatomic Fe(II) after the electro-reduction of Fe(III), thus the memristive behavior is quenched near 60 K.

Figure 5.7. Plot of $R_{ON/OFF}$ (the ratio of I_{ON} to I_{OFF} under 0.6 V bias) as a function of temperature. Inset: I - V responses of ferritin-modified ~ 12 nm nanogap measured at selective temperatures.

5.3.3 Nonvolatile Memory Performance of the Ferritin-Based MTJs

Finally, we demonstrated that such ferritin-based nanodevices with reversible resistance could be used for nonvolatile memory, for which the ability to write, read, and erase data is one important characteristic. Write-read-erase cycle tests on a ferritin-based nanogap device are shown in Figure 5.8. The upper part shows the continuous and various voltage biases (black curve) applied to control the state of the device. Various

bias strengths were used to write by setting it to the ON state (+1 V, higher than V_{set}), to read current at the ON state (+0.6 V, which is between V_{set} and V_{reset}), to erase by resetting it to the OFF state (-1 V, lower than V_{reset}), and to read current at the OFF state (+0.6 V, which is between V_{set} and V_{reset}). It was observed that the currents of the device at the ON state (~ 0.5 mA) were higher than the ones at the OFF state (~ 0.4 mA), despite the fact that they were all recorded with the same reading bias (+0.6 V), as shown in the lower part of Figure 5.8. Significantly, the programmable switching can be operated in many cycles as is revealed in Figure 5.8 and a steady ON/OFF ratio can be maintained for this ferritin-based nanogap device.

Figure 5.8. Current response (red curve) of a ferritin-based nanogap device to applied biases (black curve) during the write-read-erase cycle test. (+1 V for writing, +0.6 V for reading, and -1 V for erasing).

5.4 Conclusion

In summary, we have demonstrated protein-based nanodevices showing reproducible memristive behavior for the first time. Device fabrication is based on the chemical immobilization of ferritin molecules within OWL-generated nanogaps. This two-terminal circuit element performs hysteretic resistive switches due to the electrochemical processes in the active centre of ferritin. As proof-of-concept, such ferritin-based nanodevices with reversible resistance could be used for nonvolatile memory based on write-read-erase cycle tests. This work provides a direct proof that natural biomaterials, especially redox proteins, could be used to fabricate solid state devices with transport junctions, which have potential applications in functional nanocircuits.

The results were published in *Small* **2011**, 7, 3016-3020. Some data of this chapter are reproduced from the above publication with permission from *John Wiley and Sons*.

Chapter 6 Bioengineered Tunable Memristor Based on Protein Nanocage-fabricated Molecular Transport Junctions

Besides chemically synthesized molecules, in Chapter 5 we demonstrated that the naturally available biomacromolecules present untapped resources to fulfill the requirement of molecular devices. The rapidly developing field of biotechnology is uniquely poised to contribute significantly to the growth of functional electronic devices as a result of the tidal shift towards molecular electronics, whose core, biomacromolecules can be bioengineered. In this chapter, a protein-based nanodevice with tunable and reproducible memristive performance is fabricated by combining the unique high iron loading capacity of *Archaeoglobus fulgidus* ferritin with on-wire lithography-generated nanogaps. By tuning the amount of iron inside ferritin, the ON/OFF ratio of conductance switching of nanodevices can be modulated accordingly. Consequently, various protein molecules can be tailored using biotechnology to suit the specific requirements of molecular device development.

6.1 Introduction

Traditional electro-functional molecules in molecular electronics rely on complex chemical synthesis and assembly while use of biomolecules as functional elements represents an attractive strategy to circumvent such complex processes.^[189-192] Proteins perform specific functions in all physiological or biochemical processes such as support, catalysis, signaling, storage, charge transfer, and so forth.^[193, 194] Although the diversity of these natural molecules is vast, tailoring their structures to fit the variable and complex requirements of both the biological and non-biological world is achievable by leveraging on the rapidly developing bioengineering field. For instance, more than 10^6 variants of an individual protein may be created via genetic engineering.^[194] On a parallel note, bioengineering may provide an alternative approach to tune the structural and electronic properties of functional molecules leading to further development in the field of molecular electronics.

Memristors^[155, 156] with electrically tunable conductive switching effects have been proposed as the candidates for next generation nonvolatile memory devices,^[158] combining the advantages of Flash and DRAM (dynamic random access memories).^[157] In the last chapter, we demonstrated a bipolar memristive nanodevice by utilizing ferritin, an iron storage protein, as the electrofunctional component. The utilization of a new class of biologically derived molecules for the nanodevices as against traditional chemical molecules, creates additional choices. The key parameter that defines the successful performance of memristive devices is conductance switching. The open question that this work aims to tackle is whether the memristive performance of such nanodevices can be modulated by leveraging on bioengineering approaches.

The inorganic iron complex core is known to be the determining factor for memristive behavior and we hypothesize that the amount of iron loaded in the core, modulates the performance of the fabricated device. The archaeon *Archaeoglobus fulgidus* ferritin (AfFtn) is a nano-sized protein cage with outer diameter of 12-14 nm and four triangular pores of 4.5 nm, distinct from other ferritins reported so far.^[195] Bioengineering of the external and internal surfaces of the cage as well as inter-subunit interfaces provides new avenues to tune the properties of the AfFtn, including the expandable iron loading capacity. In this chapter, we incorporated recombinant AfFtn into precise nanogaps generated from OWL, resulting in reproducible memristive behavior. More importantly, the hysteretic resistive switching can be modulated by loading variable iron amount. The mechanism governing this process is ascribed to the higher redox activity of inorganic Fe complex core at higher iron loading.

6.2 Materials and Methods

6.2.1 Ferritin Preparation by Bioengineering

The *Archaeoglobus fulgidus* wild-type ferritin (AfFtn) was produced in *E. coli* BL21-CodonPlus[®] (DE3)-RIL (Stratagene) following a previously published method.^[195] (Scheme 6.1) Briefly, *E. coli* was transformed with the vector pAfFtn. Overnight culture of the transformed colony was inoculated in LB broth media (containing ampicillin and chloramphenicol) and the gene expression was induced by adding 1 mM isopropylthio- β -galactoside (IPTG) when OD₆₀₀ of the culture reached ~0.8. Cells were harvested after 4 hours and stored at -80°C. Cell lysate was treated at 85°C for 10 minutes and denatured proteins were removed by ultracentrifugation. The protein was finally purified by hydrophobic interaction chromatography using HiPrep 16/10 Phenyl FF (high sub)

column in ÄKTA-purifier FPLC system (GE Healthcare). The binding buffer composition was 25 mM HEPES with 50 mM NaCl and 500 mM ammonium sulfate at pH 7.5 and the same buffer without ammonium sulfate was used as the elution buffer.

Scheme 6.1. Illustration to obtain AfFtn: I protein purification, II ratio-controlled loading, III self-assembled cage formation.

6.2.2 Iron Loading

To achieve the variable iron loading, FeSO_4 solution (in 0.1% HCl) was added to 1 mg/ml AfFtn solution (in 100 mM HEPES buffer containing 50 mM NaCl, pH 7.5) to achieve the final molar ratio of 1200, 2400, 4800 and 7200 iron atoms per AfFtn cage. To avoid autoxidation of the Fe(II) ions, complete iron loading was performed in several steps. In each step, 600 Fe(II) ions were added per ferritin cage, followed by immediate mixing of the solution. This process was repeated every 10 minutes. After the final round of iron addition, the mixture was incubated at room temperature for 1 hour followed by overnight incubation at 4 °C. The protein was concentrated by membrane filtration using Centricon® (100 kDa MWCO) centrifugal device (Millipore) and any unbound metal was removed by desalting through PD-10 column (GE Healthcare). The

encapsulated iron of ferritin was quantified by inductively coupled plasma (ICP) spectrometry. After iron loading, the 5 μ M PBS solution (pH 7.4) of ferritin with different iron amount were used to functionalized $\sim$ 12 nm gaps devices, which were pre-modified by MPA, with the catalysis of EDC and NHS.

6.2.3 Raman Characterization of Ferritin-Based Nanogap Devices

Raman spectra of ferritin-functionalized nanogap were obtained using a confocal Raman microscope (WiTec Alpha300) equipped with a 100 $\times$ objective (N.A. = 1.0, Olympus) under the excitation of a He-Ne laser (633 nm ,Research Electro-Optics Inc.) with the power of approximately 20 μ W focused on an estimated area of 1 μ m upon the samples. The chips fabricated with ferritin-based nanogap devices were annealed at 400 $^{\circ}$ C for 3 h in order to exclude the protein nanocages and convert ferric oxyhydroxy core to Fe₂O₃, which can be observed Raman signals under the laser excitation. Finally, the *I-V* characteristics were also measured in the same system and condition.

6.2.4 Ferritin Redox Activity Characterization

Iron release was monitored by reducing the ferric cores. AfFtn was loaded with different quantities of iron and mixed with 1 mM ferrozine and 100 mM HEPES buffer (pH 7.5). The reaction was initiated at room temperature by adding 1 mM ascorbate and the amount of iron released was measured by monitoring the formation of Fe(II)-ferrozine complex at 562 nm. Direct electrochemistry of AfFtn nanocage with different iron loading was measured in the form of LSV curves using an electrochemical analyzer (CH Instruments 832C). LSV was carried out between 0 V and -0.6 V in 100 mM anaerobic PBS solution (pH 7.4). The platinum wire was employed as counter electrode while Ag/AgCl was selected as reference electrode for all electrochemical measurements.

6.3 Results and Discussion

6.3.1 Bioengineered Ferritin Nanocage-Functionalized Nanogap Devices

6.3.1.1 Preparation of Bioengineered Ferritin

Ferritin loaded with varying amounts of iron was readily obtained by treating the purified AfFtn sample with different amounts of Fe(II) ions to achieve the final molar ratio of 1200, 2400, 4800 and 7200 iron atoms/cage. After the addition of FeSO₄ solution (in 0.1% HCl), the mixture was incubated at room temperature for 1 hour followed by overnight incubation at 4°C. Unbound metal was removed by desalting, and the encapsulated metal was quantified by ICP spectrometry. (Table 6.1) Subsequently, AfFtn with various amounts of Fe loading (1200, 2400, 4800, and 7200 Fe/cage) were used as the active material of the electronic nanodevices according to the process as described in the previous Chapter 5.

Table 6.1 Quantification of iron loading amount.

Ferritin	[Iron](ppm)	[Iron] (μM)	[Protein cage] (μM)	Fe/Protein cage
1200Fe	14.051	251.7939	0.21	1199.019
2400Fe	27.536	493.4451	0.206	2395.365
4800Fe	54.492	976.4966	0.204	4786.748
7200Fe	78.417	1405.233	0.196	7169.554

[a] Column 2 is the data directly measured by ICP spectrometry.

6.3.1.2 Characterization of Ferritin-based Nanodevices

Figure 6.1. SEM image of (a) a fabricated nanorod device, and (b) ~ 12 nm gap in the nanorod.

Scheme 6.2. Illustrated fabrication of ferritin nanocage spanning OWL-generated ~ 12 nm gap device.

In a typical experiment, ~ 5 μm gold nanowires with ~ 12 nm gaps were synthesized by OWL,^[46] which is specifically tailored to assemble the AfFtn protein cages within the nanogaps and to thereby construct MTJIs with memristive behavior. The representative nanogap device (Figure 6.1a) and ~ 12 nm gap on the Au nanowire (Figure 6.1b) can be observed in the SEM image. The two ends of unmodified nanogaps were carboxylated by 1 mM 3-mercaptopropionic acid (MPA) via Au–S bonding. In the final

step, the as prepared AfFtn nanocages with different Fe loading were covalently assembled, catalyzed by EDC combined with NHS,^[186] as illustrated in Scheme 6.2. Due to the formation of amide bonds between MPA modified nanogap and AfFtn, the protein was immobilized as a monolayer in the nanogap. These covalent bonds have been demonstrated to ensure a strong electronic coupling between ferritin and nanoelectrodes,^[65] and to achieve the memristive conductance switching.

Figure 6.2. Raman spectra of nanogap area of blank (black curve) and 4800 Fe ferritin-based (red curve) device after annealing at 400 °C for 3 h. (Integration time: 100 s, Laser: 633 nm)

To confirm the involvement of ferritin within the nanogap, the measured devices were characterized as Raman spectra after annealing at 400 °C. The annealing process ensures that the protein nanocages are excluded and convert ferric oxyhydroxy core to Fe₂O₃. Due to the strong electromagnetic enchantment of nanogap structures,^[48, 51] the SERS signals from Raman-active component within the nanogap can be obviously

observed. Compare to the blank gap, obvious Raman bands can be observed (Figure 6.2), which are assigned to Fe_2O_3 obtained from inorganic core of ferritin, suggesting the successful immobilization of ferritin within the nanogap.

6.3.2 Memristive Performance of Ferritin-Based Nanodevices

6.3.2.1 I - V Characteristics of Ferritin-Based Nanodevices

Figure 6.3. Representative I - V curves of ~12 nm OWL-fabricated gaps before (black curves) and after immobilization of recombinant AfFtn with a) 1200, b) 2400, c) 4800, and d) 7200 Fe loading (color curves, scanned between -1 V and 1 V under vacuum).

Our previous work demonstrated that the ferric oxyhydroxy core of the commercial horse spleen ferritin was responsible for the memristive behavior of the two-terminal nanodevice. Consequently, we hypothesized that if the composition of this Fe complex core can be modulated, the switching performance of the protein-based device can be controlled accordingly. To prove this hypothesis and to achieve ferritin-based memristors with tunable performance, the I - V characteristics (1×10^{-4} torr, room temperature) of the ~ 12 nm gap devices were measured both before and after the immobilization of the AfFtn with different iron loadings. As shown in Figure 6.3a-d, all the AfFtn (1200 Fe, 2400 Fe, 4800 Fe, and 7200 Fe) functionalized nanogap devices exhibit distinct I - V responses, regardless of the amount of Fe atoms loaded in the protein. In contrast, the empty nanogap or MPA-modified nanogap device showed no conductance within the noise limit of the measurement (<10 pA, black curves in Figure 6.3). Thus, bioengineered ferritin-based transport junctions had been achieved.

The archaea-derived AfFtn functionalized nanodevices with variable iron loading demonstrated programmable conductive switching (Figure 6.3a-d) that is similar to the bipolar memristive behavior of commercial horse spleen ferritin-fabricated devices as presented in last chapter. When voltage sweep approached a set potential (V_{set} , ~ 0.7 V), the devices switched to ON state, showing stable high conductivity until reset potential (V_{reset}) was reached at around -0.8 V. Once the potentials were lower than V_{reset} , the devices returned to the original low conductivity as the OFF state.

6.3.2.2 Endurance Performance of Ferritin-Based Nanodevices

Importantly, programmable memristive switching was maintained over many cycles and retained a steady and unique ON/OFF ratio for each type of ferritin-based

nanodevice (Figure 6.4, corresponding to the Fe loading amounts). However, the difference in conductance between ON and OFF states became increasingly apparent with higher Fe loading inside the protein cage. Therefore, such bioengineered ferritin molecules have also been demonstrated to be apt as functional biomaterials for memristive nanodevices whose performance can be tuned by modulating the Fe loading inside the protein.

Figure 6.4. Endurance performance of the ferritin-based memristive nanodevices with different Fe loading. The ON/OFF ratio is the ratio of current magnitudes between ON state and OFF state, which were recorded at 0.6 V. (green curve: 1200 Fe, red curve: 2400 Fe, blue curve: 4800 Fe, and purple curve: 7200 Fe)

6.3.2.3 Repeatability of Ferritin-Based Nanodevices

The overall yield of operative devices is ~11% (the number of working devices that show memristive properties out of approximately 90 devices found on a single chip of $1\text{ cm} \times 1\text{ cm}$ are as follows: Fe 1200: 7, Fe 2400: 10, Fe 4800:11, and Fe 7200: 10.). Additionally, it should be mentioned that the current value under 1 V bias (in I - V curves)

obtained from different ferritin-based devices varied up to three orders of magnitude (Figure 6.5, Fe 1200: 10^{-10} to 10^{-9} A, Fe 2400: 10^{-9} to 10^{-7} A, Fe 4800: 10^{-8} to 10^{-6} A, and Fe 7200: 10^{-7} to 10^{-5} A). This disparity is presumably due to the different number of ferritin molecules that are actually incorporated into the nanogap, which may be caused by the non-uniform roughness and morphology of the gold surface, as discussed in the previous chapters.

Figure 6.5. Repeatability of device fabrication. ON/OFF ratio of working AfFtn-based nanogap devices in different current magnitude ranges. (green: 1200 Fe, red: 2400 Fe, blue: 4800 Fe, and purple: 7200 Fe)

5.3.2.4 Bioengineering-Tunable Performance of Ferritin-Based Nanodevices

It is worth noting that the most important advantage of such bioengineered ferritin for memristive nanodevices is the controllability in the amount of iron loaded inside the protein – a key factor for achieving the tunable switching behavior. As is shown in

Figure 6.6 (also observed the trend in Figure 6.4 and 6.5), the ON/OFF ratio of bioengineered ferritin-based memristive devices is a function of the number of Fe atoms inside the cage-like protein. When apoferritin is employed to fabricate the device, also, no memristive switching is observed in the I - V response as demonstrated in Chapter 5. As the Fe loading is increased, the ratio of conductance between the ON and OFF states becomes larger, indicating a gradual improvement in the performance of the device.

Figure 6.6. ON/OFF ratio of AfFtn-based memristive nanodevices with different Fe loading (The color intensity of the protein nanocage core indicates the density of Fe atom). Current magnitudes were recorded at 0.6 V.

6.3.3 Mechanism of Tunable Memristive Performance

6.3.3.1 Bipolar Memristive Behaviors

At this juncture, the mechanism of the ferritin-based memristive device having such bipolar memristive behavior, as illustrated in Scheme 6.3, can elucidate the link

between the Fe loading amount and the device performance. It has been demonstrated previously that the hysteretic resistive switching of such protein device is due to the ferric-oxyhydroxy core. The apoferritin-based device exhibits no conductance variation, while the memristive functionality of the same device is recovered by reconstituting the inorganic core inside the protein.

Scheme 6.3. Memristive characteristics of ferritin-based devices under voltage scanning.

Conversely, the crucial role of such ferric-oxyhydroxy core for memristive behavior of whole device has been also supported by the fact that both the ON/OFF ratio and current magnitude show dramatic decrease in ascorbate-treated 4800 Fe ferritin-based device (Figure 6.7), in which the ferric core is reduced and Fe(II) release from protein nanocages. Furthermore, the electrochemical processes of the metal oxide core (i.e., the redox activity) have been proposed to be responsible for the memristive properties. The iron atom alternates between ferric and ferrous states by net reduction

and oxidation, under sequential application of V_{set} and V_{reset} , which correspond to the low conductive and high conductive states of the device, as illustrated in Scheme 6.3.

Figure 6.7. Representative I – V characteristics of 4800 Fe ferritin-based device before (black curve) and after (red curve) the reduction by 1 mM ascorbate for 2 h.

6.3.3.2 Variable ON/OFF Ratios with Different Fe Loading

We carried out two control experiments to decipher the improved performance of the protein-based device at higher iron loading. Firstly, we monitored Fe release from the ferritin molecules loaded with four different amounts of Fe in the presence of ascorbic acid as the reducing agent. Iron released from the ferritin core involves redox reactions that result in Fe (II) ions being transported outside the protein cage. In the same reaction time and for the same ascorbate concentration, higher iron loading resulted in more Fe(II) ions being reduced and released from the protein cage cavity (Figure 6.8), implying that such ferritin underwent faster redox reaction. The chemistry behind the faster redox

reaction of the ferritin cores loaded with more Fe(III) ions is not yet established. When a ferritin molecule is loaded with different amounts of iron atoms, the core size does not change, but rather the density of the core increases with increased iron loading.^[196] At this higher iron loading, the higher core density may be responsible for faster redox reactions and the performance of the protein-based device may correspondingly improve.

Figure 6.8. Fe(III) reduction in AfFtn with different amounts of iron loading. (Reduced agent: ascorbic acid)

Secondly, the direct electrochemistry also reflects the redox activity of ferritin molecules. The linear sweep voltammetry (LSV) of electrodes containing various amounts of Fe in ferritin molecules were carried out at 10 mV/s (Figure 6.9a). During the first scan cycle, an obvious reduction peak was obtained at around – 560 mV. However, this peak disappeared during the second scan cycle, and a new reduction peak was found in much more positive position after preliminary anodic scan (Figure 6.9b), indicating

that the Fe(II) ions had been fully released from the core during the first scan.^[197] Hence, the reduction peak during the first scan reflects the redox activity of the proteins. As shown in Figure 6.9a, the reduction peak at -560 mV increases with increasing Fe amount inside the protein cage and the peak current is linearly correlated with the Fe number (Figure 6.9a, inset). These results confirm that a high ON/OFF ratio can be obtained in the device fabricated from the protein with high loaded Fe.

Figure 6.9. Linear sweep voltammograms obtained at ferritin-modified gold electrodes with (a) different Fe loading (The scan rate was 10 mV/s) for the first cycle scan, and (b) 4800 Fe for the first cycle (black curve) and the second cycle (cyan curve) scan. Inset: the plot of the reduction peak current vs the Fe-loaded ferritin amount.

6.3.3.3 The Most Improved Performance with 7200 Fe Loading

It is worth noting that the 7200 Fe ferritin-based device shows drastically improved performance (Figure 6.3d) compared to other ferritin-based devices with lesser Fe loading or the device fabricated from the commercial horse spleen ferritin. This is

consistent with the fact that the maximum stoichiometric Fe loading amount is 7200 Fe inside the AfFtn which is much higher than 4500 Fe inside other ferritin molecules.^[176] Meanwhile, as mentioned above, although the size are similar, the core density of 7200 Fe ferritin is distinctly higher than other loading amount. This high density may cause the better connection between the protein shell and inorganic core, and decrease the barrier at the interface during the electron transport, contributing high conductivity of such ferritin-based nanodevice. Additionally, in order to compare the role of the Fe core vs. the protein shell in the memristive behavior of the nanodevices, we built a nanodevice with bioengineered wild-type AfFtn^[198] with a closed pore and loaded various amounts of Fe. Although the unique structure of AfFtn with 4.5 nm open pore^[195] was modified into a closed shell in the mutant protein, similar memristive behavior was observed which confirmed that the Fe core inside the protein dominates the performance of ferritin-based devices rather than the protein shell structure.

6.4 Conclusions

In summary, the protein cage derived from *A. fulgidus* ferritin showed unique high loading capacity with tunable iron amount that directly impacted the performance of the memristive devices following the strategy for the fabrication of protein-based memristive nanodevices with stable and tunable performance developed in last chapter. It has been demonstrated that the higher Fe loading amount contributes to better memristive performance of fabricated nanodevices due to higher electrochemical activity of the ferric complex core. Most remarkably, the 7200 Fe ferritin-based device exhibits significant ON/OFF ratio and tunable conductance switching. This work provides another solid proof that hybrid nanostructures with biomolecules can be utilized in

functional nanocircuits. Besides chemical synthesis, bioengineering paves the way for future development in electronics and to gradually approach the higher-order target applications such as the construction of integrated electronic devices like neuromorphic computers.

The results were published in *Small* **2014**, *10*, 277-283. Some data of this chapter are reproduced from the above publication with permission from *John Wiley and Sons*.

Chapter 7 Conclusions and Recommendations

In this thesis, we discussed the recent developments in the emerging field of molecular electronics, by building molecular architectures as elements in electronic circuits. Varied functional molecules have been selected, designed and modified by the tools from synthetic chemistry and molecular biology. Meanwhile, the feasible and universal platform for molecular incorporation was fabricated based on the nanogap structures generated by OWL. The hybridized systems of MTJs are realized with advanced functions with the modulation of multiple external stimulations, such as switches, memristor and logic gate, which have been experimentally and theoretically investigated. And by achieving that we have provided guided and useful tools for exploiting functional molecular nanodevices for electronic nanocircuits. The main conclusions drawn from this study are shown as below.

Based on the OWL-fabricated nanogap that has been demonstrated as new testbed for molecular electronics, external stimulation was firstly introduced to such nanosystem and a photo-controllable MTJ nanodevice was achieved with a ruthenium-based organometallic molecular wire including a photochromic DTE unit. The obtained devices perform bi-directional conductive switching upon irradiation with UV and visible light, which solved the problem of the one-way transformation of previous structures with similar photochromic complex. The theoretical calculations performed on **1** reveal that the ruthenium acetylide moieties decrease judiciously the electronic coupling of the DTE fragment with the metal electrodes in its open form, allowing reversible switching.

Therefore, such the photo-controllable device demonstrates that chemical synthesis is a powerful tool to provide functional elements to electronic system.

We further improved the complexity and functionality of such photo-controllable MJTs by both the chemical tailor of organometallic molecular wire and optimization of device configuration, in order to achieve multi-modulation by external inputs. The modified devices represent the very first molecular nanodevices that perform bi-state switchable conductivity by judicious control of the orthogonal light irradiation and electrochemical stimuli. The successive structural rearrangement of the incorporated molecules, i.e. the photo-triggered reversible isomerization and especially the low potential electro-triggered metal-promoted electrochemical cyclisation, are all based on rational molecular design that allows stable Au-S bond connection between the functional molecules and two nanoelectrodes. Remarkably, the unique electronic structure of the newly synthesized longer molecule combining two DTE units offered the achievement of stepwise modulation. Therefore, depending on the properties of orthogonal modulation, these multi-addressable MTJs-based nanodevices can be designed to achieve Boolean computing, such as the presented OR operator and the 3-input device AND-OR logic operation. Importantly, in contrast to other logic gates based on chemical systems, these organometallic molecular wire-based logic gates can be simply reset by introduction of visible light, ensuring the cycled set-reset operation.

Besides chemically synthesized complex, the naturally available biomacromolecules present untapped resources to fulfill the requirement of molecular devices. Especially, proteins undertake specific functions in all physiological or biochemical processes, and thereby were firstly selected to incorporated into nanogaps.

We have demonstrated ferritin-based nanodevices showing reproducible memristive behavior for the first time. This two-terminal circuit element performs hysteretic resistive switches due to the electrochemical processes in the inorganic iron core inside protein shell. As proof-of-concept, such ferritin-based nanodevices with reversible resistance could be used for nonvolatile memory based on write-read-erase cycle tests. This work provides a direct proof that natural biomaterials could be used to fabricate solid state devices with transport junctions.

Although the diversity of these natural molecules is vast, tailoring their structures to fit the variable and complex requirements is achievable with the rapidly developing bioengineering. The protein cage can also be modified to exhibit unique high loading capacity with tunable iron amount that directly impacted the performance of the protein-based memristive devices. It has been observed that the higher Fe loading amount contributes to better memristive performance of fabricated nanodevices due to higher electrochemical activity of the ferric complex core. Most remarkably, the 7200 Fe ferritin-based device exhibits significant ON/OFF ratio and tunable conductance switching. Therefore, bioengineering will provide an alternate option to improve molecular architectures.

In conclusion, various advanced molecular nanodevices were developed based on OWL-generated nanogap with suitable gap sizes, with the help of external electro-/photo-stimulations, contributing new types of molecular electronic device as indicated in Figure 7.1. The enormous resource of functional molecules can be attained from synthetic chemistry to molecular biology. Both the chemical modification and bioengineering have been demonstrated as powerful tools to enrich and ameliorate functions and performances

of desired electronic devices. Therefore, after optimizing fabrication and operative conditions, such functional MTJs paves the way for future development in multifunctional nanocircuits and to gradually approach the higher-order target applications such as the construction of integrated electronic devices like neuromorphic computers.

Figure 7.1. Further development in the roadmap of functional MTJs.

Recommendation for Future Work

We have demonstrated that various electronic nanodevices were fabricated with OWL-generated nanogap associated with small ensembles of molecules obtained from synthetic chemistry or biosystem. With judicious modulation of external photo-/electro-stimulations, applicable electronic properties were exhibited by such multifunctional MTJs, which were determined by the controllable switches of molecular conformation of

electronic structures. So far, we can only probe such molecular motion or switching indirectly by experimental measurement of device conductivity or theoretical calculation. However, from the obtained I - V characteristics of these functional MTJs, a disparity in conductivity can be observed for different operative devices, which may range for several orders of magnitude, as presented in this thesis (Figure 3.8, Figure 5.3, Figure 6.5, and Table 4.1, 4.2) or previous reports.^[65-67] Therefore, it is crucial to clarify the mechanism of conductive changes are owing to individual behavior of single molecule or interaction of small molecular ensembles between metal junctions. Therefore, from a more fundamental point of view, we would like to recommend visualizing switching process of molecular conformation or electronic structures under external stimuli as well as current flowing, since “seeing is believing”. A possible path to tackle these unsolved challenges is to employ spectroscopic techniques, such as the SERS.

Figure 7.2. (a) Scheme of spectroscopic monitoring of DNA complex-based transport junctions (intercalator: MB); (b) Raman spectra obtained at 12 nm gap (black curve) and gold nanorod (red curve). Integration time: 10 s, Laser: 633 nm.

Note that the precisely controlled nanogap structures fabricated by OWL have been shown to act as Raman “hot spots” with enhancement factors as large as 10^8 , so molecules with a proper Raman cross section that are assembled within such

nanostructures can be identified spectroscopically by SERS measurements.^[48, 51] Therefore, besides of electrical testbeds for the molecular conductivity, these plasmonic-active nanostructures are also recommended to achieve optically monitoring of molecular structural switches, during current flow, as is schemed in Figure 7.2a. DNA chains may be ideal to be firstly selected as a model system, since the chemical assembly of such biomolecules on the gold surface has been fully investigated.^[199, 200] Furthermore, a variety of intercalator chains can be selected to enhance the conductivity of DNA chains between gold junctions, such as Methylene Blue (MB) illustrated in Figure 7.2. Meanwhile, Raman signals of such DNA-intercalator complexes can be obviously monitored with the strong electromagnetic enhancement of such nanogap structures, as the initial data shown in Figure 7.2b. More interestingly, the electromagnetic enhancement factor of such nanogap structure can be accurately tuned through the effect of the geometrical parameters as reported that a periodic electric field enhancement was observed along gold rods with proper gap size.^[53]

Figure 7.3. (a) Scheme of spectroscopic visualization of local electron transfer; (b) Electrochemical potential-dependent Raman spectra of nanoparticle-decorated Au surface during the electrochemical scanning between 0 to -500 mV.

Beyond perpendicular observation of molecular behavior, if we can optically probe the molecular reaction during the current flow in longitudinal direction, the local information of electron transport through the functional molecules, since direct electrical measurement based on either nanodevices or electrochemical techniques would only be able to measure the total electrical current passing through the lateral face.^[201] The local charge transport information (especially to relate to the local environment, near-field phenomena, and others) and the locally chemical information, such as heterogeneous reactions at the electrode surface can really reflect the mechanism of electrically driven molecular behaviors.^[202] However, such direct optical detection seems hard to achieve before further optimizing current device configuration. To simplify the system, the nanoparticle-decorated gold film is recommended to firstly simulate the lateral face of nanorods in fabricated nanogap structures, as illustrated in Figure 7.3a. From the initial data (Figure 7.3b), the regularly decreased Raman spectra can be recorded during electro-scan. Therefore, the possibility that optically explores molecular reactions during electron transfer or transport processes has been demonstrated.

List of Publications and Patent

1. **F. Meng**, C.H. Liow, P. Cai, Y. Liu, Y. Jiang, S. Li,* X. Chen,* “Spectroscopic visualization of local charge transfer along DNA Chains”, in preparation.
2. **F. Meng**, Y.-M. Hervault, Q. Shao, B. Hu, L. Norel, S. Rigault,* X. Chen,* “Orthogonally modulated molecular transport junctions for resettable electronic logic gates”, *Nature Communications* **2014**, *5*, 3023, doi: 10.1038/ncomms4023. (It was highlighted by Nanowerk Spotlight, Materials Views, and ACS Noteworthy Chemistry.)
3. **F. Meng**, B. Sana, Y. Li, Y. Liu, S. Lim,* X. Chen,* “Bioengineered tunable memristor based on protein nanocage”, *Small* **2014**, *10*, 277-283. (It was highlighted by Nanowerk Spotlight.)
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6. C.H. Liow, **F. Meng**, X. Chen,* S. Li,* “Active control of SERS intensity by tuning surface plasmon resonance position through electrochemical techniques”, submitted.

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