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TOPICAL REVIEW — Spin manipulation in solids

# Recent spinterfacial studies targeted to spin manipulation in molecular spintronic devices*

Xian-Rong Gu(谷现荣)[1,2], Li-Dan Guo(郭立丹)[1,3], and Xiang-Nan Sun(孙向南)[1,2,†]

[1] CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, China
[2] University of Chinese Academy of Sciences (CAS), Beijing 100049, China
[3] Department of Materials Science and Engineering, College of New Energy and Materials, China University of Petroleum Beijing, Beijing 102249, China

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Molecular spintronics is an emerging field which evoked wide research attention since the first molecule-based spintronic device has been reported at 2002. Due to the active study over the last few years, it is found that the interfaces in spintronic device, so called spinterface, is of critical importance for many key issues in molecular spintronics, such as enhancing spin injection, lengthening spin transport distance, as well as manipulating spin signals in molecular spintronic devices. Here in this review, recent studies regarding spinterface in molecular devices, especially those impressive efforts devoted on spin manipulation, have been systematically summarized and discussed.

**Keywords:** molecular spintronics, spin valve, spinterface, spin manipulation

**PACS:** 72.25.–b, 73.21.Ac, 73.40.Sx, 75.70.Cn **DOI:** 10.1088/1674-1056/27/10/107202

## 1. Introduction

Spintronics came into being when giant magnetoresistance (GMR) was discovered in 1988,[1,2] followed by the revolution of information storage during the 1990s. Due to the prosperous research of molecular electronics in past decades, molecular semiconductors became very attractive because of their unique electrical properties together with excellent chemical and mechanical flexibility.[3,4] In particular, the weak spin–orbit coupling (SOC)[5,6] of molecular semiconductors and therefore long spin relaxation time[7,8] also led to the arising of molecular spintronics.[9,10] Spin transport and manipulation are the core issues in molecular spintronics which are crucial for both probing in-depth physical problem[11,12] and building novel spintronic devices,[13,14] and hence attract considerable research interest in the past decade.[15–17] The intrinsic weak SOC of molecules is generally considered beneficial to the spin transport process,[18,19] surely in case of not considering the low conductivity of most molecules, while it raises great difficulties to achieve efficient spin manipulation in molecular devices. Because of their contradictory positions in spin-correlate process, it is exactly a great challenge to achieve effective spin manipulation in molecular spintronics especially when do not intend to sacrifice spin transport performances.

Molecular spin valve (MSV) is the most typical device in molecular spintronics,[20] as well in spin manipulation study, which normally shows a sandwich-like structure composed of two different ferromagnetic (FM) electrodes separated by a nonmagnetic molecular layer.[21] In a working MSV, spin-polarized carriers are generally injected through the FM/molecule interface under applied bias, and subsequently transported through the molecular layer via tunneling or hopping mode, and finally been detected by the opposite FM electrode. The measured signal in an MSV normally expresses as magnetoresistance (MR), which is defined as the percentage variation in resistances when magnetization alignments of FM electrodes are switched, e.g., from parallel to antiparallel.[8] In the vertical multilayer structure of MSV, the FM/molecule interface, also named as spinterface,[22,23] makes a key role in spin injection and transport[24] as well as spin signal manipulation.[25]

Here in this review, firstly, we introduce the fundamental studies which aimed to improve spin injection and spin transport distance based on interface engineering in molecular spintronic devices. Secondly, the spin filtering effect resulting from the hybrid interface state (HIS) and spinterface-based memory device are summarized and discussed in detail. Then, various methods attempted to achieve spin signal manipulation are highlighted, including the way that driven by strong polar molecules or ferroelectric materials. Finally, a short summary

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†Corresponding author. E-mail: sunxn@nanoctr.cn

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and prospect on spin manipulation utilizing functional molecular spintronic devices, according to several latest studies, is also presented to complete a full picture of the leading research direction in molecular spintronics.

## 2. Spinterface studies for high-quality molecular spintronic devices

Firstly, the indistinct FM/molecule interface has been regarded as an inevitable conundrum since the first prototypical MSV was built by Xiong *et al.*[21] During the fabrication of MSV, the thermally activated metal atoms can rapidly diffuse into the molecular layer and form metallic filaments between two electrodes, especially when top electrode is deposited via high-energy methods, such as magnetron sputter[8] or E-beam evaporation.[26] Meanwhile, metal filament is also likely to emerge due to the electrochemical migration of metal atoms when the device operates under applied bias.[26] The generated metal filaments can reduce the actual thickness of the molecular layer and even short out it, which is unfavorable for accurate evaluation of spin injection and transport in MSVs (Fig. 1(a)). An inserted intermedia layer between the FM and molecules, such as metal oxide,[27] is a good candidate to suppress the development of metal filaments due to the penetration of top FM electrode and the generation induced by electrochemical migration.[26] However, the robust metal oxide can also diffuse into the molecular layer during device fabrication and bring unpredictable effects on spin injection and transport in MSV. Thus, more effective and reliable methods should be developed to achieve a clear interface in MSV, which is a necessary precondition to reach high efficient spin injection, long-distance spin transport as well as spin manipulation.

Secondly, inevitable problem resulting from intrinsic property differences between FM electrodes and molecules, such as energy level alignment mismatch and dramatic difference in conductivity, always obstruct spin injection through the interface.[28] To solve the above issues, novel magnetic materials have been explored and specific FM/molecule couples with nice energy alignment have been selected. In recent studies, organic magnetic electrode[29,30] and graphene tunnel barrier[31–35] have been employed in spintronic devices, which shown clearly improved energy alignment. Besides, perfect energy matching between FM electrode and molecular semiconductor can also be achieved by simply choosing suitable FM/molecules couples, such as $La_{0.67}Sr_{0.33}MnO_3$ (LSMO)/fullerene ($C_{60}$),[36,37] $Ni_{80}Fe_{20}$/fluorinated copper phthalocyanine ($F_{16}$CuPc),[38] and $Fe_3O_4$/rubrene.[39] However, even excellent results have already been obtained, the above methods just can apply perfectly in very limited cases, thus more general solutions regarding the interfacial issue are still eagerly expected up to now.[40,41] Based on current studies, the interface engineering in MSV seems to be a very promising solution, and many researchers have already delivered considerable contributions on this topic, which are concluded as below.

### 2.1. Novel approaches to prevent metal penetration at FM/molecule interface

Recently, a low-temperature and rate-controlled deposition method has been utilized to avoid the metal penetration during top electrode deposition, by removing the extra thermal energy with liquid nitrogen and weakening the kinetic energy of metal atoms with controlled deposition rate during device fabrication.[26] With such a strategy, a sharp and clear FM/molecule interface can be obtained even on a 5-nm thick molecular layer.[26] Similar low-temperature method can also be employed to smooth the molecular layer, which is also of critical importance for fabricating reliable MSVs. In fact, most thin films of molecular semiconductors, especially those have high charge carrier mobilities, normally show rough polycrystalline morphology,[13] which is inclined to form metal filaments during the deposition of top FM electrode. Smooth amorphous molecular films can be obtained by cooling substrate with liquid nitrogen during deposition of molecules.[38] As shown in Fig. 1(b), high-quality $F_{16}$CuPc SVs with various-thickness molecular layers have been successfully prepared via low-temperature fabrication strategy for both molecular layer and electrodes. Unique photo-response performances together with very long spin transport distance, up to 180 nm at room temperature, are observed in the $F_{16}$CuPc SVs.[38]

Buffer layer-assisted growth (BLAG) method should be another option to address the interface problem in MSVs.[42] It is exploited to prevent thermally atomic deposited FM material from diffusing into molecular layer, as shown in Fig. 1(c).[42] With the BLAG method, initial Co layer deposited in the form of nanodots, and acts as a buffer layer to protect molecular layer from metal penetration.[42] Although there is still a bit Co diffusing into inhomogeneous molecular film of tris(8-hydroxyquinolinato) aluminum ($Alq_3$), MSV with high performances has been obtained successfully, which shows a large GMR value exceeding 300% at ultra-low temperatures. Increased GMR value is also observed along with growing thicknesses of $Alq_3$ thin films, which probably due to the gradually disappeared negative influences from the undefined interface and hence enhanced spin injection. In fact, this observation conflicts with a majority of related studies but paves

the different way toward better device performances from the perspective of the growth of FM electrode. Compact self-assembled molecular monolayer (SAM) has also been employed as spacer layer in spintronic devices, which is supposed to be robust enough for FM top electrode deposition.[43] It has also proved that a SAM intermedia layer can obviously enhance the operational bias of the device,[44] which is important for promoting the applications of molecular spintronic device.

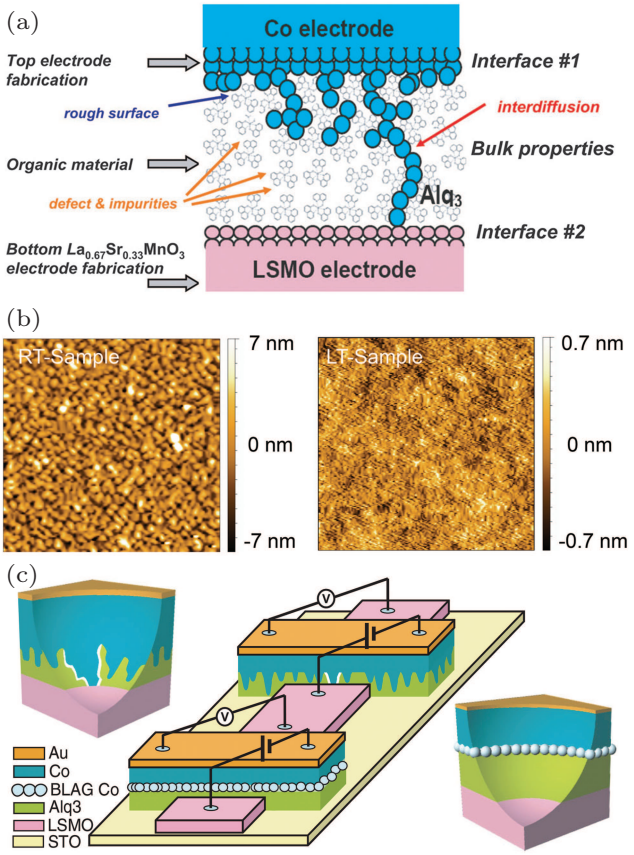



**Fig. 1.** (color online) (a) Schematic of problems in MSV, including rough interface, metal inclusion and others in molecular layer (from Ref. [16], Fig. 3). (b) Atomic Force Microscope (AFM) images of 90 nm $F_{16}$CuPc film deposited with conventional method and low-temperature and rate-controlled deposition method separately (from Ref. [38], Fig. 2(b)). (c) Structure of BLAG-spin valve and traditional spin valve (from Ref. [42], Fig. 1).

### 2.2. Interface engineering to improve spin injection and transport

To optimize the energy level alignment at the metal/molecule interface via various interface engineering processes is a common and feasible method to enhance charge carrier injection in electronic device,[40,41,45] and it is also proved to be a promising way to improve spin injection recently in MSVs.[46–50] It is found that alkali metal dopants, such as Cs or Na, can effectively bring down both highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of copper phthalocyanine (CuPc) without changing the bandgap (Fig. 2(a)), and therefore promote the efficiency of spin injection from Co electrode.[46] The doped metal atoms may play a role as impurities that can cause a strongly band bending at the energy level of FM/molecule interface, and hence form more broad spin injection route at the interface.[51] Moreover, a versatile electrostatic model has been employed to demonstrate the beneficial effect of the energy level bending at metal/molecule interface on spin injection process, while the density of state (DOS) distribution profile of molecule must be seriously considered to tailor the energy level alignment via interface engineering.[52]

Direct contact of molecule and FM electrode, especially the Co, may produce extra chemical or physical interaction which can hinder spin injection across the interface. In a recent study, a dipole barrier is proved to form at the Co/$Alq_3$ interface due to Fermi level pinning, which can effectively block the spin electrons. In this case, just very noisy output signals can be observed[49] due to the downward shift of energy level of $Alq_3$ relative to the vacuum level.[50] An inserted interface layer between FM electrode and molecules can be an efficient solution of this problem. According to previous reports, metal oxides seem to be very promising to form the intermedia thin layer to separate FM electrodes and molecules in MSVs, just as displayed in Fig. 2(b).[48] With just a very thin $Al_2O_3$ intermedia layer, the negative influences from interfacial dipoles are significantly eliminated, and therefore enhanced spin injection

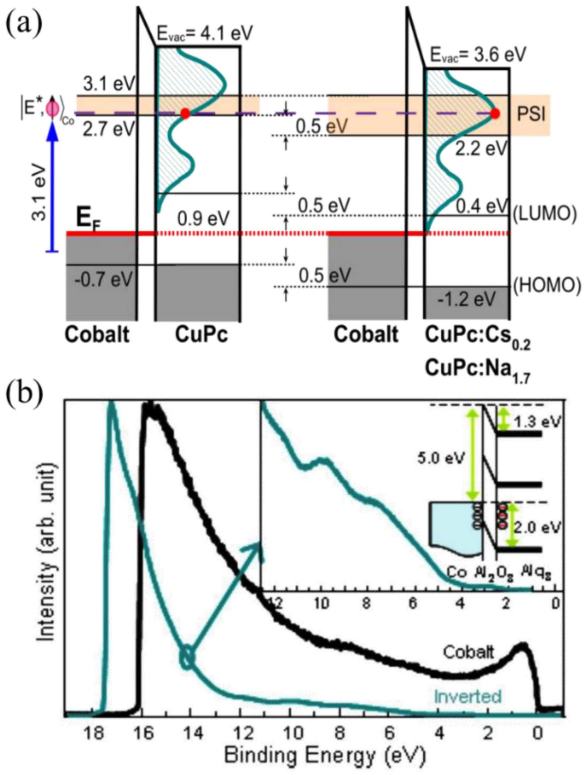



**Fig. 2.** (color online) Strategies for enhance spin injection efficiency. (a) Diagram of energy level shift by doping Cs and Na into CuPc (from Ref. [46], Fig. 2). (b) Ultraviolet photoelectron spectroscopy for interface with $Al_2O_3$ (green) and without $Al_2O_3$ (black), insert was energy level alignment of $Alq_3$/$Al_2O_3$/Co interface (from Ref. [48], Fig. 1).

is achieved in the $Alq_3$ based device.[53] Besides the $Al_2O_3$, various metal oxides, such as MgO, $MoO_x$, and ZnO,[45] might have potential to be employed as interfacial layers in molecular spintronics devices. Nevertheless, robust metal oxides are likely to penetrate into molecular layer, a specific-designed metal oxide deposited below molecular layer is found to be a better choice.

In very recent studies, semi-oxidized aluminum, named as leaky $AlO_x$ barrier, shows very different property to the full oxidized $Al_2O_3$ when employed as interfacial layer in MSV (Fig. 3(a)), which behaves much close to a bad metal rather than an insulator (as shown in Fig. 3(b)).[26] The full $Al_2O_3$ barrier normally leads to a tunneling transport in the MSV as shown in Fig. 3(c), which accords well with previous studies.[48,49] However, when a 1.5-nm leaky $AlO_x$ barrier is inserted between Co and molecules, it clearly leads to a more effective spin injection and spin transport process via thermal-active hopping mode (see Fig. 3(d)),[26] which is typically for the carriers transport in molecular semiconductors[45] but hardly been observed in MSV devices previously.[8] Moreover, the leaky $AlO_x$ barrier can obviously improve the spin transport distance especially at room temperature in MSVs, which may due to the hopping-mode spin transport. Recently, a large spin transport distance of approximately 180 nm has also been observed in MSVs based with an interface layer of semi-oxidized aluminum.[38]

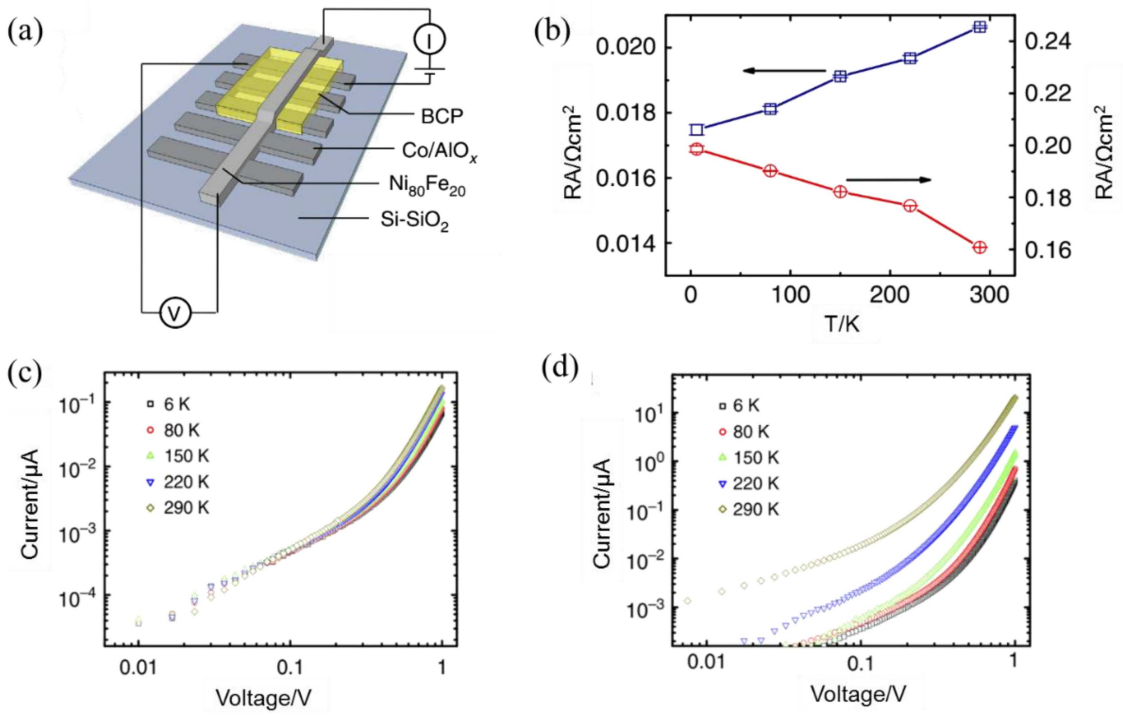



**Fig. 3.** (color online) (a) Diagram of $AlO_x$-based MSV (from Ref. [26], Fig. 1(a)). (b) Temperature-dependent resistance of Co/$AlO_x$/NiFe junction based on leaky (blue squares) or non-leaky (red circles) $AlO_x$ barriers (from Ref. [26], Fig. 2(a)). (c)–(d) Current–voltage curves of BCP-SVs with non-leaky and leaky $AlO_x$, respectively, indicating tunneling and hopping transport mode (from Ref. [26], Figs. 5(a)–5(b)).

## 3. Spin filtering effect due to hybrid interface state (HIS)

In addition to improving the reliability and performances of the device, the interface engineering is also crucial to achieve effective manipulation of spin signal in MSVs. The spin filtering effect caused by HIS, interpreted by electron trapping and interaction strength, is expected to be employed for achieving spin signal manipulation. The role of HIS at FM/molecule interface, formed due to the coupling between metal and molecules, has been frequently discussed in many recent studies, including the bonding strength and unbalanced spin-DOS of HIS. Finally, based on the spin filtering effect, a novel kind molecular spin memory device has already emerged, which hints the primary application of spin manipulation.

### 3.1. Formation and properties of HIS

In conventional MSVs, directly contacted FM electrodes (such as NiFe, Co, and LSMO) and molecules (usually $\pi$-conjugated) can cause the hybridization of 3d or 4f electrons with $\pi$-conjugated molecular orbitals and therefore form HIS at the interface. So far, several experimental and theoretical contributions have been delivered to deal with the formation mechanism of HIS. Recently, x-ray photoelectron spectroscopy has been used to analyze the surface chemical state

of Fe/$Alq_3$ HIS, and an interfacial interaction, occurred at atomic scale, has been successfully observed.[54] Besides, x-ray magnetic circular dichroism signals indicate that $Alq_3$ is magnetized via exchange coupling and behaves like a part of the spin injector.[54] By considering the interaction strength and computing the spin lifetime theoretically, Droghetti *et al.* concluded that the metal Co and surface monolayer of the $Alq_3$ molecule are strongly chemisorbed, whereas the second layer of $Alq_3$ is weakly physisorbed on Co.[55] Besides molecular semiconductors, molecular interface layer, such as 11,11,12,12-tetracyanonaptho-2,6-quinodimethane, that inserted between Co and $Alq_3$ can also form HIS with Co and hence enhancing the hole injection efficiency by shifting the HOMO level alignment.[56]

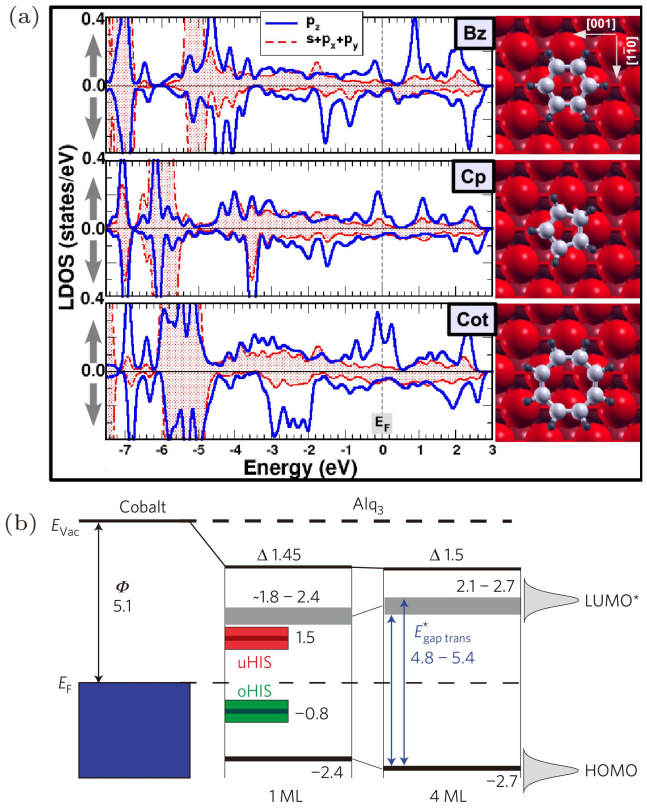



**Fig. 4.** (color online) (a) Adsorption geometries and the spin-resolved local density of states of the Bz ($C_6H_6$), Cp ($C_5H_5$), and Cot ($C_8$ $H_8$) molecules adsorbed on the 2-ML Fe=W(110) (from Ref. [57], Fig. 1(b)). (b) Energy level alignment at Co/$Alq_3$ interface with 1-ML and 4-ML $Alq_3$ (from Ref. [62], Fig. 2(a)).

The electronic and magnetic properties of HIS have been studied both theoretically and experimentally in recent reports, including spin-resolved DOS of occupied electrons, and energy level alignment. As shown in Fig. 4(a), Atodiresei *et al.* show a clear picture of local spin-resolved DOS captured from FM surface, which is influenced by a series of molecules with $\pi$-electron system.[57,58] It is observed that the spatial distributions of the majority spin state are changed at FM/molecule interface, which also corresponds to the double-exchange mechanism proposed by Zener.[59] Similarly, Ultraviolet photoelectron spectroscopy (UPS) combined with density functional theory indicates that the spin-resolved local DOS of the chemisorbed metal phthalocyanine (*M*Pc)/Co ($M$ = Cu, Fe, Co) interface exhibits totally different majority and minority spin distributions. Whereas the local DOS of pure MPc shows no spin splitting, which indicates different interactive strengths due to different central metals.[60] Spin-split HIS has also been observed when the $C_{60}$ contact directly to FM materials with different crystal directions.[61] Furthermore, several studies have found that the occupied HIS (oHIS) and the unoccupied HIS (uHIS) are formed between HOMO and LUMO levels of the surficial monolayer of $Alq_3$ (Fig. 4(b)). Consequently, spin holes and electrons can transport at uHIS and oHIS separately and freely, and therefore enhancing the spin injection process.[62]

### 3.2. Spin filtering effect induced by HIS

The spin filtering effect is a phenomenon to produce spin polarization that can be attributed to different spin selectivity for majority and minority spins under certain conditions. Based on the description of spin DOS at HIS mentioned above, many studies and interpretations of spin filtering effect induced by HIS have been demonstrated. By characterizing the HIS at Co/$Alq_3$ interface with spin- and time-resolved two-photon photoemission,[63] it is found that electrons accumulated at uHIS above 1.5 eV are spin-correlative trapped as inferred from the measured longest inelastic lifetimes. Moreover, the dramatic lifetime disparity between majority and minority spin electrons directly demonstrates a clear spin filtering process.[62] Moreover, the dynamic study of spin filtering effect indicates that the observed long spin-flip scattering lifetime is caused by the physisorbed secondary molecular layer of $Alq_3$ on the Co surface (see Figs. 5(a) and 5(b)), which can also significantly influence the spin injection and diffusion processes.[55,64]

Based on the spin filtering effect caused by physisorbed secondary molecular monolayer (Fig. 5(c)) of zinc methyl phenalenyl (ZMP) on Co, a molecular spin memory device (Fig. 5(d)) based on magnetic exchange coupling principle has been firstly achieved, in which a relatively large interface MR has been observed. This study also suggests that neutral planar phenalenyl-based molecule can be effectively transformed through the interfacial hybridization and hence lead to promising applications in spin memory devices.[65] Moreover, as an interfacial effect, the spin filtering effect can also be achieved by an inserted thin intermedia layer between the FM and molecule, such as EuS[66,67] and MgO.[68]

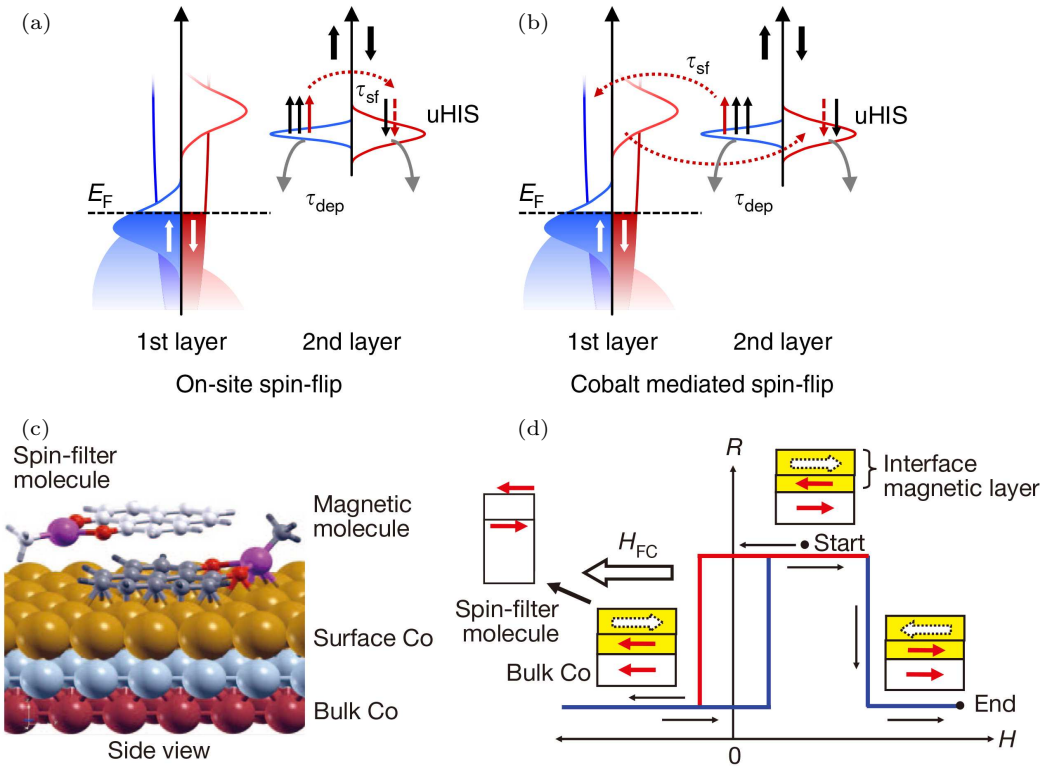



**Fig. 5.** (color online) (a) and (b) Dynamic spin filtering at the Co/$Alq_3$ uHIS (from Ref. [55], Figs. 7(a)–7(b)). (c) Absorption of ZMP molecule on Co atoms (from Ref. [65], Fig. 3(c)). (d) Relative magnetization directions of the interface with sweep magnetic field in the model of molecular spin memory device (from Ref. [65], Fig. 3(d)).

## 4. Spin signal reversal by the FM/molecule interface

Since the effective spin filtering effect of FM/molecule interface has already been observed, the HIS is widely considered as the pivotal factor to achieve spin manipulation in molecular spintronic device, although more effort is still needed to be delivered on clarifying the interaction mechanism of HIS. In the following text, recent advances regarding spin signal manipulation embodied by MR signals reversal, has been summarized, which include the study on intrinsic property of FM/molecule interface and inserted polar intermedia layer at interface.

### 4.1. Spin signal reversal due to interaction at FM/molecule interface

$Alq_3$ is one of the most widely used molecules in the molecular spintronic studies. The MSV, built with a structure of LSMO/$Alq_3$/Co, normally exhibits inversed MR sign, as shown in Fig. 6(a), instead of a common positive MR signal. According to the corrected Jullière formula, the inversed MR should be caused by opposite spin polarization of FM electrodes, which might be produced by the changed spin DOS.[21] Based on this assumption, a spin hybridization transport model has been established to describe the spin signal reversal process that caused by hybridization of the LSMO electrode and the first monolayer of $Alq_3$ (see Fig. 6(b)),[69] which is exactly coordinated to the initially observed negative MR signal in the study from Xiong *et al.*[21] Therefore, it is clear that a $Al_2O_3$ intermedia layer inserted between Co and $Alq_3$ layers, shown device architecture as LSMO/$Alq_3$/$Al_2O_3$/Co, definitely cannot change the MR signs from negative to positive.[27] However, different to the $Al_2O_3$, few kinds metal-oxide, such as $SrTiO_3$ (STO) and $Ce_{0.69}La_{0.31}O_{1.845}$ (CLO), can reverse the spin polarization of electrons when acting as tunnel barrier in magnetic tunnel junctions (MTJs),[70] which should have the potential to turn over the sign of MR in MSVs. Besides, similar reversed MR signals have also been observed in the MSV of Fe/$Alq_3$/Co[71,72] and LSMO/P3HT/$Al_2O_3$/Co[73] architectures.

As mentioned above, the introduction of organic-based magnet $V[TCNE]_x$ as two FM electrodes in MSV, shows advantages in addressing the problem of conductivity mismatch.[29] Meanwhile, combined with annealed rubrene layer, the MSV of $V[TCNE]_x$/rubrene/$V[TCNE]_x$ shows reproducible inversed MR sign since the spin carriers tunneling through the spin splitting band. To interpret the negative MR, a bias-enhanced selective tunneling model has been proposed to demonstrate that energy levels are shifted under the applied bias (Fig. 6(c)).[30] And as a consequence, the spin selectiv-

ity is completely inversed when spin signals tunnel through the molecular layer (Fig. 6(d)).[30] In fact, the all-organic spin valve have attracted considerable attentions recently because it shows the potential to achieve both improved performances of MSV and the possibility for primary manipulation of spin signal.

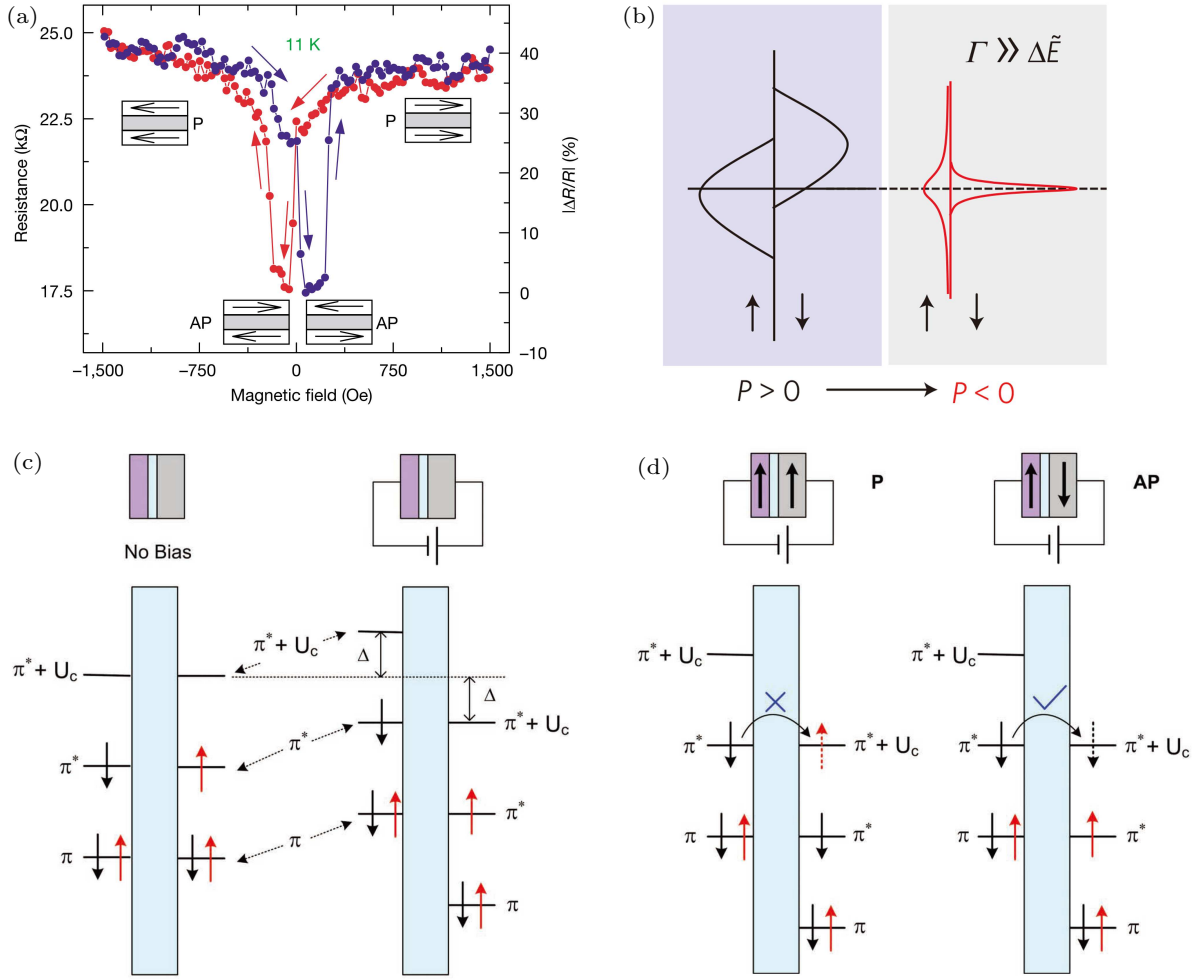



**Fig. 6.** (color online) (a) GMR of LSMO/$Alq_3$/Co spin valve measured at 11 K (from Ref. [21], Fig. 2(a)). (b) Illustration of the spin-dependent interfacial molecular hybridization to explain negative MR (from Ref. [69], Fig. 5(b)). (c) Energy level diagram for a V[TCNE]$_x$/rubrene/V[TCNE]$_x$ tunnel junction without and with external bias. (d) The tunneling process of electrons transport at energy level under parallel and antiparallel configuration. (Both panels (c) and (d) are from Ref. [30], Fig. 5). The unit 1 Oe = 79.5775 A·m$^{-1}$.

### 4.2. Spin signal reversal due to polar interfacial layer

The LiF is a polar material widely employed to modify the interface for enhancing the electron injection in molecular electronic device. In recent studies, it also shows a unique property that can invert the spin signal in MSV, when works as an intermedia layer between FM electrode and molecular layer. However, the mechanism for the spin signals reversal, caused by LiF as well as similar polar interfacial layers, is still under debated so far. The spin transport status through the modified energy level and the chemical interaction at the interface are the two main views presently.

Negative MR caused by LiF was firstly observed when it was employed as a buffer layer to protect FM electrodes from direct contact with the molecule of $Alq_3$ in MSVs,[27] which got noticed soon by many researchers. In a subsequent study, Schulz *et al.* indicated that the interface dipole generated by LiF may change the spin polarization direction via HOMO level shift and hence spin signal reversal is detected by the counter-electrode of NiFe (see Figs. 7(a) and 7(b)).[74] In another study from Hueso's group, it is found that the spin signals reversal just can be observed when the LiF layer is deposited in a specific sequence,[75] which may lead to a different mechanism to previous study. When LiF is deposited directly on the top of bottom FM electrode, whether Co or NiFe, metal fluorides are formed by chemical reaction between thermally decomposed LiF and bottom FM metals. The antiferromagnetic (AFM) layer (comprising $CoF_2$ or $NiF_2$ and $FeF_2$) has a magnetization direction that is opposite to the bottom electrode. However, MR signals are determined by the relative magnetization directions between the AFM layer and top FM electrode, which caused inverted MR in these MSVs (Figs. 7(c) and 7(d)).

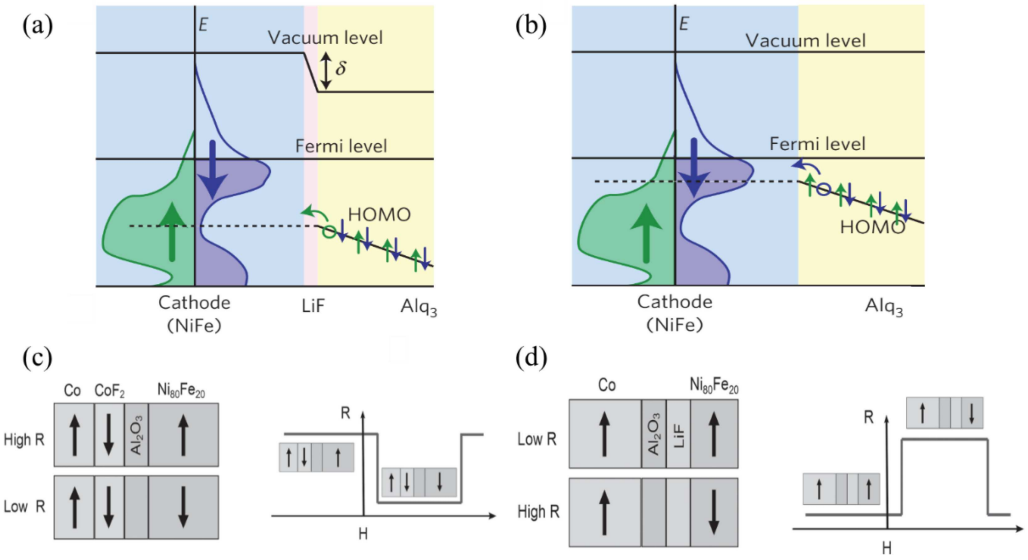



**Fig. 7.** (color online) Interpretation of negative MR based on LiF MSVs. (a) and (b) Holes extracted at LSMO/LiF/$Alq_3$ interface and pure NiFe/$Alq_3$ interface is related to the spin-DOS (from Ref. [74], Figs. 4(b) and 4(c)). (c) and (d) Relative magnetized directions at FM/LiF interface and its effect on resistance changing under switching magnetic field (from Ref. [75], Figs. 3(b) and 3(c)).

## 5. Spin signal manipulated by ferroelectric interfacial layer

Ferroelectric materials characterized by spontaneous electrical polarization at a specific temperature range originated from the transform of crystal structure, and their polarization can be reversed with a large and opposite electric field. Under a magnetic field, magnetoelectric coupling occurs as a result of the interaction between the magnetic strength of FM metals and the electric polarization of ferroelectric materials, thus an applied electrical field can be programmed to control the magnetization of the FM metals. Recently, the $BaTiO_3$ (BTO) tunnel barrier was proven have the ability to influence the spin polarization of injected carriers,[76] which indicated a possible way to achieve spin signal manipulation in spintronic devices. In the study, MTJs based with BTO spacers were constructed and characterized, in which spin polarization at the Fe/BTO interface was controlled by applied bias and therefore different magnitude tunnel magnetoresistances (TMR) were obtained.

Inspired by previous achievements in MTJs devices, ferroelectric material has also been employed to manipulate spin signals in molecular spintronic devices. The $PbZr_{0.2}Ti_{0.8}O_3$ (PZT), a perovskite material well known with large remanent polarization, has been used as intermedia layer between LSMO electrode and $Alq_3$ in MSV recently (Fig. 8(a)).[77] The ferroelectric polarization of PZT produces dipole moments at the PZT/$Alq_3$ interface and shifts the vacuum level, and as a consequence, the effective applied bias on the $Alq_3$ spacer is changed (increasing or decreasing). Therefore, the shape of the MR diagram can be controlled systematically according to the electric polarization of PZT, which includes modulating and even reversing the sign of MR in an operated MSV. A more detailed mechanism of the MR shape modulation has been concluded from an energy level alignment model, which derived from the integration of spin hybridization transport model that used to explain the negative MR[69] and the energy level model that proposed by Schulz *et al.*[74] In this model, the spin polarization of holes is reversed when injected across LSMO/PZT interface into the HOMO level of $Alq_3$, in pace with the changing on ferroelectric polarization of PZT (Fig. 8(b)).[77] Similarly, TMR signals in multiferroic tunnel junctions (MFTJs) also change accordingly to the variation of electric polarization of PZT under reversible applied bias, in which PZT was used as a tunnel barrier.[78]

Recently, the ferroelectric polymer of poly(vinylidene fluoride) (PVDF) has been employed as a robust spacer between two FM electrodes to form hybrid MFTJs (Fig. 8(c)). In this device, four resistance states can be detected, combining the relative magnetization direction of FM electrodes under recycled magnetic field and ferroelectric polarization of PVDF under reversed applied bias as shown in Fig. 8(d).[79] It is found that the sign of measured TMR is fairly depended on the atom bonding conditions at PVDF/Co interface calculated by ab initio calculations[80] (Fig. 8(d)). To further verify the role of the interfacial effect on controlling the signs of TMR experimentally, the same structure MFTJs are fabricated, merely different with a room-temperature-deposited Co top electrode. And it is found that the spin signal shows no response to the ferroelectric polarization of PVDF since the PVDF layer is shorted out by the metallic penetration of the top electrode. Furthermore, when a thin MgO layer is inserted between PVDF and Co as an intermedia layer, no obvious dependence between the TMR sign and the polarization of PVDF can be observed. All these experimental results demonstrate that the interaction at the interface of FM electrode and ferroelectric material is the key point to achieve the manipulation of MR sign in spintronics device.

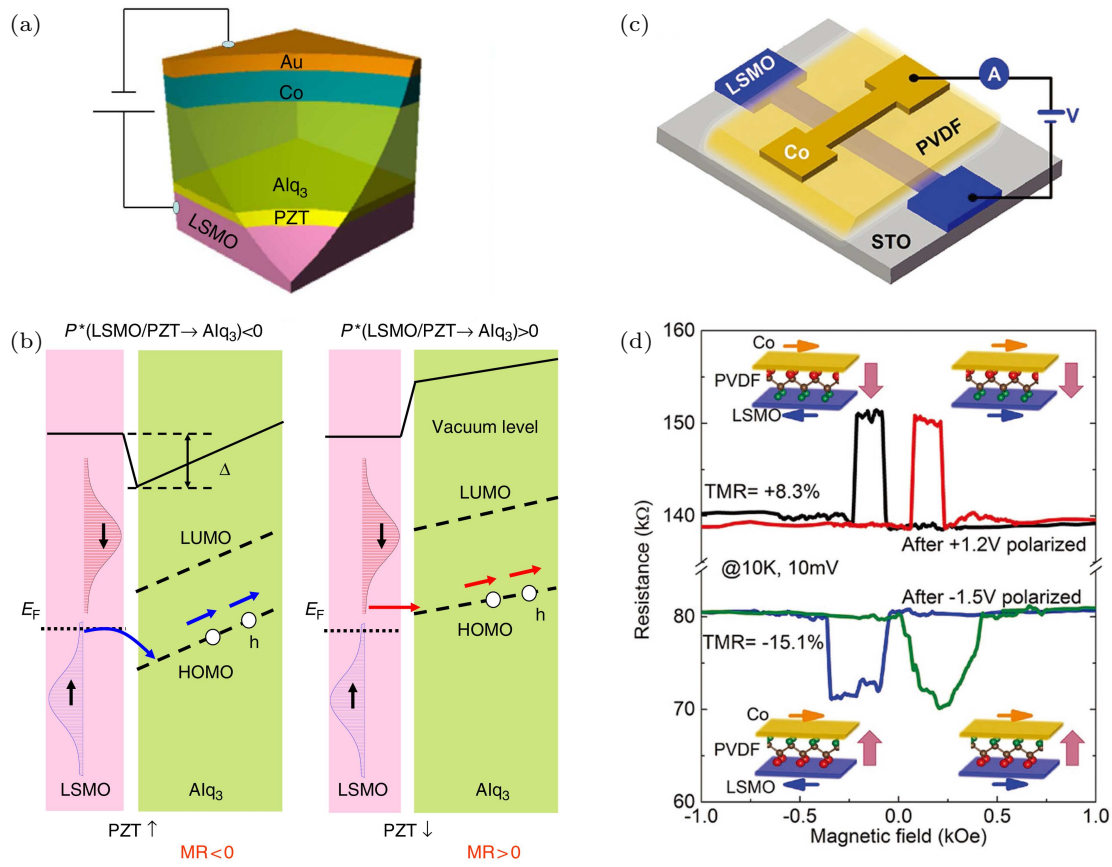



**Fig. 8.** (color online) (a) Structure of MSV based on ferroelectric PZT (from Ref. [77], Fig. 1(a)). (b) Illustration of MR sign reversal when electric polarization of PZT is up and down (from Ref. [77], Fig. 5). (c) Schematics of the LSMO/PVDF/Co MFJs (from Ref. [79], Fig. 1(a)). (d) TMR measured under 10 mV at 10 K after +1.2 V and −1.5 V polarizing the device (from Ref. [79], Fig. 2(a)).

The above studies, regarding magnetoelectric coupling effect in molecular spintronics, are all carried out at low temperatures, which cannot meet the basic demand of room-temperature operation for potential applications. Recently, room-temperature multiferroicities of Fe/BTO and Co/BTO have already been observed by the x-ray resonant magnetic scattering under a magnetic field and the piezo-response force microscopy with changing applied bias, which might result from the hybridization or even the interaction between Fe/Co and O atoms.[81] This important discovery may lead to a breakthrough on room-temperature MR sign manipulation in the near future based with ferroelectric materials in molecular spintronic devices.

## 6. Conclusion and perspectives

In this review, recent advances regarding the FM/molecule interface in spintronic device have been summarized. So far, various novel methods for interface engineering have already been developed to fabricate reliable MSV devices and improve the device performances. According to latest reports regarding spinterface, spin filtering effect at HIS has been studied and employed to initially manipulate spin signal, which is mainly driven by energy level shift and spin DOS change of the spinterfacial states. Besides, manipulation of spin signals has been preliminarily achieved in molecular device with the aids of the interfacial layer comprising polar or ferroelectric materials inserted between FM electrode and molecular layers. All these contributions have shed light on the development of the molecular spintronics, especially to the research field of spin manipulation and novel spin functions in devices based on molecules.

However, how to achieve effective spin manipulation is still one of key issues so far in molecular spintronics. Although, interfacial engineering and exploration have shown the possibility on achieving spin manipulation, the study on spinterfacial mechanism need to go further especially on illuminating the FM/molecule interaction and the role of polar interfacial layers in MSVs. More instructive theory models, like spin hybridization transport model, and necessary experimental methods need to be established to give more clear explanation that can effectively promote the development of spin manipulation in molecule-based devices. Beside the spinterfacial methods, utilizing the abundant optical–electrical proper-

ties of the molecules in spintronic device has been preliminarily demonstrated to be a possible way to achieve effective spin manipulation by the external electric field and illumination according to the recent reports of spin memory device[82] and molecular spin photovoltaic device.[83] As a prospect, multifunctional molecular spintronic devices combining spin valve effect with thermoelectric or electrical field-effect and further spinterface theoretical studies might give more powerful impetus to the development of the research on spin manipulation.

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