

Review

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Review

The Variability of the Conductance Changes Associated with the Change in the Spin State in Molecular Spin Crossover Complexes

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Abstract: We examine here the conductance changes associated with the change in spin state in a variety of different structures, using the example of the spin crossover complex $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ (pz = (pyrazol-1-yl)-borate and bipy = 2,2'-bipyridine) and $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ (Htrz = 1H-1,2,4-triazole) thin films. This conductance change is highly variable depending on the mechanism driving the change in spin state, the substrate, and the device geometry. Simply stated, the choice of spin crossover complex used to build a device is not the only factor in determining the change in conductance with the change in spin state.

Keywords: spin crossover; conductance change; substrate effects; device geometry

1. Introduction

There is often a change in conductance, sometimes by many orders of magnitude, accompanying switching between spin states in spin crossover complexes [1–37]. This change in conductance, associated with a change in spin state, can be voltage controlled [1,3,4,7,15] and when formed in a bilayer with a molecular ferroelectric a nonvolatile voltage-controlled device, based on molecular systems, is realized [1,3,6,15], as illustrated in Figure 1. For most practical memory applications, switching is required to be non-volatile, isothermal (near and above room temperature), bidirectional, and voltage controlled. The greater the change in conductance, with the isothermal switching of the spin state, the better the device fidelity [1], but what exactly controls this on/off ratio is far from settled. The objective of this review is to show that while significant conductance changes have been observed to accompany molecular spin state switching, the magnitude of this change depends on a great many factors, not all of which are completely understood. We illustrate these points noting the various results obtained from thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ (pz = (pyrazol-1-yl)-borate and bipy = 2,2'-bipyridine) and $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ (where Htrz = 1H-1,2,4-triazole as examples. In particular, we emphasize that switching mechanism [3,15], device geometry as well as contact resistance [27] greatly affect not only the on/off ratio but the conductance as well. We also point out that polymeric additives [5,35], as well as charge transfer salts [11,33,36–38], have a strong influence on conductance and frequently on the on/off ratio as well [5,33]. We also hint at a mechanism for conductance change in spin crossover complexes. $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ (pz = (pyrazol-1-yl)-borate and bipy = 2,2'-bipyridine) and $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ (where Htrz = 1H-1,2,4-triazole are very different but both complexes are now well studied. crossover complex is depicted in Figure 2, the spin transition for this complex occurs at around $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ (pz = (pyrazol-1-yl)-borate and bipy = 2,2'-bipyridine) spin 120 K [3,6,39–44]. The spin crossover polymer $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ (Htrz = 1H-1,2,4-triazole) is schematically depicted in Figure 3 and spin transition for this complex occurs above room temperature at around 340 K [2,5,21,22,24,26,28–30,35].

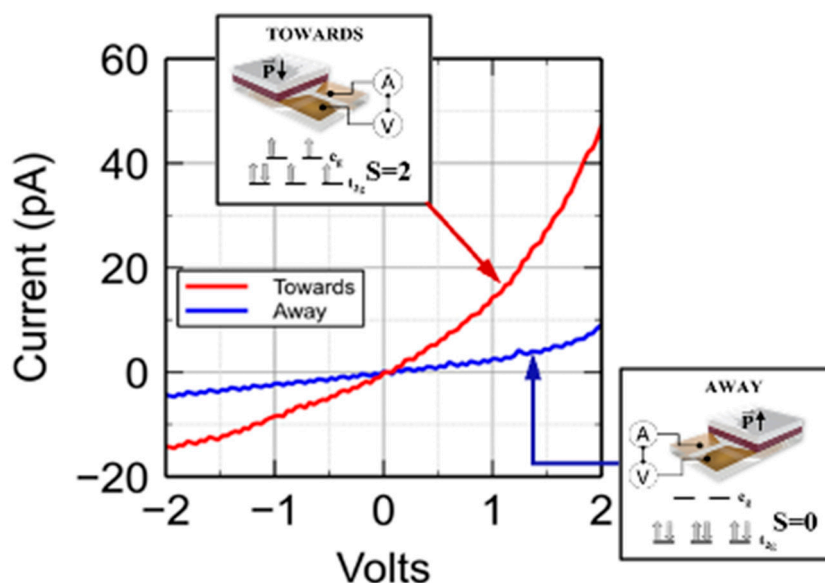


Figure 1. The change in conductance observed in a $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ thin film, 65 nm thick, with different ferroelectric polarization directions in an adjacent thin film of the molecular ferroelectric polyvinylidene fluoride hexafluoropropylene (PVDF-HFP). Transport measurements were taken across a device in the transistor geometry, at room temperature, with the ferroelectric layer adjacent to the SCO layer. Polarizing the ferroelectric towards the $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ layer results in high spin state (nominally $S=2$) with larger conductance. The polarization of the ferroelectric away from the $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ layer leads to the low spin state, a diamagnetic $S=0$ state, and lower conductance. Reproduced from [15], with permission from the American Chemical Society.

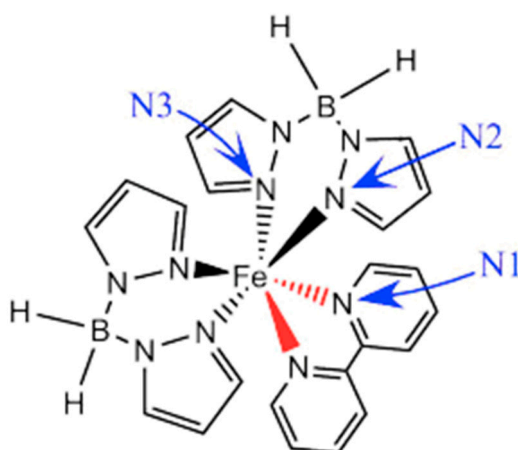


Figure 2. $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ molecular spin crossover complex depicted schematically.

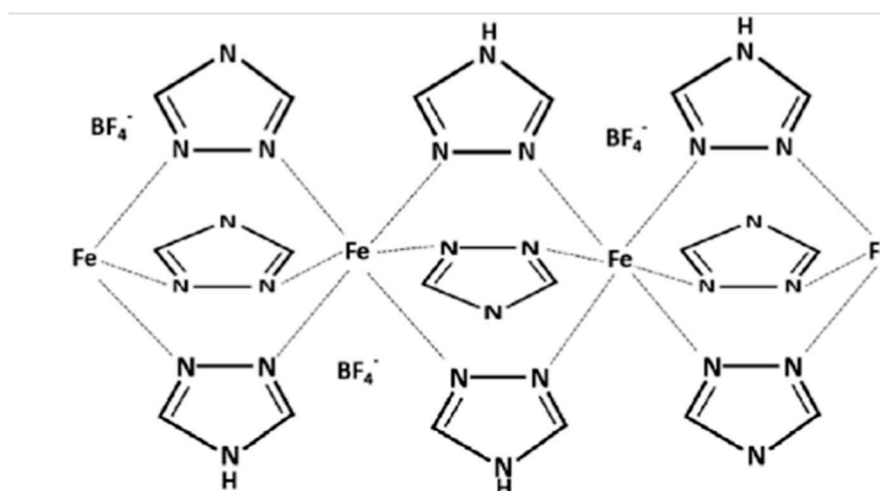


Figure 3. $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ spin crossover polymer depicted schematically. Adapted from [5] with permission from Elsevier.

2. Variability of conductance change.

Thermal versus voltage controlled switching.

It has been demonstrated that thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ can be driven through a spin crossover transition if the polarization of an underlying ferroelectric substrate is switched using an applied voltage [1,3,6,15]. This switching occurs not only for the molecules in the immediate proximity of the ferroelectric but propagates up to 24 molecular layers [45]. For thicker $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ films on an organic ferroelectric, the switching may be incomplete with the change in ferroelectric polarization, however, which translates to a lower on/off ratio [3]. Furthermore, the notion that voltage controlled switching in thicker films is incomplete, is supported by spectroscopic measurements [3,39]. Figure 1 shows the on and off state current versus voltage, $I(V)$, characteristics of a 65 nm thick $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ film on a organic ferroelectric polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) substrate. In this molecular heterolayer device geometry, an on/off ratio of about 6 is achieved through voltage controlled switching or the ferroelectric, although we now know the ferroelectric polarization retention is not always guaranteed [39]. In a similar thin geometry, however without the adjacent ferroelectric layer, a significant improvement in the on/off ratio is observed when the spin state is switched through temperature variation, as more complete molecular spin state switching is assured. As seen in Figure 4, the leakage current is drastically reduced, consistent with a more complete spin state transition with temperature.

Similar changes in the current across the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film, that are far more characteristic of a full change in spin state instead of a partial change in spin state occupancy, can be accomplished by electric field if we ensure that the entire $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film is influenced by the applied electric field. Such is the case for a $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film in a diode type structure, as seen in Figure 5. In this case, the currents for the "on" state are some 10^3 to 10^4 times larger than seen for the "off" state [1].

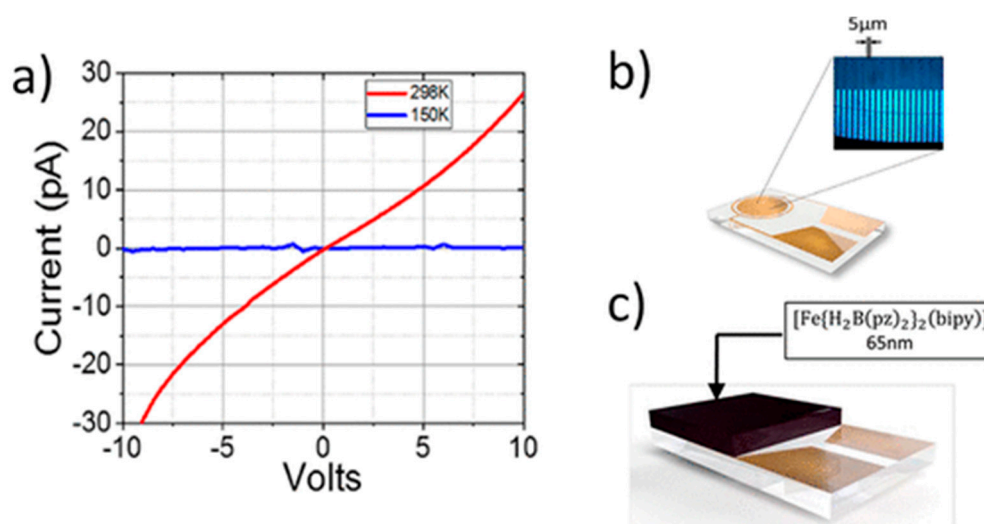


Figure 4. The differences in conductance for a 65 nm thick $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film in the high spin taken at 298 K (red) versus the low spin dominated state with the current measured at 150 K (a). The interdigitated fingers, with a spacing of $5\mu\text{m}$, used as the basis for the transport measurement is indicated in (b) with $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film deposited directly on patterned electrodes as in (c). Reproduced from [3], with permission from the American Chemical Society.

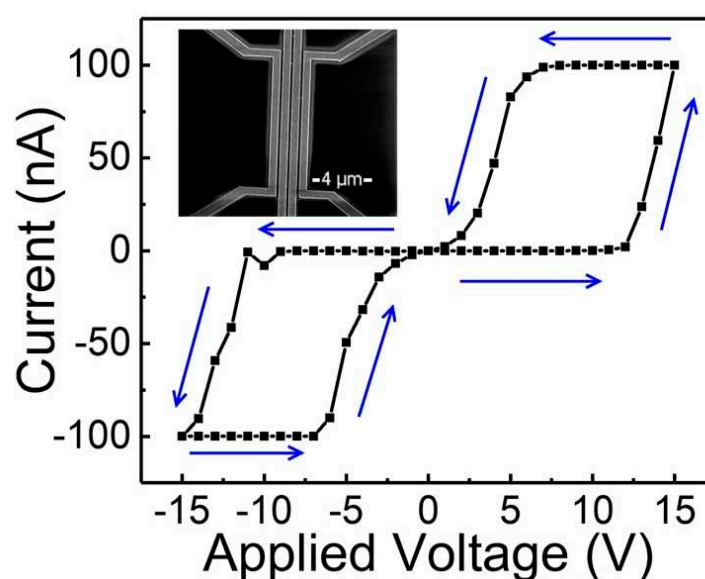


Figure 5. The evidence of conductance changes with applied voltage of a 20 nm $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film deposited on top of 200 nm thick croconic acid thin film. Longitudinal voltage was applied on different junctions and the measurement was taken at room temperature. With the very small gap between electrodes, the ferroelectric fails to lock the changing conductance state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ at zero applied voltage. In this device, the measured width and pitch of the smallest portion of the electrodes were 550 nm and 700 nm respectively. Reproduced from [1], with permission from the MDPI.

The effect of device structure

Not only is the on/off ratio a function of the spin crossover material and the switching mechanism, but the underlying device geometry also seems to play a significant role. As discussed above, in the diode geometry, more complete switching is seen with an applied voltage for a $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin film (Figure 5) than in the transistor like geometry (Figure 1). For the $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$ spin crossover polymer complex, several studies report an on/off ratio ranging

from 2 to 300 depending on whether a graphene based diode like device geometry was used or an Au/SCO/Au type arrangement was used [27], for a spin crossover (SCO) $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$ complex. In general, multilayer junctions lead to a higher on/off ratio as compared to a diode like geometry [27,34]. The effect of contact resistance in the variability of conductance changes observed for different device geometries cannot be ruled out, as is demonstrated in case of $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$ ($\text{tz} = 1,2,4\text{-triazol-1-yl}$).), in an indium tin oxide (ITO)/100 nm $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$ /Al junction, an on/off ratio of 50 was observed. This on/off ratio was shown to be enhanced up to 400 in a similar device geometry of ITO/100 nm SCO/Ca junction [27]. An on/off ratio of 1500 has been reported for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$ [23] in a structure involving multiple Au dots in an array, a much larger on/off ratio than is typical for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$, as summarized in Table 1. Nevertheless, even for comparable electrode and spin crossover materials, the effects of device geometry remain significant [34].

Table 1. Summary of the variation of conductance changes across the spin crossover transition for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$. Conductance values and ratios were determined at 15 V [22,30], 1 V [29], 20 V [26], 10 V [21], 0.4 V [24], 1.5 to 2 V [28], 1.2 V [21], while for [2], information as to the bias voltage was not clear.

On state	On/off ratio	On state current (A)	Off state current (A)	Switching mechanism	Reference
Low spin state	380	1.9×10^{-9}	5×10^{-12}	Temperature controlled	[22]
Low spin state	8	-	-	Temperature controlled	[29]
Low spin state	2	2×10^{-13}	1×10^{-13}	Temperature controlled	[2]
Low spin state	1.6	1×10^{-10}	0.5×10^{-10}	Temperature controlled	[26]
High spin state	11	5.5×10^{-9}	0.5×10^{-9}	Temperature controlled	[21]
High spin state	6	6×10^{-11}	1×10^{-11}	Temperature controlled	[30]
High spin state	1.7	9.2×10^{-10}	5.2×10^{-10}	Temperature controlled	[24]
High spin state	1.5	6×10^{-8}	4×10^{-8}	Photo induced	[28]
High spin state	1.5	-	-	Temperature controlled	[31]

3. The influence of the substrate

It has been fairly well established that the underlying substrate wields a strong influence on the spin state stability of spin crossover thin films [46]. As a key example, as mentioned above, there exists compelling evidence that the polarization direction of an adjacent molecular ferroelectric, like polyvinylidene fluoride hexafluoropropylene (PVDF-HFP), has a significant influence on the spin state of a $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ spin crossover thin film to a film thickness of 24 molecules thick [45] or about 25 to 30 nm thick. In fact, the influence of the substrate is not only limited to spin state stability, but also extends to the magnitude of the conductance itself [33,39,46].

It is important to realize that the substrate affects not only the spin state and stability of that spin state with temperature, but the actual conductance. This influence of the substrate on conductance can occur not simply because the substrate can "lock" the spin crossover molecular thin film in the low spin state [46], which is frequently the low conductance state, but because the substrate itself can enhance or suppress conductance even if the substrate is dielectric and not conducting. As an

example, the effect of ferroelectric polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) on the conductance in both the high spin (HS) and low spin (LS) states of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films as illustrated in Figure 6. This cannot be just an interface effect, as it propagates at least up to 24 molecular layers, but also because the change in the measured current is large and thus is not simply an interface effect. Additionally, this influence on the measured conductance is not a result of the ferroelectric thin film polarization directly as the ferroelectric is a very strong dielectric and thus by itself does not contribute to the net conductance. Although the mechanisms for this enhancement of the conductance is not known, we suggest that the effect arises from changes to the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ molecular packing within the thin film resulting in a significant change in the cooperative effects.

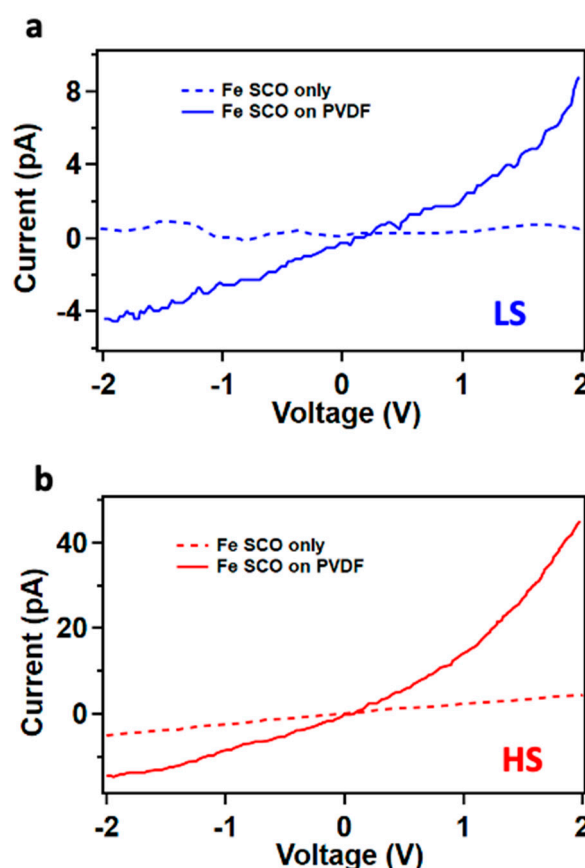


Figure 6. The current-voltage characteristics observed in a) low spin (LS) and b) high spin (HS) states for thin films of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ both on its own and on a polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) substrate. Transport measurements for the low spin state and high spin state of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films were conducted at temperatures of 150 K and 298 K, respectively. Meanwhile, for the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ film on PVDF-HFP, the measurements were carried out with the organic ferroelectric polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) polarized away from the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ film (representing the low spin state), and conversely, polarized towards the $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ film (indicating the high spin state) at room temperature.

4. Influence of additives

As noted at the outset, the on-state resistance and leakage current in spin crossover based devices, among other properties [5,11,33,35–38,40,41,47], are known to be influenced by the addition of conducting polymers [5,35], as well as charge transfer salts [11,33,36–38,47]. As an example, when $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$ spin crossover complex is formed into a composite with a semiconducting polymer like polyaniline, the on state resistance is reduced to less than 1 Ohm.cm [35]. The effect of semiconducting additives is much more nuanced, however, than meets the eye at a first glance. It was found that, $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$ plus polyaniline composites exhibit a wildly varying on/off ratio

depending on the doping routes and synthesis of the polyaniline additive [5]. The polyaniline additive synthesized from the emeraldine salt form led to a higher on/off ratio and a significantly reduced leakage current as compared to the one synthesized from the emeraldine base form. Not only did the on/off current ratios vary, but the on-state current obtained using emeraldine salt form was significantly larger than what was obtained using the emeraldine base form [5]. The addition of organic semiconducting polymers can lead to an enhancement of conductance but depends significantly on the polymer chosen to be mixed with the spin crossover [35].

The effect of mixing a charge transfer organic complex with a spin crossover complex is also highly variable [33,36,41]. For $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ when an organic acceptor molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ) is used as an additive, the complex is locked mostly in the low spin state but the conductance at room temperature is enhanced over the unalloyed $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ [33]. Polymeric and molecular additives also influence drift carrier lifetime as well as carrier mobility. Devices fabricated from $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)$ with a polyaniline additive feature a drift carrier lifetime in the excess of 10-100 micro-seconds [5]. The enhancement of the drift carrier lifetime is even more remarkable in case where TCNQ was mixed with $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ and an extremely long drift carrier lifetime of the order of 0.5 s was observed [33]. Thus, while molecular and polymeric additives can enhance conductance and carrier lifetime significantly, they also perturb the bistability of the spin state significantly and as seen in the case of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ combined with TCNQ [33] where the spin state was seen to be locked in one spin state which was seen with the addition of some other zwitterions species [40,41].

5. The mechanism of conductance change.

In many instances, the conductance changes accompanying the spin state transition in SCO complexes can be understood by considering the electronic structure changes occurring in tandem with the spin state change [3,6,15,40–43,45,48–56]. It is known that in the low spin state, energy difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular (LUMO) is large enough to allow the electrons to pair up in the HOMO, leaving the LUMO empty. This is analogous to a large band gap in conventional semiconductors. In the high spin state, this HOMO-LUMO gap shrinks and some states in the nominally unoccupied in the low spin state become occupied [2,3,15,36,45,50]. This is analogous to a narrowing of the band gap in conventional semiconductors. However, it is to be noted that molecular systems cannot be directly compared to semiconductors as the conventions of band bending don't apply very well especially if the molecules are charge neutral and the molecular films are not doped [57,58].

Changes in the HOMO-LUMO gap have been observed in optically induced transitions in $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ [51] and other spin crossover complexes while changes in the unoccupied electronic structure can be noted in X-ray absorption spectroscopy (XAS) of $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{bipy})]$ thin films [3,6,15,42,43,48–56], as illustrated in Figure 7. What is characteristic and important to the discussion here is that a new feature at lower photon energy emerges. This emerging feature at a lower photon energy indicates unoccupied states in the low energy t_{2g} orbitals that become partially unoccupied in the high spin state. This higher photon energy feature is indicative of unoccupied states in the higher energy e_g orbitals. Similarly, the conduction band appears closer to the Fermi level in inverse photoemission when the molecular thin film is in the high spin state [45], as seen in Figure 8. In both inverse photoemission (Figure 8) and X-ray absorption (Figure 7), the conduction band is indeed closer to the Fermi level. In the light of this discussion, one would expect the conductance in the high spin state should be enhanced as compared to the low spin state, owing to the narrowing of the bandgap, as suggested elsewhere [12,45]. However, problems with this rational based on a changing conductance associated with a changing band gap quickly emerge.

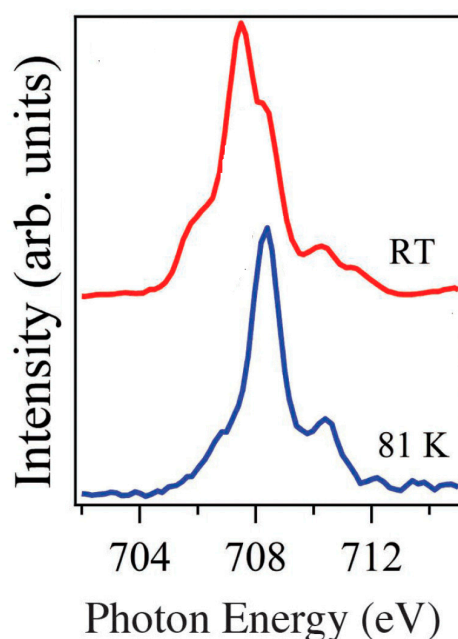


Figure 7. The temperature dependent X-ray absorption spectra of the $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ spin crossover complex, the spectrum obtained at room temperature (300 K), depicted by the red curve, signifies the complex being in the high spin state. In contrast, the blue curve representing the spectrum obtained at 81 K indicates the complex being in the low spin state. Adapted from [42] with permission from John Wiley and sons.

First among the problems with using this rational is for $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ spin crossover, the band gap is not trivial (several eV). Adding to the contention that the changing band gap does not address the changing conductivity of a molecular spin crossover thin film, there are several complexes including, $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$, where several studies [2,5,22,26,29,32], have reported that the low spin state has a significantly enhanced conductance compared to the high spin state. It is to be noted that other studies [21,22,28,30,31] have reported the opposite behavior in $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$, where the high spin state has the higher conductance as is the case for $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ discussed above. The variability of conductance change across the spin state transition for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$ is summarized in Table 1, and as noted above, the variability is significant. As seen in the table, not only does the spin state determine conductance, but the switching mechanism plays an important role as well. In addition to the examples mentioned in Table 1, an on/off ratio of 1500 was reported for $[\text{Fe}(\text{Htrz})_2(\text{trz})](\text{BF}_4)]$ [23] and, as mentioned above, this on/off ratio this is not really comparable to the examples mentioned in the table because this is in a multi-junction device. This suggests there are materials issues affecting the spin crossover molecular thin film conductance changes across the spin transition and this may include the film growth methodology and possibly the molecular polytype[5]. Just the same, the currents in the high spin state for $[\text{Fe}(\text{H}_2\text{B}(\text{pz})_2)_2(\text{phen})]$ films [16] and $[\text{Fe}(\text{HB}(\text{tz})_3)_2]$ films [17,27] and lower than the measured currents for the low spin state. Thus, we conclude that the conductance change across a spin transition is not merely due to the narrowing and widening of the HOMO-LUMO gap. What other factors influence the conductance changes associated with the spin state in spin crossover molecular thin film remain far from established. It is known that the applicable correlation energy (the Hubbard on-site potential) in the high spin state is wildly different from the low spin state [43], and while this almost certainly affects conductivity it is not yet clear the relative significance. Furthermore, an applied external magnetic field is seen to affect the spin state transition for $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ [52,54], so it is entirely plausible that there may be magneto-capacitance effects as well.

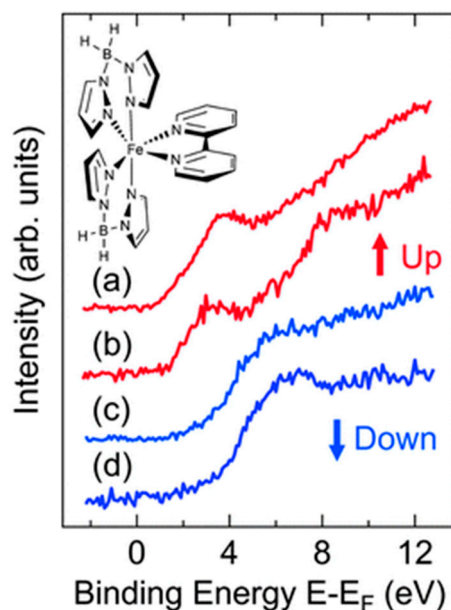


Figure 8. The inverse photoemission spectra obtained from thin films of $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ layered onto a ferroelectric poly-vinylidene fluoride – trifluoro ethylene substrate, a) and c) show spectra obtained from $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ layers consisting of 25 molecules, while b) and d) show spectra corresponding to $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ layers spanning 10 molecular layers. The blue curves delineate instances where the ferroelectric substrate's polarization is oriented away from the spin crossover thin film, representing the low spin state. Conversely, the red curves portray situations where the ferroelectric substrate's polarization is directed towards the spin crossover thin film, characterizing the high spin state. Adapted from [45] with permission of the Royal Society of Chemistry.

It should be noted that the conductance changes across the spin transition are significant, thus optical absorption becomes an unreliable indicator of band gap. As just noted, in X-ray absorption and inverse photoemission there are strong indicators that the band gap is smaller in the high spin state than for the low spin state in $[\text{Fe}\{\text{H}_2\text{B}(\text{pz})_2\}_2(\text{bipy})]$ thin films in X-ray absorption [3,6,15,40–43,45,48–56] and inverse photoemission [45], a superficial inspection of the optical spectroscopy changes across the spin state transition suggests the opposite [39]. Of course, optical absorption is subject to selection rules and a good (or better) conductor would lead to a decreased interaction with the photo-hole shifting optical absorption to shorter wavelengths (higher photon energies) [59].

6. Conclusions and outlook

Being able to control the spin state of a spin crossover molecular thin film device isothermally with voltage is vital to realizing future spintronic devices and low power molecular memory devices [1]. Interfacial interactions seem to provide a mechanism for stabilizing a spin state well above (low spin) and below (high spin) the spin transition temperature [1,3,6,39,45]. The nonvolatile stabilization of the spin state, in case of ferroelectric substrates, is shown to be amenable to modulation by an applied voltage [1,3,6,15,39] enabling bi-directional isothermal spin state switching. The isothermal spin state switching is evident in spectroscopy [3,6,15,39], as well as transport measurements [3,6,15] and confirmed by magnetometry [45]. In light of the fact that the on/off ratio of the measured currents in spin crossover molecular devices seems to be sensitive to the device geometry as well as the spin state switching methodology [1,3] and molecular additives as discussed above, it becomes imperative to map out the dependence of conductance change and the on/off ratio on the factors that influence the conductance change. Some of these have been identified here: the completeness of the spin state change or stated differently, the fraction of molecules that undergo a spin state change, influence of the substrate; the molecular packing and molecular polytype and possibly changing cooperative effects. A deep understanding is presently elusive. Knowing the possible device architectures [34], a

demonstration of conductance change is simply not enough. Little is known about the nature of charge carriers (electrons or holes), the origin of charge carriers (metal or ligand contributed) and the conduction mechanisms. It is now well established that polymer additives and charge transfer salts have an impact on the spin crossover as well as the electronic transport properties in spin crossover molecular devices [5,11,33,36,38], it is important to explore how the additives impact voltage-controlled switching. So yes, the choice of spin crossover complex affects the overall conductance, but other factors such as film thickness, choice of the substrate, underlying device geometry seem to have a strong influence as well. What remains surprising is not so much that the substrate influences a thin film of spin crossover molecules, but that in many instances, the influence of the substrate extends far from the interface, affect not just those molecules most adjacent but indeed well beyond [3,39,45,46].

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