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Progress towards the competitive multiferroic molecular transistor*

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***Abstract*— The example of spin crossover molecule [Fe(Htrz)$_2$(trz)](BF$_4$) (where Htrz = 1H-1,2,4-triazole) plus polyaniline composite thin films is used to illustrate the rapid improvement in transport properties signaling that competitive molecular devices for back end of the line (BEOL) silicon compatible nonvolatile memory arrays are increasing realistic.**

I. INTRODUCTION

Transition metal complexes, usually with a 3d^4 to 3d^7 electronic configuration, can sometimes undergo a change in spin multiplicity, and are thus known as spin crossover compounds. There has been significant success developing molecular spin crossover thin film devices, which may ultimately lead to voltage controlled molecular spintronics [1-3]. Despite significant advances in understanding spin crossover molecular films, there is only limited understanding of the underlying science [1]. There are serious deficiencies in fully understanding the voltage control of the spin state in spin crossover molecular thin film devices, the chemistry and intermolecular cooperative effects that determine spin state switching speed [4], the conduction mechanism [1], the limits to size reduction of a molecular voltage-controlled multiferroic device [1], and thermal stability of the molecular multiferroic. A key challenge to competitive multiferroic molecular devices based on spin crossover complexes, now widely recognized, is that the successful devices fabricated thus far from spin crossover complexes have a far too large on-state resistance to be fabricated into high density compact memory arrays [1]. This hurdle to competitive devices has been successfully overcome recently through the fabrication of molecular composites [5-7].

The spin crossover molecule [Fe(Htrz)$_2$(trz)](BF$_4$) (where Htrz = 1H-1,2,4-triazole) plus polyaniline composite is promising because of its much lower resistance [7], less than 1 Ω.cm, which makes the molecular composite more amenable to smaller devices [2]. While the on-state resistance of [Fe(Htrz)$_2$(trz)](BF$_4$) (where Htrz = 1H-1,2,4-triazole) plus polyaniline composite molecular devices has been reduced [5,7] to the point where competitive spin crossover molecular devices are possible [1], the change in conductance as the spin state changes remains significant as seen in Figure 1

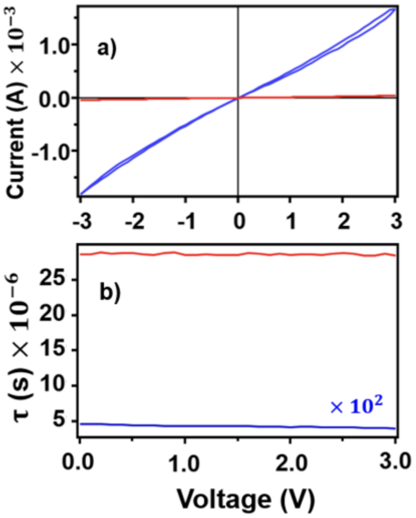

Figure 1. *(a) The I(V) characteristics of [Fe(Htrz)$_2$(trz)](BF$_4$) plus polyaniline. (b) The carrier lifetime versus voltage of [Fe(Htrz)$_2$(trz)](BF$_4$) plus polyaniline. Blue color refers to the measurement at T = 320 K (the low spin state) and red color refers to the measurement at T = 380 K (the high spin state). The carrier lifetime at T = 320 K was scaled as labeled. From [5].*

The fabrication of successful heteromolecular spin crossover thin film transistors has not only opened the door to controlled nonvolatile memory devices [1-3], but also has afforded us the opportunity to identify the majority carrier and drift carrier lifetimes [5] in thin films of spin crossover molecular complexes alloyed with semiconducting polymers like polyaniline [5,7].

II. SPIN CROSSOVER MOLECULAR TRANSISTORS

An effort has been made to determine the majority carrier and drift carrier lifetimes in the promising spin crossover molecule [Fe(Htrz)$_2$(trz)](BF$_4$) (where Htrz = 1H-1,2,4-triazole) plus polyaniline composite. The current voltage and capacitance voltage characteristics of the [Fe(Htrz)$_2$(trz)](BF$_4$) plus polyaniline composite were studied at both the low spin state and the high spin state [5]. In these composites, the drift carrier lifetimes are in excess of microseconds, and there are indications that the majority carriers are holes from the transistor mobility measurements. For the polytype of [Fe(Htrz)$_2$(trz)](BF$_4$) studied in [5], even after being combined with polyaniline, the composite

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conductance is high in the low spins state (Figure 1a), yet the drift carrier lifetime is much lower and negligible compared to the drift carrier lifetime (28 μsec.) in the high spin state [5]. This apparent contradiction between high conductance and very small drift carrier lifetime in the low spin state compared to the high spin state of $[Fe(Htrz)_2(trz)](BF_4)$ (where Htrz = 1H-1,2,4-triazole) in polyaniline can be reconciled by noting the changing carrier mobilities.

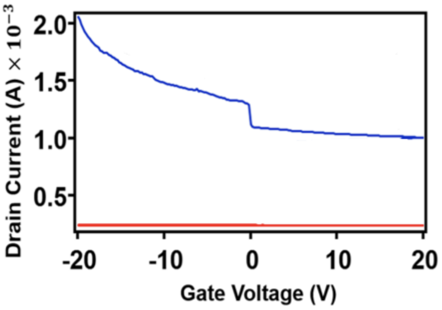

Figure 2. *The source to drain current transfer characteristics of $Fe(Htrz)_2(trz)](BF_4)$ plus polyaniline thin film transistor in the high conductivity low spin state (blue) and the low conductivity high spin state (red). respectively. The enhanced conductivity at negative gate voltages is indicative of holes as the majority carrier. From [6].*

The carrier mobility in the $[Fe(Htrz)_2(trz)](BF_4)$ (where Htrz = 1H-1,2,4-triazole) plus polyaniline composite is much higher in the low spin state, i.e. $\mu_{(\text{low spin})} \approx 10^5$ while $\mu_{(\text{high spin})} \approx 10^7$ as seen in Figure 1, so that the mobility is consistent with the higher conductivity of the low spin state. In both $[Fe(Htrz)_2(trz)](BF_4)$ plus polyaniline composite thin film transistors [5] and the well studied spin crossover complex $[Fe\{H_2B(pz)_2\}_2(bipy)]$ thin film transistors, the majority carrier is holes [6] (Figure 2). Furthermore, the carrier mobility is strongly influenced by the substrate, as the organic ferroelectric gate poly-vinylidene fluoride enhances the carrier mobility in $[Fe\{H_2B(pz)_2\}_2(bipy)]$ spin crossover molecular thin film transistors by more than 20 times [6].

TABLE I. SPIN CROSSOVER DEVICE BENCHMARKS DEVELOPMENT

Device Benchmark	*2019*	*2022*	*Realistic*
On/off	5 [2]	25	10^4 [1]
peak current density	??	$5\text{x}10^5$ A/cm^2	$3.8\text{x}10^5$ A/cm^2
switches	5	$10\text{x}10^7$ [8]	10^{12}
minumum size	3.6 nm [9]	3.6 nm [9]	10 nm
switching speed	0.3 ps [10]	0.3 ps [10]	100 ps
on state resistance	10^3 Ω.cm [1]	0.3 Ω.cm [7]	0.05 Ω.cm
upper bound operational temperature	300 K [2]	350 K [3]	375 K

Figure 1. Recent evolution of spin crossover molecular device performance benchmarks from 2019 to 2022 against a considered assessment of what might be possible for a working device in a memory array.

III. CONCLUSION

Recently, progress has been made in modifying the spin crossover molecular films for significantly lower on-state resistance [5-7] and higher carrier mobilities [5,6] in the transistor geometry. These continued improvements in the thin film transport properties have shown that the evolution of spin crossover molecular complexes, and their composites with other molecular systems, in the directions needed for competitive devices, as summarized in the table. Large conduction changes, with changes in spin state, have been retained and possibly enhanced.

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