

Unidirectional Spin-Dependent Molecule-Ferromagnet Hybridized States Anisotropy in Cobalt Phthalocyanine Based Magnetic Tunnel Junctions

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Organic or molecular spintronics is a rising field of research at the frontier between condensed matter physics and chemistry. It aims to mix spin physics and the richness of chemistry towards designing new properties for spin electronics devices through engineering at the molecular scale. Beyond the expectation of a long spin lifetime, molecules can be also used to tailor the spin polarization of the injected current through the spin-dependent hybridization between molecules and ferromagnetic electrodes. In this Letter, we provide direct evidence of a hybrid interface spin polarization reversal due to the differing hybridization between phthalocyanine molecules and each cobalt electrode in Co/CoPc/Co magnetic tunnel junctions. Tunnel magnetoresistance and anisotropic tunnel magnetoresistance experiments show that interfacial hybridized electronic states have a unidirectional anisotropy that can be controlled by an electric field and that spin hybridization at the bottom and top interfaces differ, leading to an inverse tunnel magnetoresistance.

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Organic spintronics [1] is a new effervescent research field whose founding ideas are to use organic materials as an efficient host for spin transport [2,3] while bringing new advantages such as flexibility, light weight, and low cost production. In 2010, a new opening was shown highlighting that the molecule-ferromagnet hybridization [4] (dubbed spinterface [5]) could be used to tailor the interface spin polarization and thus control the spin response of devices. However, up to now, a large amount of work has focused on spin transport through Alq₃ molecules. The main difficulty with Alq₃ comes from the dipole fluctuations from molecule to molecule spreading over the whole contact area. According to local scanning tunneling spectroscopy (STM) studies [6], this may lead to spatial inhomogeneity of the charge injection properties [7] and thus spin injection [4]. A quest for a more homogeneous system that could also be easily tuned is required. One option could turn out to be self-assembled monolayers or flat molecules like metallophthalocyanine (MPc). Contrary to Alq₃, MPc molecules form a well-organized structure once deposited on a surface [8]. Furthermore, it has been shown that the electronic properties of metal-MPc interfaces could be crafted by changing the metallic surface or the center ion [9–11]. Spin-dependent hybridizations in MPc (CoPc, H₂Pc, MnPc, FePc, or CuPc) on FM surfaces (Fe, Co) have been unveiled by spin-polarized STM [12–15] or x-ray spectroscopy studies [10,11,16], making these molecules very promising for molecular spintronics.

In this Letter, we report on direct evidence of a reversal in the sign of the spin polarization of a hybrid interface, which

we interpret in terms of changes to the spin-dependent hybridization induced by differences in geometry at each of the two nominally identical interfaces within solid-state Co/CoPc/Co magnetic tunnel junctions. Moreover, we show by tunneling anisotropic magnetoresistance (TAMR) experiments [17] that a unidirectional anisotropy occurs for the interfacial hybridized electronic states at the bottom Co/CoPc interface originating from the antiferromagnetic order of the CoPc chains.

The nanosized Co/CoPc/Co magnetic tunnel junctions (MTJs) are fabricated thanks to a conductive-tip AFM based nanoindentation technique [18] adapted to soft organic materials [4]. First, the Co bottom electrode is deposited by sublimation under UHV followed by the *in situ* evaporation of a very thin CoPc layer ranging from 5 to 15 nm. The Co/CoPc bilayers are then transferred in a glove box and capped with a protective photoresist by spin coating. The AFM tip used for nanoindentation is a diamond tip *p* doped with boron. Its final radius, which will determine the shape of the nanohole, is less than 10 nm [18] and its serial resistance is 10⁴Ω. Nanocontacts are elaborated with threshold values, at which the nanoindentation process is stopped, ranging from 10⁵ to 10⁹Ω. This leaves a thin CoPc molecular layer (in the nanometer range) acting as a tunnel barrier. The completion of the upper Co electrode is performed as described previously [4]. A schematic of the nanojunction is presented in Fig. 1(a).

In Fig. 1(b) we show an $I(V)$ curve recorded at 2 K (after field cooling at +0.1 T and 0°). The nonlinearity and low current (picoampere range) passing through the

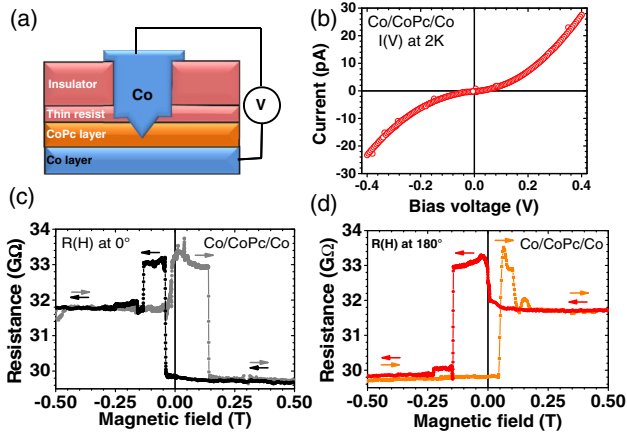


FIG. 1 (color online). (a) Schematic of the Co/CoPc/Co nanocontact. (b) $I(V)$ curve of a Co/CoPc/Co nanocontact recorded at $T = 2$ K. (c),(d) $R(H)$ curves recorded at 0° and 180° . The magnetic field is first swept from positive to negative values (black or red curve) and then from negative to positive values (gray or orange curve).

nanocontact suggest electronic transport by tunneling through the CoPc molecules. Two magnetoresistance curves with the magnetic field in the plane at 0° and 180° are plotted in Figs. 1(c) and 1(d). They are symmetric with respect to the magnetic field. While we observe that the magnetoresistance switches at low field, a striking point is that the saturation resistance is different for large positive and large negative magnetic fields. This is quite unexpected since both cobalt electrodes' magnetizations are saturated at such high magnetic fields. This means that the two directions are not equivalent and indicates the clear presence of a unidirectional anisotropy of the spin transport properties, which suggests TAMR behavior.

To clarify this behavior, we compare the $R(H)$ curve at 0° (its symmetric 180° curve is not shown) with that recorded at 90° (Fig. 2). We now focus on the gray zone of Fig. 2, within which one can clearly see three resistance

levels corresponding to 0° (30 G Ω , orange dot line), 90° (33.5 G Ω , green dot line) and 180° (32 G Ω , red dot line) saturating in-plane magnetic fields. One can see that the low magnetic field resistance states of the 0° and 180° curves correspond in fact to the 90° high field saturation resistance. Hence, the high resistance state at the low field of the 0° and 180° curves does not correspond to the conventional tunnel magnetoresistance (TMR) effect (anti-parallel magnetic configuration) but to an alignment of magnetizations along the 90° direction. We finally see that the low resistance state (at 30 G Ω) of the 90° curve (orange dot line) corresponds to the 0° high field saturation state. Overall, the variation of the resistance between the 30, 32, and 33.5 G Ω states for the $R(H)$ curves at 0° , 90° , and 180° (gray area in Fig. 2) originates from TAMR effects [17] linked to absolute magnetization directions and not from TMR. TAMR effects have already been reported in organic spin valves [19] but this unidirectional TAMR anisotropy behavior has only been observed in IrMn metallic antiferromagnet based MTJs [20,21].

Within this perspective, we plot in Fig. 3 the measured resistance (red dots) at a high field (2 T) for different magnetization directions and compare it to the expected effect for uniaxial (gray dashed line) and unidirectional (black dashed line) anisotropies. We thus infer that uniaxial and unidirectional anisotropies coexist in these Co/CoPc/Co MTJs. As the uniaxial magnetic anisotropy could be related to the cobalt electrode itself [22] the unidirectional anisotropy may be ascribed to the antiferromagnetic CoPc molecules [8,23]. This is supported by the evidence for an exchange bias effect from magnetometry measurements on our Co/CoPc bilayers (not shown). The transport properties of the device are then expected to reflect the interaction of the first interfacial molecular layer of the antiferromagnetic CoPc with the Co electrode. The understanding of the magnetotransport experiments additionally requires a specific Co/CoPc interface electronic and magnetic coupling defining a new effective electrode

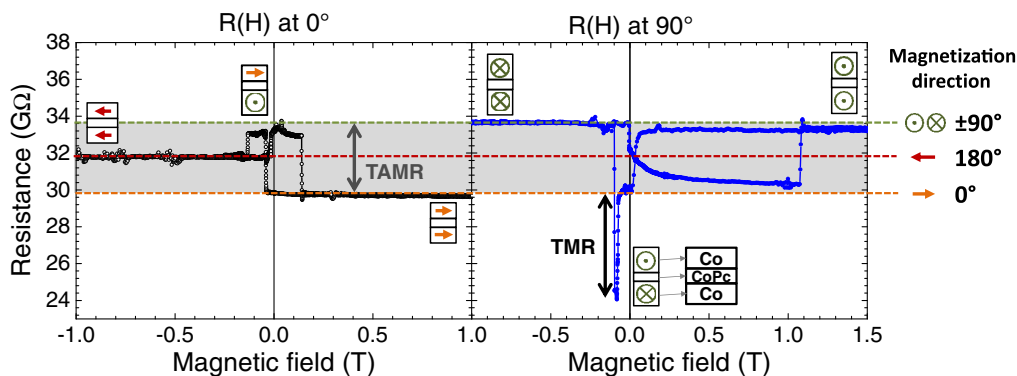


FIG. 2 (color online). Magnetoresistance curves recorded at $T = 2$ K, $V = -200$ mV at 0° and 90° . The gray area corresponds to TAMR effects. The orange, green, and red arrows and dashed lines indicate the resistance levels corresponding to magnetizations saturated in, respectively, the 0° , $\pm 90^\circ$, 180° directions (relative to field cooled). The green, orange, and red symbols in the $R(H)$ curves represent the magnetization directions of the two cobalt electrodes.

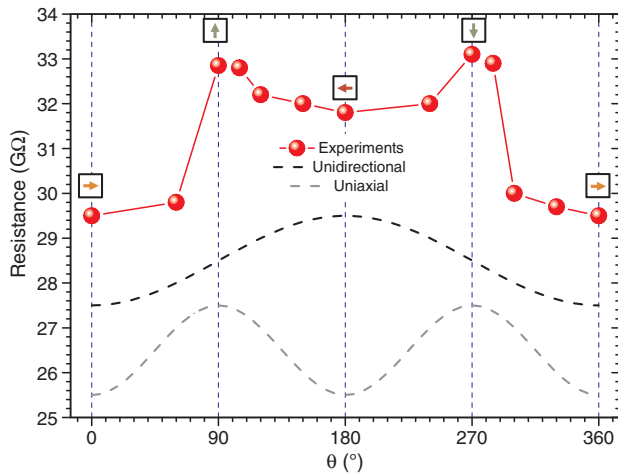


FIG. 3 (color online). Variation of the resistance as a function of the direction of the magnetic field at 2 T (red dots). The expected overall behavior (guide for the eyes) of the TAMR for uniaxial (gray dashed line) and unidirectional anisotropies (black dashed line) is also shown.

that would integrate the first molecular layer [4]. This is indeed the case as witnessed from scanning tunneling spectroscopy experiments on such interfaces [9]. Given the antiferromagnetic ordering of CoPc, this effective electrode, which integrates the first molecular layer, is then antiferromagnetically coupled to the other molecular layers. As TAMR effects reflect the anisotropy of the electrodes' density of states, these results suggest that the spin hybridized states at the Co/CoPc interface have also a unidirectional anisotropy. A unidirectional TAMR anisotropy of about 10% has been observed in devices in the 10^8 to $10^{10}\Omega$ range and thus does not seem to depend on the CoPc thickness. This suggests that the unidirectional TAMR anisotropy originates from interfacial effects.

We now focus on the TMR effect. The $90^\circ R(H)$ curve also exhibits a much lower third resistance state (Fig. 2). This resistance state does not originate from TAMR effects since this 24 G Ω resistance level is never obtained at any angle for the 2 T saturated magnetization (see Fig. 3). We thus ascribe this resistance state to the impact on the spin-dependent tunneling across the tunnel junction of a misalignment of the orientation of the magnetization of

the two electrodes, i.e., a TMR effect. The TMR has a negative sign and a magnitude of 20% for a symmetric Co/barrier/Co MTJ: the resistance when the electrodes' magnetizations are aligned parallel is larger than when they are misaligned (antiparallel magnetic configuration). This is striking because a symmetric MTJ is expected to show a positive TMR effect. Indeed, the TMR sign is usually derived in the framework of Jullière's [24] model, which gives $\text{sgn}(\text{TMR}) = \text{sgn}(P_1 P_2)$, where P_1 and P_2 are the spin polarizations of the two electrodes' interfaces. Thus, if the two electrodes are the same, the TMR sign is expected to be positive. Accordingly, a positive sign has always been reported for standard Al_2O_3 [25] or MgO [26] based devices relying on the same electrodes. Yet our symmetric Co/CoPc/Co stack shows a negative TMR sign. Up to now, the observation of a negative or inverse TMR (usually associated with a sign inversion in the bias voltage) in symmetric junctions was systematically linked to the presence of localized states or defects inside the barrier [27,28]. However, the inversion of the TMR in our junction cannot be ascribed to defects inside the CoPc layer since we observe no change of the TMR with bias voltage up to 0.8 V [Fig. 4(a)]. This quasiflat bias voltage dependence of the TMR has already been observed in molecular MTJs using self-assembled monolayers and ascribed to magnon excitation short circuits by molecular vibrations [29]. Hence, this observation means that we have symmetric electrodes but different interfaces. Indeed, the two interfacial spin polarizations have opposite signs and a clear distinction has to be made between the bottom and top interfaces ($P_{\text{Co/CoPc}}$ and $P_{\text{CoPc/Co}}$) even for the same materials. This follows the prediction that, depending on the coupling strength and position of the molecular states at the metal-molecule interface, the induced spin polarization on the first molecular levels could be inverted or enhanced [4]. *In fine*, the negative sign of the TMR observed can be explained by a strong coupling at the lower interface that inverts the spin polarization. Indeed, this would be supported by STM experiments on the same interface system (CoPc on a Co electrode) that have revealed that a strong coupling (chemisorption) induces shifts in the molecular states to the Fermi level [9] and leads to an inversion of the spin polarization [12,14,30]. The fact that this spin

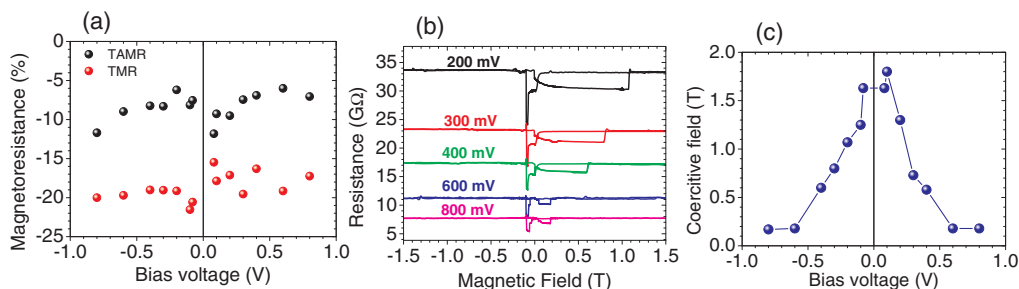


FIG. 4 (color online). (a) Variation of the TAMR and TMR as a function of bias voltage. (b) Magneto-resistance curves at 90° and 2 K recorded at different applied bias voltages. (c) Variation of the TAMR coercive field as a function of bias voltage.

polarization inversion does not occur at the top interface would then be explained by a differing strength of hybridization [4] when the metal is deposited on top of the molecules. This hybridization difference could originate from a dissimilar metal-molecule geometry induced for instance by an evolution of the stacking order of MPC films with thickness [31], by the mechanical effect of the nanoindentation process, or by cobalt atom diffusion inside the organic layer [32]. It has been even shown for apparently identical systems [Co/CoPc deposited on Cu(111) [12] or I(111) [30]] that the Co lattice parameter could modify the molecule-metal interaction [30] and therefore the hybrid interface properties.

In Fig. 4(b), we show different magnetoresistance curves obtained at 90° for voltages between +200 and +800 mV. A peculiar point is the 1-order-of-magnitude variation in the largest positive coercive field (from 0.2 to 1.7 T) with the applied bias voltage [Fig. 4(c)] corresponding to the TAMR. Note that only this coercive field shows a strong variation with the applied voltage. We now discuss the origin of this effect. While Joule heating cannot be excluded, it is tempting to ascribe this variation of the coercive field to spin transfer torque. However, since the current density in our MTJs is 4 orders of magnitude lower ($\sim 10^2$ A/cm²) than usual spin transfer currents and does not depend on the current polarity [33–35], this seems unlikely. On the other hand, it has been shown in inorganic spintronics that the surface electronic structure and thus the magnetic anisotropy can be modified by an electric field at a metal-dielectric interface [36,37]. Even if the variation of the coercive field is generally weaker (a few percent) than our observation, we may explain the exacerbation by the peculiarities of CoPc-based tunnel junctions. First, the spacer used here (CoPc) is an antiferromagnetic organic semiconductor. Second, the “effective” electrode (noted Co/CoPc^{1st layer}) involved in spin transport includes the hybridized first molecular layer. Hence, by modifying the electronic structure of the surface, an electric field could induce a variation of the Co/CoPc interfacial hybridization and also a modification of the antiferromagnetic coupling (exchange bias) at the Co/CoPc^{1st layer} and CoPc^{1st layer}/CoPc^{2nd layer} interfaces. It is also possible, given the 90° superexchange nature of the AFM interactions within CoPc [23], that spin transport may weaken the antiferromagnetic order chain through spin pairing effects [38], leading to the decrease in the coercive field with increasing applied bias. Although the exact mechanism remains an open question, these results are quite exciting since they demonstrate the possibility to shift a coercive field over an order of magnitude (1 T) with an electric field. This enables us to switch the resistance of a device by applying only a small voltage.

In conclusion, we have investigated magnetoresistance effects in molecular magnetic tunnel junctions based on cobalt phthalocyanines. The observation of inverse tunnel magnetoresistance in Co/CoPc/Co magnetic tunnel

junctions demonstrates that nominally equivalent Co/CoPc interfaces can have an opposite sign of spin polarization, which we ascribe to differing coupling strengths at the bottom Co/CoPc and top CoPc/Co interfaces. We also demonstrated by TAMR measurements that the spin dependent hybridized molecular states at the Co/CoPc interface are endowed with a unidirectional anisotropy leading to two different resistance states for positive and negative magnetic fields due to the antiferromagnetic order of the CoPc layers. Finally, we show that a strong modification of the coercive field with applied bias voltage can be achieved using CoPc molecules in magnetic tunnel junctions.

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