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Probing interfacial coupling in cobalt/metal-free phthalocyanine and cobalt/C60 heterostructures

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Co/H₂Pc and Co/C60 heterostructures are fabricated by organic molecular beam epitaxy and thermal evaporation.
- Surface phenomena in the stacks are studied by SQUID, indicating interfacial unidirectional anisotropy below 20 K.
- Coupling energy is used to calculate the interactions magnitude, being lower for the stacks compared to MPcs.
- The influence of magnetic hardening of H₂Pc and C60 molecular layers is considered for the bias field.
- The design of molecular spintronics may be made possible by the heterostructured layers serving as pinning sites.



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ABSTRACT

Exchange bias is experimentally realized when the magnetization loop is shifted from the zero magnetic field, and used in spin valve sensors to pin their hard reference layer, nullifying the subsequent effect of any variation in the sensor layers. In this regard, fundamental insights into magnetic behavior of sufficiently thin films are important for tuning their properties, and are critical for better understanding of surface phenomena in nanodevices. Here, the hysteresis loop shift phenomenon is investigated for nanoscale ferromagnetic-molecular layers using a superconducting quantum interference device (SQUID) over a wide temperature range (2–300 K). Two heterostructure systems consisting of cobalt (*Co*) nanolayers in contact with metal-free phthalocyanine (H_2Pc) planar and fullerene (*C*60) spherical molecules are fabricated using organic molecular beam epitaxy and thermal evaporation methods, demonstrating the effect of surface phenomena on magnetic characteristics. For two stacks of *Co*/ H_2Pc and *Co*/ *C*60 molecular layers, SQUID measurements indicate the presence of interfacial unidirectional anisotropy (i.e., the anisotropy that is effective only in one direction at the interface between thin films) in the temperature range below 20 K. The magnitude of the strength of interactions through the shift and coupling energy is computed for both hybrid stacks, and compared with that for *Co*-magnetic and nonmagnetic transition metal H_2Pc structures. Therefore, the influence of magnetic hardening of H_2Pc and *C*60 molecular layers is

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confirmed for the bias field. By contrast, antiparallel spin alignment inside the molecular layer results from magnetic ions in the organic layer detached from the contact area, being responsible for large value of exchange bias. Accordingly, such heterostructured layers may act as pinning sites, paving the way for designing cost effective molecular spintronics and spin logic devices with faster data processing, ecofriendly, and high flexibility.

1. Introduction

Materials employed for spintronics technology have traditionally been dominated by conventional metallic compounds and inorganic semiconductors. Building molecular components into spintronic systems with a propensity toward new characteristics that may contribute to device downsizing is a natural concept. As a consequence, organic semiconductors have prompted the interest of the spintronics community. Since the pioneering magneto-transport experiments in the early 2000s [1], the area of organic spintronics has progressed rapidly in this set of research. Organic spintronics may offer advantages such as simplicity of fabrication, tunability of electrical and magnetic properties, and most significantly, a substantially longer spin relaxation time due to the extremely small spin orbit coupling in carbon-based compounds. These materials might lead to the creation of devices that are considerably easier to fabricate and consequently much cheaper than their inorganic counterparts. prospects of organic spintronic devices include reduced power consumption (due to their lower energy consumption), downscaled ecofriendly organic flexible spin logic devices, and higher speed or faster data processing, being realized by the ability of spin states to switch more quickly than charge states [1-4]. Given the wide range of materials available, carbon-based compounds are anticipated to serve as the foundation for future multifunctional devices that could push the integration limit. By utilizing the spin degree of freedom in spintronic devices, the efficiency with which spin polarization is transferred across multiple layers and interfaces becomes critical to the performance of these devices. This complex transfer process is influenced by individual material properties as well as, most critically, the structural and electrical properties of the interfaces between the different materials and defects present in real devices [5-7]. In the late 2000s, an initial understanding of the spin-polarized solid-state tunneling mechanism emerged across amorphous tunnel barriers such as those containing Alg3 molecules [1]. Furthermore, the barrier was initially assumed to be nothing more than a mechanism of spin transport between decoupled ferromagnetic (FM) electrodes. However, due to significant charge transfer, new electronic states with potential spintronic features might emerge at the ferromagnet-molecule interface.

For instance, employing spin-polarized photoemission at room temperature (*RT*) on a wide range of interface elements (e.g., amorphous carbon) led to the discovery of a high spin polarization (*P*) of the ferromagnet/molecule interface. Nevertheless, this high *P* has only been observed in a solid-state device at low temperatures (up to 99% @ 2 K) [8,9], whereas equivalent observations of *P* at *RT* did not reach 28 % [1]. The full comprehension of magnetic exchange processes inside *FM*/molecular films involving the organic/molecular spinterface, is required to fully exploit the *RT* spintronic potential of the *FM*/molecule interface. In this regard, the two following effects have been discovered so far: magnetic hardening [10–12] of the topmost *FM* monolayer forming the organic spinterface in comparison to the underlying *FM* thin film, and the impact of molecular spin chains away from the interface and into the organic layer on magnetic properties of the organic spinterface [13–16].

Adsorption of a molecule onto an *FM* surface promotes the creation of an interface with magnetic properties different from the *FM* substrate, both on the molecule and on the highest *FM* layer. Magnetic hardening, in turn, might cause magnetoresistance at *RT* [12], which, depending on the strength of the interaction with the *FM* substrate, can cause additional macroscopic phenomena such as exchange bias (*EB*), thereby shifting the center of the *FM*'s hysteresis loop away from H = 0 by a magnetic field (H_{shift}). The *EB* is associated with the exchange anisotropy created at the interface between an anti-*FM* and an *FM* material. Magnetic hardening effects that do not require anti-*FM* ordering of molecular spin chains within the organic layer should be unaffected by the thickness of the molecular film deposited atop the *FM* layer. This is in contrast to the increased *EB* by increasing molecular film thicknesses of several nanometers, which is typical for inorganic materials. Nevertheless, little is known about *EB* in inorganic and carbon-based heterostructured layers.

Localized *d* states in metal organic frameworks of planar geometry and *Pc* molecules of spin-bearing transition metal (TM) centers stack into columns within films. The magnetic properties of these molecules are significantly influenced by their stacking structure. Moreover, the single ion anisotropy of the molecular framework stabilizes the localized TM spin centers, affecting the M - H response. In the case of H_2Pc with no net spin, the strong orbital overlap resulting in *d*–*p* hybridization effects is realized by the planar geometry of the molecule [8,13,14,17].

The *d* states of the *Co* atoms, primarily the d_{z^2} , d_{xy} and d_{yz} orbitals, strongly hybridize with the p_z atomic-type orbitals of the planar H_2Pc molecule to form hybrid molecule-metal $p_z - d$ interface states with bonding and anti-bonding characteristics. Anti-FM coupling is provided by the surface layer of *Co* atoms ($J_{Co-H_2Pc} = 0$), resulting in a decrease in the surface Co moment per atom. Compared to the bulk state, magnetic exchange interactions at the ferromagnet surface may be weaker. The interatomic magnetic exchange coupling (J) can decrease significantly and approach or surpass the surface anisotropy due to a decrease in the moment and fewer magnetic neighbors at the interface. Under these circumstances, the bulk magnetization may change before the surface magnetization. With regard to the hybridized surface Co layer, the observation of an *EB* for the H_2Pc implies a weakening of the magnetic exchange coupling J_{Co-H_2Pc} , giving rise to an independent magnetization switching of the magnetic molecular dimer from parallel to antiparallel alignment and vice versa.

On the other hand, due to its many advantageous characteristics, including low spin-orbit coupling and mechanical and thermal endurance, *C*60 is a great choice for charge transfer applications [18]. Despite being typically diamagnetic, *C*60 has shown intriguing magnetic properties for organic spintronics, including a remarkably large spin diffusion length (110 *nm*) at *RT* [19,20], transient triplet states, and a magnetic ordering state at low *T*. For this reason, there has been a concentrated effort to fabricate spintronic devices (e.g., spin valves) using *C*60 [21,22]. The Fermi level pinning and first electron affinity is high (2.6 *eV*) for *C*60, leading to a spin doping effect at the TM/organic interfaces [23,24].

Despite its potential, spintronics still faces limitations such as developing scalable manufacturing processes for spintronic devices, increasing integration density, achieving effective spin injection, and propagation, and detection at room temperature. In this paper, organic molecular beam epitaxy (OMBE) and thermal evaporation (TE) methods are used to fabricate inorganic (cobalt/phthalocyanine (Co/H_2Pc)) and carbon-based (Co/C60) heterostructured layers. Structural and magnetic characteristics of these layers are investigated by various techniques. In particular, interfacial coupling properties are studied over a temperature range from 2 to 300 K. Herein, the nonmagnetic planar and spherical molecules are selected for a thorough examination of the properties of organic/*FM* interfaces, thereby focusing on the impact of magnetic ions and molecular anti-*FM* ordering on *EB*, while also com-

prehending the mechanisms of *EB* brought on by magnetic hardening, which include the influence of molecular geometry on coupling energy. Meanwhile, the following relevant issues are investigated: (i) the magnetic interaction between the nonmagnetic (planar *Pc* and spherical *C*60) organic molecular film and the inorganic *FM* Co layer, and (ii) the characteristics of the coupling energies upon contact with the Co layer when compared to the planar TM counterparts.

2. Experimental details

The hybrid stacks ($Co(10nm)/H_2Pc(12nm)$, Co(10nm)/C60(12nm), Co(10nm)/MnPc(12nm) and Co(10nm)/ZnPc(12nm) were fabricated using a variety of growth methods, as explained in Supplementary Material. Briefly, OMBE was utilized for growing phthalocyanine molecular layer, and TE was employed to deposit cobalt and gold capping layers (see Figs. S1 and S2 in Supplementary Material). To protect the cobalt layer against oxidation, the radial distribution robot chamber (served as a transfer medium with the ability to connect the various deposition chambers) allowed the sample to be maintained in an ultra-high vacuum (UHV = $10^{-9} - 10^{-11}$ mbar) throughout the entire deposition process. Accordingly, there was no contamination in any of the samples examined in this work. Complete surface coverage was observed by *FM*'s large scan characterization of the layers grown on *Si/SiO*₂ (500 nm) substrates.

To evaluate layer thicknesses and roughness of the samples under investigation in more detail, X-ray reflectivity (XRR), atomic force microscopy (AFM), and scanning tunneling microscopy (STM) were used (Figs. S3-S6 in Supplementary Material). X-ray photoelectron spectroscopy (XPS) revealed that there was no oxidation or contamination of the deposited FM layers (Fig. S7 in Supplementary Material). A superconducting quantum interference device (SQUID) magnetometer was used to investigate temperature dependence of magnetic properties. The most important step to eliminate the moisture and contaminants was to perform UHV storage of the source material at high temperatures. The objective of OMBE was to deposit thin, highly oriented films of organic materials at an extremely high vacuum (10^{-10} mbar). Specifically, Pcs and C60 molecular stacks were evaporated using hot lip effusion cells. A quartz crystal thickness sensor was used to measure the growth rate, and temperature regulation was utilized to fine-tune it. At rates starting from 1 Å/min, the best results were achieved, making it possible to produce and preserve extremely pure stacks. Fig. 1 (A and B) are photographs of the samples taken prior to measurements, Fig. 1 (C) is a representative diagram of bilayer systems with Au capping layers, Fig. 1 (D and E) are two and three-dimensional AFM images for *Co*, Fig. 1 (F and G) for H_2Pc molecules, and Fig. 1 (H and I) for the *Au* capping layer. Schematic representations of the hybridized interface by the planar H_2Pc and *C*60 molecules are shown in Fig. 1 (J and K), respectively.

It should be noted that the names of the layers match the order in which they were deposited, starting with the substrate bottom Si/SiO2(500 nm). Various molecules (*C*60 and H_2Pc , ZnPc, and *MnPcs*) with a thickness of 12 *nm* are represented by the molecule in the green section (see Fig. 1 C). Large scan AFM characterization with layer roughness ranging from 0.27 to 0.4 *nm* showed full coverage of cobalt layer. Full coverage of Au grown on molecules shows roughness in the range (0.8 to 1.2*nm*).

3. Results and discussion

In simple terms, the EB is an interface phenomenon. In turn, the strength of the interface exchange coupling is determined by the nature of the interface. The magnetic proximity effect is another intriguing phenomenon that could result from the interface exchange coupling, involving the combination of at least two dissimilar materials that possess different long-range magnetic ordering behaviors and/or functionalities [25–27]. The magnetization of FM-anti-FM systems with only one easy direction (being commonly referred to as unidirectional anisotropy, as opposed to uniaxial anisotropy) involves two equivalent easy configurations in opposite directions. The spins of the anti-FM system adjacent to the FM align ferromagnetically with those of the FM system when cooling to below Néel temperature of anti-FM in the presence of the field because of the interaction at the interface (assuming FM interaction). The zero net magnetization is achieved when the other spin planes in the anti-FM system follow the anti-FM order. The FM spins begin to rotate when the field is reversed. However, the anti-FM spins do not change for sufficiently large anti-FM anisotropy.

In order to ferromagnetically align the *FM* spins with the anti-*FM* spins at the interface, the *FM*– anti-*FM* spins interact with one another at the interface. To put it another way, the *FM* spins are kept in their initial (ferromagnetically aligned) position by the microscopic torque applied by the anti-*FM* spins at the interface. Consequently, the anisotropy is unidirectional, meaning that the *FM* spins have a single stable configuration. Since an additional field is necessary to overcome the microscopic torque, the field required to fully reverse an *FM* layer will be greater if it is in contact with an anti-*FM* layer. However, because of the



Fig. 1. A and B are photographs of the actual samples taken prior to measurements, C is an exemplary bilayer system with Au capping layers, and D and E are two and three dimension AFM images for Co, F and G for H_2Pc molecules, and H and I for the Au capping layer. J and K are symbolics of hybridized interface by the planar H_2Pc and spherical C60 molecule respectively.

interaction with the anti-FM spins exerting a torque in the same direction as the field, the FM spins will begin to rotate at a smaller field once the field is rotated back to its original direction. Therefore, the FM hysteresis loop is shifted in the field axis or EB, indicating the presence of an additional (internal) biasing field applied to the material. Exploring exchange anisotropy at the interface between 3d TM conventional ferromagnets such as cobalt and metal-free H_2Pc molecule represents an appealing challenge due to the electronic properties of the combination of FM layer and planar molecule, leading to the focus of the utmost previous experimental work on inorganic materials. The new concept of employing organic semiconducting molecules to pin the FM-metal is based on the fact that at the metal/organic interface, the hybridization of the molecular orbitals with the surface spin-polarized bands provides new interface states with distinct electrical and magnetic properties. Extensive research using X-ray magnetic circular dichroism has demonstrated this fact [14].

The temperature dependence of magnetic properties for $Co(10nm)/H_2Pc(12nm)$ hybrid bilayer structure is shown in the following in order to demonstrate the existence of *EB*, while also examining the differences in the strength of interfacial coupling of the sample under investigation. As revealed by magnetostatic investigations in our previous studies, the hybrid bilayers form a complete *EB* system, with the exchange interaction at the *Co/MPc* interface contributing to the pinning of the magnetization of the *Co* layer [17]. To explore the temperature dependence of hysteresis loops of $Co(10nm)/H_2Pc(12nm)$ structure, SQUID measurements were performed, and the results obtained are shown in Fig. 2.

In this regard, the sample was cooled from 300 K (above the Néel temperature of H_2Pc molecules) to below the target temperature of 2 K when applying a magnetic field of $H_{FC} = +3$ T closely along the easy axis (in-plane) of the sample magnetization. This magnetic field was sufficient to saturate the cobalt magnetization. For each desired temperature, the procedure was repeated. Following this field-cooling protocol, the $(Co(10nm)/H_2Pc(12nm)$ structure's hysteresis loop is observed to shift along magnetic field axis towards the opposite (negative) direction to the cooling field, as depicted in the right panel of Fig. 2.

In fact, the absolute value of coercive field for decreasing $(-H_{C1})$ and increasing $(+H_{C2})$ fields differs from each other, indicating the presence of unidirectional anisotropy. This kind of anisotropy hinders spins at the $Co(10nm)/H_2Pc(12nm)$ interface from rotating towards the negative branch of the magnetic field because they require a higher magnetic field. It is also important to compare the field cooling (*FC*) with the second protocol called zero field cooling (*ZFC*), whose measurement was performed without applying a static magnetic field during the cooling down of the structure, as shown in the left panel of Fig. 2. The unwanted background signals from the substrate were subtracted (see Fig. S8 in Supplementary Material).

The most significant distinction between the two loop shapes is that they both have remnant magnetization M_r (*FC*) > M_r (*ZFC*). In turn, this results in *EB* field (H_{EB}) and H_C that are larger in the course of *FC*, thereby emphasizing the more prominent alignment of spins at the interface, with a greater energy product ($(M_rH)_{max}$). The hysteresis loop shift is commonly referred to as *EB*, or H_{EB} . The $Co(10nm)/H_2Pc(12nm)$ heterostructure's hysteresis loop also has a higher H_C value following the *FC* protocol compared to the *Co/Au* structure with no *EB* and a modest $H_C \sim 8$ *Oe*. Then the field is first reduced to negative values, an abrupt magnetization reversal is observed at H_{C1} . When the field is increased to positive values, the magnetization curve at H_{C2} becomes more rounded in shape that might be due to a different reversal mechanism.

Fig. 3 shows temperature variation of H_{EB} , and the inset of the figure represents temperature variation of coercive switching fields (H_{C1} and H_{C2}) for $Co(10nm)/H_2Pc(12nm)$ sample. Note that H_{C1} and H_{C2} values were extracted directly from the hysteresis loops measured at temperatures ranging from 2 to 300 K. Moreover, the corresponding H_{EB} was calculated at these temperatures by the following relation: $H_{EB} = (H_{C1} + H_{C2})/2$. Meanwhile, coercivity was calculated by: $H_C = (-H_{C1} + H_{C2})/2$. A more detailed analysis of the graph in Fig. 3 reveals that the H_{EB} disappears at about 20 K, being in contrast to the interpretation of these data published by Boukari et al. [17] who demonstrated strong *AFM* coupling with an exchange energy reaching 100 K for *MnPc*, *CoPc*, and *FePc* thin films.

The results (inset of Fig. 3) also show that under this specific temperature (20 K), H_{C1} increases strongly, whereas H_{C2} increases more slowly with temperature. This characteristic implies that at lower temperatures, the *FM*-molecular layer interface's spin structure becomes magnetically stiff, which is consistent with our magnetic findings on heterostructures. In general, it is clear that at temperatures below 20 K, the H_2Pc layer becomes magnetically rigid and acts as a pinning substance, with the effect of pinned spins (via unidirectional anisotropy) exceeding the effect of reversible spins (via magnetocrystalline anisotropy), resulting in the observed *EB* and H_c enhancements.

The magnetic anisotropy of the cobalt layer has been found to be strongly enhanced by orbital hybridization at the Co/C60 interface, producing such hybrid systems with desirable components for memory and sensing devices. As a result, the same hybridization can produce a spin-filtering effect and cause significant variations in the Co/C60 interface basis to support spin-polarized currents [28]. The weak spin-orbit coupling and hyperfine interaction of C60 molecule are particularly promising for obtaining a long spin diffusion length of more than 100 nm [19,20,29]. The ferromagnet/molecule interface appears to play a major role in transport properties, while also regulating the so-called spinterface. The magnetic anisotropy can be significantly altered due to the molecule-ferromagnet interaction.

The $C_{pz} - Co_{dz^2}$ hybridization, for example, has been shown to be the source of increased perpendicular anisotropy at the Co/C60 interface, resulting in magnetic hardness in either out-of-plane or in-plane



Fig. 2. Zero-field and 3 T field cooling hysteresis loops (left panel), and *M*-*H* curves of $Si/SiO_2(500 \text{ nm})/Co(10 \text{ nm})/H_2Pc(12 \text{ nm})/Au(10 \text{ nm})$ sample measured by SQUID at different temperatures after cooling in an applied static field of +3 T (right panel).



Fig. 3. Exchange bias field (H_{EB}) with temperature for *Si/SiO*₂(500 nm)/*Co*(10 nm)/*H*₂*Pc*(12 nm)/*Au*(10 nm) sample measured by SQUID after cooling in an applied static field of +3 *T*. The inset represents the variations of coercive switching fields (H_{C1} and H_{C2}).

magnetized samples [22,24,29]. Considering these facts, it seems tempting to compare the planar molecular layer of H_2Pc with a spherical molecule (e.g., *C*60) in order to examine the relationship between magnetic properties and fine features of the interface structure. The SQUID measurements were utilized to explore the temperature dependence of M - H curves of *Co/C*60 structure, as shown in Fig. 4. At multiple target temperatures, the sample was cooled from *RT* to 2 *K* with a magnetic field of $H_{FC} = +3 T$ applied closely to the easy axis (in-plane) of the sample magnetization, being sufficient to saturate the *Co* layer. This procedure was resumed for each desired temperature.

The temperature variations of H_{EB} , Hc, and switching fields $(H_{C1} \text{ and } H_{C2})$ for $Si/SiO_2(500nm)/Co(10nm)/C60(12nm)/Au(10nm)$ sample are depicted in Fig. 5. In this respect, H_{C1} and H_{C2} values were derived directly from the hysteresis loops measured at temperatures ranging from 2 to 300 K. In this context, it appears reasonable to compute coupling energies and compare the two different hybrid bilayer structures.

Since Meiklejohn-Bean model [25] assumes parallel orientation of all

moments throughout the whole process of coherent rotation, the *FM*/anti-*FM* layer interface magnetization can be interpreted as macroscopic moments. Therefore, *FM* spins fulfill the following condition: $S_i^{FM} = S_i^{FM} \prec i$, making it possible to transform the microscopic spin interaction at the interface into the interaction of macroscopic interface moments according to $\sum_{i,j} S_i^{FM} S_i^{Anti-FM} \propto S^{FM} S^{Anti-FM}$.

Essentially, the interface magnetizations (i.e., $S S^{FM}$ and $S^{Anti-FM}$) are coupled via *J*, which is the exchange interaction constant. In order to compare different types of *EB*, a coupling energy of $E = H_{EB}M_SV_{FM}$ (where M_S is the saturation magnetization and V_{FM} is the volume of the ferromagnet) is evaluated instead of using the loop shift itself. If this energy is normalized to the coupling area (A), one will obtain the following relation: $E_A = E/A = H_{EB}M_SV_{FM}/A$. For a bilayer structure, this energy is expressed as: $E_A = H_{EB}M_St_{FM}$ (where t_{FM} is the thickness of the *FM* layer) [26,27].

As can be inferred, both $Co(10nm)/H_2Pc(12nm)$ and Co(10nm)/C60(12nm) structures exhibit almost an equal small amount



Fig. 4. Zero-field and 3 *T* field cooling hysteresis loops (left panel), and *M*-H curves of $Si/SiO_2(500 \text{ nm})/Co(10 \text{ nm})/C60(12 \text{ nm})/Au(10 \text{ nm})$ sample measured by SQUID at different temperatures after cooling in an applied static field of +3 T (right panel).

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Fig. 5. Exchange bias field (H_{EB}) with temperature for $Si/SiO_2(500 \text{ nm})/Co(10 \text{ nm})/C60(12 \text{ nm})/Au(10 \text{ nm})$ sample measured by SQUID at different temperatures after cooling in an applied static field of +3T.The inset represents the variations of coercive switching fields (H_{C1} and H_{C2}).

of loop shift with a blocking temperature of around 20 K. To understand the mechanism of these planar and spherical molecules as molecular pinning sites, it is necessary to compare the above structures with a *Pc* molecule that contains a core magnetic ion of already computed bias field [17]. Accordingly, one can confirm the mechanism of the interfacial interaction that causes the *EB* present in $Co(10nm)/H_2Pc(12nm)$ and Co(10nm)/C60(12nm) hybrid structures. As depicted in Fig. 6, the coupling energies of $Co(10nm)/H_2Pc(12nm)$ and Co(10nm)/C60(12nm)structures are compared with those of a bilayer with a nonmagnetic center element consisting of a *Co* layer and another *Pc* molecule with a full shell Zn atom (*ZnPc* molecule) [17] that is not anticipated to carry any magnetic moment. In this case, the origin of unidirectional anisotropy is unlikely to be explained by the concept of exchange interaction



Fig. 6. Comparison of coupling energies of $Co(10nm)/H_2Pc(12nm)$ and Co(10nm)/C60(12nm) structures with those of their counterpart Co(10nm)/ZnPc(10nm) (as a nonmagnetic molecule) and Co(10nm)/MnPc(10nm) (as a magnetic molecule) structures within the temperature range of 2–300 K after 3 T field cooling.

between *FM* and anti-*FM* ordering in molecular layers. The Co(10nm)/MnPc(12nm) and Co(10nm)/ZnPc(12nm) stacks were fabricated under the same chamber conditions as those for $Co(10nm)/H_2Pc(12nm)$ Co(10nm)/C60(12nm) stacks. As well, the M - H curves were recorded using the same protocol as those for the previous magnetization measurements. The results of the comparison are indicative of very large coupling energies in hybrid system containing a core magnetic ion with a blocking temperature of about 100 K.

In fact, the results of exchange energy of all the fabricated systems were calculated after cooling them in a static magnetic field through the anti-*FM* Néel temperature. The exchange coupling at the interface between *FM* and anti-*FM* spin structures and the magnetic hardening typically cause the unidirectional anisotropy. A magnetic moment is produced by certain TMs in *MPcs*, leading to an intriguing magnetism in organic semiconductors. At low temperatures, *MnPc* (having a magnetic moment of 3μ B) displays anti-*FM* ordering in thin-film form when grown on *Co* with a blocking temperature of about $T_B \sim 100 \text{ K}$, as supported by density functional theory calculations, X-ray circular dichroism (XMCD) experiments and SQUID measurements [13,17].

The stabilization of the magnetization of *Co* layers has also been confirmed by XMCD and X-ray absorption spectroscopy for *MnPc* grown on *Co*. These techniques unambiguously demonstrated the occurrence of: (i) *EB*, (ii) *FM* interaction at the interface between *Co* and Mn, and (iii) intermolecular anti-*FM* interactions in *MnPc* [13,14,17,30]. The subtle balance occurring between molecule-molecule and molecule-*FM* interactions can be adjusted by the central metal ions of the *MPc* molecules and the metal *FM* layer, being the source of the various self-assembling behaviors of *MPc* molecules on the *Co* layer. Nonetheless, the unexpected H_{EB} in Co(10nm)/ZnPc(12nm) system (where the full shell *Zn* nonmagnetic *Pc* exhibited *EB*), was significantly lower than that in the magnetic *MnPc*.

Similar to Zn *Pc*, it has been shown that the interface magnetoresistance induced by the interfacial chemical modification can be caused by charge transfer and hybridization of the molecular orbitals with the *d* orbitals of the *FM* layer [31]. This planar system with a nonmagnetic central element grown on *Co*, creating new hybrid metal-organic interface states that directly affect the electronic and magnetic properties of the adsorbed molecule. According to the mechanism proposed, the *EB* observed in the present study is therefore the combination of two effects: one arising from the interfacial *FM*/ molecule hybridization and the other from the anti-*FM* ordering of the bulk molecular layer.

On the other hand, for $Co(10nm)/H_2Pc(12nm)$, the exchange coupling energy was slightly smaller than that found in Co(10nm)/ZnPc(12nm). This might be due to central atoms or the different symmetry of the adsorbed molecule. Recent results have shown that, on metallic surfaces, the planar H_2Pc symmetry is typically adsorbed with its molecular plane parallel to the surface. A mismatch between the symmetry of the molecule and the underlying surface reduces the symmetry of the H_2Pc molecule [32]. Still much less than in Co(10nm)/ZnPc(12nm), spherical C_{60} layer showed comparable results of exchange coupling energy with H_2Pc counterpart (see Fig. 5), having the same blocking temperature ($T_B \sim 20 K$).

Some results showed that, the morphology of the interface has a significant impact on the electronic properties of FM/C60 according to STM experiments. This finding raises the possibility of fine-tuning the electronic properties of organic/inorganic heterostructures by modifying the structural coupling with the substrate. Furthermore, it may have implications for hybrid magnetic interfaces, where the development of hybrid magnetic states can be aided by the molecular and magnetic order harmonization [33–35]. The huge difference between the values of coupling energies can be explained by the effect of spin chains or anti-*FM* ordering induced by *Mn* ions in *Pc* molecules, giving rise to an additional major influence on the increased coupling causing the *EB*.

It is worth noting that, despite their potential as a spacer layer and an effective way to pin the *FM* layer, nonmagnetic molecules have been

neglected in earlier research on organic EB spin valves. The measurements of the temperature bias dependence of the M-H loops revealed that the adsorption of H_2Pc and C60 alters the magnetic anisotropy of interfacial *Co* atoms. The strong *p*–*d* hybridization causes the *Co* atoms to be bound to the H_2Pc and C60 atoms to have an interfacial magnetic moment and enhanced anisotropy. The existence of spin-polarized currents at a near-zero magnetic field is necessary for many spintronic devices, being frequently achieved through spin EB. Coupled FM and anti-FM thin film layers make up a large number of spintronic device designs. The EB, which is required to pin the magnetization in a specific orientation, is generated at the interfaces between these layers. The coexistence of nonmagnetic spacer layers spontaneously biasing the FM layers could pave the way for the development of innovative spintronic devices. The absence of magnetic ions in their structures, which results in spin-flipping and scattering, makes H₂Pc and C60 molecules superior to TMPc molecules as a spacer layer. These results suggest that when designing spintronic devices, it is particularly important to consider the nonmagnetic molecules as pinning sites at the interface as well as the spin polarization sources. By taking into account that the hyperfine interactions of H_2Pc and C60 are significantly weaker than those of other TMPcs, it is possible to create a more effective spin transport. Meanwhile, the nearly isotropic nature of the highly symmetric C60 produces spin-polarized carriers with tiny spin flip amplitude and energy loss.

4. Conclusions

 $Co(10nm)/H_2Pc(12nm)$ and Co(10nm)/C60(12nm) heterostructures have been fabricated using OMBE and TE methods, and characterized by XRR, AFM, STM, XPS and SQUID techniques. The SQUID measurements examined the magnetic hardening of the organometallic interfaces, indicating that the molecular layers of the resulting heterostructures acted as pinning materials for temperature ranges lower than 20 K. In this regard, both planar and spherical molecular stacks slightly pinned the *Co* layer, as determined by calculating the values of low temperature *EB* and coupling energies of the two stacks.

While the comparison between coupling energies of the heterostructures and those of cobalt-magnetic (Co(10nm)/MnPc(12nm)) and cobalt-nonmagnetic (Co(10nm)/ZnPc(12nm)) TM phthalocyanines confirmed the effect of magnetic hardening for temperatures below 20 *K*, *Mn* molecular spin chains or anti-*FM* ordering in the organic layer (separated from the contact region of the organic spinterface's magnetic characteristics) was found to contribute to the enhanced *EB* of Co(10nm)/MnPc(12nm). Overall, due to the lacking of magnetic ions in their structures (thus resulting in spin-flipping and scattering), H_2Pc and *C*60 molecules can function as pinning sites at the interface, making them especially crucial to be taken into account when designing spintronic devices.

Declaration of competing interest

I wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome. I confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing I confirm that we have followed the regulations of our institutions concerning intellectual property. I confirm that I have provided a current, correct email address which is accessible by the Corresponding Author.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matchemphys.2025.130816.

Data availability

Data will be made available on request.

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