Robust Monolayer Exchange-Bias Effect in Molecular Crane-Pulley Response at Magnetic Surface

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Exchange-bias effect is a widely investigated topic for spintronic applications in magnetic data storage read heads and spin-valve sensors. This effect is observed in bilayers of magnetic materials comprising of a soft ferromagnet (FM) and an antiferromagnet (AFM). In the last few years, unexpected observations of such an effect in ferromagnet-molecule heterostructures has raised curiosity in probing their underlying mechanism for potential technological applications. Here, we report our interface study between thin films of Fe and monolayer metal-phthalocyanine (MPc) molecules providing evidence of a robust exchange bias in zero-field cooled devices that is stable even after multiple training cycles. We ascribe the underlying mechanism to a combination of surface magnetic hardening and weakening of interlayer magnetic exchange that decouples the surface MPc-Fe hard magnetic layer from the soft switchable Fe layer underneath. We refer to this combined response to a molecular crane-pulley effect arising from the strong $\pi - d$ hybridization induced changes in the magnetization properties of surface Fe relative to the underlying film. Furthermore, analysis of our in-plane angle-dependent anisotropy magnetoresistance measurements reveal a surprisingly large biaxial anisotropy of the hard-surface layer with switching field exceeding 7 T. These studies provide us the opportunity to engineer the form of magnetic anisotropy at these spin interfaces.

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I. INTRODUCTION

In conventional FM and AFM bilayer systems [1–3], exchange-bias setting (H_{ex}) is achieved by cooling the devices below the Neel or blocking temperature of the AFM material in the presence of a magnetic field (H_{FC}), where FC means field-cooling. Such a process results in a horizontal shift by H_{ex} in the soft magnetization curve (M vs H) of the FM film that has played an indispensable role in commercial magnetic read heads for magnetic hard-disk drives and in other nonvolatile magnetic memory technologies [4,5]. This process of bias setting depends critically on the structural compatibility of AFM material with the FM film, anisotropy properties of the AFM layer and also on the sign and magnitude of H_{FC} [3]. As a result, this process suffers from scalability challenges that causes disappearance of exchange bias with decreasing thickness of AFM layer (and also FM). Hence, these procedures lead to implementation challenges for their future integration with low-dimensional spintronic devices [6,7].

In this regard, recent developments of molecular exchange-bias effect [8–12] reported in magnetotransport studies provide promise. In the earlier studies of Co/CoPc [9] and Co/MnPc [8,10] interfaces, requirement of thicker molecular films [> 10 monolayers (ML)] for the observation of exchange bias had suggested antiferromagnetic ordering of molecular spin chains to play a crucial role. This ordering is predicted to stabilize by the magnetic interaction with the FM substrate. However, recent observations of exchange bias using molecules such as metalloporphyrin [11] and C_{60} [12], which do not readily form antiferromagnetically coupled spin chains in bulk state, has opened an interesting debate. An alternative explanation for the origin of exchange bias may be attributed to surface magnetic hardening—an effect that is reported in a number of FM and molecule systems over the last decade [13–17]. This effect arises due to the formation of hybridized $\pi - d$ interface states that render new magnetic properties to the surface [18–20]. Here, the enhancement in film coercivity (H_c) can be approximated by the weighted volumetric average (H_c^{ave}) of switching fields of the hard-surface ($H_c^{surface}$) and soft-bulk layer (H_c^{bulk}). Such artificially engineered bilayers of hard-surface and soft-bulk layer can show exchange-spring effects—in which case the magnetization rotation can show a completely reversible path in the low-field range [21]. Additionally, if the hard ferromagnetic layer has a sufficiently large anisotropy than the soft layer, an exchange-bias response may also arise [22]. Evidence of these effects was recently

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provided in Co/C_{60} interfaces [12]. However, in this study, the device required field-cooling to observe a combination of exchange-spring and exchange-bias response that lasted only for one magnetization reversal cycle.

A phenomenon that so far has not received much attention is the effect of interface interactions on the intralayer ($J_s^{\parallel}$) and interlayer ($J_s^{\perp}$) exchange at the magnetic surface [19] [see top left inset of Fig. 1(a)]. Callsen *et al.* [15] have shown a strong modification in $J_s^{\parallel}$, an increase by a factor of 3, between the surface Fe atoms bonded to a top 2,2-paracyclophane molecule. Also, Raman *et al.* [14] reported using computational studies that $J_s^{\perp}$ at the surface due to molecular adsorption can drop by nearly 70% of the bulk value. Here, a suitable choice of FM material and layer thickness can also enhance the relative strength of surface magnetic anisotropy over $J_s^{\perp}$. Such additive modifications in exchange strength at a magnetic hard surface can play a crucial role in decoupling the surface magnetization from the bulk for the observation of a stable and robust exchange-bias response. Achieving such a feat has generally been an engineering challenge because the typical strength of magnetic exchange in bulk

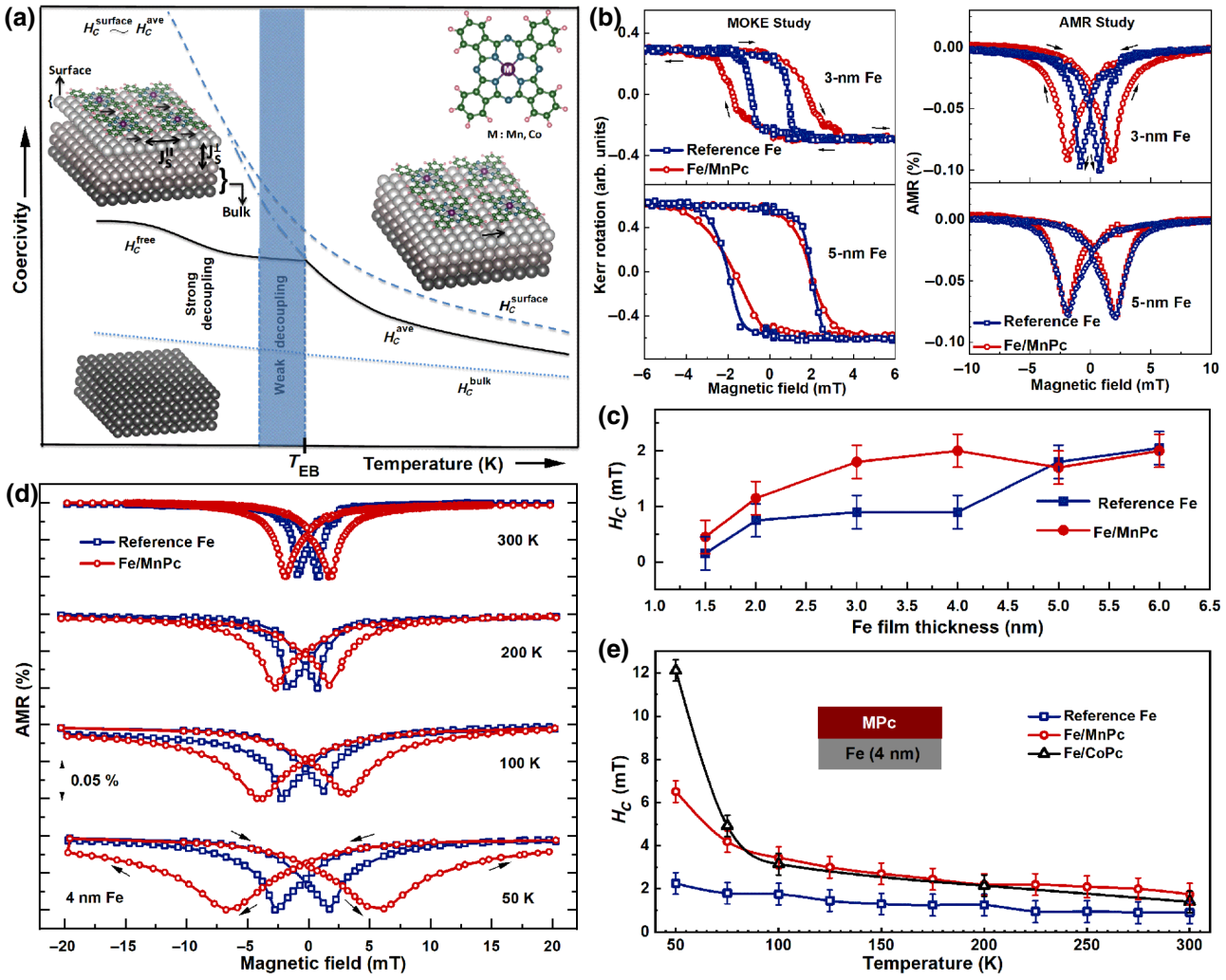

FIG. 1. (a) Crane-pulley effect: adsorption of MPc molecule (top right) on Fe surface enhances surface anisotropy, thereby increasing H_c^{surface} (dashed lines) with cool down. Above T_{EB}, measured H_c (shown by the solid line) equals weighted volumetric average (H_c^{ave}, dashed-dotted line) of H_c^{surface} and the switching field of the reference bulk Fe film (H_c^{bulk}, dotted lines). Below T_{EB}, the magnetically hard surface, with large anisotropy and weaker interlayer exchange, decouples from the bottom Fe layer. Here, the measured H_c corresponds to the magnetization reversal of the bottom Fe layer (H_c^{free}) through an exchange-bias response from the hard magnetization layer at the surface. (b) Room-temperature MOKE and AMR study of Fe/MnPc (4 ML) (red circle) and reference Fe (blue square) films. (c) Variation in H_c, extracted from room-temperature MOKE and AMR data, with the thickness of Fe. The error bar corresponds to statistical maximum deviation of H_c from its mean value over repeated measurement cycles. (d) Temperature dependence of AMR of Fe (4 nm)/MnPc (4 ML) (red circle) and reference Fe (4 nm) (blue square) films. (e) H_c vs T for Fe (4 nm)/MnPc (4 ML) (red circle), Fe (4 nm)/CoPc (4 ML) (black triangle) and Fe (4 nm) (blue square) films. Arrows in the plots indicate the direction of field sweep.

(approximately meV/atom) that aligns the adjacent spins in parallel configuration is at least 2 orders of magnitude stronger than the surface magnetic anisotropy (approximately 10 s of μeV/atom) [14,23,24]. Evidence for such a decoupling response, that we refer to as the *molecular crane-pulley effect*, can be probed experimentally by studying the temperature dependence of switching field of the hybrid hard-soft magnetic film [see Fig. 1(a)]. With an enhancement in surface-layer magnetic anisotropy during cool down, the onset of surface-bulk decoupling and hence exchange bias at T_{EB} leads to a drop in the slope of H_c, as shown by the solid line in Fig. 1(a). Conceptually, this is marked by a bifurcation of switching response of the hard-surface and the soft-bulk layer. Through our experimental investigations in the present work, we provide evidence of such a response supporting a strong molecular interaction force responsible for the crane-pulley effect.

II. RESULTS AND DISCUSSIONS

We began our study by investigating the magnetization switching response of thin films of Fe (3.5 to 8 nm) with approximately 1–4 ML coverage of MPc (M:Co or Mn) molecules [top right inset of Fig. 1(a)]. MPc is a widely researched planar aromatic molecule that offers chemical versatility in functionalizing its electronic, optical, magnetic, and chiral properties [25]. We calibrate the monolayer growth of the molecule and confirm its structural integrity on the Fe surface using scanning tunneling microscopy and spectroscopy studies (see Supplemental Material [26] and Refs. [27,28]). Patterned Fe (as reference) and Fe/MPc films are prepared in a single deposition run using the shadow-mask technique under ultrahigh vacuum conditions to avoid variations in the Fe film thickness. The films are capped with Al/Al_2O_3 to prevent oxidation of Fe (see Supplemental Material [26] for details on capping-layer uniformity).

In Fig. 1(b), we show a combination of room-temperature magneto-optical kerr effect (MOKE) and anisotropic magnetoresistance (AMR) measurements indicating an enhancement in H_c of Fe/MnPc (4 ML) films compared to the reference films. With an increase in Fe film thickness ($\geq$ 5 nm), the enhancement in H_c is no longer observed, which may be explained by the larger bulk contribution [see Fig. 1(c)]. We attribute this increase in H_c to the enhancement in the magnetic anisotropy of the top Fe surface due to the Fe/MnPc interface chemistry [19]. Also, at lower thickness of Fe ($\leq$ 2 nm), H_c enhancement is not clearly visible at room temperature due to weaker film magnetism and is limited by the sensitivity of our experimental apparatus.

Adsorption energy of MPc molecules on the surface of Fe is found to be significantly large approximately 6 eV [29]. However, this adsorption energy is distributed over the entire molecule involving multiple bonding sites with the Fe surface atoms underneath [inset of Fig. 1(a)]. Thus, the Fe/MPc interface is expected to show a strong temperature dependence of its magnetic properties. This is indeed observed in Figs. 1(d) and 1(e) where the temperature dependence of AMR for Fe (4 nm)/MnPc films show an increased magnetic hardening compared to the reference Fe films. While H_c in Fe/MnPc films increase by threefold compared to the reference film at 50 K, the Fe/CoPc films show a larger increase, by a factor of 6.

Interestingly, with further cool down to 1.5 K in zero field, AMR studies of Fe/MPc films show an unusual trend. In an increasing cycling field of upto 50 mT, a completely reversible AMR behavior is observed indicative of an exchange-spring response [see Fig. 2(a)]. Subsequently, at higher cycling fields, an hysteretic AMR appear with the center of the loop shifted towards the left indicative of the exchange-bias effect. In contrast, our reference Fe films show a symmetric AMR with low H_c [Fig. 2(b) top plot]. In Fig. 2(b), we plot the AMR data of Fe/CoPc devices (in the first sweep) acquired during warm up after cooling the device in zero field and $H_{FC} = 0.3$ T. In field-cooled measurements, we observe a strong asymmetry, i.e., positive sweep cycle showing a larger AMR signal than in the negative sweep cycle. After multiple training cycles, this asymmetry is found to reduce and approach the AMR curve of zero-field cooled measurements with a much weaker asymmetry. Similar asymmetric response of AMR is also noted in the study of Fe/metalloporphyrin [11] and Co/C_{60} [12] interfaces. Such a strong asymmetry in the initial set of sweep cycles of field-cooled devices may be suggestive of overcoming an activation barrier by domain-wall nucleation and propagation arising due to the formation of pinned domains perpendicular to the Fe/MPc interface [30–32]. In contrast, a rather weakly asymmetric AMR response in the zero-field-cooled measurements (or in field-cooled devices after sufficient training cycle) may suggest the dominant role of domain rotations in the process of magnetization reversal [33–35]. In Fig. 2(c), the extracted value of H_{ex} and H_c as a function of temperature is plotted. Here, the data for 1-ML coverage of MnPc on 3.5-nm Fe film is also included that shows stable and stronger exchange-bias signal. Interestingly, we observe that the steeper increase in H_c with cool down (labeled as H_c^{ave}) transitions abruptly to a plateaulike response (labeled as H_c^{free}) at T_{EB}, below which the exchange-bias effect is observed. In Fe/MnPc, T_{EB} appear at approximately 30 K, while in the case of Fe/CoPc, it shows up at approximately 50 K. These observations are in agreement with our molecular crane-pulley model described in Fig. 1(a).

Next, the stability of the exchange-bias response is checked by performing training-effect studies in our 1-ML MnPc devices at 1.5 K. For these studies, a training field of ± 0.2 T is used to study the evolution of H_{ex} and H_c with training cycle [see Fig. 3(a)]. Comparing with all previous

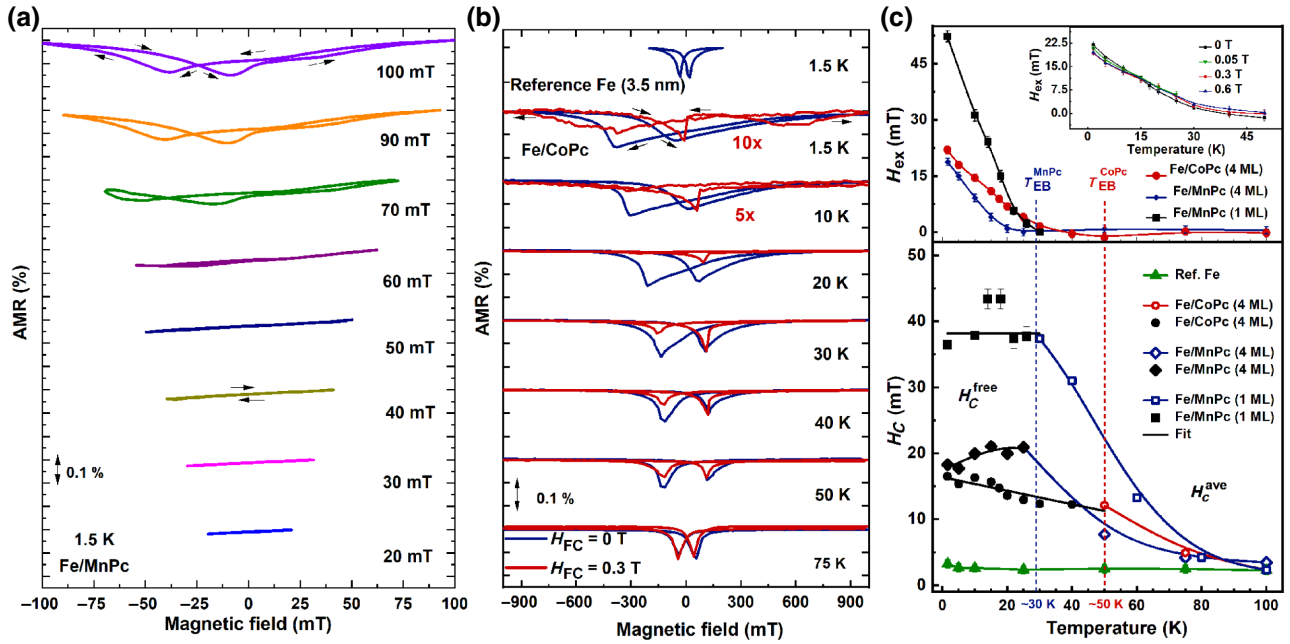

FIG. 2. (a) AMR of Fe (4 nm)/MnPc (4 ML) films measured at 1.5 K after zero-field cooling. AMR is measured in increasing cycling field ranges from 20 to 100 mT. (b) AMR of Fe (3.5 nm)/CoPc (4 ML) films at different temperatures (value labeled in the inset), measured during warm up after cooling the films in $H_{FC} = 0$ T (blue) and 0.3 T (red). AMR of reference Fe film (3.5 nm) at 1.5 K is shown in the topmost plot. The y scale for the AMR plots of $H_{FC} = 0.3$ T at 1.5 and 10 K are multiplied by factors of 10 and 5, respectively, for visibility. (c) H_{ex} vs T (top) and H_c vs T (bottom) of Fe/MnPc and Fe/CoPc films, extracted from AMR measurements, showing the onset of exchange bias. Below T_{EB}, only the coercivity of the bottom Fe layer (H_c^{free}) is measured (solid black symbols). Here, the lines are a guide to the eye.

studies of molecular-exchange bias, we find H_{ex} in our devices to decay gradually and saturate to a large value of 49 mT. We further investigate the effect of high destabilizing fields (fields opposite to the pinned hard magnetization axis) on the robustness of the exchange-bias signal. For this study, the devices are again cooled down in zero field and the training process is performed with a training field of ± 0.2 T for each cycle [see Fig. 3(b)]. However, at the beginning of fifth, sixth, seventh, and eighth training cycles, progressively large one-sided destabilizing fields of 1, 2, 3, and 7 T is applied, respectively, before starting the AMR measurement of that cycle. Interestingly, a temporary healing process in terms of a marginal increase in H_{ex} in the subsequent training cycles is observed. These results confirm a very robust nature of our interface response with a sufficiently large anisotropy and switching field of the hard-surface Fe/MPc layer that is suggested to exceed 7 T from our above studies. Additionally, we observe this effect to disappear in thicker 8-nm film of Fe. This can happen due to an enhancement in anisotropy and magnetic exchange strength of bulk Fe film that weakens the crane-pulley response of the modified surface (see Fig. S6 within the Supplemental Material [26]). In our above experimental investigations, observation of large H_{ex}, independent of field-cooling conditions [inset of Fig. 2(c)], may suggest that (i) internal remnant field of Fe film is sufficient to give rise to a strong surface magnetic hardening and (ii) there is no variation in effective thickness of the surface layer (because any increase in pinning layer thickness should enhance H_{ex}) [2,3].

In the literature, the presence of residual asymmetric AMR in exchange-bias systems, similar to our observations in Fig. 2(b) for zero-field-cooled measurements, may also be associated to the difference in magnetization rotation pathways of the bottom soft layer during the ascending and descending branches of field sweep [36,37]. This rotation asymmetry is driven by the presence of unidirectional anisotropy (K_{UD}) and possibly a new anisotropy axis induced in the soft layer (K_{ex}^{i}) due to proximity exchange with the pinning surface layer [3]. Hence, a study of magnetization switching response of the bottom soft Fe layer may allow us to probe the origin and symmetry of the anisotropy axis in the top surface magnetic layer (K_{SML}).

In this effort, in-plane angular dependence of AMR in Fe (3.5 nm)/MnPc (1 ML) devices is measured at 1.5 K (see Fig. 4). Before performing these measurements, the devices are sufficiently trained (at least > 15 cycles in training fields of ± 0.35 T) to have subsequent overlapping and reproducible AMR curves. In Fig. 4(c), we observe that AMR becomes highly asymmetric as the angle (ϕ) between H_{FC} and the applied field (H_a) is increased. We quantify this asymmetry by measuring the magnitude of

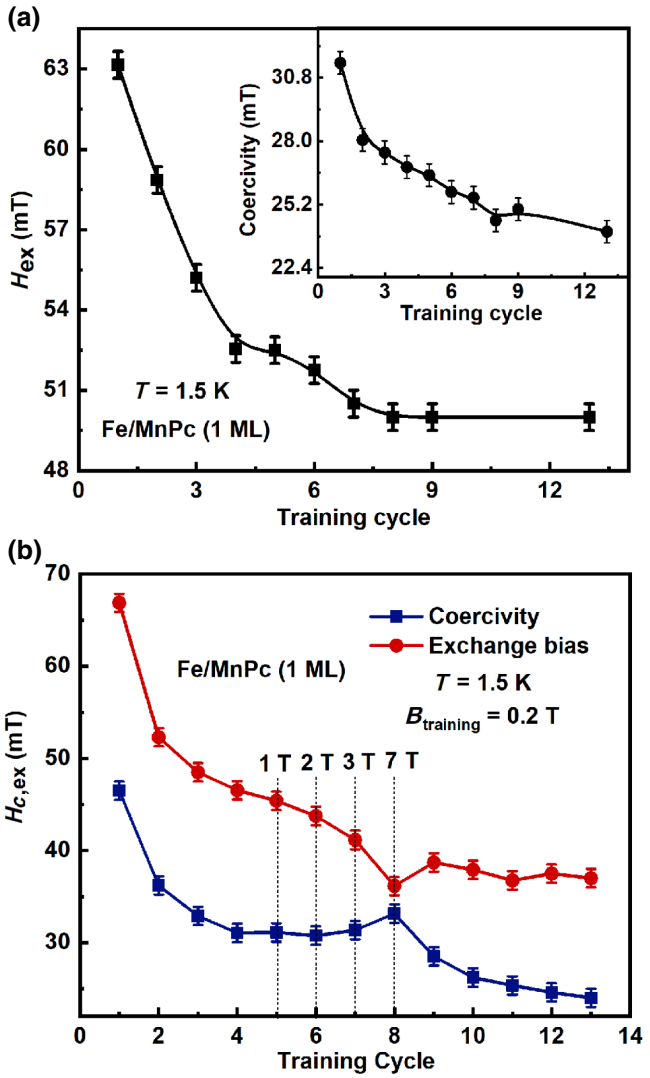

FIG. 3. (a) Training effect (H_{ex} vs training cycle) in Fe (3.5 nm)/MnPc (1 ML) devices with a training field of $pm0.2$ T at 1.5 K. Inset shows corresponding variation in H_c. (b) Variation in H_{ex} (red circle) and H_c (blue square) in Fe (3.5 nm)/MnPc (1 ML) devices during another training effect study similar to (a). Here, at the beginning of fifth, sixth, seventh, and eighth training cycles, progressively large one-sided destabilizing fields of 1, 2, 3, and 7 T is applied, respectively. A process of healing effect is observed subsequently. In the above measurements, the training field in each cycle is fixed at ±0.2 T.

difference in the saturation resistance value in high positive and negative magnetic fields of ±0.35 T ($|\Delta R|$) at each angle and plotted them in Fig. 4(d). Here, a cyclic response in $|\Delta R|$ with a periodicity of 90° is noted. To understand these results, angular dependence of magnetization reversal of the bottom soft Fe layer is simulated using the Stoner-Wohlfarth (SW) coherent rotation model [38] by considering different symmetries viz. uniaxial, biaxial and/or sixfold anisotropy of K^i_{ex}. In addition, K_{UD} in the direction of H_{FC} is included to simulate the exchange-bias shift in our AMR plots. Interestingly, we find that the experimental AMR plots of Figs. 4(c) and 4(d) are qualitatively captured well by our model assuming a biaxial anisotropy of K^i_{ex} [see Fig. 4(b)].

In the SW model, the free energy per unit area (E) of the bottom Fe layer is estimated by [2]

$$E = -K_{UD}\cos(\theta-\phi) - K^i_{ex}\cos[4(\theta-\phi-x)] - \mu_o H_a M_{Fe} t_{Fe}\cos(\theta),$$

where μ_o is the magnetic permeability, M_{Fe} is the Fe magnetization per unit volume, θ is the angle between M_{Fe} and H_a, x is the angle between H_{FC} and K^i_{ex} [see Fig. 4(a)] and t_{Fe} is the thickness of the Fe layer. The relatively much larger value of switching field in our Fe/MPc films (H_c^{free}) than in reference Fe films [see Fig. 2(c)] allows us to neglect the contribution of the internal anisotropy of the soft Fe film in our model. The above equation can be rewritten in terms of the anisotropy fields as

$$E = -H_{UD}\cos(\theta-\phi) - (H_{BA}/16)\cos[4(\theta-\phi-x)] - H_a\cos(\theta),$$

where $H_{UD} = K_{UD}/\mu_0 M_{Fe} t_{Fe}$ is the exchange-bias field and $H_{BA} = 16K^i_{ex}/\mu_o M_{Fe} t_{Fe}$ is the anisotropy field for a biaxial system (see Supplemental Material [26]).

We consider random orientational absorption of the MPc molecules on the Fe surface and simulated the average AMR response by $< \text{AMR} > = < \cos^2\theta > -1$, where $<>$ represents an average over the in-plane azimuthal rotation of angle x. Our fitting to the experimental data of Fig. 4(c) reveal $H_{BA} \sim 0.12$ T and $H_{UD} \sim 51$ mT. Considering proximity effects, the strength of internal anisotropy of the surface layer, K_{SML}, can be at least an order of magnitude larger than K^i_{ex}. Hence, taking a conservative estimate of $K_{SML} \sim 10K^i_{ex}$, we obtain anisotropy field of the surface layer, $H_a^{SML} \sim 10H_{BA}(M_{Fe}/M_{SML})(t_{Fe}/t_{SML})$, where $M_{SML}t_{SML}$ gives the surface magnetization per unit area with t_{SML} as the thickness of surface hard layer. Considering $M_{Fe} \sim M_{SML}$, $t_{Fe} \sim 3.0$ nm, and $t_{SML} \sim 0.4$ nm, we find H_a^{SML} exceeding 9 T that explains our robust surface magnetic hardening response with extremely large switching field.

We also explore the possibility to observe exchange-bias response in thinner films of Fe ~ 1.5 nm under zero-field conditions. In this thickness regime, the reference Fe films show negligible H_c (< 0.5 mT at 1.5 K) approaching the superparamagnetic limit [see Fig. 4(e)]. On the other hand, Fe/MnPc devices show magnetic hardness with cool down without any plateaulike signature of crane-pulley effect observed previously in our thicker Fe films. Correspondingly, no exchange-bias effect is observed suggesting unfavorable interface conditions for the crane-pulley response. This could arise if the bottom Fe layer exchange couples

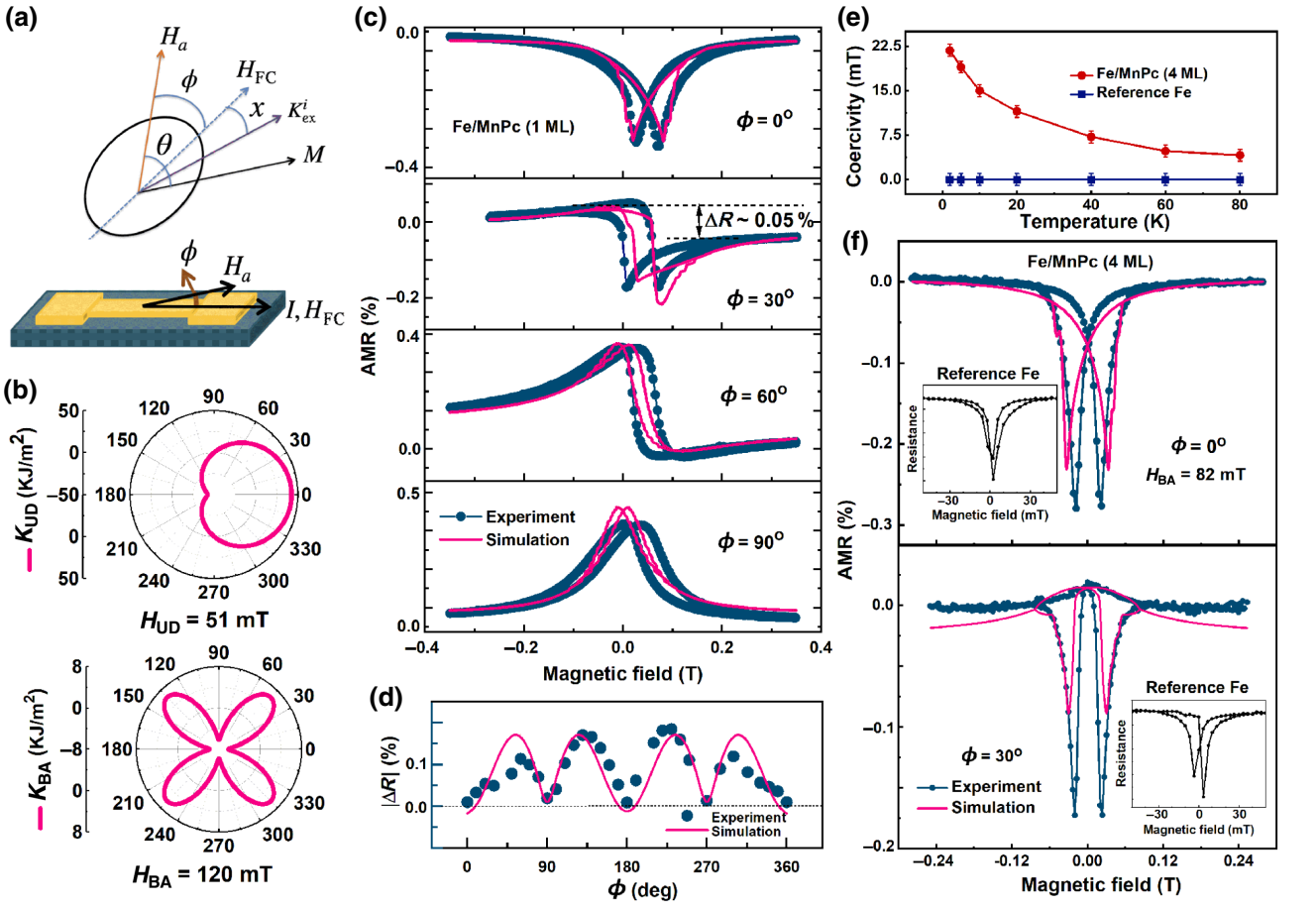

FIG. 4. (a) Schematic showing description of the SW model with our experimental setup for performing in-plane angular-dependent AMR study. Here, direction of current (I) and H_{FC} is kept in the parallel configuration. (b) In-plane contours of K_{UD} and K_{BA} with biaxial anisotropy used for fitting the experimental data of (c),(d). The vertical scale shows the corresponding values of the contour on the minor circles of the plot. Corresponding anisotropy fields, H_{UD} and H_{BA}, are provided. (c) Angular- (ϕ) dependent AMR measurements (blue circle) in Fe (3.5 nm)/MnPc (1 ML) at 1.5 K fitted using the SW model (solid line). (d) Magnitude of $|\Delta R|$ [shown in (c), blue circle] vs ϕ show a fourfold symmetry, also captured in our simulation fits (solid lines). (e) H_c vs T of Fe (1.5 nm)/MnPc (4 ML) (red circle) showing a nearly 100-fold enhancement compared to the reference Fe (1.5 nm) (blue square). (f) AMR of Fe (1.5 nm)/MnPc (4 ML) device measured at $\phi = 0$ and 30°, at 1.5 K (blue circle), fitted to the SW model (solid line) using a biaxial anisotropy capturing the characteristic upward-hump feature near zero field for $\phi = 30°$. Inset shows AMR response of reference Fe (1.5 nm).

strongly to the surface than within the film leading to an exchange-coupled hard-soft magnetic layer with enhanced film coercivity. We also perform angular-dependent AMR studies in these devices and compare the plots with the reference Fe films [see Fig. 4(f)]. We observe an upward-pointing shoulder peak around zero field at $\phi = 30°$ in Fe/MnPc films, not found in the corresponding reference samples. We fit the AMR plots with our SW model and observe the requirement of a biaxial anisotropy, with $H_{BA} \sim 82$ mT, to capture this shoulder peak. Therefore, these results may further confirm the origin of biaxial anisotropy to the formation of Fe/MPc interface hybridized states. The possibility of fourfold symmetry of the MPc molecule contributing to this anisotropy field may need further investigation and is subject of interest in the future.

III. SUMMARY

In summary, our work shows that in molecular spinterface research [19,39,40], surface magnetic hardening and magnetic exchange should be together tailored in observing a crane-pulley response with a robust exchange-bias effect. On one hand, our observation of surface magnetic hardening with switching fields exceeding 7 T offer technological potential in the development of non-rare-earth-based hybrid molecular magnets [12]. While, on the other hand, these surfaces also provide the potential to develop strong pinning layers for the development of newer classes of all-ferromagnetic [41] low-dimensional exchange-bias systems. This monolayer molecular exchange-bias effect presents several unique advantages compared to

commercial FM and AFM exchange-bias systems for their integration with future spin-valve-based spintronic technologies. Firstly, replacement of commercially used expensive intermetallic AFM materials, such as FeMn, NiMn, IrMn, or their alloys, with low-cost monolayer molecules simplify the structural integration with the FM layer without the need for any high-temperature growth or annealing procedures. Secondly, our observation of a robust value of H_{ex}, even in zero-field-cooled devices, further simplify the procedure for bias setting the FM layer. In intermetallic AFM systems, bias setting is achieved by either heating the film above the Neel and blocking temperature and then cooling the devices in a setting field or by growing the AFM layer over the FM in the presence of a setting field. All these above procedures can now be avoided, thereby simplifying the device integration. Presently, low-temperature effects limit our work. However, a careful molecular design can tune surface magnetic hardening and magnetic exchange to envision room-temperature molecular exchange-bias devices in the future. Also, our interface anisotropy study reveals the presence of a surprisingly large induced biaxial anisotropy due to $\pi - d$ hybridization effects. These results provide a number of opportunities for fundamental study in terms of controlling the symmetry of the anisotropy term through molecular design, such as by molecular symmetry or by chirality [42,43]. Additionally, extending the spinterface study to other exotic topological spin surfaces can offer significant exploration of interfacial phenomena.

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