

Supporting Information for:

Effect of Chiral Molecules on the Electron's Spin Wavefunction at Interfaces

Supriya Ghosh,¹ Suryakant Mishra,² Eytan Avigad,³ Brian P. Bloom,¹ L. T. Baczewski,⁴
Shira Yochelis,³ Yossi Paltiel,^{3*} Ron Naaman,^{2*} and David H. Waldeck,^{1*}

¹ Chemistry Department, University of Pittsburgh, Pittsburgh PA 15260, USA

² Department of Chemical and Biological Physics, Weizmann Institute, Rehovot, 76100
Israel

³ Applied Physics Department, the Hebrew University of Jerusalem, Jerusalem 91904, Israel

⁴ Magnetic Heterostructures Laboratory, Institute of Physics, Polish Academy of Sciences Al.
Lotnikow 32/46, 02-668 Warszawa, Poland

Content:

Figure S1 Coercivity measurements on substrates with Co wedge

Figure S2 Topographic image and electrostatic potential map of L-Ala5 SAM

Sample preparation

Different types of magnetic samples were used for the KPFM measurements; however, all of the experiments showed similar magnetization trends. For the experiment illustrated in Fig. 1 in the main text, ITO substrates were coated with 3 nm of Ti buffer layer, followed by 10 nm of polycrystalline Ni, and 10 nm of Au using a Plassys evaporator. For the experiments describe in Fig. 4, E-beam evaporation of Ti/Ni/Au-10nm/120nm/10nm on Si-100 was used as the substrate.

Epitaxial thin films with a cobalt ferromagnetic layer, were used in Figures 2 and 3. The films were grown using PREVAC molecular beam epitaxy system (MBE) with a base pressure of 10^{-10} Torr, according to the following configuration Al_2O_3 (0001)/Pt (5 nm)/Au (20 nm)/Co (1.5nm)/Au (5 nm). A Pt buffer layer was deposited at 650°C to ensure an atomically flat buffer layer surface allowing the epitaxial growth of consecutive layers. Sharp streaks were visible in the in-situ obtained RHEED images for each growth step. The crystallographic orientation of the epitaxially grown layers was as follows: Pt(111), Au(111), Co(0001), and Au(111). The Pt buffer and Co layers were deposited using an electron gun; Au layers were deposited from high temperature effusion cells. The sample with the flat uniform Co thickness of 1.5 nm has a perpendicular anisotropy and features a rectangular hysteresis loop for a magnetic field direction perpendicular to the sample plane, which is characteristic of the out-of-plane easy axis. Wedge type samples were also studied and they were deposited using a movable shutter controlled by a step motor. Two types of wedge samples were also grown:

an Au-wedge

Al_2O_3 (0001)/Pt (5 nm)/Au (20 nm)/Co (1.5nm)/Au wedge (2-10 nm)

and a Co-wedge:

Al_2O_3 (0001)/Pt (5 nm)/Au (20 nm)/Co (1.6 -3 nm)/Au (5 nm).

For a Co layer thickness above 2 nm a spin reorientation transition occurs, and the magnetization easy axis changes from perpendicular to in-plane direction, resulting in the in-plane anisotropy. Hysteresis loops were measured by the polar magneto-optic Kerr effect (P-MOKE) along the Co wedge direction and by SQUID, for the sample with flat Co layer (see figure S1).

The standard, phenomenological relationship based on Neel predictions

$$K_{1\text{eff}}(d) = -2\pi M_s^2 + K_{1v} + 2K_{1s}/d$$

where d denotes thin film thickness and M_s saturation magnetization,¹ is used for describing the anisotropy in the thin films, containing the demagnetization term (shape anisotropy) and two anisotropy terms: volume K_{1v} and surface term K_{1s} originating from the interfaces with buffer layer and the overlayer. As the K_{1s} is inversely proportional to the thin film thickness d , for a higher value of d a spin reorientation transition takes place and the easy axis direction rotates from perpendicular to in-plane direction.

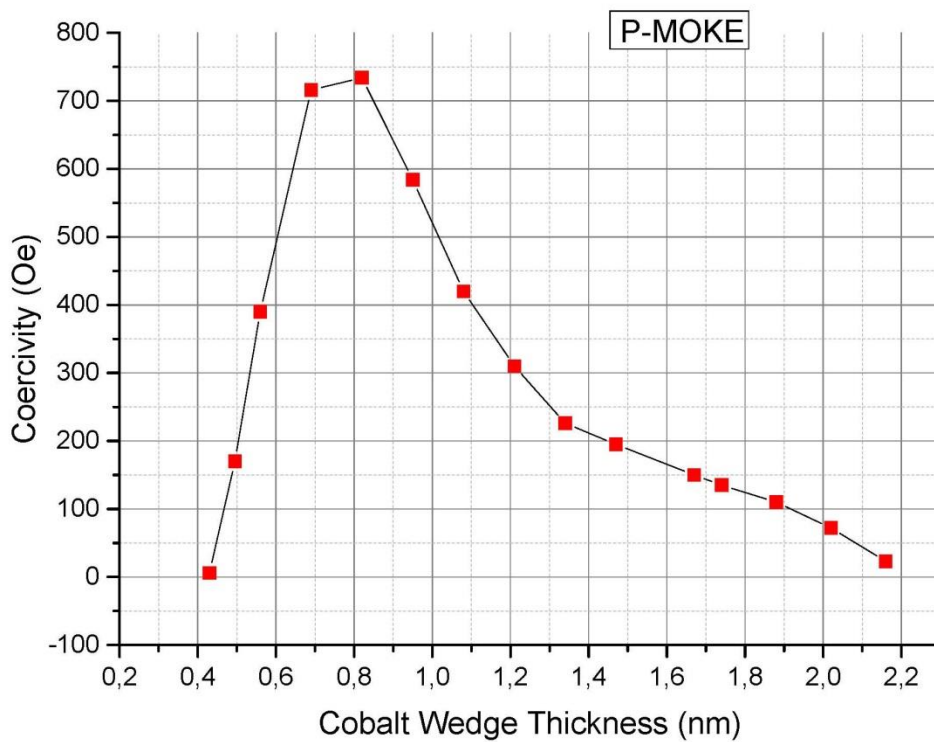


Figure S1. Coercivity dependence on the thickness of the Co layer for epitaxial Au/Co/Au substrates Cobalt was deposited as a wedge using a computer controlled movable shutter.

KPFM measurement

KPFM measurements were made using an Asylum Research MFP-3D atomic force microscope. Experiments were done under ambient conditions in a nitrogen atmosphere. Electric cantilevers, ELEC-01 silicon chip with a Titanium/Iridium coating ($K \sim 2.8$ N/m, $F \sim 75$ KHz) from Asylum Research, were used to conduct the experiments. The surface potential

measurements were performed at a 20 nm distance from the surface. Because of the dielectric nature of the monolayers, the sample was not grounded. For the magnetic field experiments, a permanent magnet was placed underneath the substrate such that ~ 200 mT magnetic field (measured using a Gauss meter) was applied to the substrate. Because the measurements are susceptible to environmental conditions and dust the acquired data are only used for measurements with reproducible KPFM scans. Figure S2 shows an example of a topography and KPFM image for one of the samples.

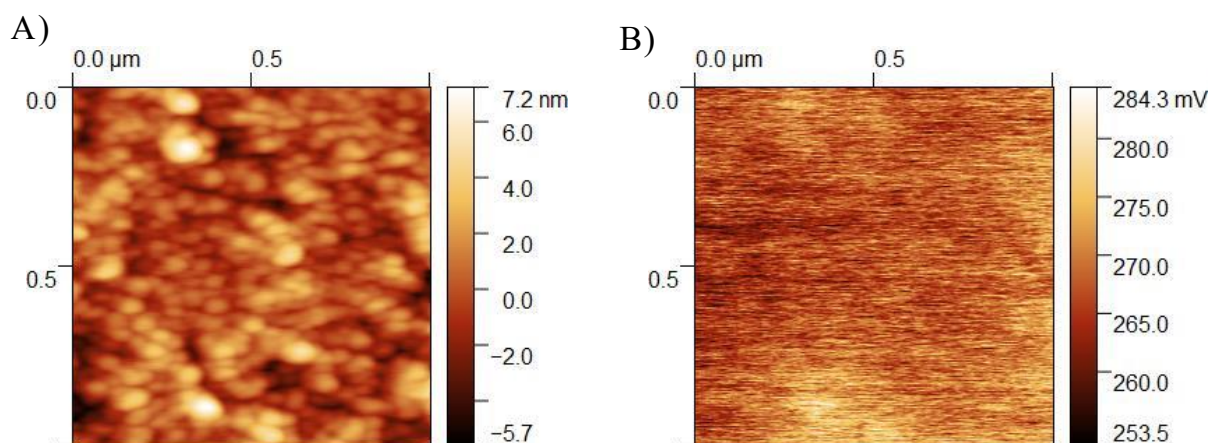


Figure S2. The left panel shows a representative topographic image of an L-Ala5 coated ferromagnetic nickel substrate. The right panel image shows an electrostatic potential map corresponding to the image in the left panel.

Peptide SAM preparation

Measurements were performed on two different peptides (D- and L- HS-CH₂-CH₂-(Ala-Aib)₅-COOH) and an achiral molecule (HS-(CH₂)₁₅-COOH). The D- and L-peptides were synthesized by Genemed Synthesis, Inc. and the achiral molecules were purchased from Sigma Aldrich.

To prepare the SAM, the substrates were first cleaned by immersing them in absolute ethanol for 10 minutes and then drying them under a stream of argon gas. The substrates were then incubated in a 1mM peptide / achiral molecule ethanoic solution for 48 hours. After adsorption, the samples were washed in absolute ethanol to remove excess unbound molecules and dried with argon. All of the substrates were stored under vacuum prior to KPFM measurements.

Macroscopic CPD measurements

The CPD of the surfaces was determined using a commercial Kelvin probe instrument (Delta Phi Besocke, Jülich, Germany) within a Faraday cage at atmospheric pressure. The reference probe consisted of a gold grid. The CPD signal was allowed to stabilize before recording, where ΔCPD is the difference in the direction of magnetic field.

Substrate preparation and cleaning: Substrates used for the CPD measurement are grown by electron-beam (ODEM evaporator) where Si-100 wafer used as substrate to grow Ti/Ni/Au-10nm/120nm/10nm with 0.5Å/sec deposition rate at 10^{-8} Torr pressure. Surfaces were cleaned by first boiling in acetone and then boiling in ethanol for 10 minute each. The surfaces then underwent UV-Ozone treatment for 10 minutes and were subsequently immersed in ethanol for 30 minutes. Immediately afterwards, the substrates were dried with a nitrogen stream and then used for monolayer deposition.

DNA SAM preparation: The self-assembled monolayers (SAM) of DNA were prepared using DNA oligomers 3'- functionalized with thiol groups on one strand. DNA duplexes were used for monolayer preparation and spin polarization studies in the following way: First, a 100 μ M stock solution of DNA was prepared in deionized water. Before monolayer preparation, the stock solution was mixed with 0.8 M PBS (K_2HPO_4/KH_2PO_4) buffer (pH = 7.2) in equal quantity – thus making a 50 μ M DNA solution in 0.4 M PBS buffer. The solution was then mixed with the same quantity of 10 mM Tris(2-carboxyethyl)phosphine hydrochloride (TCEP, purchased from Sigma Aldrich) in 0.4 M PBS buffer (pH 7.2). The solution was left in Tris buffer for 2 hours, then was purified by filtering through a Micro Bio-Spin P-30 column (purchased from Bio Rad). The final concentrations of all DNA were measured with UV-vis spectroscopy using a Nanodrop spectrometer and was found to be between 20-30 μ M. This DNA solution was drop cast onto the substrate. The sample was left for 20-24 hours in a humid environment and then rinsed twice with 0.4 M PBS and twice in de-ionized water.

DNA Sequence:

20bp dsDNA:

5'-CGC TTC GCT TCG CTT CGC TT/3ThioMC3-D/-3'
5'-AAG CGA AGC GAA GCG AAG CG-3'

30bp dsDNA:

5'-CGC TTC GCT TCG CTT CGC TTC GCT TCG CTT /3ThioMC3-D/-3'
5'-AAG CGA AGC GAA GCG AAG CGA AGC GAA GCG-3'

40bp dsDNA:

5'-CGC TTC GCT TCG CTT CGC TTC GCT TCG CTT CGC TTC GCT T/3ThioMC3-D/-3'
5'-AAG CGA AGC GAA GCG AAG CGA AGC GAA GCG AAG CGA AGC G-3'

50bp dsDNA:

5'-CGC TTC GCT TCG CTT CGC TTC GCT TCG CTT CGC TTC GCT TCG CTT CGC
TT/3ThioMC3-D/-3'

5'-AAG CGA AGC GAA GCG AAG CGA AGC GAA GCG AAG CGA AGC GAA GCG AAG
CG-3'

Oligopeptide SAM preparation: For growing monolayers of oligopeptide, the substrates were prepared using the same cleaning procedure as that used for DNA. Following cleaning, the substrate was immersed in a peptide solution (0.625 mg mL^{-1} , using a 1:1 mixture of pH 7.0, 10 mm sodium phosphate buffer and TFE) for 36 hours and then rinsed twice with de-ionized water.

Oligopeptide Sequence:

1. SHCH₂CH₂CO-{Ala-Aib}₃-COOH
2. SHCH₂CH₂CO-{Ala-Aib}₄-COOH
3. SHCH₂CH₂CO-{Ala-Aib}₅-COOH
4. SHCH₂CH₂CO-{Ala-Aib}₆-COOH
5. SHCH₂CH₂CO-{Ala-Aib}₇-COOH

References

1 Kisielowski, M.; Maziewski, A.; Tekielak, M. ; Wawro , A.; Baczewski, L.T.; New possibilities for tuning ultrathin cobalt film magnetic properties by a noble metal overlayer, *Phys. Rev. Lett.* **2002** *89*, 087203.