Enantiospecific adsorption on a ferromagnetic surface at the single-molecule scale

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Abstract

The recently discovered chirality-induced spin selectivity has opened a new strategy for enantioselective processes that exploits the interaction between molecular handedness and electron spin. Despite successful experimental reports of enantiospecific adsorption of chiral molecules on ferromagnetic substrates, comprehensive and quantitative theoretical models are still lacking. This is mainly due to the
complex experimental conditions, which include adsorption from solution, protective Au layers on the ferromagnetic surface to avoid oxidation, and detection schemes that address ensembles of molecules. Here, we report enantioselective adsorption of chiral molecules on uncoated single-crystalline perpendicularly magnetized Co nanoislands by sublimation under ultra-high vacuum. Detection of the handedness of each molecule and the magnetization direction of the underlying island by spin-polarized scanning tunneling microscopy provides unequivocal evidence for enantioselective adsorption. Analysis of more than 740 molecules yields an enantiomeric adsorption energy difference of \((9 \pm 2)\) meV. Due to the well-defined experimental conditions, our results are readily accessible for theoretical modeling.

**Keywords:** chiral molecules, ferromagnetic substrate, enantiospecific adsorption, CISS effect, single-molecule scale

**Introduction**

Chiral molecules, ubiquitous building blocks of the molecules of life, have been extensively studied in various scientific disciplines such as medicine, pharmacy, and chemistry. Despite identical chemical composition and physical properties under achiral conditions, enantiomers behave differently in chiral biological and physiological environments, where they often exhibit disparate pharmacological and toxicological responses \([1]\). The fact that more than half of drugs currently in use are chiral molecules, emphasizes the importance of developing robust and simple enantioseparation techniques \([2]\). Most chiral separation techniques are based on purely spatial aspects like steric matching, including various types chromatography, electrophoresis, and their combinations \([3]\).

The recently discovered effect of chirality-induced spin selectivity (CISS) \([4, 5]\) not only gives rise to spin-selective transport of charge carriers through chiral systems \([6–11]\), but also offers a new approach for chiral separation by exploiting the CISS-induced enantiospecific interaction of chiral molecules with a perpendicularly magnetized ferromagnetic substrates \([12–15]\). Despite the steadily growing body of experimental evidence for the CISS effect, theoretical models continue to be sought to close the still large gap between experimentally reported and substantially smaller theoretically calculated values for the degree of CISS-induced spin polarization in electron transport through chiral systems \([16–23]\). Theory related to the more recent CISS in enantiospecific adsorption reactions is much more limited and is only now starting to emerge \([23]\).

The few previous experimental reports on enantiospecific adsorption of chiral molecules on ferromagnetic substrates \([12–15]\) reported the deposition of the molecules under ambient conditions from solution onto ferromagnetic substrates coated with 5 to 10 nm Au for oxidation protection. Enantiospecific adsorption was revealed by either using enantiopure solutions and enantio-unspecific determination of the adsorbed amounts of molecules \([12–15]\) or, in
the case of racemic solutions, by enantiospecific circular dichroism spectroscopy [12, 13]. In all cases, evidence of enantiospecificity was provided integrally over large ensembles of adsorbed molecules.

Here it is shown that enantiospecific adsorption occurs on single-crystalline ferromagnetic cobalt surfaces in ultra-high vacuum (UHV). By using this well-defined approach, external influences, such as undesired co-adsorption of other species or the need of a gold capping layer to prevent oxidation are excluded. The direct determination of molecular handedness of each single adsorbed molecule as well as the local substrate magnetization guarantees unequivocally analysis of the origin of enantiospecificity. Moreover, it is shown that the effect relies on single-molecular properties and not on ensemble or cooperative effects. Low sub-monolayer coverages of chiral heptahelicene C_{30}H_{18} molecules ([7]H) are deposited in UHV by sublimation from a racemic powder onto ferromagnetic bilayer Co nanoislands on a Cu(111) single-crystal surface held at room temperature (RT). Such Co islands are known to have out-of-plane magnetization [24–29]. The handedness of each [7]H molecule and the magnetization direction of the Co nanoislands are determined by using low-temperature spin-polarized scanning tunneling microscopy and spectroscopy (SP-STM/STS). Statistical analysis of more than 700 molecules on 110 islands revealed a pronounced imbalance of the absolute handedness of adsorbed [7]H molecules with respect to the direction of the out-of-plane substrate magnetization. This enantiospecific adsorption is attributed to different adsorption energies for the different combinations of molecular handedness and magnetization direction.

Results

The adsorption of helical molecules with their helix axis normal to the substrate plane on a perpendicularly magnetized substrate allows in principle four possible alignments of substrate magnetization \( M \) and helix vector \( h \), where the latter distinguishes the two enantiomers. \( h = \uparrow \) represents the (P)-[7]H enantiomer and \( h = \downarrow \) the (M)-[7]H enantiomer. An exact definition of \( h \) is given in Supplementary Section S1. The incidences of the four possible configurations are denoted by \( N_{Mh} \), where \( M = \uparrow \text{ or } \downarrow \) and \( h = \uparrow \text{ or } \downarrow \). \( M \) and \( h \)

Suppl. Fig. 1 Adsorption configurations of [7]H on Co nanoislands Both enantiomers, (P)-[7]H and (M)-[7]H, can adsorb on Co nanoislands with (a) up and (b) down magnetization. The incidence of the four configurations are denoted by \( N_{Mh} = N_{\uparrow \uparrow}, N_{\uparrow \downarrow}, N_{\downarrow \uparrow}, \text{and } N_{\downarrow \downarrow} \), where \( M = \uparrow, \downarrow \) indicates the magnetization direction of the island and \( h = \uparrow, \downarrow \) the direction of the helix vector.
Enantiospecific adsorption on a ferromagnet at single-molecule scale can be parallel and point either into $+z$- or $-z$-direction ($N_{↑↑}$ and $N_{↑↑}$, i.e., up or down, respectively) or $M$ and $h$ are antiparallel with $h$ pointing either in $+z$- or $-z$-direction ($N_{↑↓}$ and $N_{↑↓}$), see Fig. 1.

Enantiospecific adsorption of $[7]$H molecules on perpendicularly magnetized Co is here evidenced by counting the incidences $N_{Mh}$ in topographic STM images measured simultaneously with spin-polarized spectroscopy maps. Hence, the handedness ($h$) for each molecule and the magnetization direction $M$ of the respective Co island are simultaneously determined.

The triangular Co islands are formed by in-situ thermal evaporation of a sub-monolayer (ML) of Co onto the pre-cleaned Cu crystal [30]. Deposition of racemic $[7]$H is performed by sublimation at about 400 K under UHV conditions [31]. Figure 2a shows a constant current topographic STM image of a sub-ML of $[7]$H molecules deposited on Co/Cu(111) at RT and imaged at 5 K. The molecules adsorb with the proximal phenanthrene group aligned parallel

Suppl. Fig. 2 [7]H molecules deposited on ferromagnetic Co bilayer nanoislands on Cu(111). a, Constant-current topographic image showing $[7]$H molecules attached only to Co nanoislands. b, Simultaneously with a measured $dI/dV$ map revealing magnetic contrast (blue versus yellowish) between Co nanoislands with opposite out-of-plane magnetization ($V_{bias} = -600 \text{ mV}$, $I_t = 950 \text{ pA}$, $V_{mod} = 20 \text{ mV}$, $f_{mod} = 752 \text{ Hz}$, 5 K, Co-functionalized W tip). c and d, High-resolution topographic image of the areas framed in (a and b) by dashed and dotted lines, respectively, after Gaussian high-pass filtering. Green and red circular arrows indicate the handedness of the respective $[7]$H molecules. The insets represent the number of right-handed ($P$) and left-handed ($M$) molecules adsorbed on the corresponding island ($V_{bias} = 1000 \text{ mV}$, $I_t = 50 \text{ pA}$, 5 K).
to the surface. The triangular Co nanoislands are decorated with molecules on the top and at the edges, while the Cu substrate remains bare. Hence, the surface mobility of the [7]H molecules during deposition allows them to travel to the Co nanoislands, where they accumulate as a result of stronger binding to the Co [32]. The differential conductance (dI/dV) map in Fig. 2b recorded simultaneously with the topography in Fig. 2a reveals magnetic contrast of the Co nanoislands, demonstrating ferromagnetism also in the presence of chemisorbed [7]H molecules [31]. The dI/dV contrast arises from different spin-polarized tunnelling probabilities between the oppositely out-of-plane magnetized Co nanoislands and the magnetic Co-functionalized tungsten (W) tip (see Methods) of the STM [25, 26, 28, 29]. The dI/dV contrast also depends on the direction of the tip magnetization, which is fixed during the acquisition of a dI/dV map but is generally not readily known. Hence, there is no unique assignment of blue and yellowish contrast to the absolute direction of the magnetization $M$ (i.e., $M$ pointing into vacuum or substrate). Without loss of generality, bright contrast can be designated for analysis as up magnetization ($M = \uparrow$) and dark contrast as down magnetization ($M = \downarrow$).

Figure 2c presents a high-resolution topographic image of the dashed framed area in Figs. 2a and b after applying Gaussian high-pass filtering, which enhances the fine structure of the molecular features [31, 33]. Technical information on the implementation and application of the Gaussian high-pass filter is detailed in Ref. [31]. The sub-molecular fine structure can be mainly attributed to the apparent topographic profile of the adsorbed molecules, which have their helix axis perpendicular to the surface. Therefore, the fine structure reveals the handedness of the molecules, as indicated by red and green circular arrows for $(M)$-[7]H and $(P)$-[7]H molecules, respectively.

The island in Fig. 2c shows blue contrast in Fig. 2b and therefore has $M = \downarrow$. The enantiomer count yields $N_{\uparrow\uparrow} = 10$ for the $(P)$-[7]H and $N_{\downarrow\downarrow} = 5$ for the $(M)$-[7]H molecules, suggesting enantiomeric imbalance. For 2 molecules, the handedness cannot be determined, probably due to adsorption on a defect in the substrate or fragmentation of a molecule.

Figure 2d presents a similar analysis for an island (dotted framed area in Figs. 2a and b) with $M = \uparrow$, i.e., for an island with opposite magnetization compared to that in Fig. 2c. On the $M = \uparrow$ island, the enantiomer count yields $N_{\uparrow\uparrow} = 4$ for the $(P)$-[7]H and $N_{\downarrow\downarrow} = 9$ for the $(M)$-[7]H molecules. The reversed imbalance in Figs. 2c and d suggests enantiospecific adsorption of [7]H on ferromagnetic Co islands that depends on the direction of the islands magnetization: Molecules of different handedness preferentially adsorb on islands with opposite magnetization direction.

To support this conjecture with better statistical data, two independent data sets were measured using separately prepared Co/Cu(111) substrate systems, different runs of [7]H deposition, and newly Co-functionalized STM tips. The first data set is shown in Fig. 3 and the second in Supplementary Fig. S2. A topographic overview image featuring several dozen Co bilayer nanoislands decorated with [7]H molecules and the simultaneously recorded dI/dV
Suppl. Fig. 3 Enantiospecific adsorption of [7]H on ferromagnetic Co nanoislands. a and c, Constant-current topographic image of [7]H molecules on Co nanoislands on Cu(111). b and d, Simultaneously with a and c measured dI/dV maps. The scan area of c and d is vertically shifted relative to that of a and b to enlarge the data set. The red frames in b and d indicate a common island in the two consecutive scans showing the same magnetic contrast (V_{bias} = −350 mV, I_{t} = 340 pA, V_{mod} = 20 mV, f_{mod} = 752 Hz, 5 K, Co-functionalized W tip).

Suppl. Table 1 [7]H adsorption on Co nanoislands. Incidence of the four combinations of M and h in the two data sets presented in Fig. 3 and Supplementary Fig.S2. The number of molecules for which the handedness could not be determined and the total number of analyzed molecules are also listed.

| Data sets | N_{↑↑} | N_{↑↓} | N_{↓↑} | N_{↓↓} | Unknown handedness | Analyzed molecules |
|-----------|--------|--------|--------|--------|--------------------|--------------------|
| Set 1     | 39     | 61     | 98     | 78     | 15                 | 291                |
| Set 2     | 63     | 94     | 172    | 114    | 14                 | 457                |
| Total     | 102    | 155    | 270    | 192    | 29                 | 748                |
this is not the case in this data set. Therefore, the enantiomer counts obtained from high-resolution topographic images of all 48 islands visible in the two scans (like those in Figs. 2c and d) can be added. The incidence numbers $N_{Mh}$ for 291 analyzed $[7]$H molecules are listed in the first row of Table 1. The results for the second even larger data set presented in Supplementary Fig. S2 are compiled in the second row of Table 1. For both data sets, $N_{\downarrow\uparrow} > N_{\uparrow\uparrow}$ and $N_{\downarrow\uparrow} > N_{\downarrow\downarrow}$, meaning that the $\langle M\rangle$-$[7]$H enantiomer preferably adsorbs on nanoislands with a certain magnetization direction (denoted as $M = \uparrow$), whereas the $\langle P\rangle$-$[7]$H enantiomer preferably adsorbs on nanoislands with the opposite magnetization direction (denoted as $M = \downarrow$).

### Discussion

Enantiospecific adsorption on a ferromagnetic surface implies a dependence of the adsorption probability on the relative alignment of magnetization $M$ and handedness $h$ [12]. Therefore, we divide the adsorbed molecules into the two classes: (1) $M$ and $h$ are parallel and (2) $M$ and $h$ are antiparallel. $N_1 = N_{\uparrow\uparrow} + N_{\downarrow\downarrow}$ and $N_2 = N_{\uparrow\downarrow} + N_{\downarrow\uparrow}$ are the number of molecules in class 1 and 2, respectively. Enantiospecificity is characterized by an enantiomeric ratio $r = \frac{N_1}{N_2}$ that differs significantly from one. The statistical analysis of our data in the framework of a trinomial distribution (see Supplementary Section S3) yields for both data sets an enantiospecific ratio $r \approx 0.7 \pm 0.05$, i.e. significantly lower than one (Table 2 and Fig. 4). Therefore, our data demonstrate that the absorption probability of $[7]$H molecules on a ferromagnetic Co(111) surface clearly depends on the relative alignment of the helix vector $h$ and the substrate magnetization $M$. On a homogeneously magnetized Co surface, one $[7]$H enantiomer adsorbs preferentially over the other.

### Suppl. Table 2 Statistics of the $[7]$H adsorption on Co nanoislands.

$N_1$ and $N_2$ are the number of molecules in classes 1 and 2. $N_3$ is the number of molecules with unknown handedness. The ratio $r = \frac{N_1}{N_2}$ is significantly lower than one and reveals a clear dependence of the adsorption probability on the relative alignment of island magnetization $M$ and molecular handedness $h$. The error bar of $r$ is calculated according to Equation (S1) in Supplementary Section S3. $\Delta E$ is the difference in adsorption energy of the two molecule classes derived from $r$ using Equation (2).

| Data sets | $N_1$ | $N_2$ | $N_3$ | $N_1 + N_2 + N_3$ | $r = \frac{N_1}{N_2}$ | $\Delta E$ (meV) |
|-----------|-------|-------|-------|-------------------|----------------------|-----------------|
| Set 1     | 117   | 159   | 15    | 291               | 0.74 ± 0.09          | 8 ± 3           |
| Set 2     | 177   | 266   | 14    | 457               | 0.67 ± 0.06          | 10 ± 3          |
| Total     | 294   | 425   | 29    | 748               | 0.69 ± 0.05          | 9 ± 2           |
Suppl. Fig. 4 Enantiomeric ratio for [7]H adsorption on Co nanoislands. For both data sets, $r$ is significantly lower than one, demonstrating enantiospecific adsorption. The error bar of $r$ is calculated according to Equation (S1) in Supplementary Section S3.

[7]H molecules sublimed from a racemate arrive on the sample surface at random positions and with uniformly distributed handedness. However, the STM data reveal a more ordered state. All molecules are attached to Co nanoisland leaving the Cu regions between the Co islands free of molecules, and the [7]H molecules adsorbed on each island show an enantiomeric excess that depends on the direction of the island magnetization. This implies surface mobility of the [7]H molecules after deposition and before cooling to 5 K, which allows them to diffuse across the surface and explore the energy landscape for adsorption without kinetic hindrance. Co nanoislands provide preferential adsorption sites due to their higher binding energy compared to Cu [32]. And the enantiomeric excess on top of each island suggests an enantiospecific adsorption energy that depends on the relative alignment of molecular helix vector $h$ and island magnetization $M$. If $E_{1(2)}$ denote the adsorption energies for the two classes defined above, (1) $M$ and $h$ are parallel and (2) $M$ and $h$ are antiparallel, the occupation numbers at temperature $T$ are proportional to the Boltzmann factor, $N_{1(2)} \propto \exp(-E_{1(2)}/k_B T)$, and the enantiomeric ratio of the occupation numbers is related to the energy difference $\Delta E = E_1 - E_2$ by

$$r = \frac{N_1}{N_2} = \exp \left( - \frac{\Delta E}{k_B T} \right).$$

The STM data presented in Fig. 3 and Fig. S2 and compiled in Tables 1 and 2 were measured at 5 K and therefore represent the enantiomeric ratio at the freezing temperature $T_{\text{freeze}}$, below which surface diffusion of [7]H molecules between Co nanoislands is kinetically hindered. In order to estimate the freezing temperature $T_{\text{freeze}}$, we observed the adsorption positions of [7]H molecules at 78, 285, and 296 K (RT) for up to 5 hours by recording time series of topographic STM images of a selected sample area and determined $T_{\text{freeze}} = 296$ K as a lower bound of estimation (see Supplementary Section S4). This finding suggests that the magnetization-dependent enantiomeric excess on the Co nanoislands observed by STM at 5 K is established immediately after the adsorption process, when the kinetic energy of the molecules exceeds the substrate temperature. Consequently, the enantiospecific adsorption of [7]H...
molecules observed in our experiments requires that the superparamagnetic blocking temperature of the Co bilayer nanoislands is approximately RT on the time scale of the adsorption process and the subsequent molecular diffusion between Co nanoislands. Otherwise, the island magnetizations $M$ would fluctuate thermally and could not cause the enantiomeric excess on the islands. We verified this premise experimentally by performing spin-polarized measurements at RT, which yielded clear and stable magnetic contrast for equally sized and identically stacked Co nanoislands (see Supplementary Section S5).

Using $T_{\text{freeze}} = 296$ K as a lower bound for the freezing temperature, a lower bound for the energy difference due to enantiospecific interaction of $[7]$H molecules with the ferromagnetic Co surface can be obtained by rewriting Equation (1),

$$\Delta E = -k_B T_{\text{freeze}} \ln(r).$$

Both data sets yield consistent values (see last column of Table 2) that can be combined to $\Delta E = (9 \pm 2)$ meV. This result is based on the analysis of two independently measured data sets comprising a total of 748 $[7]$H molecules adsorbed on 110 Co nanoislands. Note that the assignment made above of bright $dI/dV$ contrast to $M = \uparrow$ depends on the direction of the unknown tip magnetization. If bright contrast corresponded to $M = \downarrow$, $E_1$ and $E_2$ would have to be swapped and the sign of $\Delta E$ would reverse. Therefore, the present analysis can only indicate the magnitude of the enantiospecific adsorption energies, but not which alignment of magnetization and helix vector directions is more stable.

**Conclusion**

We demonstrated for the first time that enantiospecific adsorption of helical molecules on a ferromagnetic surface occurs in UHV and for discrete molecules. Enantiospecificity thus results from single-molecule properties. Cooperative or ensemble effects can be excluded. The approach of depositing the molecules by sublimation onto clean and uncoated single-crystalline surfaces eliminates external influences due to Au capping layers and co-adsorbed species.

Enantiomer separation takes place during deposition on the substrate kept at RT, when the surface mobility of the $[7]$H molecules allows them to explore the energy landscape for adsorption. After deposition, the adsorption state is frozen as surface diffusion between Co nanoislands is kinetically hindered.

The observed enantioselective adsorption for the model system $[7]$H on Co bilayer islands is phenomenologically consistent with the CISS-related mechanism proposed in [12] and with previous reports on application-oriented systems [12–15]. In the present case, 3 of the 7 C-rings forming the helix of $[7]$H are involved in chemisorption to the Co substrate, whereas in the previous studies the molecules were bound to the Au capping layer via thiol, amide, or carboxylic groups. This emphasizes the universality of the phenomenon of enantioselective adsorption on ferromagnetic surfaces. We expect that the presented model system $[7]$H on Co bilayer islands and the straightforward and
well-defined experimental conditions are readily accessible for theoretical analysis and quantitative modeling of enantiospecific adsorption on ferromagnetic surfaces.

**Methods**

Measurements were performed in an UHV ($< 10^{-8}$ Pa) cluster tool equipped with a preparation chamber for substrate preparation and analysis, a separate molecule deposition chamber, and a LT-STM (Omicron Scienta) operating down to 5 K.

**Molecule synthesis**

Racemic mixtures of heptahelicene were synthesized from a stilbene precursor by photocyclyzation as described previously [34].

**Sample preparation**

Co bilayer nanoislands were grown on an atomically clean Cu(111) surface by in-situ deposition at RT from a 99.99% pure Co rod using e-beam evaporation. The deposition rate was $0.2 \text{ML/min}$ and pressure during deposition was $< 2 \times 10^{-8}$ Pa. The cleaning procedure of the Cu(111) single crystal by repeated cycles of Ar$^+$ sputtering followed by annealing and further details about the Co deposition can be found in Ref. [31]. After Co deposition, the shape and density of the Co bilayer islands as well as the cleanness of the deposition were checked by means of topographic STM images. Simultaneously, spin-polarized STM measurements were performed to confirm the presence of a well-defined magnetization of the islands perpendicular to the surface. Then, the Co/Cu(111) substrate was transferred at RT to the molecule chamber and exposed to the molecular vapour sublimed from a carefully heated glass crucible. The crucible temperature was about 400 K, the exposure time typically less than one minute, and the pressure during sublimation less than $10^{-7}$ Pa [31]. Finally, the sample was transferred to the STM chamber within a few minutes and immediately cooled for the STM experiments, which were performed at a pressure in the mid $10^{-9}$ Pa range and at 5 K unless otherwise specified. Higher measurement temperatures $T_{\text{meas}}$ were achieved by cooling with liquid N$_2$ instead of liquid He ($T_{\text{meas}} = 78$ K), during the slow warming of the system to RT ($T_{\text{meas}} = 285$ K), or by measuring immediately after [7]H deposition at RT without any cooling ($T_{\text{meas}} = 296$ K).

**STM measurements**

Electrochemically etched (polycrystalline W wire in 5 M NaOH solution) were used for all STM measurements. Co-functionalized W tips providing magnetic contrast were obtained by intentionally bringing the tip in near mechanical contact with a remote ferromagnetic Co nanoisland and by applying short bias
voltage pulses to transfer Co atoms from the island to the tip. The functional-
ization procedure was repeated until successful acquisition of a spin-polarized
d$I$/d$V$ map from a Co nanoisland confirmed the sensitivity of the tip to the
out-of-plane magnetization component.

We present two types of STM data: (i) Topographic STM images were
taken in constant-current mode. The bias voltage $V_{\text{bias}}$ was applied to the
sample, and $I_t$ denotes the setpoint current of the STM feedback loop. (ii)
Differential conductance ($dI/dV$) maps that were taken simultaneously with
constant-current topographic images, i.e. with the STM feedback loop closed.
d$I$/d$V$ maps represent, to a good approximation, the local density of states
as a function of the lateral position and at the energy $eV_{\text{bias}}$, where $V_{\text{bias}} = 0$
corresponds to the Fermi energy. The $dI$/d$V$ signal for the conductance maps
was obtained by modulating $V_{\text{bias}}$ with a small sinusoidal signal (rms ampli-
tude $V_{\text{mod}} = 20 \text{ mV}$; frequency $f_{\text{mod}} = 752 \text{ Hz}$) and detecting the resulting
modulation of the tunneling current at $f_{\text{mod}}$ using a lock-in amplifier.

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