

Towards Comprehension of Chiral Induced Spin Selectivity

775. WE-Heraeus-Seminar

05 - 08 December 2022

at the Physikzentrum Bad Honnef/Germany

**WILHELM UND ELSE
HERAEUS-STIFTUNG**



Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see <https://www.we-heraeus-stiftung.de>

Aims and scope of the 775. WE-Heraeus-Seminar:

When electrons are moving through helical molecules, one spin orientation has a larger chance of making it through than the other, despite the helices being diamagnetic. This observation termed chiral induced spin selectivity is an intriguing phenomenon that rests on a foundation of structural chirality, spin-orbit interactions, and strongly non-equilibrium conditions. Its underlying mechanism is not fully understood.

What might be further aspects fitting into the set of fundamental mechanisms lying behind this phenomenon? This question is one, among several others, that we aim to discuss and, hopefully, clarify in this seminar. Leading experts working in the field of chiral induced spin selectivity as well as expert physicists, chemists, engineering and biology-oriented scientists aiming to focus research in this direction will provide lectures with a broad scope to facilitate a wider comprehension and open discussions of this enigmatic issue.

Scientific Organizers:

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Introduction

Venue :

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Registration:

Mojca Peklaj (WE Heraeus Foundation)
at the Physikzentrum, Reception Office
Sunday (17:00 h - 21:00 hrs) and Monday morning

Program

Program (CET)

Sunday, 04 December 2022

17:00 – 21:00 ARRIVAL and REGISTRATION

18:30 *BUFFET SUPPER*

Monday, 05 December 2022

07:30 *BREAKFAST*

08:30 – 09:30 Ron Naaman **Why It Is Difficult to Understand the Mechanism of the CISS Effect?**

09:30 – 10:30 Helmut Zacharias **Chirality Induced Spin Selectivity: The Photoelectron View**

10:30 – 11:00 *COFFEE BREAK*

11:00 – 12:00 Yonatan Dubi **The “Spinterface” Model for the CISS Effect – Connecting Theory and Experiment**

12:00 – 13:00 Vladimiro Mujica **Field-Mediated Chirality Information Transfer and Dispersion Intermolecular Forces**

13:00 – 13:15 **Conference Photo (outside at the main entrance)**

13:15 – 14:30 *LUNCH BREAK*

Program (CET)

14:30 – 15:30	José Lorenzo Alonso Gomez	Ad Hoc Chiroptical Systems through Synthesis
15:30 – 16:30	Solmar Varela	The Chiral-Induced Spin Selectivity Effect and the Chiro-Optical Activity of a Helix
16:30 – 17:00	<i>COFFEE BREAK</i>	
17:00 – 18:00	Mayra Peralta	Electron and Spin-phonon Interaction in DNA: A Minimum Analytical Model
18:00 – 19:00	Tianhan Liu (ONLINE)	Control of Chirality, Spin, and Orbital in Chiral Molecular Semiconductor Junctions
19:00 – 20:30	<i>DINNER</i>	
20:30	Poster Flash Presentation	

Program (CET)

Tuesday, 06 December 2022

07:30	<i>BREAKFAST</i>	
08:30 - 09:30	David Waldeck	CISS and Electrocatalysis
09:30 - 10:30	Narcis Avarvari	CISS Effect with Helicene and Tetrathiafulvalene Derivatives
10:30 - 11:00	<i>COFFEE BREAK</i>	
11:00 - 12:00	Ora Entin-Wohlman	Spin-orbit Active Weak Links
12:00 - 13:00	Hiroshi Yamamoto	Symmetry Considerations on the CISS Effect
13:00 - 14:30	<i>LUNCH BREAK</i>	
14:30 - 15:30	Binghai Yan	Spin Polarizer, Electric Magneto-Chiral Anisotropy, and Higher-order Magnetoresistance in CISS
15:30 - 16:30	Per Hedegård	CISS and Equilibrium Spin Currents
16:30 - 17:00	<i>COFFEE BREAK</i>	
17:00 - 19:00	Poster Session	
19:00	<i>DINNER</i>	

Program (CET)

Wednesday, 07 December 2022

07:30	<i>BREAKFAST</i>	
08:30 – 09:30	Magalí Lingenfelder	Chiral Molecular Layers: A New Twist for Clean Energy
09:30 – 10:30	Amparo Ruiz Carretero	The CISS Effect in Next Generation Organic Photovoltaics
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 12:00	Jean-Philippe Ansermet	Magnetic Resonance Characterization of the CISS Effect
12:00 – 13:00	Giovanni Cuniberti	Model- and First-principle Based Investigations of Chiral Molecules and the CISS Effect
13:00 – 13:15	Stefan Jorda (ONLINE)	About the Wilhelm and Else Heraeus Foundation
13:15 – 14:30	<i>LUNCH BREAK</i>	
14:30	Excursion	
18:30	<i>HERAEUS DINNER</i> at the Physikzentrum (cold & warm buffet, with complimentary drinks)	

Program (CET)

Thursday, 08 December 2022

07:30	<i>BREAKFAST</i>	
08:30 – 09:30	Yossi Paltiel	Chiral Spintronics
09:30 – 10:30	Clarice Aiello	From Nanotech to Living Sensors: Unraveling the Spin Physics of Biosensing at the Nanoscale
10:30 – 11:00	<i>COFFEE BREAK</i>	
11:00 – 12:00	Best Poster Prizes	
12:00 – 13:00	Concluding Remarks	
13:00	<i>LUNCH</i>	

End of Seminar / Departure

Posters

Poster Session: Tuesday, 06 December, 17:00 h (CET)

- 1 Alexandre Abhervé Chiral Halide Perovskite Materials for Optoelectronic and Spintronic Devices
- 2 Seif Alwan „Spinterface“ Origin for the CISS Effect – From Low Temperature Effect to the Thermo-electric CISS Effect
- 3 Gregory Amato Chirality Induced Spin Selectivity in Contact Electrification
- 4 Neeraj Bangruwa CISS-based Label-free Novel Electrochemical Impedimetric Detection of UVC-Induced DNA Damage
- 5 Prashant Kumar Bhartiya Chiral-induced Enhanced Electrocatalytic Behaviour of Cysteine (Chiral) Coated Bifunctional Au/Ni Bilayer Thin Film Device for Water Splitting Application
- 6 Jorge Cardenas-Gamboa Study of Electron Transport in a DNA Model
- 7 Tapan Kumar Das The New Functionalities of Spintronic Device and Spin Selective Electron Transfer
- 8 Niccolò Giaconi High Spin Selective Electron Transport of Thia[4]helicene Radical Cations Monolayer Chemisorbed on Surface
- 9 Kars Huisman Current-Voltage Characteristics of Coulomb Interactions
- 10 Sebastian Kalhöfer Green-Function-Approach to explain Chirality-dependent Helix-Metal-Binding-Energies
- 11 Fabian Kammerbauer Tuning Skyrmion Diffusion by Adhesion of Chiral Molecules

Poster Session: Tuesday, 06 December, 17:00 h (CET)

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| 12 | Alessandro Lodesani | Investigating Quantum Electron Transport Through Chiral Molecules at the Single Spin Level |
| 13 | Emilio Macaluso | Detecting Chiral-Induced Spin Selectivity in Electron-Transfer Processes Using Time-Resolved EPR: From Theory to Experiments |
| 14 | Shinji Miwa | Effective Magnetic Field from Chiral Phthalocyanine due to Thermally Driven Spin Polarization |
| 15 | Paul Valerian Möllers | Chirality-Induced Electron Spin Polarization in Chiral CuO and CoO _x Catalyst Surfaces |
| 16 | Shuichi Murakami | Theory of Kinetic Magnetoelectric Effect in Chiral Metals and Topological Insulators |
| 17 | Alberto Privitera | Spectroscopic Detection of Spin Polarisation in Photoinduced Charge Transfer through a Chiral Bridge |
| 18 | Shammi Rana | STM: A Tool to Probe the CISS Effect in Self-assembled Molecular Networks? |
| 19 | Lokesh Rasabathina | Control of Magneto-optical Properties of Cobalt-layers by Adsorption of α -helical Polyalanine Self-assembled Monolayers |
| 20 | Massimiliano Remigio | Synthesis and Chiral Resolution of [2.2]Paracyclophane Derivatives on Graphite: Self-assembled Molecular Networks of a 3D Molecular Nanostructure |
| 21 | Rebecca Rodrigues de Miranda | Functionalised Spin Crossover Complexes for Exploring Chirality-based Effects in Thin Films |

Poster Session: Tuesday, 06 December, 17:00 h (CET)

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|----|----------------------|---|
| 22 | Reza Mohammad Safari | Enantiospecific Adsorption on a Ferromagnetic Surface at the Single-molecule Scale |
| 23 | Aida Saghatchi | Transfer of Spin-Orbit Coupling of Molecule-Metal Interfaces |
| 24 | Mahroo Shiranzaei | Intrinsic Contribution of Spin-orbit Coupling in Phonon-assisted Magnetization |
| 25 | Christoph Tegenkamp | Studying the CISS Effect on the Molecular Scale with Non-spin-polarized STM |
| 26 | Pius Theiler | Kelvin Probe Force Microscopy on Chiral Single Crystals |
| 27 | Sytze Tirion | Detection of the CISS Effect in the Linear and Non-linear Regime as a Two- and Four-terminal Magnetoresistance Measured in Spin Valve Devices |
| 28 | Adrian Urban | Metalloporphyrins Open Up Towards Enantioseparable and Fully sp^2 -hybridized Helical Complexes |
| 29 | Clemens Vittmann | Spin-Dependent Momentum Conservation of Electron-Phonon Scattering in Chirality-Induced Spin Selectivity |
| 30 | Laura Alicia Völker | The Importance of Dipolar Decoupling for Detecting Chiral-Induced Spin Selectivity in Radical-Pairs with NV Centres in Diamond |
| 31 | Artem Volosniev | Dissipative Dynamics of an Impurity with Spin-Orbit Coupling |

Abstracts of Lectures

(in alphabetical order)

**From nanotech to living sensors:
unraveling the spin physics of biosensing at the nanoscale**

Substantial *in vitro* and physiological experimental results suggest that similar coherent spin physics might underlie phenomena as varied as the biosensing of magnetic fields in animal navigation and the magnetosensitivity of metabolic reactions related to oxidative stress in cells. If this is correct, organisms might behave, for a short time, as “living quantum sensors” and might be studied and controlled using quantum sensing techniques developed for technological sensors. I will outline our approach towards performing coherent quantum measurements and control on proteins, cells and organisms in order to understand how they interact with their environment, and how physiology is regulated by such interactions. Can coherent spin physics be established – or refuted! – to account for physiologically relevant biosensing phenomena, and be manipulated to technological and therapeutic advantage?

Bio

Prof. Clarice D. Aiello is a quantum engineer interested in how quantum physics informs biology at the nanoscale. She is an expert on nanosensors harnessing room-temperature quantum effects in noisy environments. Aiello received her Ph.D. from MIT in Electrical Engineering and held postdoctoral appointments in Bioengineering at Stanford, and in Chemistry at Berkeley. She joined UCLA in 2019, where she leads the Quantum Biology Tech (QuBiT) Lab.

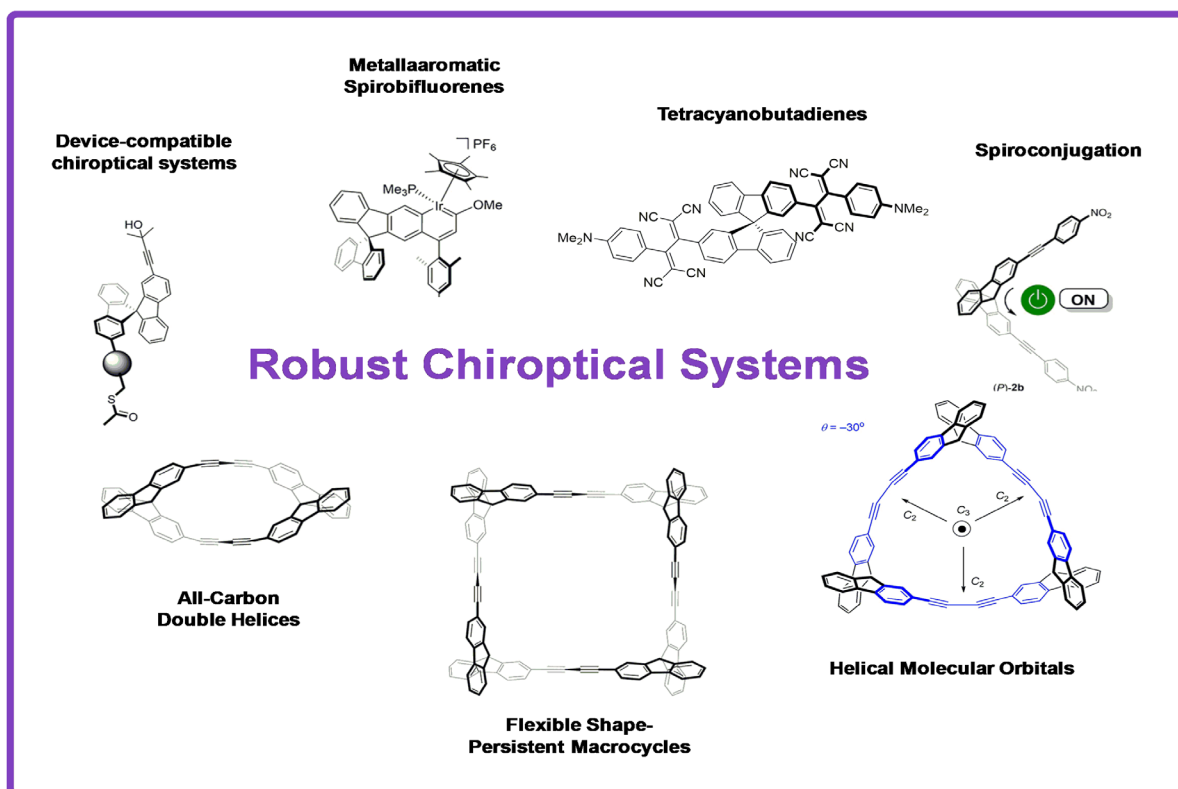


Ad Hoc Chiroptical Systems through Synthesis

Ani Ozcelik,¹ R. Pereira-Cameselle,¹ Stefano Chiussi,¹ Ángeles Peña-Gallego,¹ and J. Lorenzo Alonso-Gómez¹

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The development of chiroptical sensing, imaging, catalysis or spin filtering applications among other needs the use of systems with specific requirements. With the aim of contributing to this field, we have used spirobifluorenes for the synthesis of robust chiroptical systems of very distinct nature: device compatible systems for surface functionalization, metallaaromatic and tetracyano[1] derivatives with absorption in the near infrared region of the spectra, or macrocycles with different ring strain providing all-carbon double helices, flexible shape-persistent macrocycles or even systems presenting helical molecular orbitals.[2] These synthetic possibilities along with the understanding of the mechanisms originating the chiroptical responses represent a toolbox for the development of chiroptical systems *ad hoc*.



References

- [1] A. Ozcelik, Á. Peña-Gallego, R. Pereira-Cameselle, J. L. Alonso-Gómez, *Eur. J. Org. Chem.* e202101333 (2022)
- [2] A. Ozcelik, D. Aranda, S. Gil-Guerrero, X. A. Pola-Otero, M. Talavera, L. Wang, S. Kumar Behera, J. Gierschner, Á. Peña-Gallego, F. Santoro, R. Pereira-Cameselle, J. L. Alonso-Gómez, *Chem. Eur. J.*, **26**, 17342 (2020)

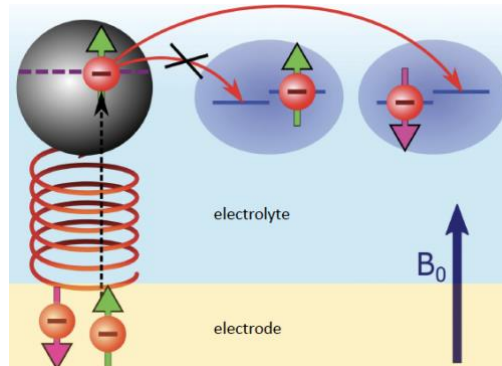
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Magnetic resonance characterization of the CISS effect

In the past 30 years, Ansermet has worked on spintronics and several magnetic resonance techniques, including dynamic nuclear polarization (DNP). These two lines of research merged when doing electrically-detected magnetic resonance (EDMR). For example, he detected the ferromagnetic resonance of just 100'000 Bohr magnetons in a spin valve [1]. That experiment combined giant magnetoresistance and spin torque effects. Another example was the conductance change of an organic light emitting diode (OLED) when the electron spin resonance was excited [2].

The EDMR strategy was used to verify that chiral biomolecules attached to an electrode act as spin filters. The experiment consisted in exciting the spin resonance of free radicals in the electrolyte and detecting the change of the reduction current at resonance (see cartoon). Quantitative analysis of the spin polarization of electrons transiting through the biomolecule was consistent with photoemission data obtained in UHV conditions with the same molecules.

CISS could potentially offer a breakthrough in electrochemical DNP applications. A preliminary result was the NMR signal enhancement produced in an electrolyte in which free radicals were produced or quenched at will via a redox process on an electrode [4].



[1] N. Bizière, E. Murè, J-Ph. Ansermet, Current-driven, electrically detected ferromagnetic resonance in electrodeposited spin valves, *J. Mag. Mag. Mat.* 322(9-12) 1357-1359 (2010)

[2] F. Comandè, J-Ph. Ansermet, Time-resolved spin processes in Alq(3) light-emitting diodes, *Phys. Rev. B* 90(20), 201201(R) (2014)

[3] F. Blumenschein, M. Tamski, C. Roussel, E.Z.B. Smolinsky, F. Tassinari, R. Naaman, J-Ph. Ansermet, *Spin-dependent charge transfer at chiral electrodes probed by magnetic resonance*, *Phys. Chem. Chem. Phys.* 22(3), 997-1002 (2020)

[4] F. Saenz; M. Tamski, *Blatter-type radicals as polarizing agents for electrochemical overhauser dynamic nuclear polarization*, J. Milani; C. Roussel, H. Frauenrath, J-Ph Ansermet, *Chemical Communications*, 58 (5), 689-692 (2022)

CISS effect with helicene and tetrathiafulvalene derivatives

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A sustainable future requires highly efficient energy conversion and storage processes, where electrocatalysis plays a crucial role. The activity of an electrocatalyst is governed by the binding energy towards the reaction intermediates, while the scaling relationships prevent the improvement of a catalytic system over its volcano-plot limits. To overcome these limitations, unconventional methods that are not fully determined by the surface binding energy can be helpful. In this respect, thiadiazole-[7]helicene and bis(thiadiazole)-[8]helicene have been used to boost the oxygen evolution reaction (OER) by up to ca. 130 % (at the potential of 1.65 V vs. RHE) at state-of-the-art 2D Ni- and NiFe-based catalysts *via* the CISS effect (Nat. Commun. 2022, 13, 3356). Our results show that the chirality of the helicene molecules is accountable for a great enhancement in the activity of state-of-the-art OER catalysts. The enhancement is related to the electron spin polarization at the catalyst surface. The comparison of different electrode configurations provides a clear guideline for optimizing the enhancement. In this contribution we will discuss as well evidences for the occurrence of the CISS effect in chiral tetrathiafulvalenes (TTF).

Model- and first-principle based investigations of chiral molecules and the CISS effect

M. Geyer,¹ A. Dianat,¹ R. Gutierrez,¹ V. Mujica,^{2,3} G. Cuniberti^{1,4}

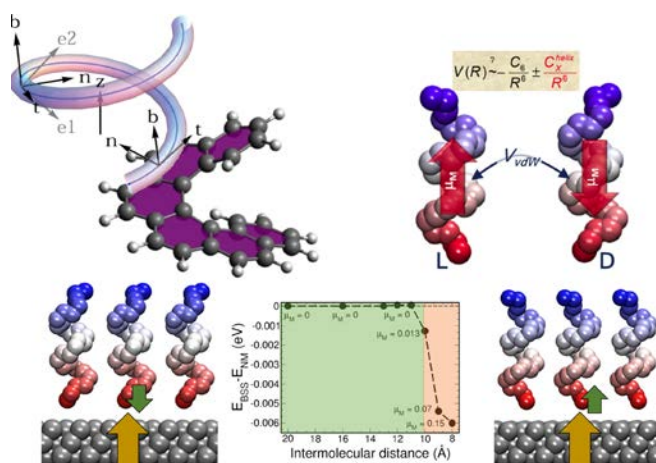
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Chirality-induced spin selectivity (CISS) was discovered nearly 10 years ago, but so far, its precise microscopic origin has not been fully elucidated. In this presentation, we will provide an overview of our most recent activities in the field. First we will discuss, relying on a previous model by K. Michaeli and R. Naaman [1], an effective



1D model derived as the limit of a 3D quantum system with strong confinement and including spin-orbit coupling (SOC) [2]. We use adiabatic perturbation theory to provide a mathematically sound procedure applicable to a large class of spin-dependent continuum models and compute the corresponding spin polarization in the model. In the second part of the presentation, two issues will be addressed: a)

experimental studies have clearly revealed that electronic exchange interactions play a key role in the magnetic response of chiral molecules. We have used spin-polarized density functional theory calculations to address the influence of exchange contributions to the interaction of helical molecules in periodic arrays as well as of helical molecules with magnetized substrates [3]. We show that exchange interactions result in differences in the interaction properties with magnetized surfaces, shedding light into the possible origin of two recent important experimental results: enantiomer separation and magnetic exchange force microscopy with AFM tips functionalized with helical peptides; b) A recent proposal to describe the mutual induction of charge and spin-density fluctuations in a pair of chiral molecules leading to intermolecular SOC. Within second-order perturbation theory these contributions manifest as an effective intermolecular exchange interaction scaling as R^{-6} with the intermolecular separation, similar to the London dispersion interactions [4].

References

- [1] K. Michaeli and R. Naaman, J. Phys. Chem. C **123**, 17043 (2019)
- [2] M. Geyer, R. Gutierrez, G. Cuniberti, J. Chem. Phys. **152**, 214105 (2020)
- [3] M. Geyer, R. Gutierrez, V. Mujica, J. F. Rivas Silva, A. Dianat, G. Cuniberti, J. Chem. Phys. **156**, 234106 (2022)
- [4] A. Dianat, R. Gutierrez, H. Alpern, V. Mujica, A. Ziv, S. Yochelis, O. Millo, Y. Paltiel, G. Cuniberti, Nano Letters **20**, 7077 (2020)

The “Spinterface” model for the CISS effect – connecting theory and experiment

S. Alwan¹ and Y. Dubi¹

¹*Department of Chemistry, Ben Gurion University, Beer-Sheva, Israel*

The “spinterface” model for the chirality-induced spin-selectivity (CISS) effect [1] is a model which can explain the CISS effect to great detail with no need for unrealistic parameter renormalization, fit experimental (raw) data, and provide reliable and testable predictions. We show several examples for this, including old [2] and new [3,4] experimental data. We also show a generalization of the “spinterface” model for the CISS effect in photo-emission experiments, and provide new predictions for these experiments.

References

- [1] S. Alwan & Y. Dubi, Spinterface Origin for the Chirality-Induced Spin-Selectivity Effect, *J. Am. Chem. Soc.* **2021**, 143, 35, 14235.
- [2] Y. Dubi, Spinterface chirality-induced spin selectivity effect in bio-molecules, *Chemical Science* **2022** (just accepted).
- [3] C. Yang, Y. Li, S. Zhou, Y. Guo, C. Jia, Z. Liu, K. N. Houk, Y. Dubi & X. Guo, Stereochemistry identified by single-molecule chirality-induced spin selectivity, **2022** *in press*.
- [4] Q. Qian *et al.*, *Chiral molecular intercalation superlattices*, *Nature* **2022**, 606, 902=908.

Spin-orbit active weak links

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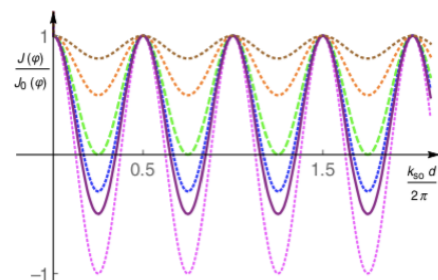
The spin-orbit interaction, which allows for an interplay between charge and spin currents in all-electrical devices, substantially alters the transport properties of semiconductors. This interaction affects even more dramatically transport in ballistic one-dimensional conductors, where an additional spin-dependent phase, termed “Aharonov-Casher phase” [1] is accumulated by propagating electrons. This Aharonov-Casher phase gives rise to quite a number of new spintronic functionalities in devices formed by weak links bridging bulk conductors in configurations, where spin-orbit interaction is active solely in the weak link [2]. They are particularly striking in quantum networks built of spin-orbit active weak links where the Aharonov-Casher phase dominates the interference of the electronic spinors.

In this talk several aspects that can be realized in spin-active weak links are described: Magnetoconductance anisotropy (with respect to the direction of the magnetic field) of a single weak link where the spin-orbit coupling is controlled by an external electric field. We show that such a device allows for a direct detection of the Aharonov-Casher phase, and does not require observing interference patterns [2]; Spin-orbit induced splitting of Cooper pairs [3]. We show that in the Coulomb-blockade regime of single-electron tunneling, a weak link acts as a “spin splitter” of the spin states of Cooper pairs tunneling through the link. The Josephson current is sensitive to the Aharonov-Casher phase, resulting in a periodic function of the strength of the spin-orbit interaction (see Figure); Spin selectivity through time-reversal symmetric helical junction [4].

References

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- [2] R. I. Shekhter, O. Entin-Wohlman, M. Jonson, and A. Aharony, Magnetoconductance Anisotropies and Aharonov-Casher Phases, [Phys. Rev. Lett. 129, 037704 \(2022\)](#).
- [3] R. I. Shekhter, O. Entin-Wohlman, M. Jonson, and A. Aharony, Rashba splitting of Cooper pairs, [Phys. Rev. Lett.116, 217001 \(2016\)](#).
- [4] U. Utsumi, O. Entin-Wohlman, and A. Aharony, Spin selectivity through time-reversal symmetric helical junction, [Phys. Rev. B 102.035445 \(2020\)](#).

Figure 1: The Josephson current $J(\varphi)$ divided by its value without the SO interaction, $J_0(\varphi)$, for the genuine Rashba configuration, as a function of $k_{so}d=/(2\pi)$. The largest amplitude is for the zero bending angle, $\theta = 0$, decreasing gradually for $\theta = \pi/6, \pi/5, \pi/4, \pi/3, \pi/2.5$.



CISS and equilibrium spin currents

Per Hedegård

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Abstract

Understanding the CISS effect has proven difficult. The main obstacles are the smallness of the spin-orbit coupling in most organic molecules, and the constraints imposed by the Onsager reciprocity principle, which is a consequence of time reversal invariance of the basic Hamiltonian (including the transformation of an external magnetic field and/or a magnetization somewhere in the system). This rules out explanations of CISS relying on vibrational degrees of freedom. Strictly speaking, the Onsager principle, only has consequences to linear order in a field driving the system out of equilibrium. It is now established experimentally, that CISS is *not* obeying the Onsager principle. In the present work, a way out of this conundrum is presented. In the class of experiments, where a magnetized leads are present, there can exist equilibrium spin currents, which will alter the steady state magnetizations of the system, and hence explain the observed magnetoresistance observed in many CISS experiments.

Chiral molecular layers: a new twist for clean energy

Y. Liang¹, Priscila Vensaus¹, Martina Lihter¹ and M. Lingenfelder¹

¹Max Planck-EPFL Lab for Molecular Nanoscience and IPHYS, EPFL, CH 1015, Lausanne, Switzerland.

A pressing challenge of our modern society is the transition from a carbon-energy dependent economy towards renewable energy schemes. The development of efficient catalysts, that could either convert chemical energy into electricity or use electrons to produce chemical energy, is a key milestone in our path to clean energy (Figure 1). In general, electrocatalysis studies focus on the interactions (e.g., electron transfer) between the catalyst surface and the reaction intermediates. However, the role of electron spin has commonly been overlooked. In this talk, I will show you how using chiral self-assembled monolayers we can enhance and tune the activity and product selectivity at state-of-the-art 2D catalysts via chiral-induced spin selectivity (CISS) effects. This approach opens new directions for the design of efficient hybrid catalysts to power the transition towards clean energy [1-2].

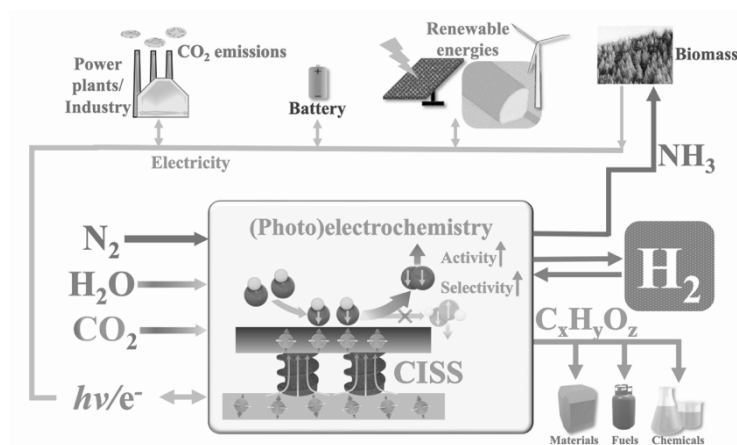


Figure 1. The potential use of chiral induced spin selectivity effects (CISS) to enhance activity and selectivity of (photo)electrodes used in energy conversion of small molecules.

References

- [1] Liang Y, Banjac K, Martin K, Zigon N, Lee S, Vanthuyne N, Xile Hu, Narcis Avarvaris, and Magali Lingenfelder. *Nature Communications*, **13**, Article number: 3356 (2022).
- [2] Liang Y, Lihter M, Lingenfelder M. Spin-control in electrocatalysis for clean energy. *Review, Israel Journal of Chemistry*, Early View e202200052 (2022).

Control of Chirality, Spin, and Orbital in Chiral Molecular Semiconductor Junctions

Tianhan Liu^{1,2}, Yuwaraj Adhikari², Hailong Wang³, Binghai Yan⁴,
Vladimiro Mujica⁵, Jianhua Zhao³, Peng Xiong², Paul Weiss¹

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³ State Key Laboratory of Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, China

⁴ Department of Condensed Matter Physics, Weizmann Institute of Science, Rehovot, Israel

⁵ School of Molecular Sciences, Arizona State University, Tempe, AZ

Chirality-induced spin selectivity (CISS) is an effect in which structural chirality engenders spin polarization in the electrical current from a nonmagnetic electrode. This phenomenon has profound fundamental implications on the intricate interplay between structural chirality, electron motion, and spin polarization. The spin-valve effect and the Hanle effect are two main electrical approaches to study spin transport in molecular junctions.

First, we fabricated junctions of (Ga,Mn)As/alpha-helix polyanilines (AHPA-L)/Au [1]. We quantitatively analyzed the spin-valve effect by measuring the magnetoconductance. The use of a ferromagnetic semiconductor facilitated a reliable examination of its bias dependences. The experiment provided definitive evidence for a nontrivial linear-response component in the spin-valve effect. We further resolved the fundamental mechanism how chiral geometry influences the electronic spin, by unambiguously identifying the origin of necessary spin-orbit coupling (SOC). We compared the Au and Al electrodes and found qualitative differences, demonstrating the essential role of electrode SOC [2].

Next, the Hanle effect was examined in junctions of GaAs/AHPA-L/Au. Our results showed the suppression of spin accumulation by a transverse magnetic field, which has presented a scheme of semiconductor spintronics free of any magnetic materials. More recently, we have taken an interdisciplinary approach to study the fundamental principles and device applications of CISS. We take advantage of magnetic substrates with perpendicular magnetic anisotropy and study the spin-dependent electron transport by electrochemistry. In addition to DNA and peptides, we plan to fabricate devices with twisted van der Waals materials and measure the possible magnetism generated from such inorganic chiral heterostructures.

References

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Field-Mediated Chirality Information Transfer and Dispersion Intermolecular Forces.

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Abstract: Chirality transfer is a well-known phenomenon in molecular structures and interfaces, where chirality is inherited in supramolecular structures from chiral motives that intervene in the overall structure or interface. Less known is the fact that a chiral-like Raman response can be observed in an otherwise achiral molecule adsorbed on a plasmonic nanoparticle, due to the interaction of an electromagnetic field with a chiral molecule adsorbed on the same nanoparticle, and located tens of nanometers apart, hence preventing direct chemical interactions from being responsible of this phenomenon. The underlying physical mechanism is related to chirality-induced space inversion symmetry breaking, which couples the electric and magnetic molecular susceptibilities. The outgoing propagating field carries information about the

molecular chirality in its circularly polarized components, which become different in magnitude due to the interaction with the chiral molecule.

In a different direction, intermolecular London dispersion forces, responsible for van der Waals interactions, are due to induced-electric dipole induced-electric dipole interaction, and they can also be affected by chirality in an unexpected way that provides a path for chiral discrimination, which plays a fundamental role in molecular recognition of bio-molecules.

In this contribution, we will explore the parallelism between these two different phenomena, whose analysis can lead to a unified description of the Chiral-Induced Spin Selectivity (CISS) effect and molecular chiro-optical properties, a theoretical problem we are currently exploring.

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Why is it difficult to understand the mechanism of the CISS effect?

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The CISS effect presents a challenge to our understanding of conduction through molecules and to its spin dependent. It was found that it relates to the optical activity of the molecule and in many cases it is temperature activated. It will be shown that explaining the effect requires the breaking of the Born Oppenheimer and the single electron approximations. Experiments will be present as well as some models that point to a possible way to explain the effect.

Chiral spintronics

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Chiral spintronics technology has the potential to overcome the limitations of other magnetic-based memory technologies and to facilitate the fabrication of inexpensive, high-density memory and other spintronics elements [1]. Recently, by utilizing the CISS effect we demonstrated a simple magnetless spin based magnetic memory [2,3]. When chiral molecules are adsorbed on the surface of thin ferromagnetic film, they induce magnetization perpendicular to the surface, [4] on s wave superconductor a triplet is induced [5]. CISS effect based devices were scaled down to the 30nm size replacing the continuous ferromagnetic layer with magnetic nano platelets [6,7]. Atomic layer deposition of Chiral oxides can supply 99% spin polarization [8]. In my talk I will present the latest chiral spintronics results and discuss what are the critical missing steps towards applications.

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Electron and spin-phonon interaction in DNA: A minimum analytical model

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We analyze the influence of electron-phonon and spin-phonon interaction in a model for electron transfer (ET) processes in DNA in terms of the envelope function approach. We are specifically concerned with the effect of these interactions on the coherence of the ET process and how to model the interaction of DNA with phonon reservoirs of biological relevance. We assume that the electron bearing orbitals are half filled and derive the physics of the electron-phonon and spin-phonon coupling in the vicinity in reciprocal space. In a first model for spinless electrons We find that at half filling, the acoustical modes are decoupled to ET at first order, while optical modes are predominant [1]. The latter are associated with inter-strand vibrational modes in consistency with previous studies involving polaron models of ET [2]. Coupling to acoustic modes depends on electron doping of DNA, while optical modes are always coupled within our model. When the spin is included, through the Spin-orbit coupling whose intensity is geometry dependent, we find that acoustical phonons become coupled independently of the doping, as in the case of optical phonons.

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The CISS effect in next generation organic photovoltaics

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One of the main challenges of our generation is securing the global energy supply while fighting global warming. In this sense, solar energy is a great alternative since several materials can convert sun light into electricity. Despite the high efficiency of silicon panels, our unstoppable energy consumption demands additional alternative materials. Particularly, organic materials are the most versatile choice since it is possible to control the materials' properties by molecular design. Our goal is contributing to these efforts by importing supramolecular chemistry strategies into the organic electronics field. More specifically, we explore the role of chiral supramolecular assemblies in charge transport processes following the recently reported Chiral Induced Spin Selectivity (CISS) effect. It states that electrons of certain spin can go through chiral assemblies of preferentially in one direction depending on their handedness. This strategy has great potential to reduce charge recombination, since charge carriers, which are spin-containing species, could have directionality through chiral assemblies (Figure 1). For this purpose, we couple chiral substituents to electroactive segments, containing hydrogen-bonding (H-bonding) motifs to form chiral supramolecular π -conjugated assemblies,² and follow charge and spin transport using electrodeless techniques.³ We expect to screen the best chiral supramolecular structures and show the potential of chiral materials in organic photovoltaics.

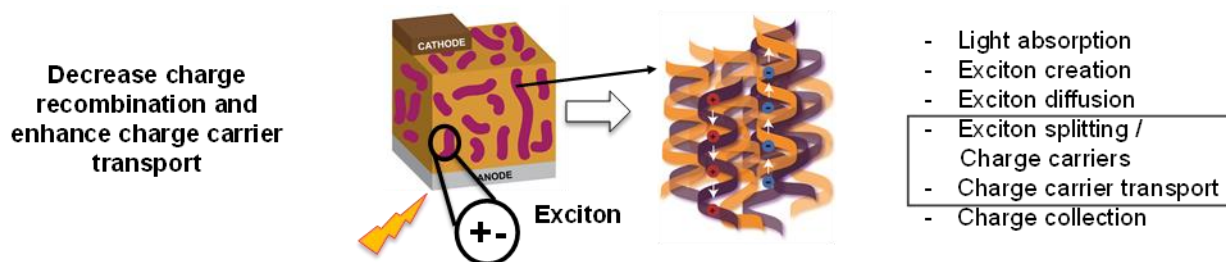


Figure 1. Illustration of the main objective for the presentation

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The Chiral-Induced Spin Selectivity Effect and the Chiro-Optical Activity of a Helix

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We have obtained a connection between the chiro-optical activity and the spin-orbit interaction for a model system of an electron constrained to a helix, taking explicitly spin into account, in the presence of an electromagnetic field as a perturbation. Because of the chiral nature of the system, spatial inversion symmetry is broken, which in turn induces a connection between the electric and the magnetic responses of the system to the external electromagnetic field, that is absent in achiral systems. Despite the apparent simplicity of the model, it contains most of the relevant physics involved in this problem, and we have established a relationship between the optical activity response, via the Rosenfeld's tensor and the spin polarization, defined as the average value of the Pauli spin-1/2 matrices. This relationship between the optical response and the CISS responses, can guide new efforts in the fields of reticular chemistry and material design for spintronics, and spin-selective chemistry.

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CISS and Electrocatalysis

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I will describe experimental studies that investigate the effects of electron spin in electron transfer and electron initiated chemical reactions at electrodes. First, I will discuss how charge polarization and charge transfer in chiral molecules and assemblies is accompanied by spin polarization and spin transfer, because of the chiral induced spin selectivity (CISS) effect. Then I will report on electrochemical and electrocatalysis studies which show how the CISS effect can be used to affect reaction mechanisms and can modulate electron transfer rates in chiral assemblies.

Symmetry considerations on the CISS effect

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Chirality-Induced Spin Selectivity (CISS) is attracting recent attention as a new source of spin polarized current. It also provides unique methods for enantio-separation [1], enantio-selective electrochemical reactions, and an efficient water oxidation. The mechanism of CISS effect is, however, yet to be clarified, as the effect is much larger than expected one estimated with small spin-orbit coupling for organic molecules. In a hypothetical consideration, it is proposed that an enhancement of spin polarization is associated with anti-parallel spin polarizations at two opposite ends of a chiral molecule created [1]. It is interesting to note that such an anti-parallel spin pair is time-reversal (T) odd state, while the chiral molecular structure is T -even. We think symmetry conversion from T -even to T -odd quantities gives an essential clue to understand CISS effect that can generate huge spin polarization in a non-equilibrium condition.

We have made such a symmetry consideration based on multipole basis and found that a T -odd chirality can emerge from an accumulation of spin current (= electrical toroidal monopole) at reservoirs [2]. The source of spin current may be an electron-molecular vibration coupling that can be described by pseudo Jahn-Teller effect [3]. In case of solids, the molecular vibration can be replaced by phonons, in which case the effect appears as spin polarizing one [4] rather than spin filtering one. In addition, we have shown that chiral organic superconductor can exhibit spin accumulation at two opposite crystal edges whose directions are anti-parallel to one another [5]. This can be regarded as a macroscopic-size emulation of chiral molecules that has T -odd spin accumulations at their opposite ends. A connection to falsely chiral influence [6] will be also discussed. This work has been done in collaboration with R. Nakajima, D. Hirobe, G. Kawaguchi, Y. Nabei, T. Sato, T. Narushima, H. Okamoto, A. Kato, J. Kishine, and Y. Kusunose.

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Spin polarizer, electric magneto-chiral anisotropy and higher-order magnetoresistance in CISS

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We propose that the chiral molecule plays a role of spin polarizer, instead of spin filter, in CISS, where the transmitted and reflected electrons exhibit the same spin polarization. If we perturbate the system where the chiral molecule connects the magnetic electrode by applying a bias, it generates electric Magneto-chiral anisotropy (EMCA) with a diode-like behavior that obeys the Onsager's reciprocal theorem, presenting a different symmetry from the CISS magnetoresistance. To violate the reciprocity, we propose that EMCA builds up a charge accumulation at the molecule – metal interface as a nonequilibrium state. The extra charge accumulation, which depends on signs of magnetization and chirality, modifies the tunneling potential barrier through the chiral molecule and thus generate the CISS magnetoresistance as a higher-order effect. We predict strategies to examine our theory in experiments.

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Chirality induced spin selectivity:

The photoelectron view

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This talk describes the manifestation of the chirality-induced spin selectivity (CISS) effect by photoelectron spectroscopy experiments with direct spin analysis. Various systems, from initially investigated monolayers of molecular biosystems and organic hepta-helicene, to recent chirally grown solid oxide films are evaluated. On selected systems the spin orientation of free electrons and magnetotransport and spin-resolved voltammetry is compared. High spin polarization up to $P = 60\%$ have been observed for samples at room temperature. For all classes it was shown that the longitudinal spin orientation changes sign with a change of the enantiomeric form. Recent advances allow to distinguish the contributions of electrons with different kinetic energies to the electron spin polarization, and thus to distinguish the CISS effect from bulk contributions to the spin originating from different mechanisms.

Abstracts of Posters

(in alphabetical order)

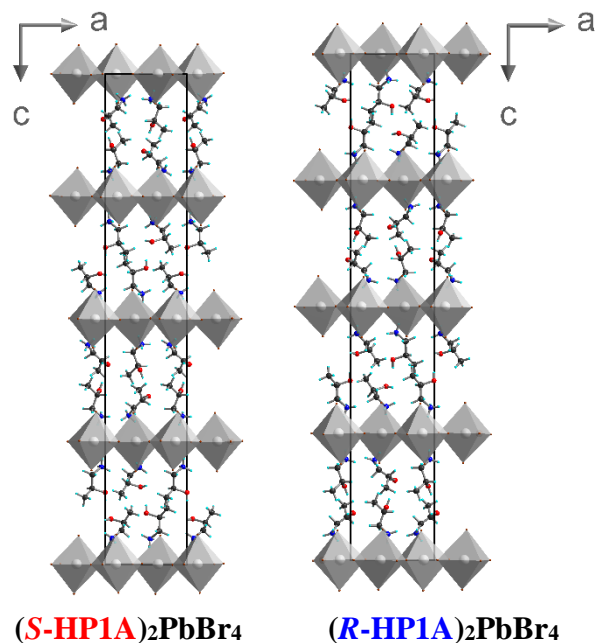
Chiral Halide Perovskite Materials for Optoelectronic and Spintronic Devices

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Chiral Halide Perovskites (HPs) bring new perspectives for chiroptical applications, such as circularly polarized luminescence (CPL), and spintronic applications.¹ By combining the optoelectronic properties of HP networks with chirality transfer from inserted organic cations, we aim to reveal the potential of chiral HP materials for CPL and chiro-spintronics. Therefore, we prepared a series of chiral lead-bromide networks starting from enantiopure and racemic forms of 1-hydroxypropyl-2-ammonium (HP2A) and 2-hydroxypropyl-1-ammonium (HP1A) cations. CD and SHG-active 1D networks of formula (S/R-HP2A)₃PbBr₅ and luminescent 2D (S/R-HP1A)₂PbBr₄ have been structurally characterized and the chirality-induced spin selectivity (CISS) effect has been investigated.



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“Spinterface” Origin for the CISS Effect – from low temperature effect to the thermo-electric CISS effect

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The effect of spin filtering in electrons passing through a helical chiral molecule (dubbed the chirality-induced spin selectivity (CISS) effect) has been suggested to emerge from the interplay between the spin-orbit interactions and the helicity of the molecule. However, the main premise of such theories requires unreasonably large spin-orbit interaction strength not typically found in the organic molecules most prevalent in the experiments. Therefore, the origin of the CISS effect is yet to be determined and has been hailed as an outstanding problem in the field of molecular electronics. Here we present a generalized model which explains the origin of the CISS effect based on the interplay of the spin-orbit interaction of the electrode (which is mostly Au or Ag, although this theory is not limited to the use of these metals) with the chirality of the molecule. We argue that the initial field generated by the chiral helical structure, which is a classical solenoidal field, allows for a drift in the magnetic moment of the surface states of the electrode in the direction of the molecular axis resulting in a spin-transfer torque at the electrode-molecule interface. We demonstrate how this “spinterface” mechanism can explain recent experiments in intercalated chiral molecules [3,4], and demonstrate how thermopower experiments of the CISS effect can serve as a “smoking gun” to differentiate this mechanism over other suggested mechanisms.

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Chirality Induced Spin Selectivity in Contact Electrification

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Contact electrification, also known as triboelectrification, is a phenomenon by which electric charges move between dissimilar materials upon contact.¹ Contact electrification for spin-selective electron transfer has only recently been explored in ferrimagnetic materials.² Another method for spin-selective electron transfer relies on the use of chiral molecules through the chirality induced spin selectivity (CISS) effect.³ Herein, we have designed and built a triboelectric nanogenerator (TENG) to investigate the CISS effect during contact electrification. To this end, we demonstrate a contact separation TENG device that generates a stable electrical output, where we have monitored the voltage and current under various spin filter conditions. Specifically, we have prepared ferromagnetic Ni-coated substrates functionalized with chiral hybrid organic–inorganic perovskites (HOIPs; (R-MBA)₂CuCl₄ and (S-MBA)₂CuCl₄).⁴ Given their high spin polarization,⁴ facile synthesis and ease of thin film preparation by spin coating, we present preliminary results of their use in a TENG coupled with a Kapton surface to investigate the CISS effect under the influence of a permanent magnet.

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CISS-based Label-free Novel Electrochemical Impedimetric Detection of UVC-Induced DNA Damage.

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In this work, we demonstrate chiral-induced spin selectivity (CISS)-based label-free electrochemical impedimetric detection of radiation-induced DNA damage using electrons' spin as a novel tool of sensing. For this, self-assembled monolayers (SAMs) of short ds-DNA (of length 7.14 nm) are prepared on arrays of multilayer thin film devices comprising of gold overlayer (500 μ m diameter with 10nm thickness) on nickel thin film (100 nm) fabricated by the physical vapour deposition technique. Subsequently, SAMs of ds-DNA is exposed to ultra-violet C (UVC) radiation for a prolonged period of 8h to induce structural perturbations in DNA. The susceptibility of DNA to the radiation-induced damage was probed by recording the spin-dependent electrochemical impedimetric spectra, wherein a continuous sinusoidal wave of the amplitude of 10 mV was superimposed on DC bias in the frequency range of 10⁰ Hz-10⁵ Hz, with simultaneous spin injection through the attached DNA. The inherent correlation between the charge transfer resistance (R_{ct}) and the spin selectivity of electrons through DNA was taken into account for the detection of DNA damage for the first time with a limit of detection achieved up to 10 picomolar concentrations of DNA. As the spin-polarized electrons directly probe the structural symmetry, it is robust against perturbation from electronic signals usually found in conventional electrochemical biosensors.

Chiral-induced enhanced electrocatalytic behaviour of cysteine coated bifunctional Au/Ni bilayer thin film device for water splitting application

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We prepare an organic chiral molecule modified Au/Ni bilayer thin film electrode to examine the chiral induced spin selectivity (CISS) effect on water splitting. Electrodes with bilayer configuration consisting of thin Ni layer (100 nm) with an Au over layer (10 nm) are prepared on glass substrates by combined sputtering, thermal evaporation techniques. Subsequently, self-assembled monolayer of chiral L-Cysteine molecule is immobilized on the as-prepared Ni/Au surface by chemisorption method. The electrocatalytic behaviour of as-modified chiral electrodes (Ni/Au/L-Cys) has been investigated in 0.1 M KOH solution. Our results show that for achieving the current density of 5 mAcm⁻². The reaction over potential decreases by 390mV while 5-fold increase in the current density value is achieved at a fixed over potential with chiral Ni/Au/L-Cys thin film compared to the achiral (bare) bilayer Ni/Au thin film during oxygen evolution reaction (OER). The dramatic reduction of over potential for OER has been attributed to the spin specific reaction occurring at the chiral Ni/Au/L-Cys electrodes during water splitting. On the other hand, we observe that there is a decrease of 260 mV over potential with more than 11-fold increase in the absolute current density value (~153 mAcm⁻² at 0.6 V) for Ni/Au/L-Cys thin film than bare Ni/Au thin film in hydrogen evolution reaction (HER). The excellent bifunctional catalytic property of Ni/Au/L-Cys has been attributed to the synergistic effect of chirality and bilayer configuration present in the primary structure of cysteine molecule and Ni/Au thin films respectively.

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Study of Electron Transport in a DNA model

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In this work, we use the Landauer-Buttiker formula as implemented in the package KWANT (Python library) for studying quantum transport in a DNA molecule based in an analytical tight-binding Hamiltonian recently developed. In our simulation, we used a Hamiltonian considering a kinetic term, a term for intrinsic Spin-Orbit (SO) interaction related to the atomic SO coupling, and a Rashba interaction due to the electric dipoles associated with hydrogen bonds between the bases of the double strand of DNA and we tested the effect of magnetic and no-magnetic leads in the spin-selectivity of the molecule. We obtained that in our model, the spin-orbit coupling associated with the molecule can not be enough to explain the spin selectivity, however, in a system with presence of ferromagnetic leads, enhance the spin selectivity when it is included, which could explain the selectivity observed in similar experiments

Keywords: DNA, Spin selectivity, Intrinsic spin-orbit, Rashba interaction, Tight-binding model

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The new functionalities of spintronic device and spin selective electron transfer

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Chiral molecules and spin selective charge transport process provide a better performance and new functionalities to spintronic device. This was possible due to the mechanism of chiral induced spin selectivity (CISS) process. Here we describe recent experimental results on the CISS effect, which include the length dependent spin polarization and vibrational contribution to the spin orbit coupling.¹ We also developed a spin transistor using chiral metallo-bio-organic crystals.² The spin properties are monitored by Hall signal and by external magnetic field. The spin transistor exhibits nonlinear drain-source currents, with multilevel controlled states, generated by the magnetization of the source.

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High Spin Selective Electron Transport of Thia[4]helicene Radical Cations Monolayer Chemisorbed on Surface

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A key step in understanding CISS effect^[1] is the structuring of chiral molecules on surfaces. Recently, we investigated the deposition of an enantiopure helicene radical cations monolayer on gold via non-covalent interactions.^[2]

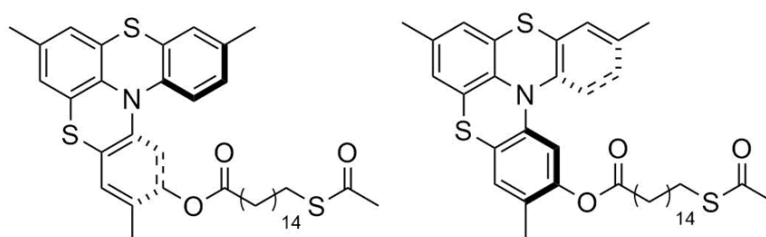


Figure 1. Molecular structures of (P)- and (M)- thioacetyl thia[4]hetero helicene.

Here, we describe the synthesis, the assembly, and spin selective conductivity studies of a novel thioacetyl derivative of a thia[4]heterohelicene (Figure 1) that is suited for direct chemisorption on an Au(111) surface. An in-depth characterization was performed to investigate the morphology (STM) and the chemical structure (XPS and XNCD) after the deposition process. A monolayer of the corresponding radical cation was assembled as well and characterized with EPR spectroscopy. Finally, a comparative investigation was carried out on both neutral and radical cations monolayers using magnetic conductive-Atomic Force Microscopy (mc-AFM) and assembling a multilayer molecular-based spintronic device for magnetoresistance measurements, studying the spin-filtering behavior induced by the occurrence of the CISS effect. High spin polarization values at room temperature were obtained in a surprisingly low applied voltage range; slight differences in spin selective conduction were observed employing paramagnetic species.^[3]

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CISS Effect: Current-Voltage Characteristics of Coulomb Interactions

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One of the manifestations of chirality-induced spin selectivity (CISS) is the appearance of a magnetocurrent. Magnetocurrent is the observation that the charge currents at finite bias in a two terminal device for opposite magnetizations of one of the leads differ [1-4]. Magnetocurrents can only occur in the presence of interactions, either of the electrons with vibrational modes or among themselves, through the Coulomb interaction. In experiments on chiral molecules assembled in monolayers the magnetocurrent seems to be dominantly cubic (odd) in bias voltage while theory finds a dominantly even bias voltage dependence [5,6]. Thus far, theoretical work has predicted a magnetocurrent which is even bias. Here we analyze the bias voltage dependence of the magnetocurrent numerically and analytically involving the spin-orbit and Coulomb interaction (through the Hartree-Fock and Hubbard One approximations). For both approximations it is found that for strong Coulomb interactions the magnetocurrent is dominantly odd in bias voltage, confirming the symmetry observed in experiment.

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Green-Function-Approach to explain Chirality-dependent Helix-Metal-Binding-Energies

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ABSTRACT

In [1] it is experimentally shown, that the binding energy of a helix-shaped molecule (with a certain orientation) inside a magnetized, atomically flat gold layer, depends on the direction of the magnetization (or, equivalently, on the orientation of the helix). We use an effective model for the DNA that proved to be successful in the past [2] to reproduce this phenomenon by calculating the binding-energy with the help of Green-functions.

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Tuning skyrmion diffusion by adhesion of chiral molecules

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Numerous phenomena in nature exhibit a degree of freedom of chirality, favoring one chiral state over the other, e.g. the L-chirality of amino acids and the D-chirality of sugar. Magnetic materials can exhibit chiral spin structures that have a defined rotation of electron spin orientation from one magnetic domain to a domain of opposite magnetization direction. This chirality is induced by the Dzyaloshinskii-Moriya interaction that breaks inversion symmetry and thus stabilizes spin structures [1]. Chiral-induced spin-selectivity (CISS) can provide new ways to manipulate magnetic materials, and it recently it was shown that the adhesion of chiral molecules can switch the magnetization of a thin Co layer [2].

We have fabricated magnetic thin films exhibiting magnetic skyrmions [3] with a particularly flat energy landscape, which allows thermal diffusion of the skyrmions [4]. We selectively adhere chiral molecules on top of the film and show that regions with adhered chiral molecules demonstrate a change of mean-square displacement of diffusing skyrmions.

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Investigating quantum electron transport through chiral molecules at the single spin level

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Chiral induced spin selectivity (CISS) is an effect that links the electron spin to the handedness of chiral molecules. When a current is driven through a chiral molecule, it gains a spin polarization whose sign is dictated by the molecular handedness [1]. Over the last couple decades, many studies have been performed using electronic and optical methods, both on ensembles and single molecules [2,3]. However, the ability of chiral molecules to transport quantum information in the form of spin superpositions still remains widely unexplored experimentally. We propose to study how spin superpositions evolve through a chiral molecule by using an electron spin resonance scanning tunneling microscope (ESR-STM) setup, which is a novel technique that enables magnetic resonance and spin manipulation at the single electron level with nanosecond time resolution. Here, we discuss the different experiments we are preparing with the aim of elucidating the ability of chiral molecules to sustain (and possibly evolve) spin superposition states. Such a fundamental study will unequivocally reveal if CISS can be used for applications in spin-based quantum computing.

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Detecting Chiral-Induced Spin Selectivity in Electron-Transfer Processes Using Time-Resolved EPR: From Theory to Experiments

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We identified single-molecule photoinduced electron-transfer processes as the ideal testbeds to study chiral-induced spin selectivity (CISS). In fact, by removing high-SOC leads and steady-state currents typical of transport experiments, we can focus with greater emphasis on the properties of the chiral molecule.

To this end, we designed time-resolved electron paramagnetic resonance (tr-EPR) experiments on simple donor–chiral bridge–acceptor (D– χ –A) systems¹, given the technique’s capability of detecting spin-polarized states. Extensive simulations allowed us to demonstrate how these experiments are indeed able to detect a signature of CISS in tr-EPR spectra, even in isotropic solutions if in presence of anisotropic dipolar interaction J_{DA} . Moreover, we proved that the inclusion of a qubit to the system as a magnetic sensor (D– χ –A–Q) can improve the detection of spin polarization, as well as introduce practical implementations of CISS in the field of quantum computing.

We were also able to faithfully reproduce tr-EPR spectra experimentally measured on a photoinduced electron-transfer process of a D– χ –A system with CdSe QD as D and C60 as A². Although we did not get an unambiguous detection of CISS from the comparison between simulations and experiments, these results are of paramount importance in identifying the ideal experimental setup and system for analogous tr-EPR experiments in the near future.

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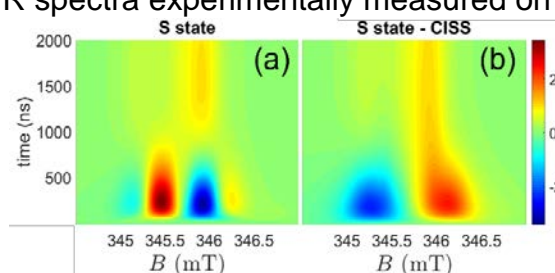


Figure 1: tr-EPR simulations for a singlet precursor state as a function of time and magnetic field. Panel (a) is simulated for non-spin selective ET, whereas (b) includes CISS along the chiral bridge.

Effective magnetic field from chiral phthalocyanine due to thermally driven spin polarization

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The current-induced spin polarization is widely recognized as a fundamental principle of chiral-induced spin selectivity (CISS) [1]. However, several studies have recently reported that chiral molecules at an interface behave like magnets [2-5]. Remarkably, no bias charge current flows through the molecule, implying that magnetization, that is, spontaneous spin polarization, may emerge in the chiral molecules. In this study, we have employed the multilayer system consisting of a ferromagnet and a chiral phthalocyanine (Pc) and have tried to characterize the CISS-related spontaneous spin polarization [6,7].

We employed (*P*)-PbPc-DTBPh and (*M*)-PbPc-DTBPh as the chiral Pc molecules, which have right- and left-handed helicities, respectively. Multilayer including Fe(0.7 nm)/(*P*)- or (*M*)-PbPc-DTBPh/MgO(2 nm) was deposited on a MgO(001) substrate. Magnetization hysteresis loops of Fe were collected via the magneto-optical Kerr effect. After careful consideration of the result, we have concluded that the experimental result indicates the presence of a finite exchange bias effect from the chiral Pc, where the polarity of the effective magnetic field depends on molecular chirality [6]. We have also conducted magnetoresistance measurements in a similar multilayer stack (Ni/(*P*)- or (*M*)-PbPc-DTBPh/MgO), and have found a chirality-induced magnetoresistance that strongly depends on the temperature [7]. We believe that the experimental results above originate from the CISS-related thermally driven spin polarization in the chiral Pc, which is qualitatively consistent with the recent theoretical work [5].

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Chirality-Induced Electron Spin Polarization in Chiral CuO and CoO_x Catalyst Surfaces

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Spin-polarized catalytic surfaces can greatly enhance the selectivity of chemical reactions, e.g., in a photoinduced water splitting process. Here, we confirm that spin-polarized currents can be obtained from chiral cupric oxide [1] (CuO) and cobalt oxide [2] (CoO_x) layers, and explore the underlying mechanism. Thin chiral oxide layers were deposited using a method pioneered by Switzer et al. [3] Photoelectrons were excited with deep-UV laser pulses and their average spin polarization (SP) was measured.

For CuO thin films, correlating the SP values with electron energy spectra reveals that the measured SP values could be rationalized assuming an intrinsic SP in the chiral oxide layer and a chirality-induced spin selectivity (CISS)-related spin filtering of the electrons. [4] On chiral CoO_x layers, the SP was found to depend on the Co oxidation state, which allows for reversible switching of the preferred spin orientation. The results support efforts towards a rational design of further spin-selective catalytic oxide materials.

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Theory of kinetic magnetoelectric effect in chiral metals and topological insulators

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We theoretically propose the kinetic magnetoelectric effect (orbital Edelstein effect), where the charge current induces orbital magnetization. It occurs in chiral crystals [1-3], and it is analogous to a solenoid in electromagnetism [1,2] (Fig. 1). Nevertheless, the effect itself is much enhanced by orders of magnitude from that naively expected from the classical solenoid, due to quantum effect [2]. A related experiment has been reported in tellurium [4,5], and ab initio calculation has been performed on current-induced orbital and spin magnetization [6]. This effect occurs also in polar systems [7]. Remarkably, we find that in topological insulators, this kinetic magnetoelectric effect becomes gigantic, due to the topological surface currents (Fig. 2(a)) [8]. We propose that Chern insulators and Z_2 topological insulators can be a platform with a large kinetic magnetoelectric effect, compared to metals, because the current flows only along the surface. We propose $\text{Cu}_2\text{ZnSnSe}_4$ as a potential candidate (Fig. 2(b)) [8].

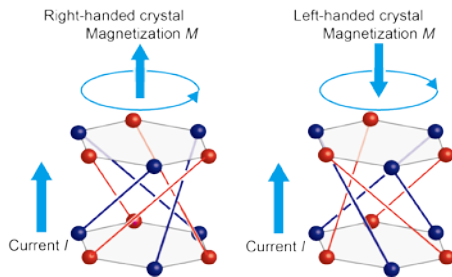


Figure 1: Schematic figure of the kinetic magnetoelectric effect.

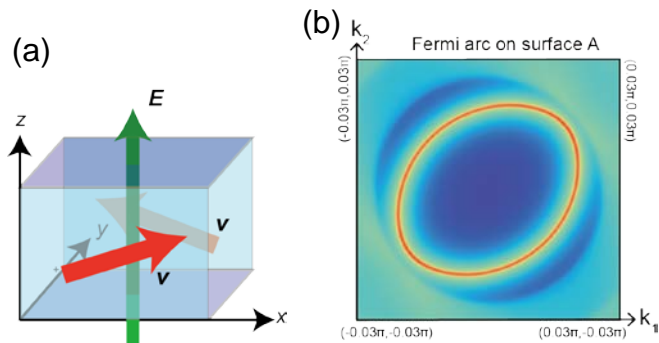


Figure 2: (a) Schematic figure of the kinetic magnetoelectric effect in topological insulators. (b) Surface Fermi surface of $\text{Cu}_2\text{ZnSnSe}_4$.

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Spectroscopic Detection of Spin Polarisation in Photoinduced Charge Transfer through a Chiral Bridge

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The direct detection of the chiral-induced spin selectivity (CISS) effect via spin-sensitive spectroscopies can provide direct access to the subtle relation between spin and chirality at molecular level.¹ In particular, determining the charge transfer (CT) dynamics in donor-chiral bridge-acceptor systems following photoexcitation is of utmost importance to understand CISS on the coherent spin dynamics and establish future guidelines to finely control photo-driven spin selectivity in chiral structures.²⁻³

In this contribution, we provide direct proof that photoinduced CT through a chiral bridge generates long-lived enhanced spin polarization in organic molecules. We propose a system comprising CdSe quantum dot (QD), as a donor, and C60, as an acceptor, covalently linked through a saturated peptidic helical bridge (χ). The proposed chiral system is favourable for many reasons: (1) QDs are effective reservoirs of electrons that can be donated via CT towards C60, (2) C60 molecules are excellent electron acceptors, and (3) the used chiral bridge is one of the shortest rigid saturated helicoidal systems possible. To investigate the photoinduced CT from the QD to the C60, we combine optical and electron spin resonance (ESR) spectroscopic techniques. Notably, time-resolved ESR spectroscopy shows that the CT in this model system is delayed with respect to the intersystem crossing on the C60 and results in a strong spin-polarization on the C60 radical anion. The modelling suggests that the observed spin-polarisation is compatible with a CISS-mediated photoinduced CT.

This work lays the basis for the direct observation of photoinduced CISS, as a fundamental step towards the optical generation and direct manipulation of spin polarisation induced by chirality and the advancement of the burgeoning field of chiral spintronics.

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STM: a tool to probe the CISS effect in self-assembled molecular networks?

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For the case of electrons, the spin is associated with two states, commonly referred to as spin “up” and spin “down”; in the absence of a magnetic field, these two states are degenerate. In the presence of magnetic interactions, this degeneracy is removed, and the spin states split; however, the energy gap between spin orientations is typically small as compared to the thermal energy, kT , at room temperature. In electron-transfer processes, spin effects normally are seen either in magnetic materials or in systems containing heavy atoms that facilitate spin-orbit coupling. Chiral-induced spin selectivity (CISS) denotes the effect in which the electron’s spin current acquires a substantial polarization after passing through a monolayer of chiral molecules. Under certain conditions, molecules may assemble into chiral self-assembled molecular networks (SAMNs) on surfaces. Here, we suggest the use of scanning tunneling microscopy (STM) as a tool to explore the CISS effect for the enantioselective formation of SAMNs of organic molecules on graphite.

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Control of magneto-optical properties of cobalt-layers by adsorption of α -helical polyaniline self-assembled monolayers

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High spin polarization was achieved in helical polyaniline molecules, allowing mainly transport of electrons with a well-defined spin direction to pass (spin filtering), depending on the handedness of the molecule as well as on the direction of the electric field acting on the electron within the chiral molecule.^[1] This phenomenon is called Chirality Induced Spin Selectivity (CISS) and has the potential to open a new perspective for organic spintronic devices.^[2] Furthermore, it was recently reported that the adsorption of the pure enantiomers of α -helical polyaniline (AHPA-L or AHPA-D) on a gold-covered ferromagnetic thin film could switch the out-of-plane magnetisation of the ferromagnetic thin film in a direction dictated by the chiral nature of the enantiomer.^[3] This effect is called Magnetism Induced by the Proximity of Adsorbed Chiral molecules (MIPAC). The specific spin exchange interactions can be utilized to separate by chemisorption the two enantiomers from their racemic mixture using Au-capped ferromagnetic thin films.^[4] Thus, it is of utmost importance to understand the self-assembling processes of helical molecules at the macro-scale (mm-range) and its influence on the magnetic properties of the substrate. In this work, we used spectroscopic ellipsometry in combination with Magneto-Optical Kerr Effect (MOKE) spectroscopy and wide-field MOKE microscopy to provide the first magneto-optical experimental characterisation of AHPA-L SAMs on ferromagnetic thin films capped with a noble metal. The result obtained from this study were published in ref.^[5]

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Synthesis and Chiral Resolution of [2.2]Paracyclophane derivatives on HOPG surface: Self-assembled monolayer of 3D nanostructure

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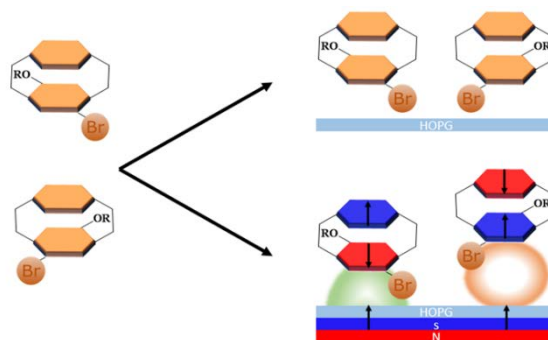
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Electron spin is a basic property of matter and plays a huge role in determining the stability of matter. The Pauli exclusion principle requires that two electrons in a single spatial eigenstate have opposite spins. This fact directs the chemical bond formation and basic features of atomic and molecular states. The recent development of Chiral Induce Spin Selectivity (CISS-effect) has shown promising results for the resolution of a racemic mixture based on the Spin-Dependent Charge Reorganization (SDCR) of chiral molecules.

In this work, we propose a system based on chiral paracyclophane (PCP) derivatives that self-assemble on highly oriented pyrolytic graphite (HOPG) surface and generate organized chiral domains on the surface. The presence of the two-benzene rings in a sandwich-like disposition allows the exact positioning of vertical structural elements. Using the well-known chemistry of PCP we functionalize this molecule. Herein, scanning tunneling microscopy (STM) was employed to investigate the surface chirality of racemic and enantiopure PCP derivatives in self-assembled domains at the solution/solid interface. Current analysis has shown different domains that can be related to the homochiral aggregation of the racemic adsorbate.



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Functionalised spin crossover complexes for exploring chirality-based effects in thin films

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Spin crossover (SCO) complexes are transition metal complexes that exhibit reversible state switching at ambient conditions, with their bistability making them promising candidates for molecular electronics. In iron (II) complexes, switching occurs between a low spin ($S=0$) and a high spin ($S=2$) state. The switching is photo- or thermally-induced, and accompanied by a change in the electronic and magnetic properties. The change in electronic properties means that the conductance of these complexes changes depending on the spin state.

A major advantage of SCO thin-film devices is that the organic ligands can be tailored to add any number of desired properties, such as photoactivity [1] or the ability to self-assemble on a surface [2]. Another possibility is tailoring chiral ligands: this would enable the study of chirality-related phenomena on the nanoscale.

Moreover, it is possible to vary the SCO-substrate interface in order to explore spin effects. Two ways to do this are 1) by using anchoring groups to graft complexes directly onto the surface, and 2) by changing the substrate material, for example by using a ferromagnetic substrate or a ferroelectric substrate that can be electrically polarised [3].

This research aims to increase our understanding of the SCO phenomenon at the nanoscale while exploring the subtleties of the (sp)interface and chiral phenomena.

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

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Previous experimental reports on enantiospecific adsorption of chiral molecules on ferromagnetic substrates [1-4] reported the deposition of the molecules under ambient conditions from solution onto ferromagnetic substrates coated with 5 to 10 nm Au for oxidation protection. Evidence of enantiospecificity was provided integrally over ensembles of adsorbed molecules. Here, we present detailed adsorption studies of chiral heptahelicene sublimed under ultra-high vacuum (UHV) conditions onto uncoated ferromagnetic substrates, such as two monolayers Fe on W(110) and Co bilayer nanoislands on Cu(111), and investigated by low-temperature spin-polarized scanning tunneling microscopy (STM). This well-defined approach eliminates external influences, such as undesired co-adsorption of other species or the need of a Au capping layer, and we investigate single-molecular properties rather than ensemble or cooperative effects. We find that the sublimed molecules remain intact and adsorb with the proximal phenanthrene group aligned parallel to the surface, permitting determination of the handedness of each molecule from topographic STM images. Three degenerate in-plane orientations on Co(111), reflecting substrate symmetry, and only two on Fe(110), i.e., fewer than symmetry permits, indicate a specific adsorption site for each substrate [5]. Based on these results, we show that enantiospecific adsorption occurs for discrete heptahelicene molecules on single-crystalline perpendicularly magnetized Co surfaces in UHV [6]. High-resolution and spin-polarized STM images enable direct determination of the enantiomeric adsorption ratio R . Statistical analysis of more than 700 molecules on 110 islands yields $R = 0.69 \pm 0.05$, which we attribute to different enantiospecific adsorption energies. We expect that our well-defined molecule-substrate system is readily amenable to theoretical modeling.

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Transfer of Spin-Orbit Coupling of molecule-metal interfaces

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Inter-System Crossing (ISC) is a dynamical process that arises from spin-orbit Coupling (SOC) between electronic states of different electron spin multiplicities. Reports are showing an unexpected increase in cis-trans isomerization rate of molecules involving azobenzene in contact with an Au(111) surface [1]. The acceleration rate depends on spin density distribution which is proportional to the coupling matrix element for the ISC between the singlet (S0) and triplet (T1) states due to gold surface.

Based on our results in the context of Chiral induced spin selectivity [2,3,4], we attempt to gain information about transferring SOC as measured by the imaginary parts in the effective single-particle Hamiltonian matrix due to the presence of a Au layer.

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Intrinsic contribution of spin-orbit coupling in phonon-assisted magnetization

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Chiral-induced spin selectivity (CISS) is a phenomenon that has been attributed to chirality, spin-orbit interactions, and non-equilibrium conditions. Until very recently, the role of vibrational modes in the CISS effect was neglected by which the temperature dependency of the effect can be explained. A conventional model to describe electron-phonon interaction ignore the spin dependent contributions originating from the spin-orbit coupling (SOC). However, in Ref. [1], it was demonstrated that the SOC gives rise to a spin-dependent electron-phonon interaction.

In this work, we address the emergence of a magnetic state in a local electronic structure when coupled to a phonon reservoir. We examine a system consisting of a single-level molecule connected to vibrational modes. The electron-phonon coupling involves charge and spin contributions which derives from SOC [1]. The phonon-assisted magnetic moment of the molecule is evaluated using the equation of motion for the Green's function.

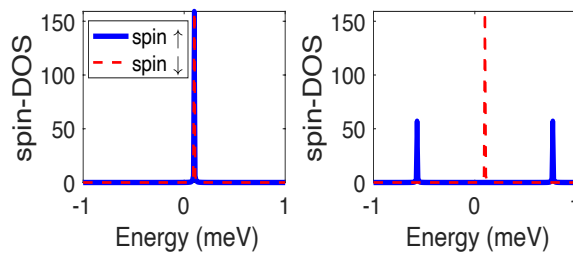


Fig. 1. Spin density of states in z-direction as a function of energy. Left panel shows spin-degeneracy in case of bare localized level molecule while right panel demonstrates the spin-DOS for the case coupled to vibrational modes.

The density of electron states for the isolated molecule is spin degenerate (Fig. 1, left). However, through a combination of charge and spin dependent couplings with phonons, the degeneracy of the spin channels is lifted (Fig. 1, right). In other words, vibrational modes coupled to the electronic level through both spin-independent and spin-dependent hybridization terms, may induce a magnetic moment even for an initially unpolarized level. Furthermore, the contributions of phonons provide a direct temperature dependence of the magnetic moment. Our results show that the sign of magnetic moment may also change with increasing temperature.

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Studying the CISS effect on the molecular scale with non-spin-polarized STM

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Helical polyalanine (PA) molecules gathered a lot of interest as the propagation of electrons along the helical backbone structure comes along with spin polarization of the transmitted electron. Via liquid–solid scanning tunneling microscopy (STM) we studied the ordering of physisorbed and chemisorbed PA molecules on HOPG and Au and achieved submolecular resolution, which allows us to deduce the molecule density for the PA films that are used for magnetic devices [1,2]. Moreover, using magnetic Au/Co/Au heterostructures for adsorption we determined the spin polarization of transmitted electrons by means of STS using non-spin-polarized tips via current–voltage (feedback open) and tip height measurements (feedback closed) for different directions of the magnetization of the Co layer. The highest spin polarizations were found for well-ordered PA monolayer structures, where the cysteine termination of the PA molecule binds to the Au surface and the PA molecules form a self-assembled monolayer. Therefore, the CISS effect in helical molecules depends on the helical molecule ordering type, proving that it is a cooperative effect, and also on the surface roughness of the capping layer in Au/Co/Au nanostructures. For both the SAM and cluster types of PA molecule ordering, the spin polarization obtained for electrons tunneling along the unoccupied states of the molecules is larger compared to electron transmissions along the highest occupied states. We correlate this finding with a larger orbital overlap resulting in a higher electron mobility along this molecular channel [3,4]. Recently, we started with co-adsorption of L- and D-PA molecules and found a phase separation, i.e. hexagonal phases, comparable to results obtained from the enantiopure adsorption, and heterochiral dimers with a rectangular unit cell for DL-PA. Despite the steric hindrance, the packing density of the PA heterophase is increased by 25% compared to the enantiopure PA structure. Apparently, this is achieved by shifting the racemic species along their helical axis. The separation is supported by STS measurements, revealing a lower spin polarization for PA molecules embedded into a quasi 1D helical chain.

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Kelvin Probe Force Microscopy on Chiral Single Crystals

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Kelvin probe force microscopy is an atomic force microscope technique used to quantify the local electrostatic potential of a surface. The technique is based on the electrostatic interaction between tip and sample, and as such limited to the measurement of relative local potential differences. Furthermore, existing Kelvin Probe Force techniques average the electrostatic interaction over the mechanical oscillation cycle of the cantilever.

For the study of the chiral induced spin selectivity (CISS) effect, these factors hinder reliable and mechanistically insightful measurements. An improved measurement protocol circumvents the above problems [1]. We replicated selected experiments of Ghosh et al. [2] with an L-AL5 peptide (-S- CH₂-CH₂-(Ala-Aib)₅-COOH) monolayer deposited on a gold-capped ferromagnetic layer and found similar experimental results.

To demonstrate the potential of electrical non-contact measurements for the CISS effect, we apply the method to chiral single crystals of L-phenylalanine sublimated on ferromagnetic substrates. To our knowledge, this material system has not been studied before, and we see magnetically induced electric polarization as well as ordinary electric polarization effects. These preliminary results on this new crystalline material system might challenge some assumptions of current theoretical models.

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Detection of the CISS effect in the linear and non-linear regime as a two- and four-terminal magnetoresistance measured in spin valve devices

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An actively discussed topic in the research on Chirality Induced Spin Selectivity (CISS) is the detection of the CISS effect as a magnetoresistance in the linear and non-linear regime in a two-terminal electric measurement where a chiral material is contacted by a ferromagnet and a nonmagnetic metal [1-5]. Regarding this discussion, it was shown in a Landauer-Büttiker transmission model, that the magnetoresistance measured in the linear regime, in a two-terminal electrical measurement, has to be zero to satisfy Onsager reciprocity [2-4]. Theoretically, it was found that a non-zero magnetoresistance can be detected in a two-terminal measurement in the non-linear regime due to energy-dependent transport and energy relaxation [3]. Similar results have been obtained in tight binding calculations [5].

We experimentally investigate the charge transport in a chiral system in the linear and non-linear regime. For this, we have fabricated spin valve devices consisting of a ferromagnetic electrode, an oxide spacer, a thin film of chiral molecules and a nonmagnetic electrode. The charge transport in the chiral film is characterised by applying a current through the chiral film and ferromagnet and measuring both the two terminal and the four terminal voltages in a current-voltage sweep. To probe the magnetoresistance, an external magnetic field is applied perpendicular to the sample plane to control the magnetisation of the ferromagnetic electrode. By repeating the current-voltage measurements with alternating magnetic field directions, the effect over time can be characterised.

In our experiments, we find that the magnetisation direction of the ferromagnetic electrodes does not affect the two- and four-terminal resistance of the chiral thin film. Instead, we find that the two- and four-terminal resistances change over time, independently of the magnetisation direction of the ferromagnetic electrodes.

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Metalloporphyrins open up towards enantioseparable and fully sp^2 -hybridized helical complexes

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We report the selective synthesis of brown nickel and copper complexes of 19-benzoyl-5,10,15-triphenyl-bilatrien-1-one (H_2 TPBT) over the blue covalent water adducts that occur as a byproduct in established literature procedures [1][2]. Metalation of TPBT with Mn, Zn, Cd and Hg using our protocol were unsuccessful. The crystal structure obtained from Ni(TPBT) shows the TPBT ligand to adapt a syn-periplanar (sp -) conformation, contrary to previous predictions for both the ligand and the complex as a whole [2][3]. The molecular helix consists of one-and-a-quarter turns with a 5.7 Å radius, a 3.2 Å pitch and spans 26 participating atoms. The ligand is completely sp^2 -hybridized. Calculations based on density functional theory using various combinations of functionals and basis sets predict the sp -isomer to be energetically favored by 11.9 ± 6.3 kJ/mol with an activation barrier ($ap \rightarrow sp$) of 14.0 ± 2.0 kJ/mol, due to attractive π - π interactions. Both TPBT complexes are redox-active in the ± 1.0 V region via two subsequent one-electron reactions. Cu(TPBT) was paramagnetic and gave a Landé factor of $g = 1.933$ for the ligand, allowing formulation as $Cu^{II}(TPBT^{\bullet})$, an air-stable helical radical. Both complexes emit in the 600–700 nm region without notable absorption when excited at 360 nm or 450 nm (Cu(TPBT) and Ni(TPBT), respectively), making them interesting for CPL emission studies. The helical enantiomers can be separated on a Daicel Chiralpak IG column and are stable in $CHCl_3$ over several weeks. Similar complexes that were previously reported in literature [4] (all unsubstituted in the 20-position) cannot be resolved into their respective (M)- and (P)-enantiomers due to a lack of sterical hindrance. Synthesis of Ni(TPBT) and Cu(TPBT) is possible upwards of 500 mg at a time and from readily available starting materials.

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Spin-Dependent Momentum Conservation of Electron-Phonon Scattering in Chirality-Induced Spin Selectivity

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The elucidation of the mechanisms underpinning chiral-induced spin selectivity remains an outstanding scientific challenge. Here we consider the role of delocalized phonon modes in electron transport in chiral structures and demonstrate that spin selectivity can originate from spin-dependent energy and momentum conservation in electron-phonon scattering events. While this mechanism is robust to the specific nature of the vibrational modes, the degree of spin polarization depends on environmental factors, like the specific temperature and phonon relaxation rates, as well as the presence of external driving fields. This parametric dependence is used to present experimentally testable predictions of our model.

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The Importance of Homonuclear Decoupling for Detecting Chiral-Induced Spin Selectivity in Radical-Pairs with NV Centres in Diamond

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Chiral-induced spin selectivity (CISS) refers to spin dependent interactions between electrons and inversion asymmetric materials.¹ Charge transfer in photoexcited donor-chiral bridge-acceptor (D-B-A) molecules is an ideal system to probe the influence of chirality in these electron transfer reactions, with implications in biology for the radical pair mechanism and for quantum information science using spin qubit pairs.^{2,3} However, whether charge transfer through the chiral bridge results in a spin-polarized or correlated state remains an open question.⁴

We propose to exploit near-surface nitrogen-vacancy (NV) centre in diamond as a nanoscale, innocent sensor for spin polarisation in radical pairs generated by D-B-A systems adsorbed on diamond surfaces.⁵ In such an experiment, the distance to the NV centre would greatly exceed the spatial separation of the radicals, thus, the dipolar interaction within the radical pair would exceed their coupling to the NV sensor spin. Therefore, the pseudo-secular part of the radical pairs' dipolar coupling results in rapid spin flip-flop dynamics and full averaging of effective spin polarisation on the timescale of the sensing experiment.

Using spin dynamics simulations, we demonstrate that Lee-Goldberg decoupling⁶ can efficiently mitigate flip-flop processes in cases where the radical pair to NV distance greatly exceeds the radical pair separation. Moreover, we provide an analytical solution for the scaling factor by which Lee-Goldberg decoupling reduces the effective spin polarisation seen by the NV centre and discuss the implications of the dipolar coupling on the general design of our proposed experiment.

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Dissipative dynamics of an impurity with spin-orbit coupling

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Brownian motion of a mobile impurity in a bath is affected by **spin-orbit coupling** (SOC). We discuss a **Caldeira-Leggett-type** model that can be used to propose and interpret quantum simulators of this problem in **cold Bose gases** [1]. First, we derive a master equation that describes the model and explore it in a one-dimensional (1D) setting. To validate the standard assumptions needed for our derivation, we analyze available experimental data without SOC; as a byproduct, this analysis suggests that the quench dynamics of the impurity is beyond the 1D Bose-polaron approach at temperatures currently accessible in a cold-atom laboratory – motion of the impurity is mainly driven by dissipation. For systems with SOC, we demonstrate that 1D spin orbit coupling can be ‘gauged out’ even in the presence of dissipation – the information about SOC is incorporated in the initial conditions. Observables sensitive to this information (such as spin densities) can be used to study formation of steady spin polarization domains during quench dynamics.

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