The Chiral Induced Spin Selectivity- Why it is so special?

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Weizmann Institute, Israel

Dedicated to my late friend and collaborator Dave H. Waldeck

Chirality

Even though homochirality in biological organisms represents an entropy reduction, that increases the organisms Gibbs free energy, the question:

“Why nature kept chirality so persistently through evolution?”

The Chirality Induced Spin Selectivity (CISS) Effect

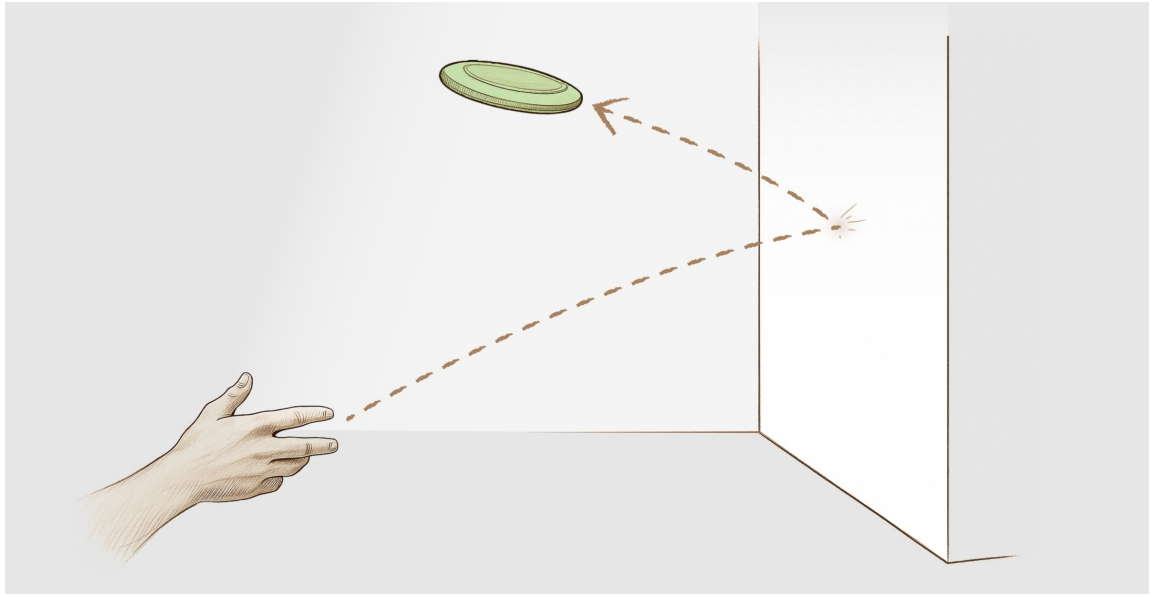
Any motion of electrons in chiral medium depends on the electrons' spin.

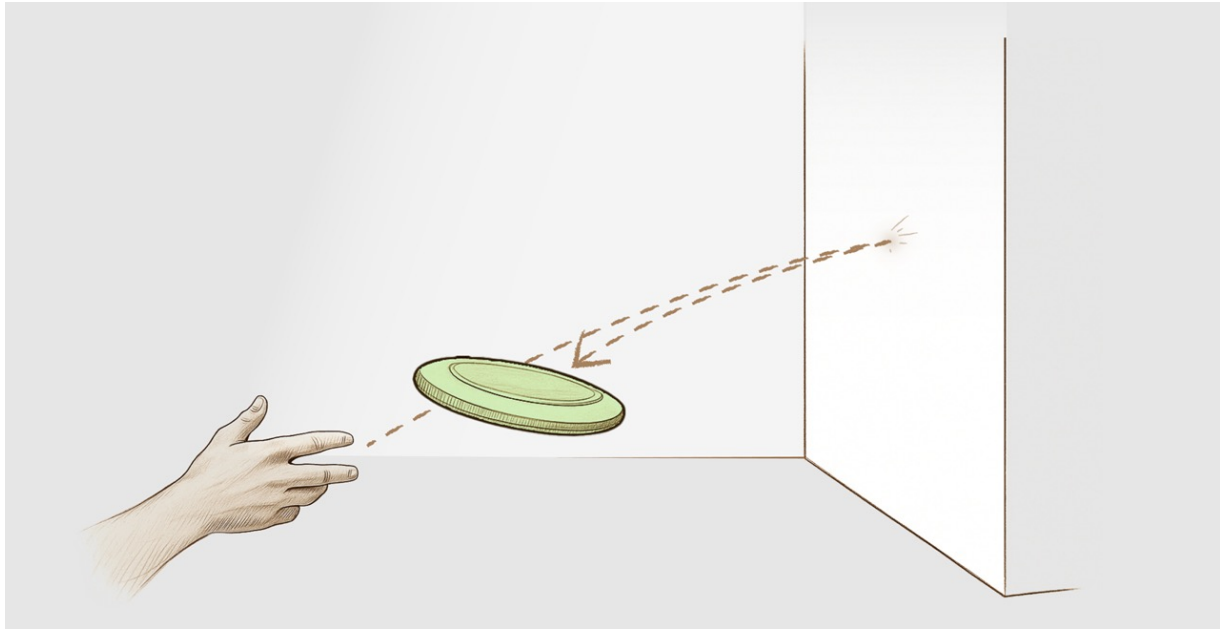
Which spin is preferred depends on the handedness of the system and the direction of the electron's motion.

The Frisbee effect

What is required for the effect ?

- Angular momentum
- Breaking symmetry
- Friction- **Spin orbit coupling** +dissipation.





Before discussing the CISS effect we have to notice the role of the electron's spin:

- Spin specific properties are assumed to require either ferromagnetic or paramagnetic properties.
- It is believed that in general the electron spin is not coupled in a significant way to the molecular frame.

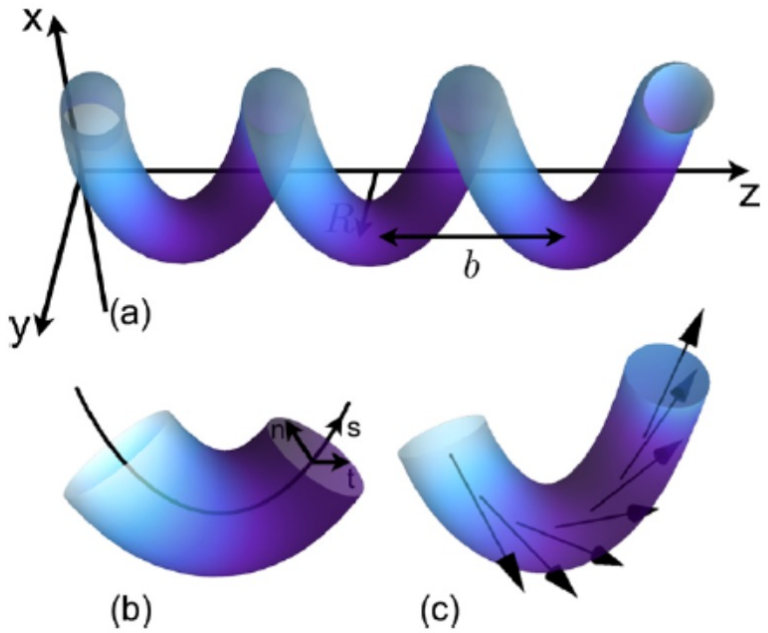
We found that chiral molecules have unique electronic and spintronic properties despite being usually closed shell systems - namely singlet.

Momentum conservation

The electron moving in helical potential must exchange momentum with the system

In solids, that ha ns can exchange momentum with t

In insulators/m are localized and therefore momen ency vibrations that have angular ons.



Works by:

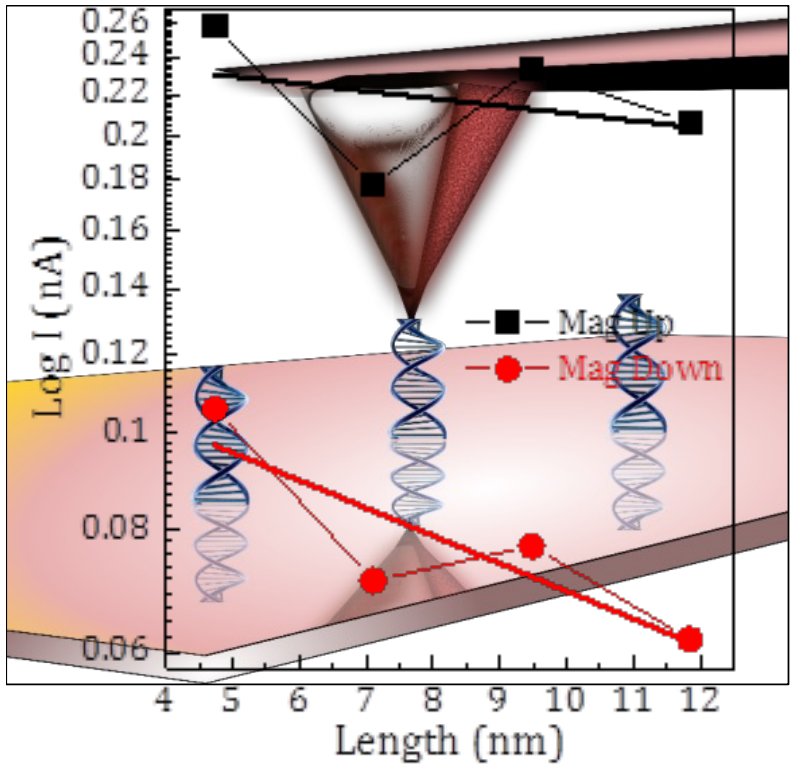
Joe Subotnik: Phys. Rev. B **106**, 184302 (2022); *Nat. Comm.* **12**, 700 (2021); *Phys. Chem. C* **127**, 14155 (2023).

Jonas Fransson: Nano Lett., 21, 3026 (2021); Phys. Rev. **B** 102, 235416(2020);

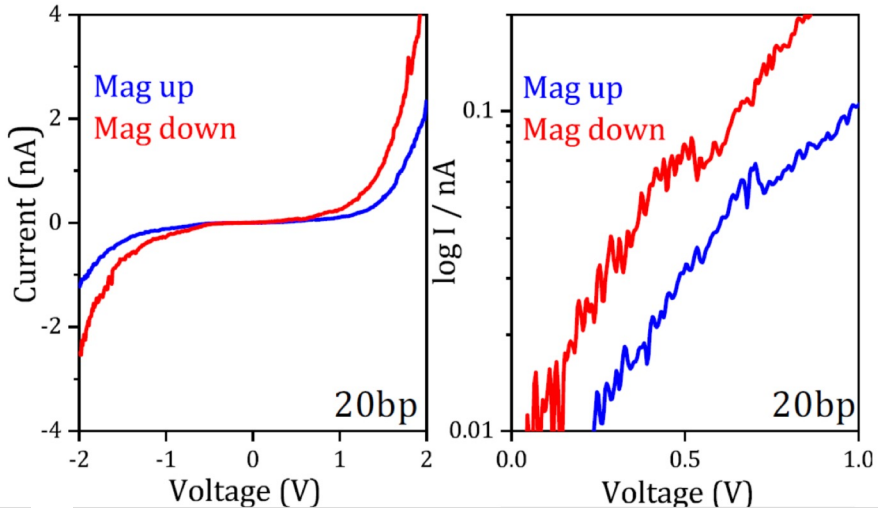
Why the CISS effect surprised both chemists and physicists?

- As mentioned above- spins are typically ignored by chemists when closed shell systems are concerned.
- Hydrocarbons suppose to have very small spin orbit coupling (SOC).
- How one get large spin polarization at room temperature?

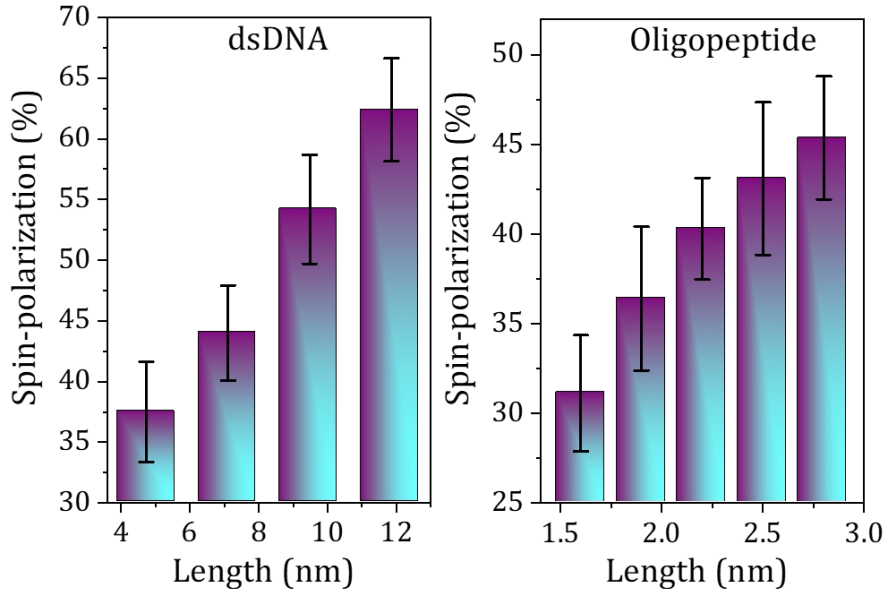
Length dependent of the CISS effect



Typical I *vs* V curves



Length Dependent Spin Polarization



S. Mishra, A. K. Mondal, S. Pal, T. K. Das, E. Z. B. Smolinsky, G. Siligardi, R. Naaman, *JPC C* 124, 10776-10782 (2020).

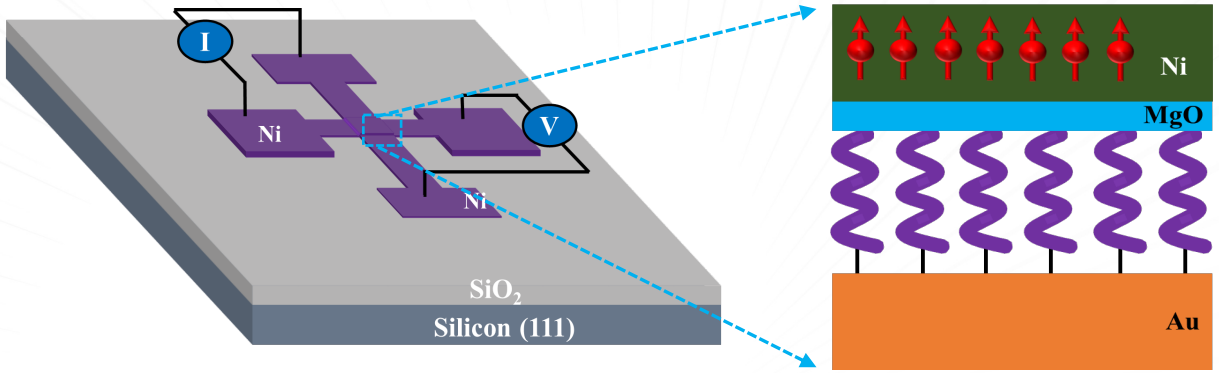
Hence:

- While for electrons moving in straight line phonons/vibrations are interfering with the straight path, in chiral potentials they are essential (especially if there are no unlocalized electrons).
- The CISS samples the electrons that **did interact** with the vibrations/phonons.

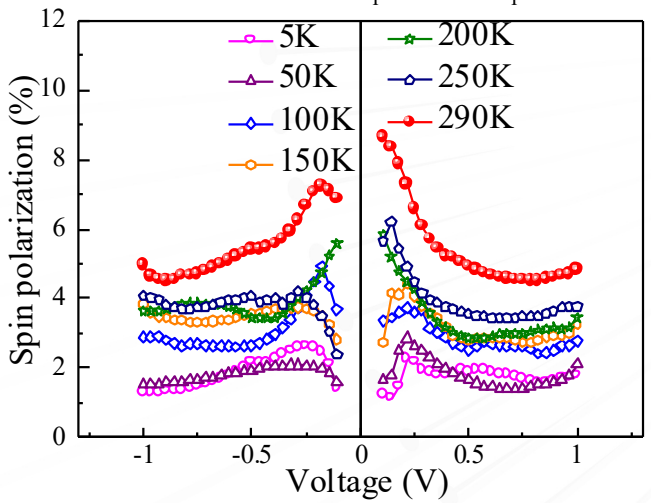
Longlong Zhang, Yuying Hao, Wei Qin, Shijie Xie, Fanyao Qu, PHYSICAL REVIEW B 102, 214303 (2020). Role of polarons.

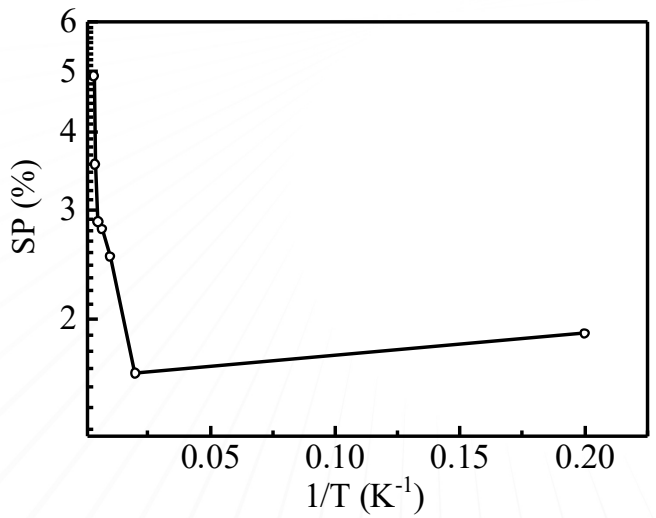
Gui-Fang Du, Hua-Hua Fu, Ruqian Wu. PHYSICAL REVIEW B 102, 035431 (2020) Role of phonons in DNA

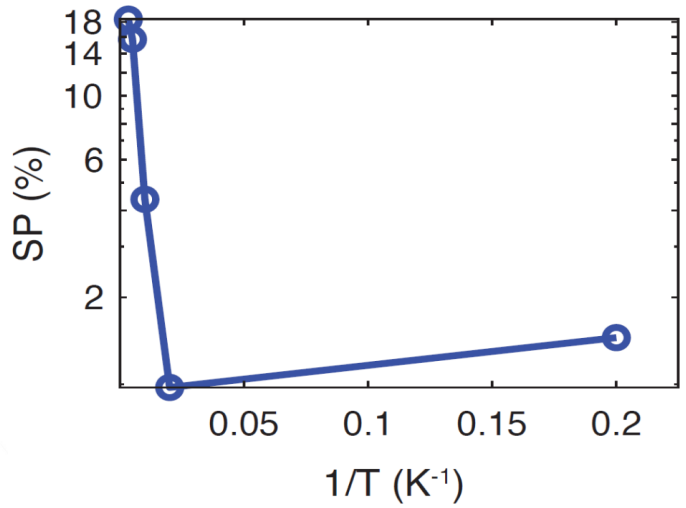
The role of phonons



Spin polarization (%)=(I_{up}-I_{down})/(I_{up}+I_{down})*100







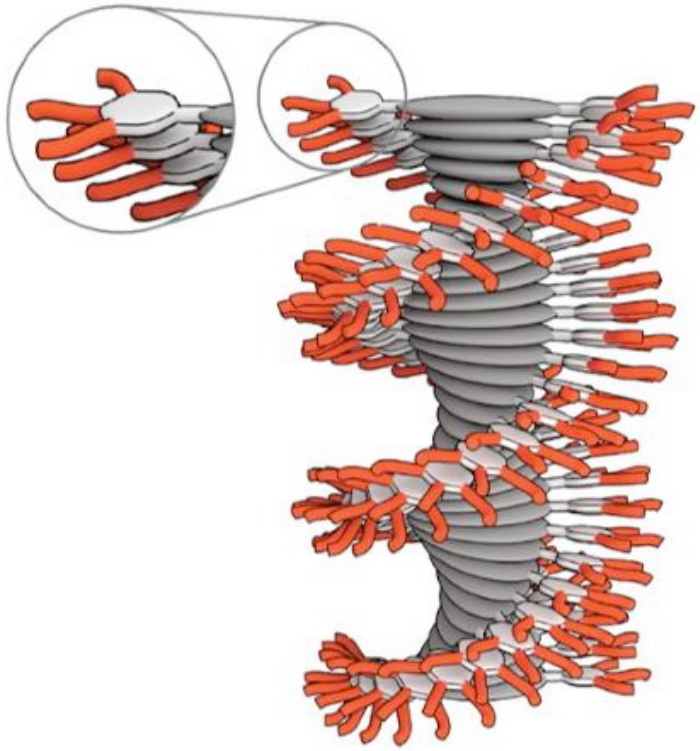
Theory by:
Jonas Fransson, Uppsala University

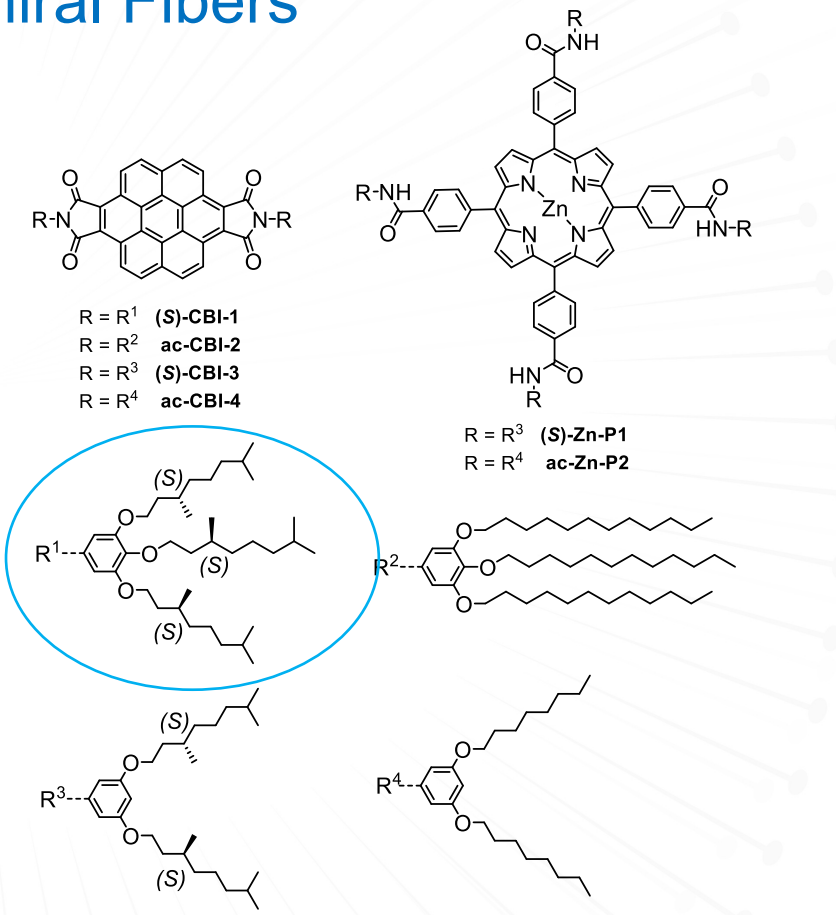
T. K. Das, **F. Tassinari,** R. Naaman**, J. Fransson,** *J. Phys. Chem. C*, **126**, 3257 (2022).

CISS and Optical Activity

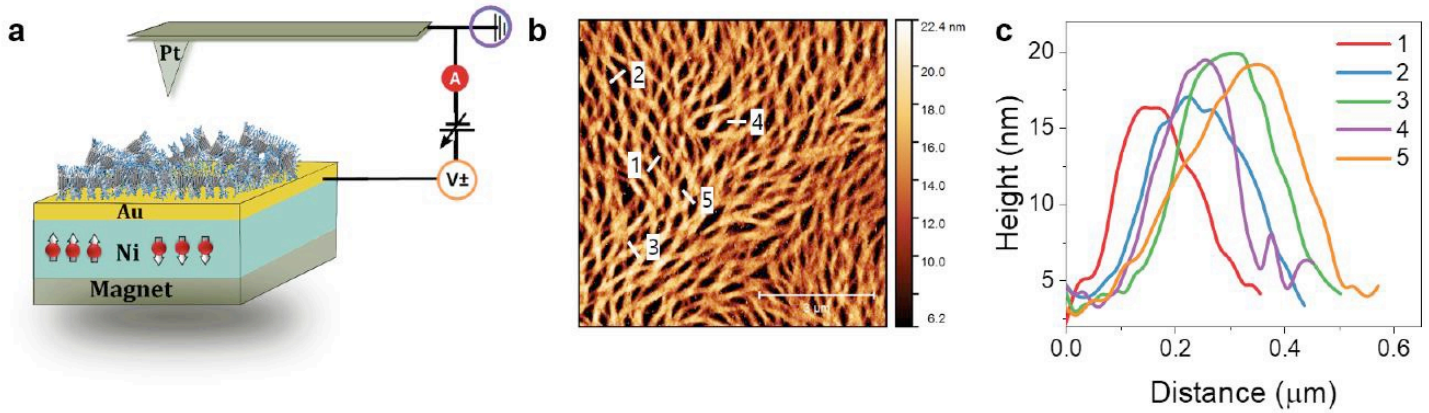
In collaboration with E.B. Meijer- Eindhoven

Chiral and Achiral Fibers



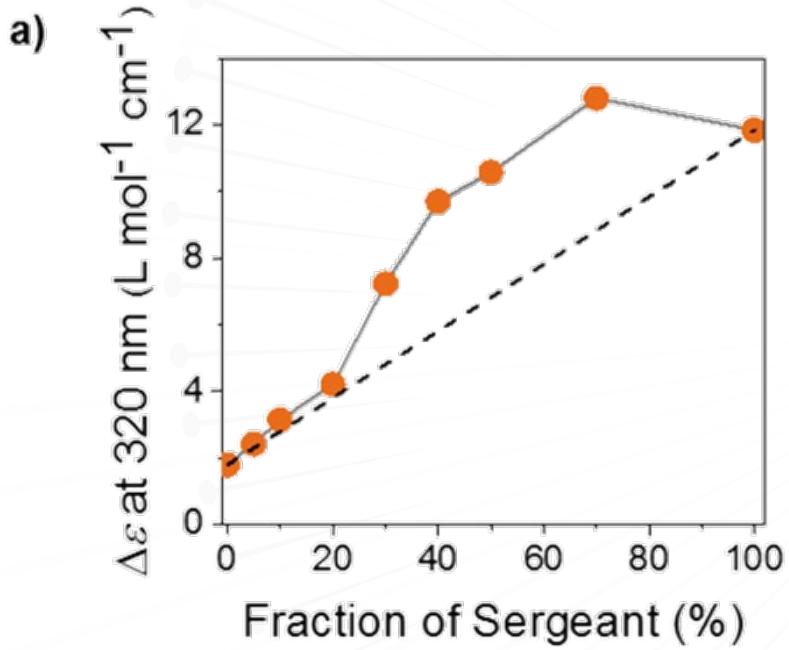


C. Kulkarni, A. K. Mondal, T. K Das, G. Grinbom, F. Tassinari, M. F. J. Mabesoone, E. W. Meijer, R. Naaman, *Adv. Mat.* 1904965 (2020).


a
Pt
A
V±
Au
Ni
Magnet
b
1
2
3
4
5
22.4 nm
20.0
18.0
16.0
14.0
12.0
10.0
6.2
c
Height (nm)
Distance (μm)
0.0
0.2
0.4
0.6
5
10
15
20
1
2
3
4
5

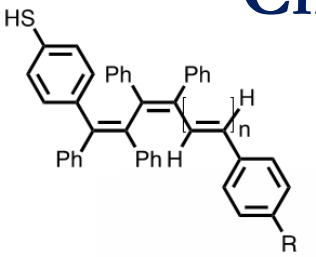
Sergeant and Soldier (S&S) principle for CBI-35 system

Intensity of the CD peak at 320 nm

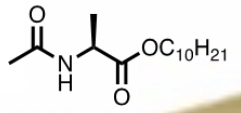


There is correlation between the optical activity and the spin polarization

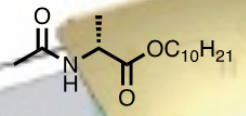
Charge polarization is accompanied by spin polarization



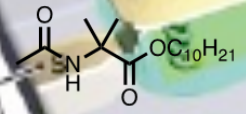
poly-1L:



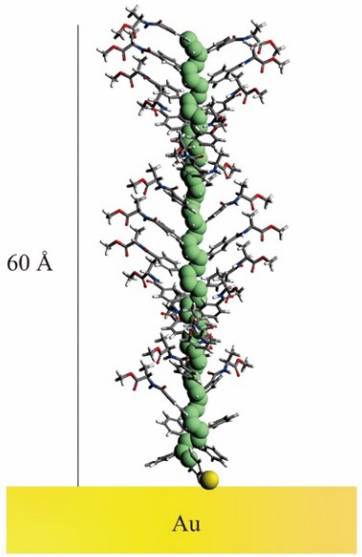
poly-1D:



poly-2:



Hall Device

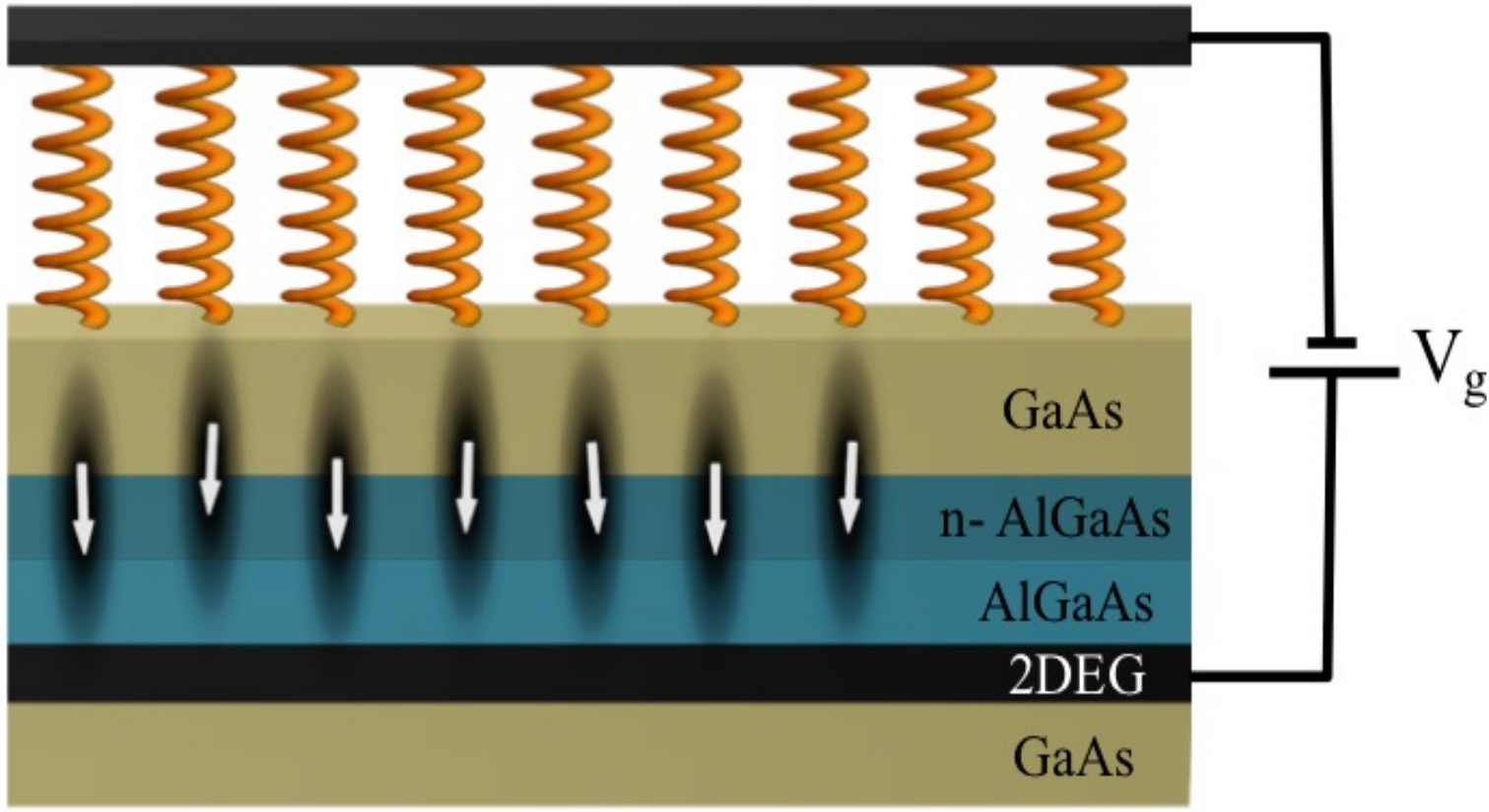


S. Mishra, A. Kumar Mondal, E. Z. B. Smolinsky, R. Naaman, K. Maeda, T. Nishimura, T. Taniguchi, T. Yoshida, K. Takayama, E. Yashima, *Angew. Chemie* **59**, 2–8 (2020

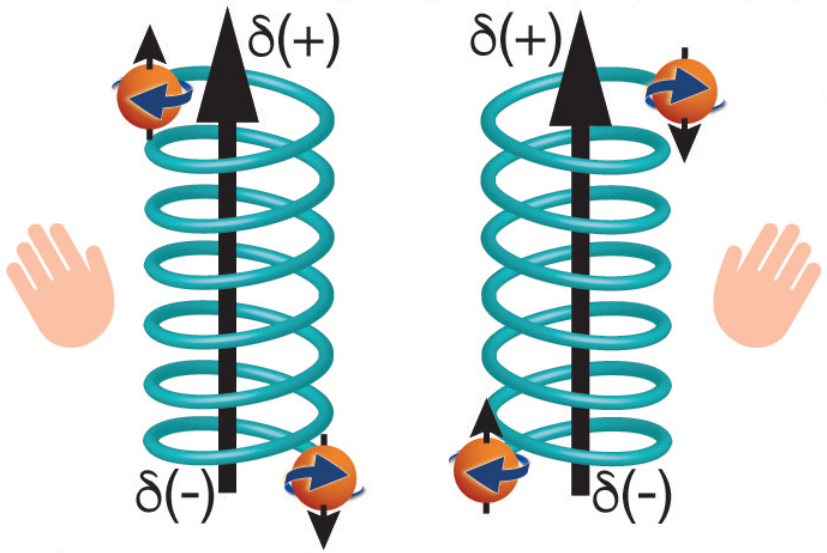
1. Spins are injected by applying voltage on the gate.

2. Due to Indirect exchange interaction (RRKY) through the 2DEG, magnetic phase is stable as long as the voltage is applied.

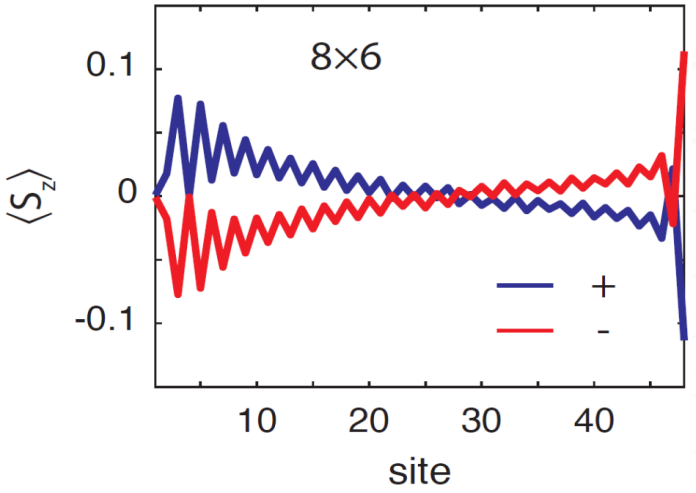
Anomalous Hall effect



E. Z. B. Smolinsky, A. Neubauer,
A. Kumar, S. Yochelis, E.Capua, R. Carmieli,
Y. Paltiel, R. Naaman, K. Michaeli,
J. Phys. Chem. Lett. **10**, 1139–1145 (2019).



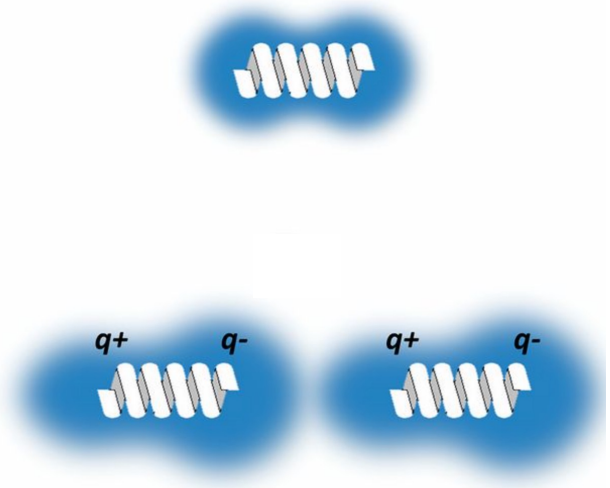
Theoretical verification:



Jonas Fransson, Uppsala University.
Phys. Rev. B, 2020, *102*, 235416; *Nano Lett.* 2021, 21, 3026.

- Upon electron being transferred through chiral system, the entanglement in the singlet state brakes.
- The electron's spin is strongly coupled to the molecular frame.

Enhancement of Enantiorecognition



In chiral molecules charge polarization is accompanied by transient spin polarization.

This introduces new electronic interaction term which is enantio-specific when two chiral molecules interact.

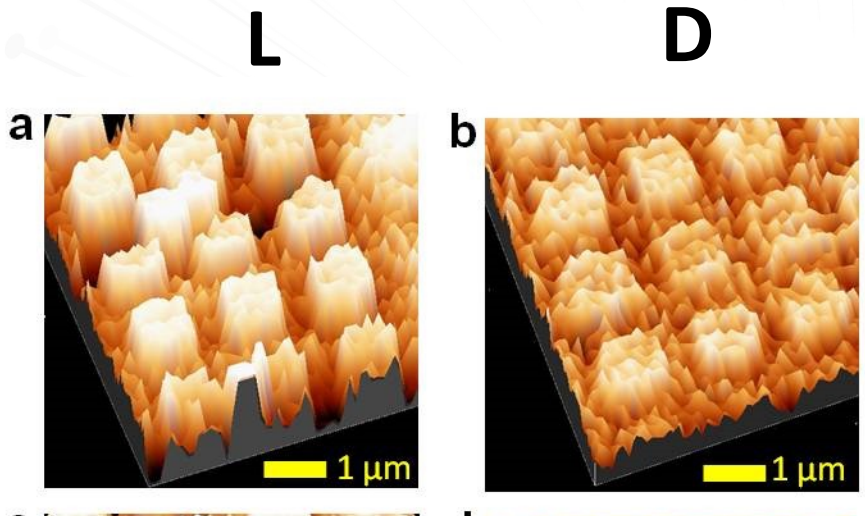
A. Kumar, E. Capua, M. K. Kesharwani, J. M. L. Martin, E.Sitbon, D. H. Waldeck, R. Naaman, *PNAS,* **114**, 2474–2478 (2017).

Chirality and Magnetism

Induced Magnetization Switching by Local Adsorption of Chiral Molecules on Ferromagnets

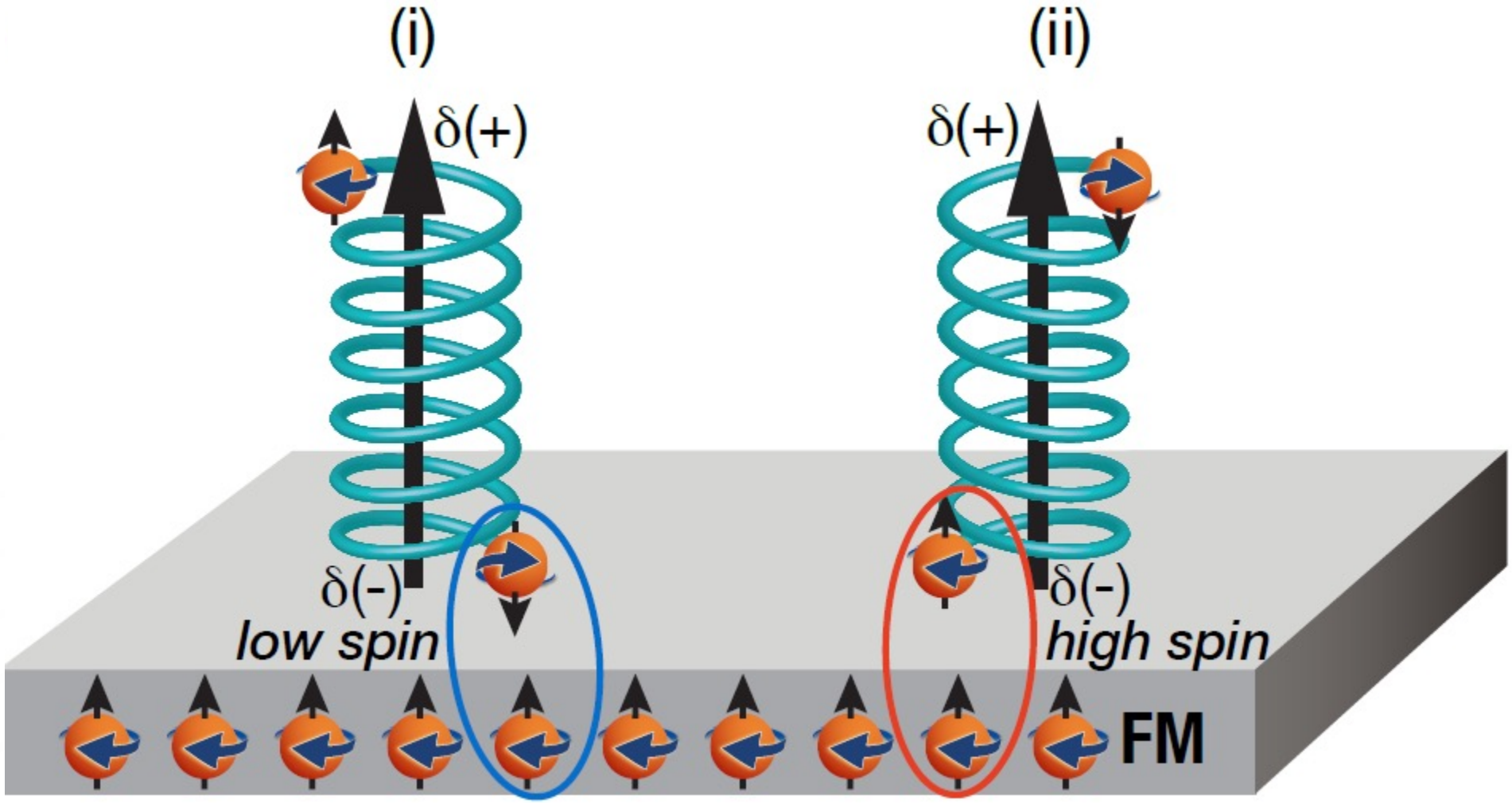
O. Ben Dor, S. Yochelis, A. Radko, K. Vankayala, E. Capua, A. Capua, S.-H. Yang, L. T. Baczewski, S. S. P. Parkin, R. Naaman, and Y. Paltiel, *Nat. Comm.* **8**:14567 (2017).

Chiral molecules were adsorbed on ferromagnetic layer coated with 2 nm gold

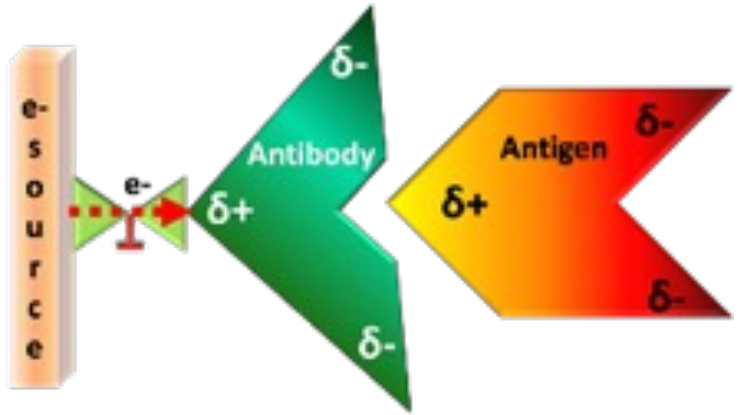


Topography with AFM

Magnetic AFM Measurements


(i)
δ(+)
δ(-)
low spin
(ii)
δ(+)
δ(-)
high spin
FM

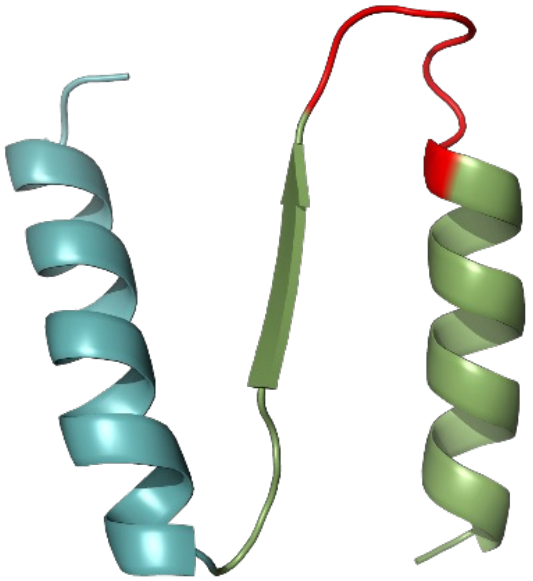
Importance of Spin Polarization in Protein Activity



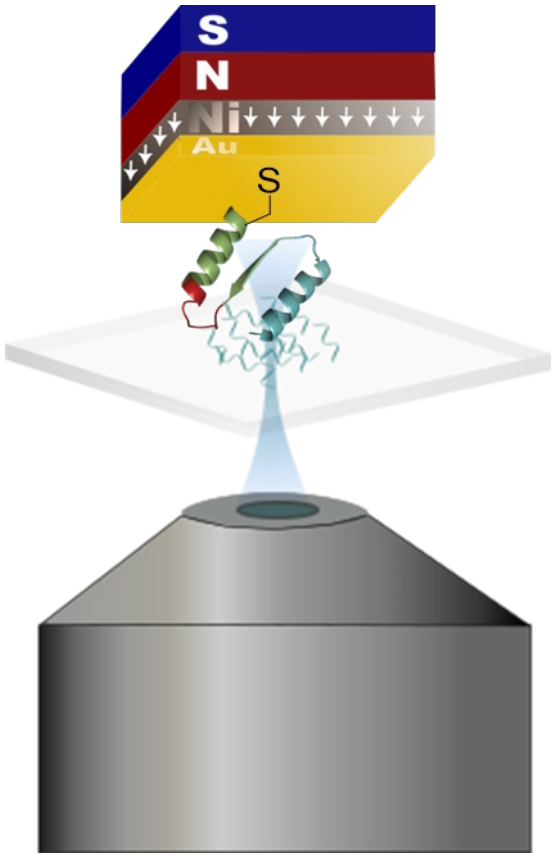
In collaboration with the group of **Gilad Haran**

K. Banerjee-Ghosh, S. Ghosh, H. Mazal, I. Riven, G. Haran, R. Naaman, *JACS* **142**, 20456–20462 (2020).
S. Ghosh, K. Banerjee-Ghosh, D. Levy, I. Riven, R. Naaman, G. Haran, *J. Phys. Chem. Lett.* **12**, 2805-2808 (2021).

The role of spin in protein-DNA interaction



N-αβα prototype
$\alpha_2\beta_1$-(P-loop)-α_1

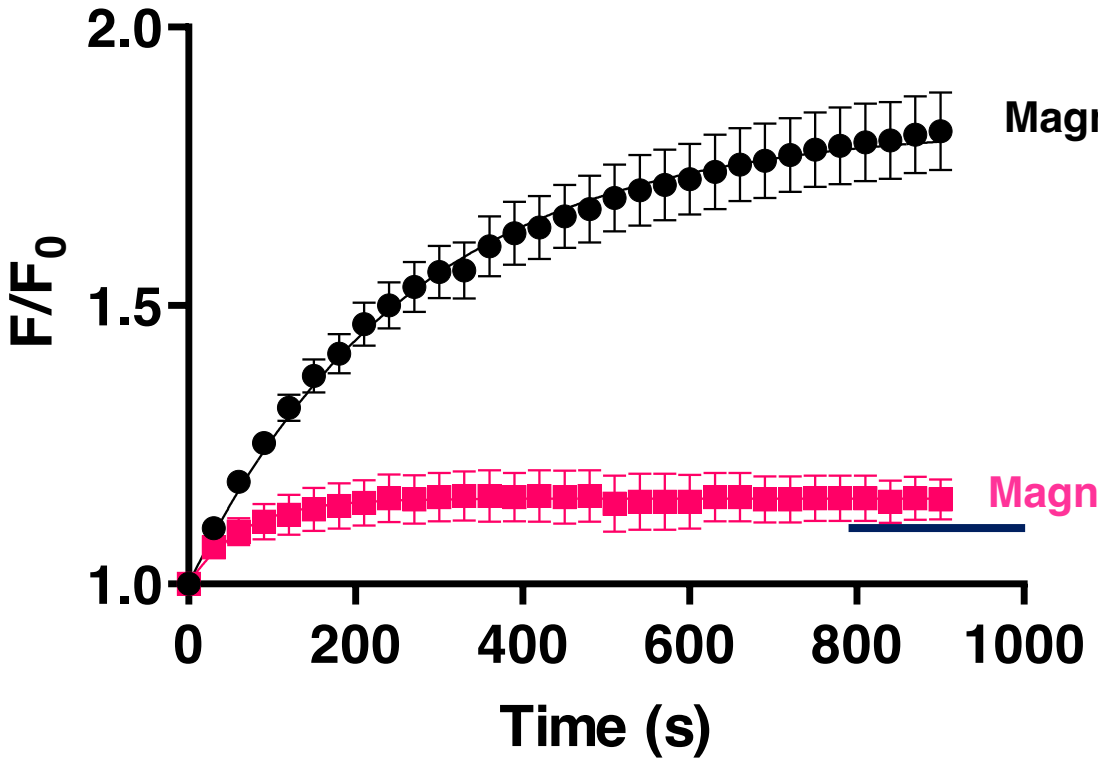


It was hypothesized that proteins and enzymes emerged via duplication and fusion of relatively short 'seeding' peptides with simple secondary structures.

Romero MLR, Rabin A, **Tawfik DS**. Functional Proteins from Short Peptides : Dayhoff s Hypothesis Turns 50. Angew Chem Int Ed Engl. 2016;1980:15966-15971.

Vyas P, Malitsky S, Itkin M, **Tawfik D**. On the origins of enzymes: Phosphate-binding Polypeptides Mediate Phosphoryl Transfer to Synthesize ATP. J Am Chem Soc. 2023;Accepted.

ssDNA binding is 'spin-selective'

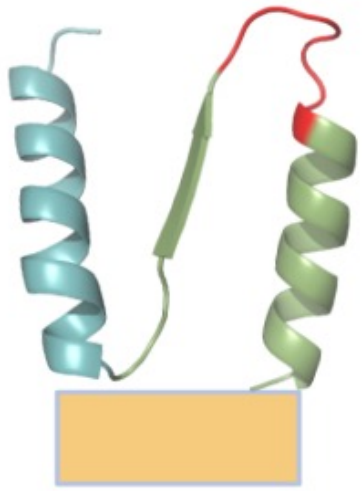


F—AGGATCTCTTCTCTCTCCTCTCCT

TC-ssDNA

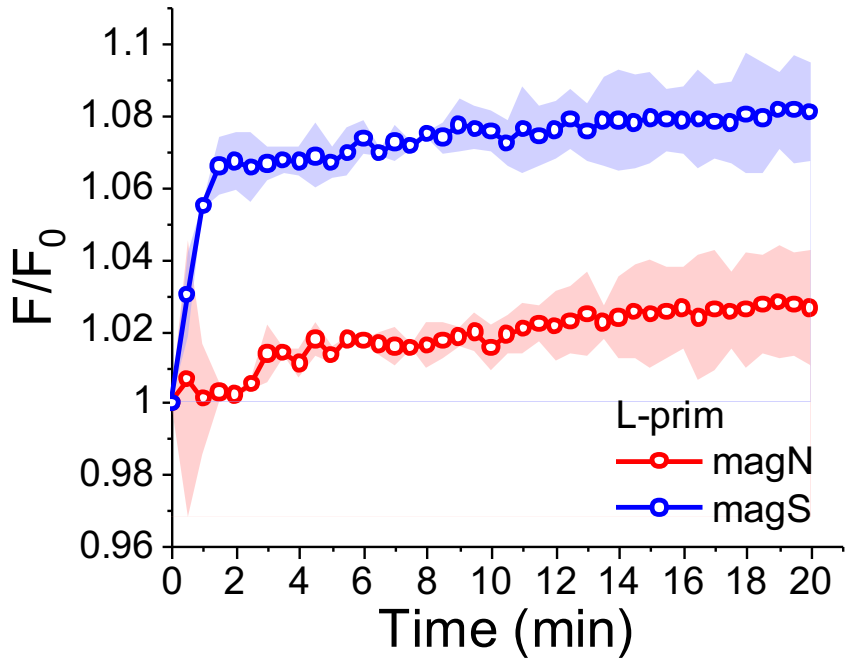
Vyas, Santra and Naaman, in preparation

In this experiment:



The “effective polarizability” of the protein affects the binding to the DNA.

Effect of spin on the interaction between primordial protein and double helix DNA



Prof. Norman Metanis
Hebrew University, Jerusalem

Dr. Kakali Santra

L-Primordial(29-60) *Sequence*
CSIERIRRASVEELTEVPGIGPRLARRILERL

Sequence for DNA binding:
Top strand
5'-6-FAM/TAGATCGATCGC-3'
Bottom strand
5'-GCGATCGATCTA-3'

The role of the spin in interactions of proteins

- The "correct" spin enables charge redistribution in the proteins, namely it increases the polarizability.
- Very long-range information transfer.
- Perhaps we do not really understand electron transfer through proteins. –

R. Naaman, D. H. Waldeck, J. Fransson, J. Phys. Chem. Lett. 13, 11753 (2022).

Enantiomers

The common perception is that beside being mirror image of each other, enantiomers are identical.

This is based on their energy levels being identical (except of very tiny difference due to the weak force).

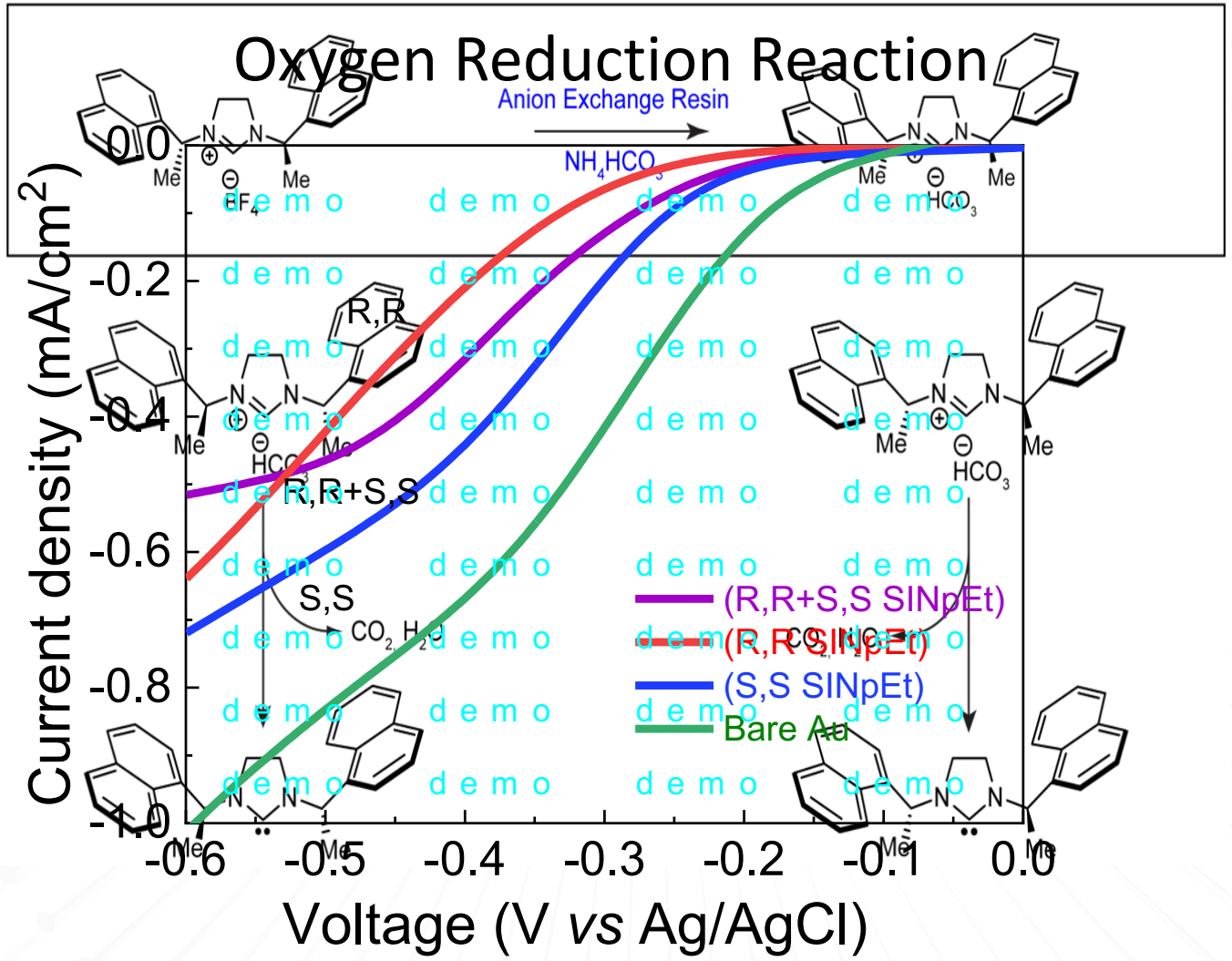
Is this true also about their spin related properties?

Asymmetry in several systems
Anomalous Hall asymmetry

We define asymmetry, A, as: $A = \frac{S_L - S_D}{S_L + S_D} \times 100$

	System	A %
1.	Chiral Golds	30±10
2.	Chiral Silver	10±5
3.	Polyalanine adsorbed on gold	34±10
4.	Polyalanine on Gold+3nm Oxide	12±5

Anu Gupta in collaboration with Frank Glorius and Himad Sasmal, Munster University



The Spin Orbit Coupling in Chiral Molecules

- The spin orbit coupling (SOC) in chiral systems has two type of contributions-

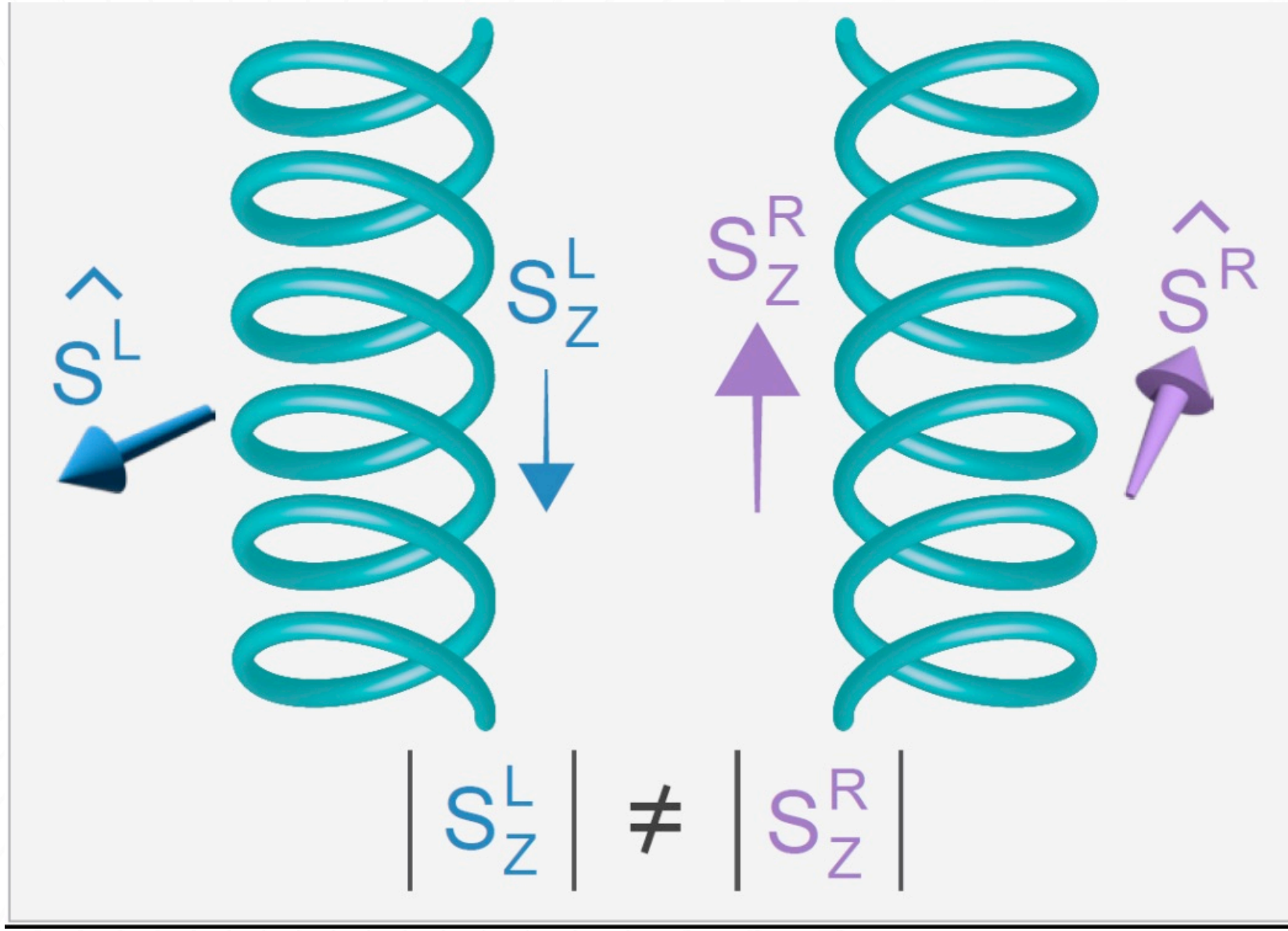
The atomic (SOC) and the topological one that results from the chirality.

- The SOC has a phase ("direction") it is fixed for the atomic one but it changes sign for the two enantiomers.

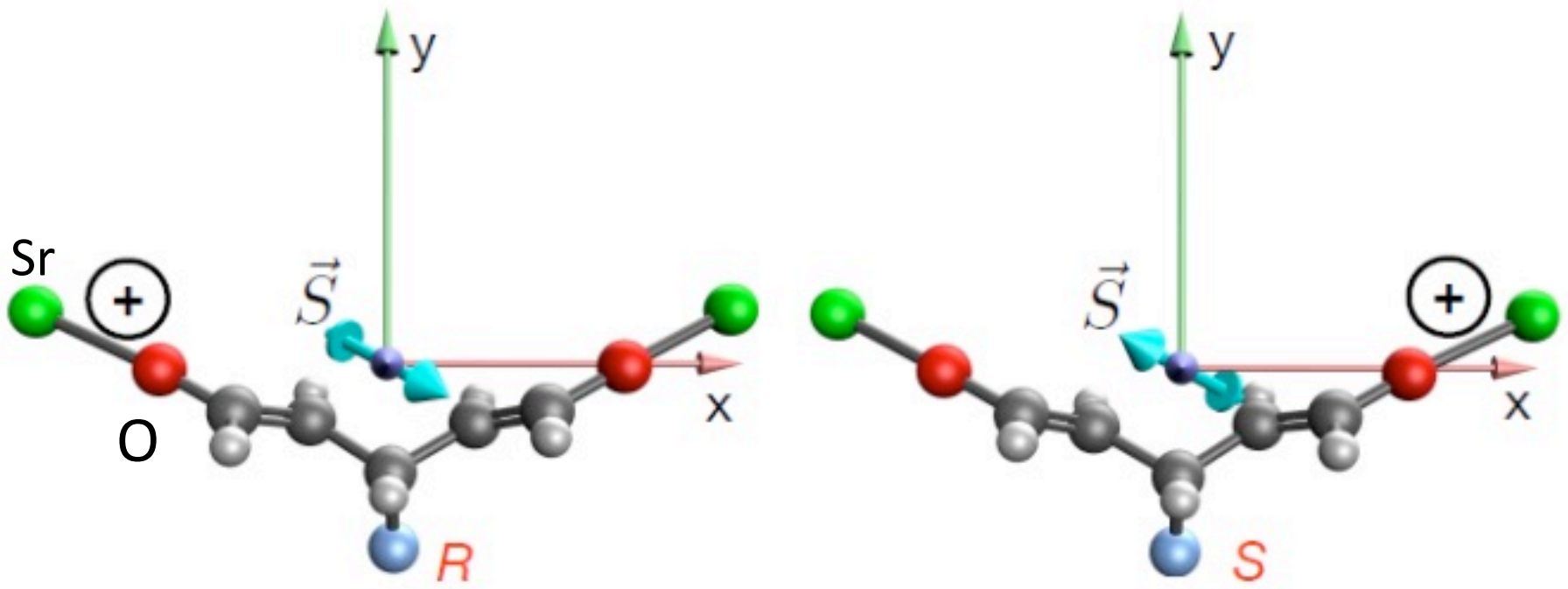
The outcome:

Although the real part of the SOC is the same for both enantiomers, the imaginary part is different and may give rise to a different orientation of J relative to the molecular frame in the two enantiomers.

- The total SOC has different direction relative to the molecular frame for the two enantiomer. As a result, the effective total spin, **S**, of the system is pointing in different direction for each enantiomer.
- For electron passing in a well defined path, the ratio between the spins states will be different.



C. Seibel, J. H. Soh, S. Zilberg, A. I. Krylova, "Ultrafast Transversal CISS Effect Observed in a Chiral Photoswitching Molecule." J. Phys. Chem. Lett., 16, 8514 (2025).



The angle between $\vec{S}$ and $\vec{\mu}$ is 124° and 82° for R and S enantiomers

Any interaction of molecules involves charge reorganization.

The charge reorganization is spin dependent.

Therefore, it is possible that the two enantiomers interact differently.

This may be the origin of homochirality in Nature.

Conclusions

1. Spin enables long range electron transfer- essential for Biology.

2. Polarizability must be considered as is evident from the correlation between optical activity and spin polarization. The connection is through the anisotropic polarizability of the system.

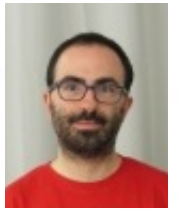
3. Angular momentum considerations must be included, especially when interaction between electron-phonons/vibrations is involved.

4. The model for the mechanism of the CISS effect requires non-BO interactions and introducing of many electrons effects.


A. K. Mondal


K. Santra


Y. Sang


F. Tassinari


E. Z. Smolinsky


S. Mishra


K. Banerjee-Ghosh


T.K. Das


A. Kumar


N. Preeyanka


Q. Zhu


P. Vyas


D. Bhowmick


A. Kumar

Thank you

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Thanks to my long-time collaborators: the late Dave Waldeck, Yossi Paltiel, Jonas Fransson