Designing Thiol-Functionalized Chiral Adsorbates for CISS-Driven Spin Polarization

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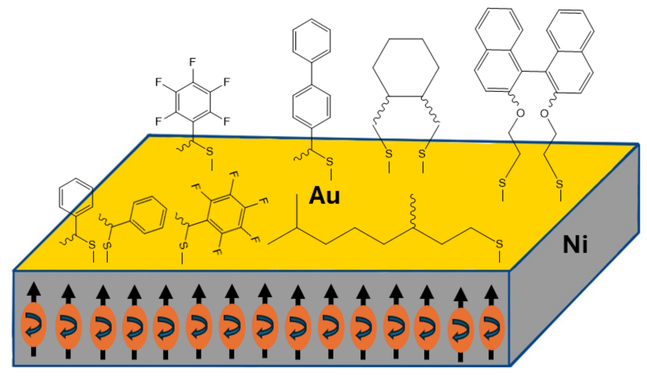
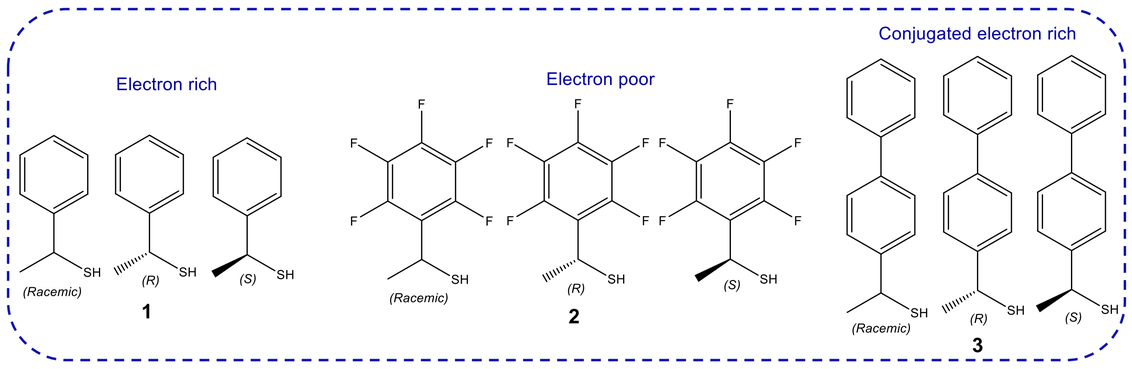
1. Introduction

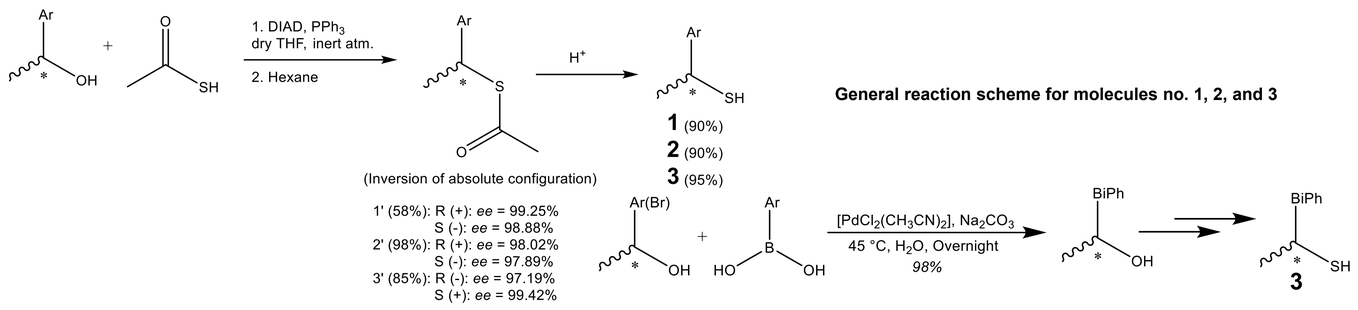
Chiral-induced spin selectivity (CISS) couples molecular chirality and spin-orbit interactions at molecule-metal interfaces, enabling enantiomer-specific spin filtering with applications in catalysis, sensing, and spintronic information processing. Yet, the molecular design rules governing CISS remain elusive. Here, we synthesize a library of **thiol-functionalized chiral adsorbates** with **>97 % enantiomeric excess** (HPLC), independently tuning each compound's **dipole moment**, **stereochemistry**, and **chemical environment**. Self-assembled monolayers on Au(111) and spin-polarized Au/Ni substrates were characterized by scanning tunneling microscopy (STM) revealing **well-ordered enantiopure networks**, while scanning tunneling spectroscopy (STS) measurements under applied magnetic fields demonstrated clear **enantiomer-specific spin-polarization** signals. Correlating these spin responses with molecular parameters establishes direct structure-property relationships that enable rational, CISS-driven surface functionalization. These findings lay the groundwork for developing next-generation, enantioselective technologies based on CISS.



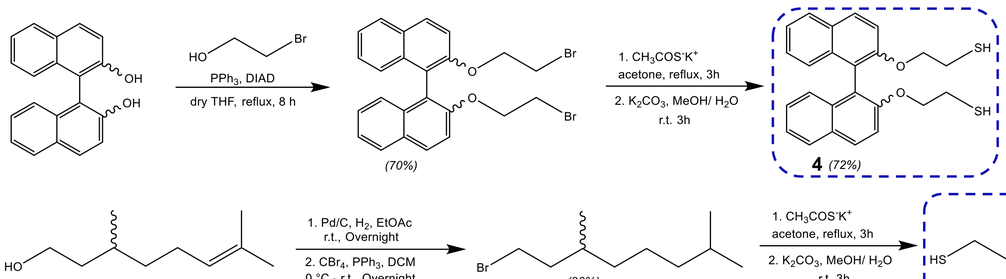
2. Synthesis



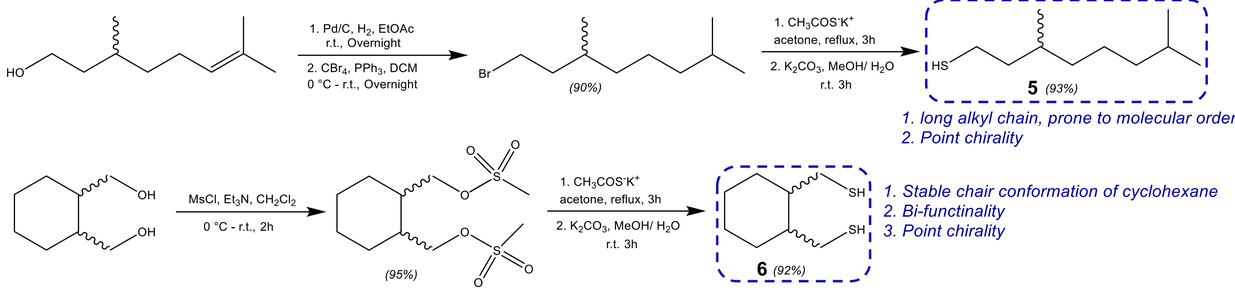
1. Different dipole-moment upon adsorbing on the surface
2. Directly attached thiol functional group with the chiral center
3. Point chirality



General reaction scheme for molecules no. 1, 2, and 3



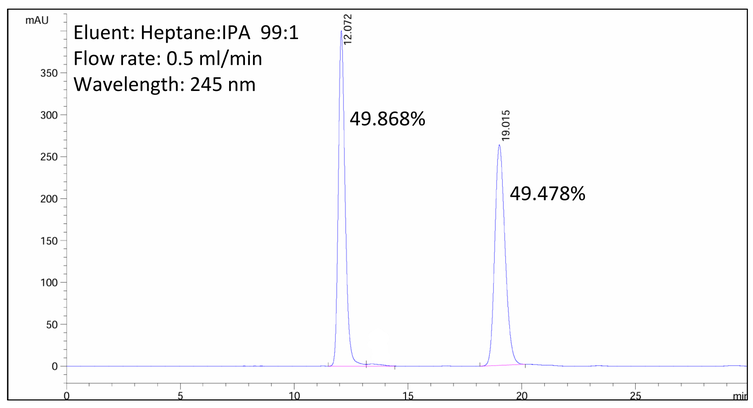
1. Binaphthyl group, prone to form self-assembly on sorface
2. Bi-functinality
3. Axial chirality

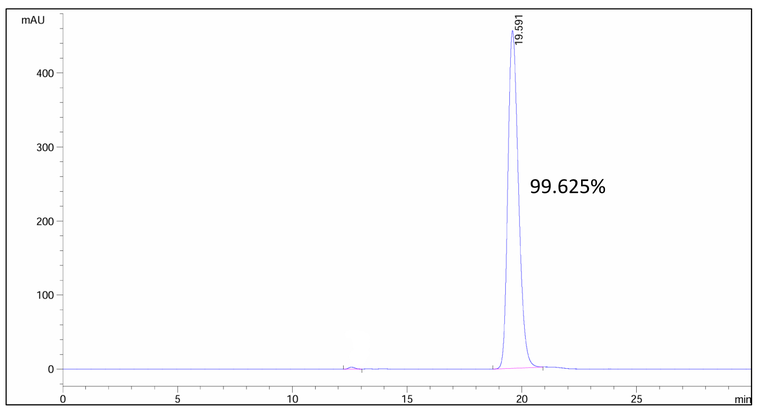


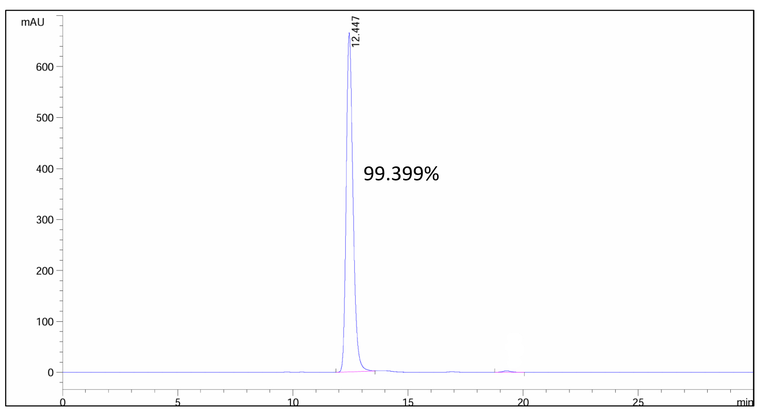
1. long alkyl chain, prone to molecular ordering
2. Point chirality

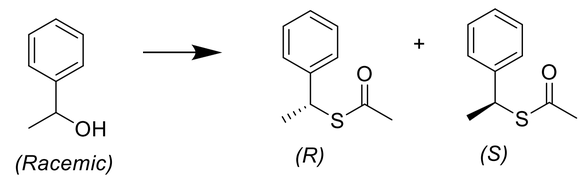
1. Stable chair conformation of cyclohexane
2. Bi-functinality
3. Point chirality

3. HPLC Analysis

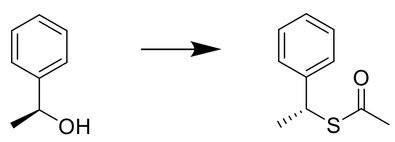








Inversion of Absolute configuration

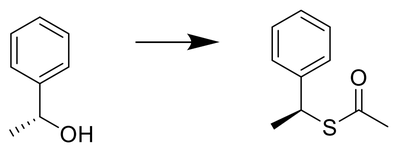


Optical rotation: -0.0256
Specific rotation: -51.240

Optical rotation: +0.1471
Specific rotation: +294.214

R(+) ee = 99.25 %

Inversion of Absolute configuration



Optical rotation: +0.0242
Specific rotation: +48.452

Optical rotation: -0.1438
Specific rotation: -287.613

S(-) ee = 98.88 %

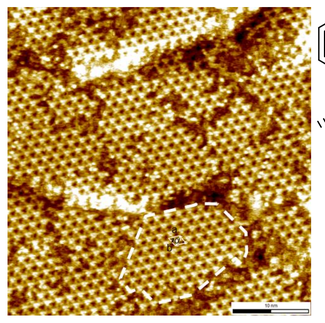
$$[\alpha] = \frac{\alpha}{c \times l}$$

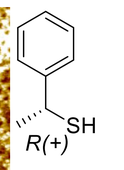
[α] - specific rotation
α – observed rotation
c - concentration (g/ml)
l - path letght (dm)

Conc.: 0.0005 g/ml
Path length: 1.0 dm

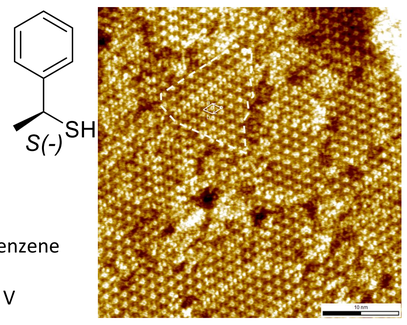
Similarly, molecules 2 and 3 show over 97 % enantiomeric excess and inversion of configuration in the final product, as verified by HPLC analysis and polarimetry.

4. STM and STS Measurements



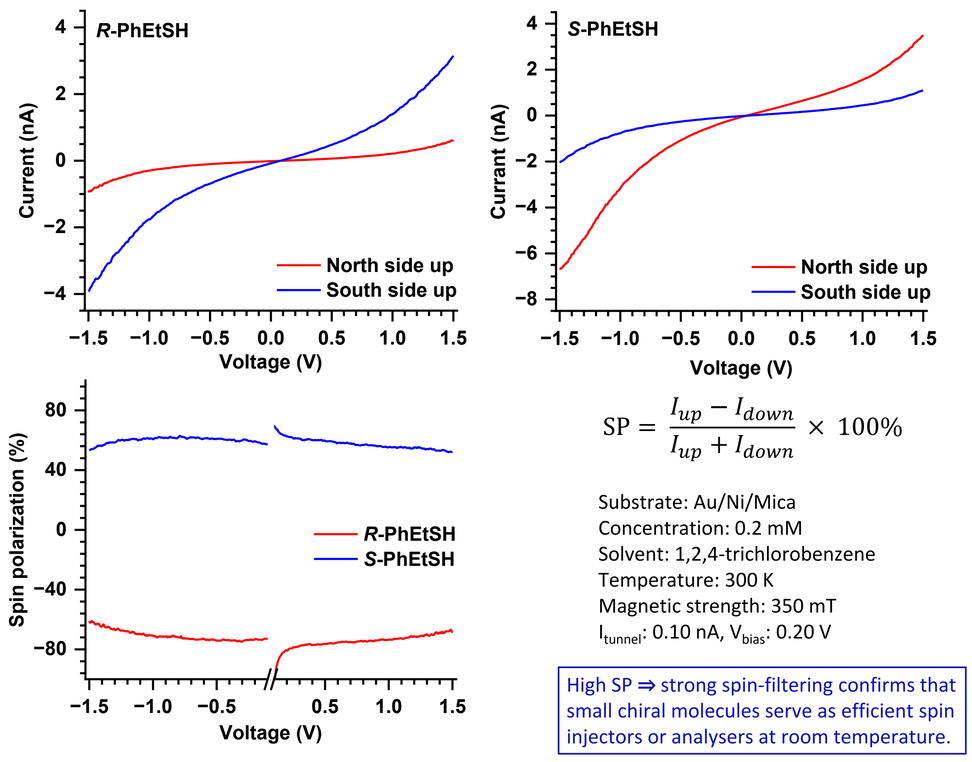


Substrate: Au (111)
Concentration: 0.2 mM
Solvent: 1,2,4-trichlorobenzene
Temperature: 300 K
I_{tunnel}: 0.10 nA, V_{bias}: 0.20 V



a: 1.49 ± 0.2, b: 1.34 ± 0.3, α: -59.80°
Inner area of the unit cell: 1.73 nm²

a: 1.42 ± 0.4, b: 1.35 ± 0.3, α: -57.30°
Inner area of the unit cell: 1.78 nm²

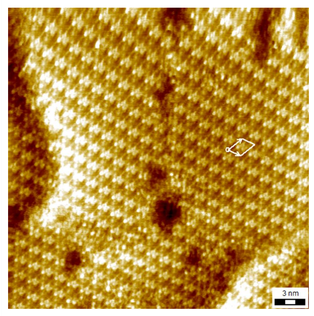


$$\mathrm{SP} = \frac{I_{up} - I_{down}}{I_{up} + I_{down}} \times 100\%$$

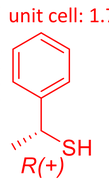
Substrate: Au/Ni/Mica
Concentration: 0.2 mM
Solvent: 1,2,4-trichlorobenzene
Temperature: 300 K
Magnetic strength: 350 mT
I_{tunnel}: 0.10 nA, V_{bias}: 0.20 V

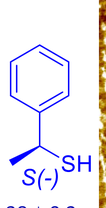
High SP ⇒ strong spin-filtering confirms that small chiral molecules serve as efficient spin injectors or analysers at room temperature.

Chirality + Spin-Orbit Coupling ⇒ Spin Filtering (CISS effect)

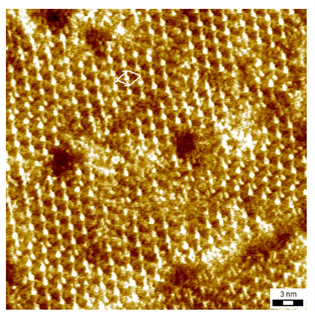


a: 1.45 ± 0.3, b: 1.37 ± 0.2, α: -58.60° Inner area of the unit cell: 1.76 nm²



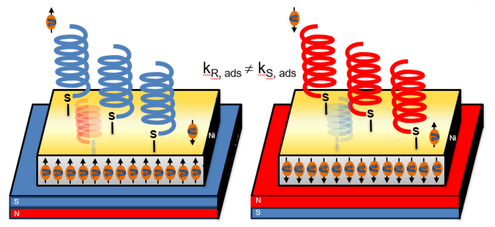


a: 1.47 ± 0.2, b: 1.38 ± 0.2, α: -59.31° Inner area of the unit cell: 1.68 nm²



5. Future Plan

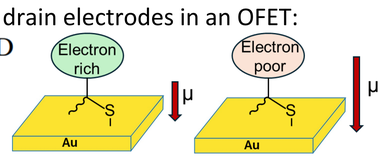
❑ Adsorption kinetics measurement with electrochemical quartz crystal microbalance (EQCM).



$$P = \frac{k'_{ads,N} - k'_{ads,S}}{k'_{ads,N} + k'_{ads,S}} \times 100\%$$

❑ SAM-modified Au surfaces as the source and drain electrodes in an OFET:

a. Electrode work function $\Delta\Phi = \Delta V_{SAM} + BD$
b. Surface energy of the modified electrodes
c. Tunnelling resistance of the SAM



❑ The high SP value of *R*- and *S*-PhEtSH has broad implications for molecular spintronics: building up organic spin valves, spin-based logic gates, or enantioselective sensors without ferromagnets.

6. Conclusion

❑ We have synthesized, fully characterized, and purified various chiral compounds to study the structure-property relationship in relation to the CISS effect.
❑ Purity and thermal stability of the enantiopure compounds has been checked by HPLC, TGA and DSC measurements.
❑ Adsorption studies on Au (111) via STM and on Au/Ni/Mica via STS measurements have been conducted for both the enantiomers of 1-Phenyethanethiol.

7. References and Acknowledgements

[1] *Chem. Rev.* **2024**, *124*, 1950−1991. [2] *Phys. Rev. Materials*, **2023**, *7*, 045002. [3] *J. Phys. Chem. C* **2023**, *127*, 14155−14162, [4] *Small* **2023**, *19*, 2302714.

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