Thiol-Functionalized Chiral Molecules: Structure-Property Relationships, Enantioselective Surface Interactions, and CISS Effect

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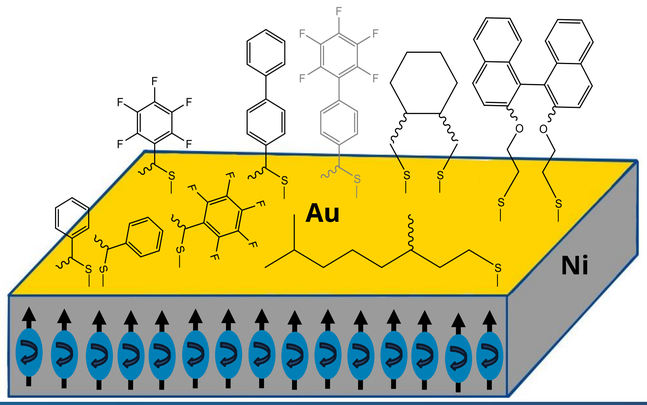
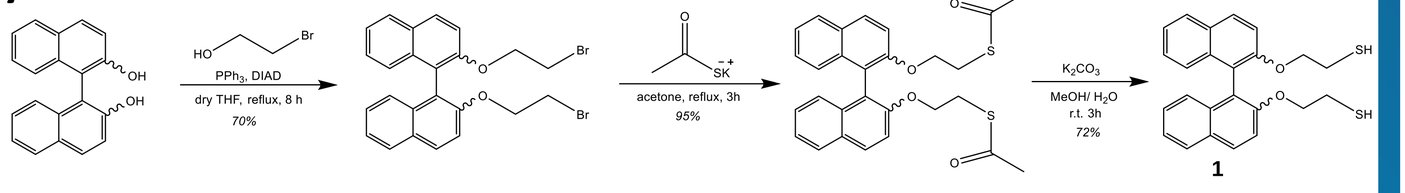
Introduction

Chirality, a fundamental property of molecules, plays a significant role in their interaction with spin-polarized surfaces. The Chiral Induced Spin Selectivity (CISS) effect links the handedness of chiral molecules to their spin-polarization, resulting in **spin-dependent enantioselective adsorption**[1] **on spin-polarized surfaces**. Our study focuses on how molecular **dipole moments**, **chemical environments**, and **stereoisomeric configurations** impact the CISS effect. We synthesized **thiol-functionalized chiral molecules** with high enantiomeric purity and the enantiomeric excess, ***ee* > 97%** is measured by High-performance liquid chromatography (HPLC) to examine their enantioselective adsorption on Au-Ni surface using scanning tunneling microscopy (STM), atomic force microscopy (AFM) and electrochemical quartz crystal microbalance (EQCM).[2,3] Understanding these spin-selective behaviors aids in designing **self-assembled monolayers (SAMs)** for organic field-effect transistors (OFETs),[4] pharmaceutical and industrial applications and selective surface interactions.



Synthesis

1.



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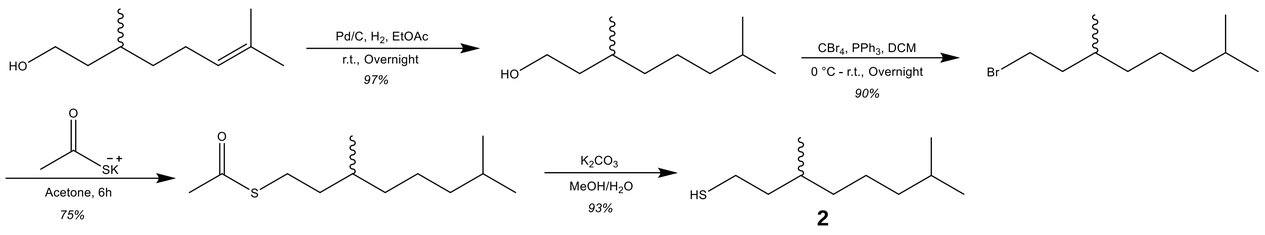

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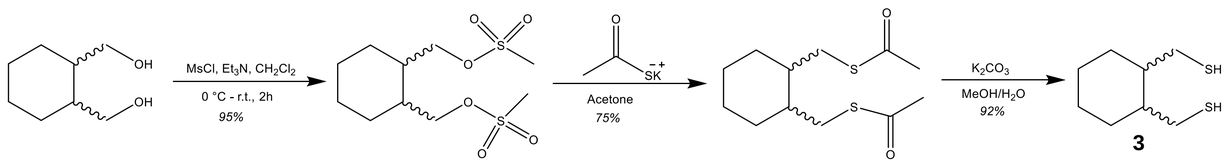

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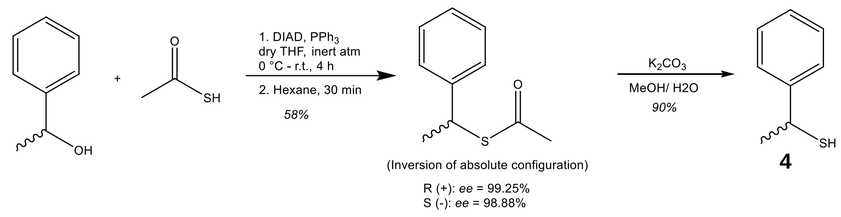
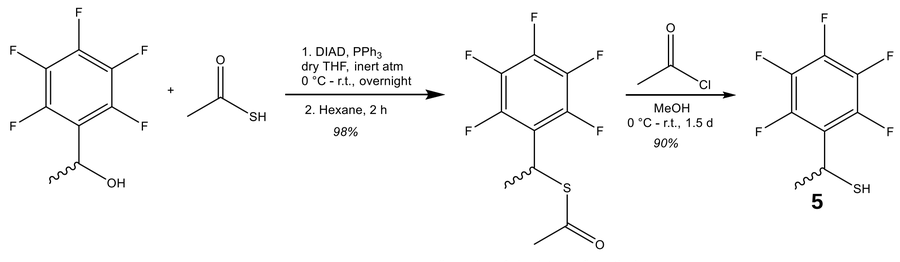


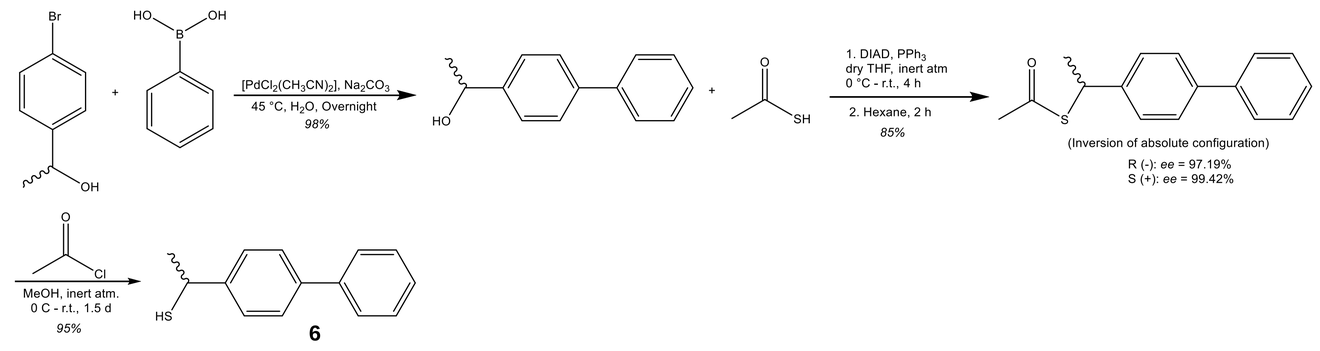
R (+): *ee* = 99.25%
S (-): *ee* = 98.88%

5.



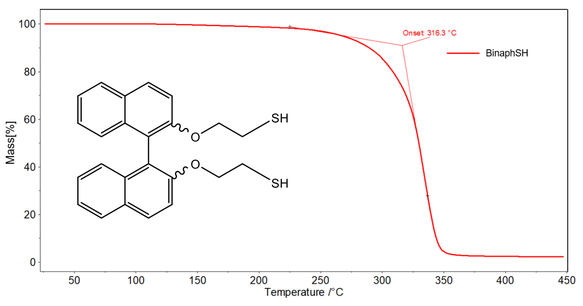
R (+): *ee* = 98.02%
S (-): *ee* = 97.89%

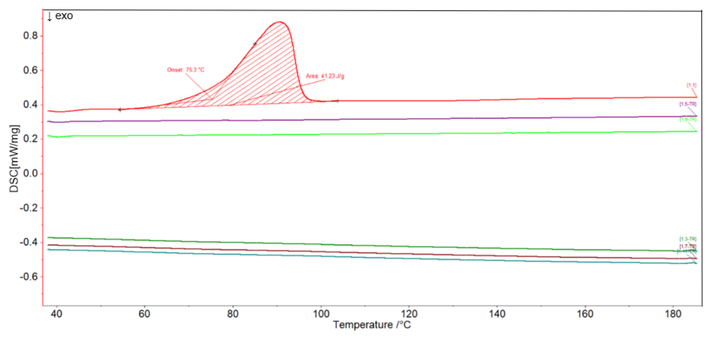
6.

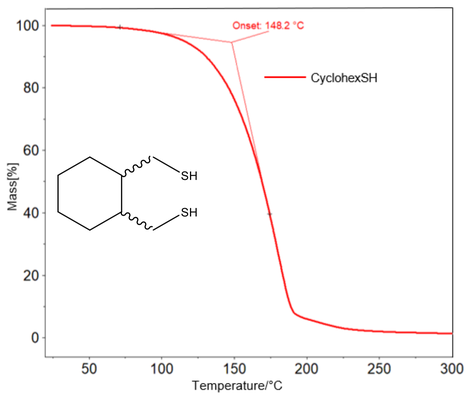


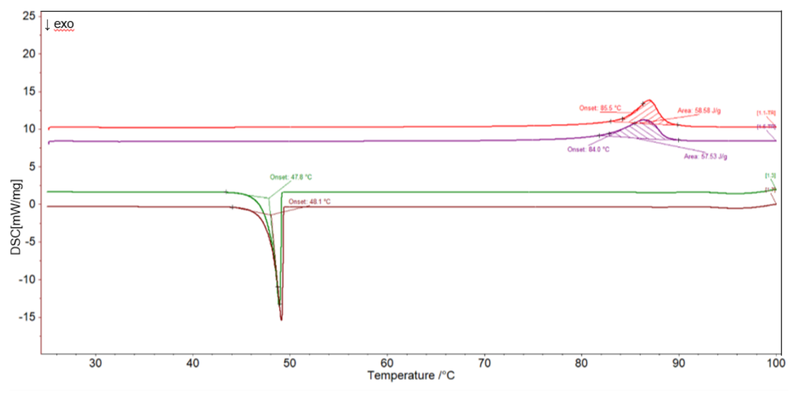
R (-): *ee* = 97.19%
S (+): *ee* = 99.42%

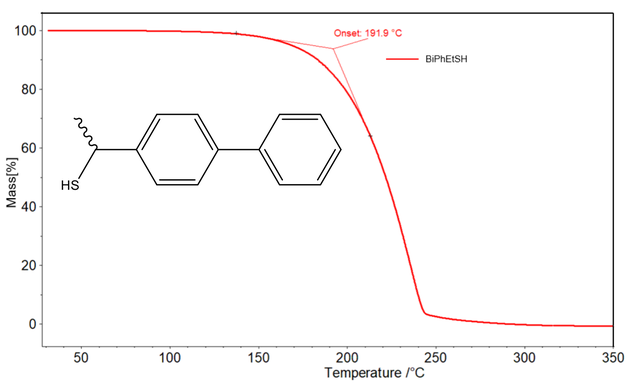
Thermal Analysis

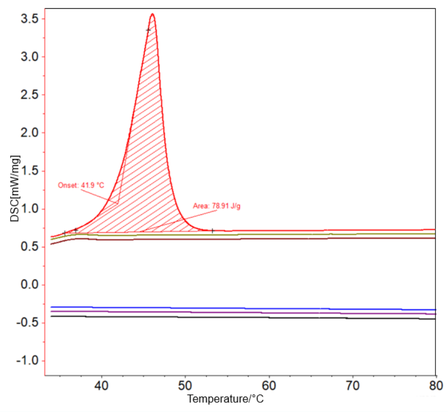




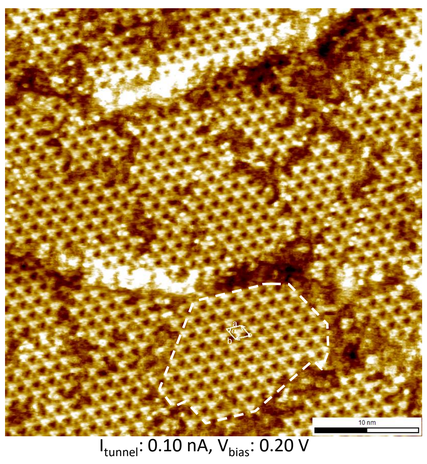




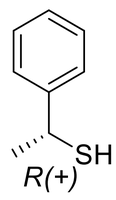




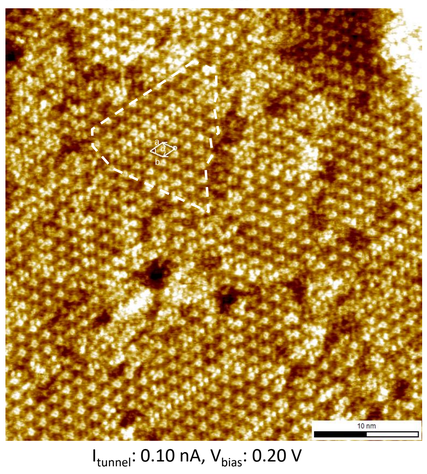
STM Measurements



I_{tunnel}: 0.10 nA, V_{bias}: 0.20 V



Substrate: Au(111)
Solvent: TCB
Concentration: 0.2 mM



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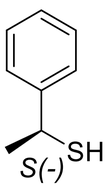
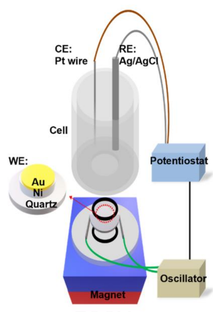


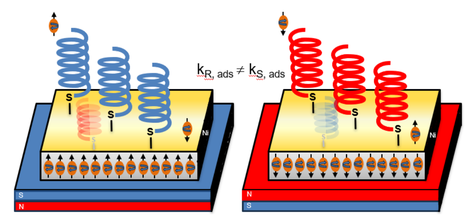
Substrate: Au(111)
Solvent: TCB
Concentration: 0.2 mM

Future Plan

❑ Study spin polarization of R and S enantiomer on Au (111)/Ni surface.



EQCM



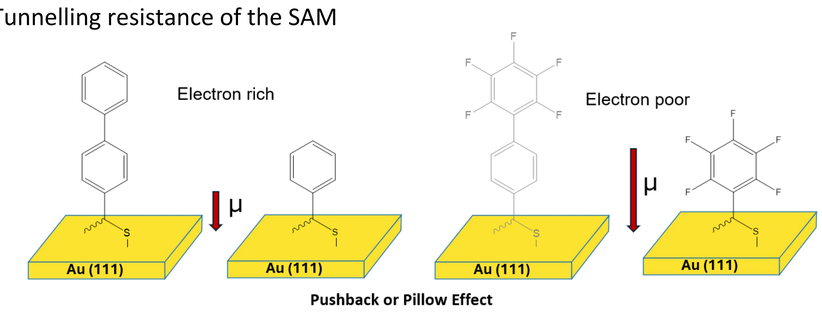
$$P = \frac{k'_{ads,N} - k'_{ads,S}}{k'_{ads,N} + k'_{ads,S}} \times 100\%$$

❑ Work function measurements depend on the surface dipole, which arises from both the intrinsic dipole of the molecules in the SAM layer (ΔV_{SAM}) and the dipole formed when the thiol anchoring groups bind to the gold surface (BD).

$$\Delta\Phi = \Delta V_{SAM} + BD$$

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

a. Electrode work function
b. Surface energy of the modified electrodes
c. Tunnelling resistance of the SAM



Pushback or Pillow Effect

❑ Synthesis of 2`,3`,4`,5`,6`-Pentafluoro-α-methyl[1,1`-biphenyl]-4-methanethiol.
❑ Further experiments will be performed to measure the CISS effect and investigate enantioselective adsorption on spin polarized ferromagnetic surface in different chiral molecules.

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.
❑ Preliminary adsorption studies Au (111) have been conducted on both enantiomers of 1-Phenyethanethiol.

References and Acknowledgements

[1] *Phys. Chem. Chem. Phys.*, 2020,22, 21570-21582. [2] *J.Phys.Chem. Lett.,* 2021,12,7854−7858. [3] *J. Phys. Chem. C*, 2023, *127*, 14155-14162. [4] *J. Mater. Chem. C*, 2015, 3, 3007-3015.

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