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

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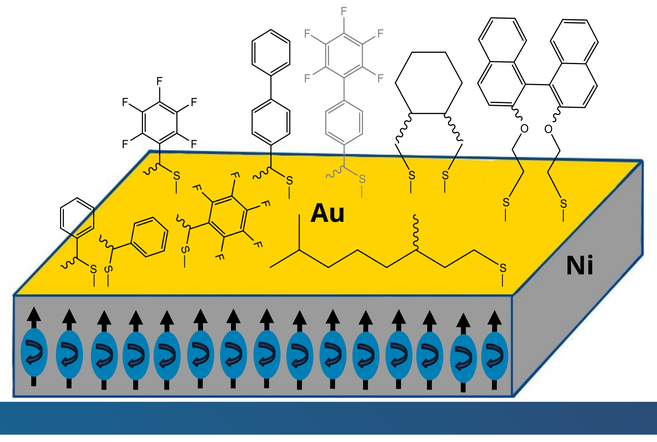
Introduction

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. PPh_3, DIAD, dry THF, reflux, 8 h, *70%*; acetone, reflux, 3h, *95%*; K_2CO_3, MeOH/ H_2O, r.t. 3h, *72%* → **1**

2. Pd/C, H_2, EtOAc, r.t., Overnight, *97%*; CBr_4, PPh_3, DCM, 0 °C - r.t., Overnight, *90%*; Acetone, 6h, *75%*; K_2CO_3, $MeOH/H_2O$, *93%* → **2**

3. MsCl, Et_3N, CH_2Cl_2, 0 °C - r.t., 2h, *95%*; Acetone, *75%*; K_2CO_3, $MeOH/H_2O$, *92%* → **3**

4. 1. DIAD, PPh_3, dry THF, inert atm, 0 °C - r.t., 4 h; 2. Hexane, 30 min, *58%*; K_2CO_3, MeOH/ H2O, *90%* → **4**

(Inversion of absolute configuration)

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

5. 1. DIAD, PPh_3, dry THF, inert atm, 0 °C - r.t., overnight; 2. Hexane, 2 h, *98%*; MeOH, 0 °C - r.t., 1.5 d, *90%* → **5**

(Inversion of absolute configuration)

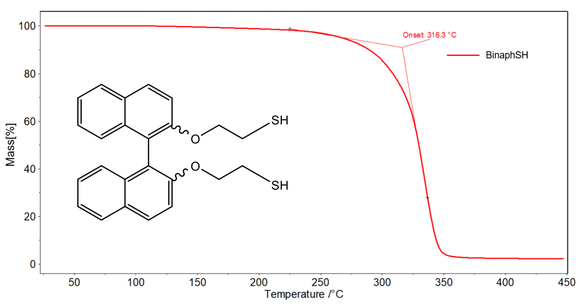
R (+): *ee* = 98.02%
S (-): *ee* = 97.89%

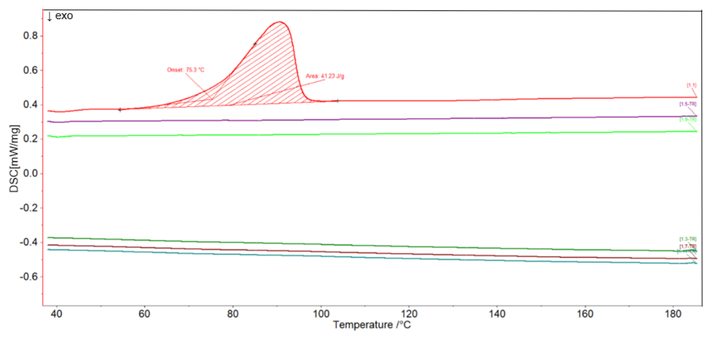
6. $[PdCl_2(CH_3CN)_2]$, Na_2CO_3, 45 °C, H_2O, Overnight, *98%*; 1. DIAD, PPh_3, dry THF, inert atm, 0 °C - r.t., 4 h; 2. Hexane, 2 h, *85%*

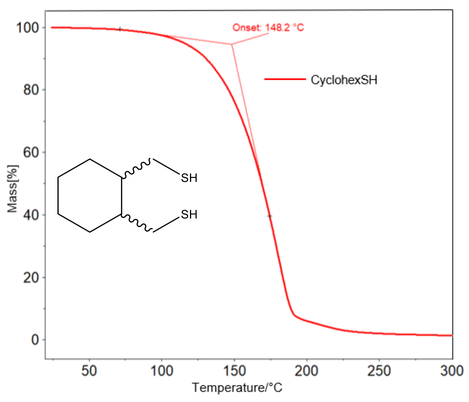
R (-): *ee* = 97.19%
S (+): *ee* = 99.42%

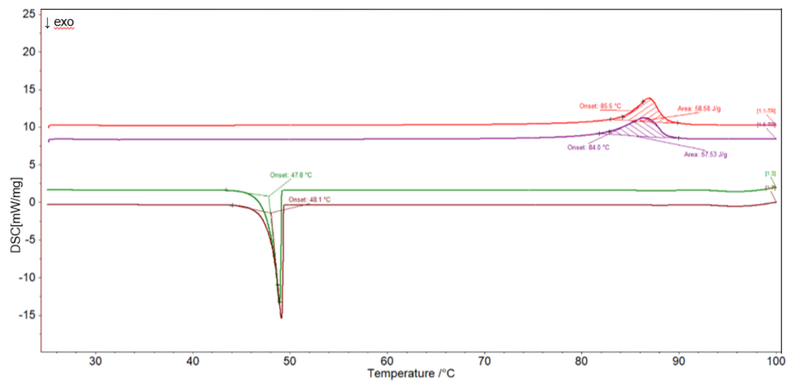
MeOH, inert atm. 0 C - r.t., 1.5 d, *95%* → **6**

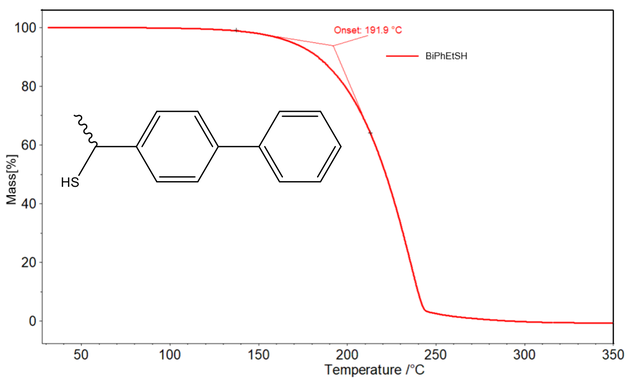
Thermal Analysis

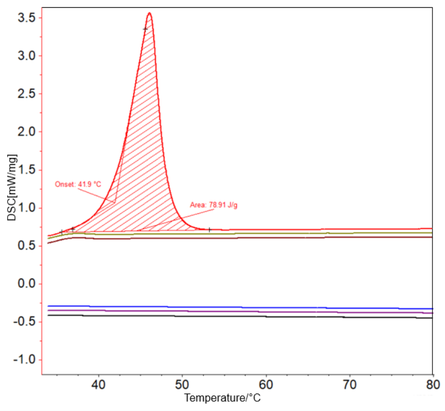




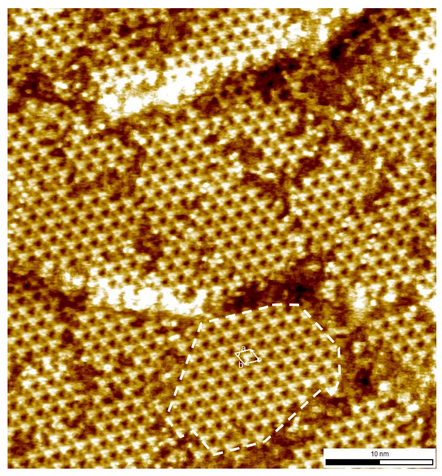


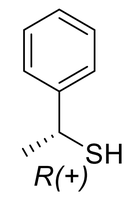




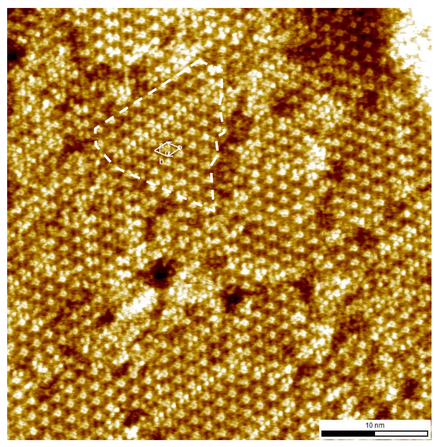


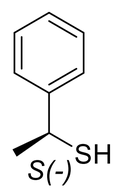
STM Measurements





Substrate: TCB/Au(111)
Concentration: 0.2 mM
I_{tunnel}: 0.10 nA
V_{bias}: 0.20 V
a: 1.49±0.2, b: 1.34±0.2, α: -59.80°
Inner area of the unit cell: 1.73 nm²

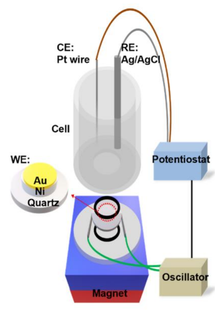




Substrate: TCB/Au(111)
Concentration: 0.2 mM
I_{tunnel}: 0.10 nA
V_{bias}: 0.20 V
a: 1.41±0.2, b: 1.38±0.2, α: -57.90°
Inner area of the unit cell: 1.66 nm²

Future Plan

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



EQCM

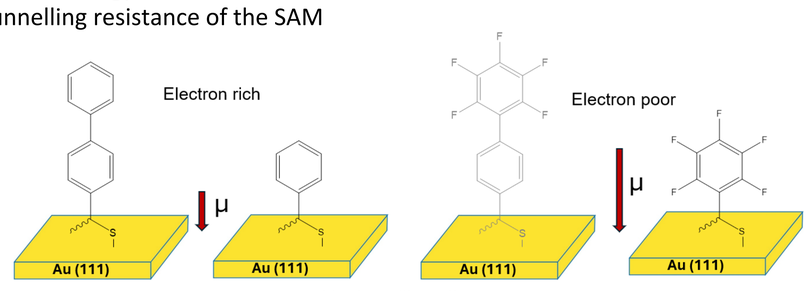
$$P = \frac{k'_{ads,N} - k'_{ads,S}}{k'_{ads,N} + k'_{ads,S}} \times 100\%$$

❑ 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.

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 on TCB/Au (111) have been conducted on both enantiomers of PhEtSH.
❑ Further experiments will be performed to measure the CISS effect and investigate enantioselective adsorption on spin polarized ferromagnetic surface in different chiral molecules.

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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