

Preparation of Chiral Surfaces from Achiral Liquid Crystals?

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Liquid crystals (LC) have been the subject of extensive research due to their unique characteristics and potential applications in various fields, including displays, sensors, and optical devices. The cyanobiphenyl family, which includes compounds like 4'-n-octyl-4-cyano-biphenyl (8CB) and 4-cyano-4'-n-dodecylbiphenyl (12CB), that are prochiral molecules, has been widely investigated for their assembly behaviour on different substrates such as graphite and gold. These achiral molecules upon adsorption onto a solid surface form chiral surfaces with domains of opposite handedness as the 2D space hinders its conformational mobility, thereby also breaking the molecular symmetry.

Expression of Chirality in Two Dimensions

Molecules confined in a plane

Achiral Molecule

Achiral

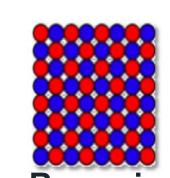
Enantiopure Molecules

Homochiral

Surface

Surface

Chiral Molecule



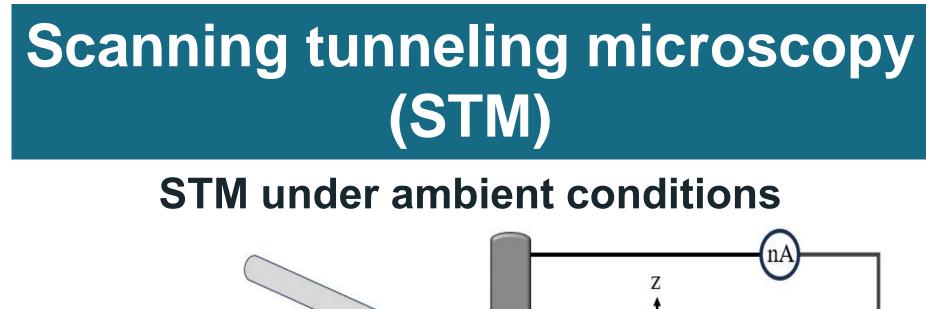
Racemic compound solution conglomerate

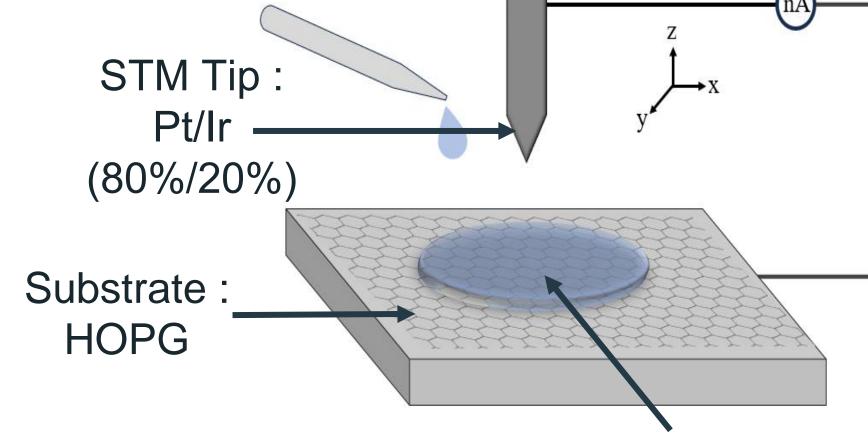
Racemic Mixture

Induction of Chirality in **Two Dimensions**

Physical means - e.g., application of magnetic field, geometric confinement.

Chemical means - *e.g.*, majority rules, "sergeant-soldiers" principle, chiral auxiliary.

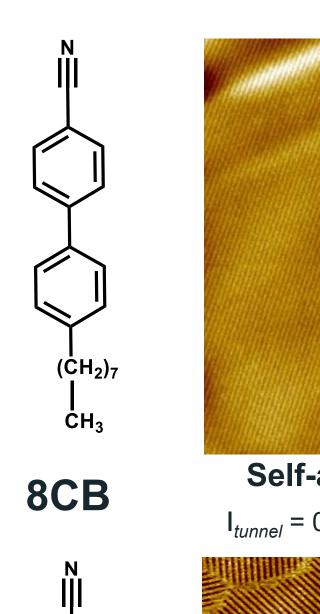




Cyanobiphenyl in ethanol

Assembly of 8CB and 12CB

8CB and 12CB assembles in a similar fashion. However, 12CB forms smaller domains compared to 8CB. There is equal surface coverage of left-handed domains and right-handed domains.



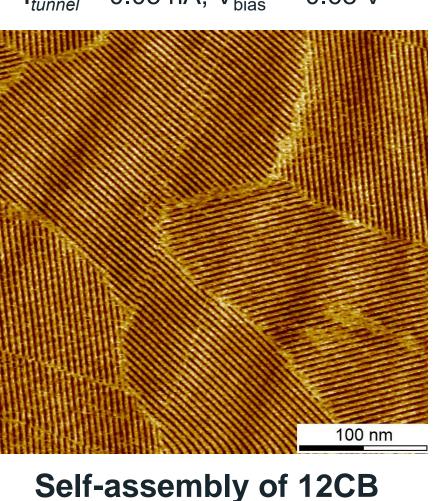
 $(CH_2)_{11}$

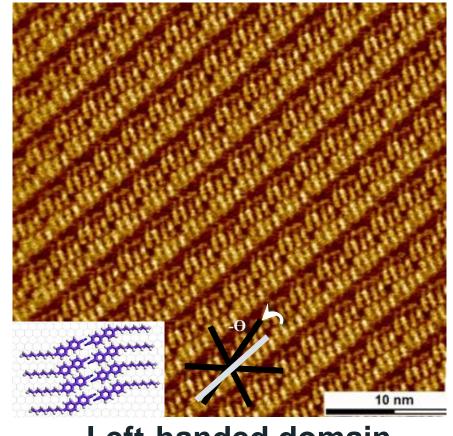
12CB

100 nm **Self-assembly of 8CB**

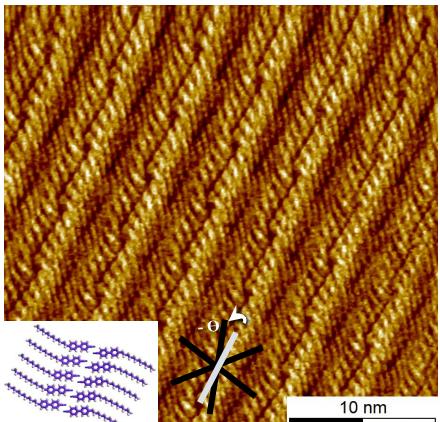
 $I_{tunnel} = 0.05 \text{ nA}, V_{bias} = -0.68 \text{ V}$



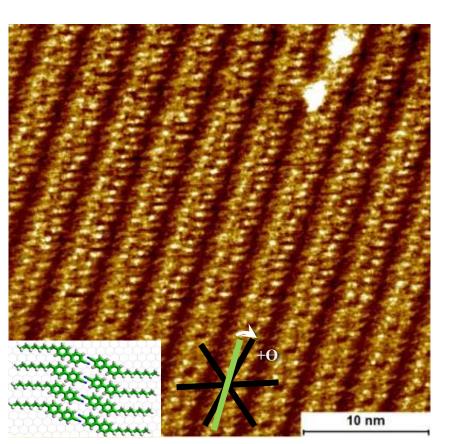




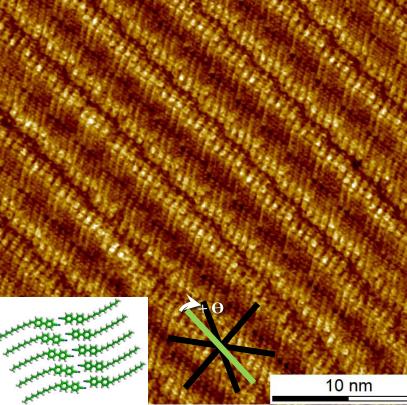
Left-handed domain 0.06 nA, 0.69 V



Left-handed domain 0.03 nA ,0.69 V

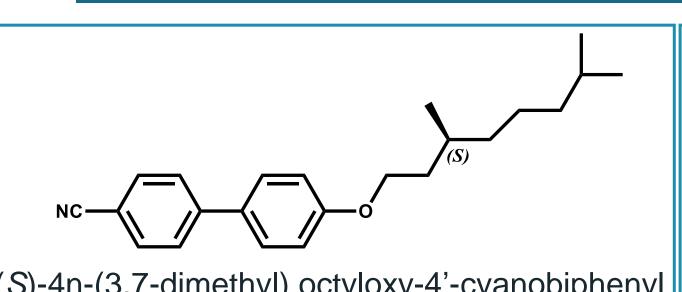


Right-handed domain 0.10 nA, 0.65 V

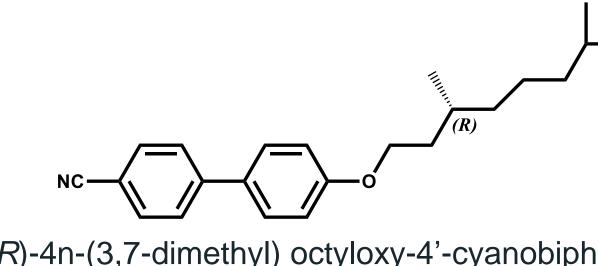


Right-handed domain 0.04 nA ,0.70 V

Influence of chiral auxiliary on the assembly of 12CB



(S)-4n-(3,7-dimethyl) octyloxy-4'-cyanobiphenyl (R)-4n-(3,7-dimethyl) octyloxy-4'-cyanobiphenyl (S)-DM8OCB



(R)-DM8OCB

3:1 mixture of 12CB and (S)-DM8OCB

In 3:1 mixture of 12CB and (S)-**DM8OCB**, of 4 sessions with 50 domains each, (59 \pm 2) % were right-handed domains.

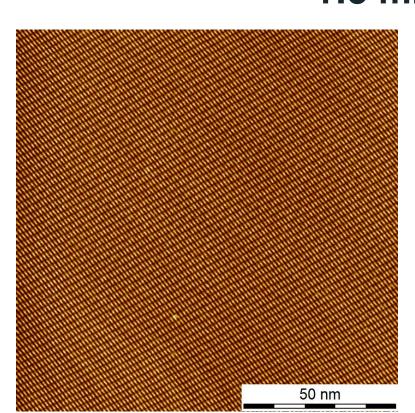
Experiments Experiments Left-handed domains Right-handed domains

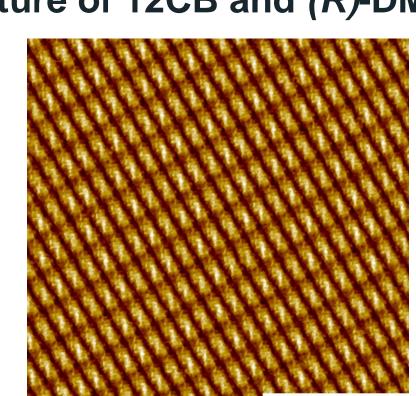
3:1 mixture of 12CB and (R)-DM8OCB

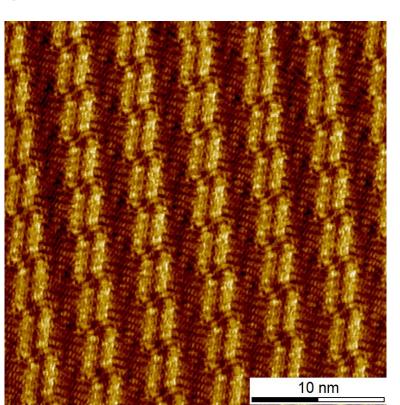
In 3:1 mixture of 12CB and (R)-DM8OCB, of 4 sessions with 50 domains each, (69 \pm 2) % were left-handed domains.

Hot-deposition of the mixtures did not increase the preference to a particular handedness.

1:3 mixture of 12CB and (R)-DM8OCB







Phase separation of 12CB and the chiral auxiliary was observed.

Conclusion and Outlook

- **12CB** forms **smaller domains** compared to 8CB and they self assembles into left- and right-handed domains in equal probability.
- Addition of chiral auxiliaries, (R)-DM8OCB and (S)-DM8OCB, to 12CB influences the supramolecular chirality of the self-assembly of 12CB.

What Next: Produce **net excess of one enantiomorph** over other using magnetic field and by changing the concentration of the auxiliary.

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"Funded by the European Union, in the frame of the Marie Skłodowska-Curie Actions (MSCA), Doctoral Network (DN) CISSE project n° 101071886. Views and opinions expressed are, however, those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Executive Agency (REA). Neither the European Union nor the granting authority can be held responsible for them."





References

- Berg, A. M., and Patrick, D. L. Angew. Chemie. 2005, 44, 1821-1823.
- Mougous, J. D., Brackley, A. J., Foland, K., Baker, R. T., and Patrick, D. L. *Phys. Rev. Lett.* **2000**, *84*, 2742.
- Parschau, M., Romer, S., and Ernst, K. H. J. Am. Chem. Soc. **2004**, *126*, 15398-15399.