

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 prochiral molecules like 4'-n-octyl-4-cyano-biphenyl (8CB) and 4-cyano-4'-n-dodecylbiphenyl (12CB), has been widely investigated for their assembly behaviour on graphite and gold. They form chiral surfaces with domains of opposite handedness, with the overall surface remaining achiral due to the formation of equal areas of both handed domains. This study investigates the influence of chiral auxiliaries and magnetic fields on the handedness of the domains. The structure and handedness of the domains formed after the addition of the chiral auxiliary were analyzed using scanning tunneling microscopy (STM). Our findings show that the introduction of a chiral auxiliary can bias the chirality of the domains. This study helps to understand the possibilities for controlling molecular orientation and chirality in self-assembled molecular networks.

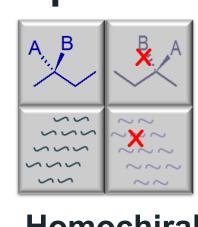
Expression of Chirality in Two Dimensions

Molecules confined in a plane

Achiral Molecule Achiral

Surface

Enantiopure Molecules



Homochiral Surface

Racemic Mixture

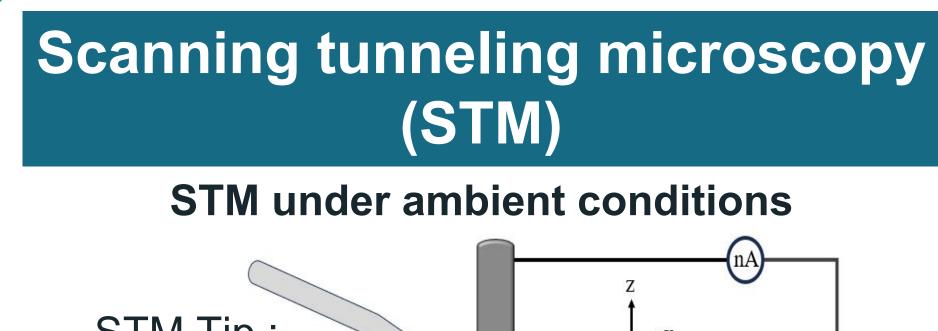
Chiral Molecule

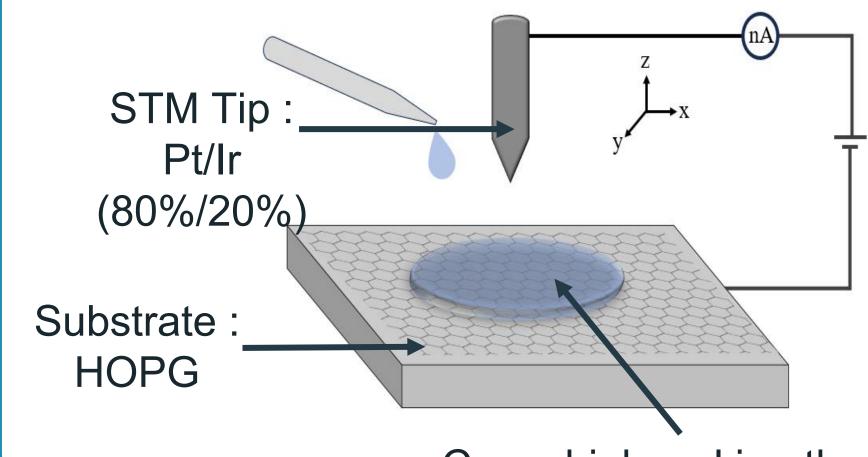
Racemic Solid compound solution conglomerate

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.

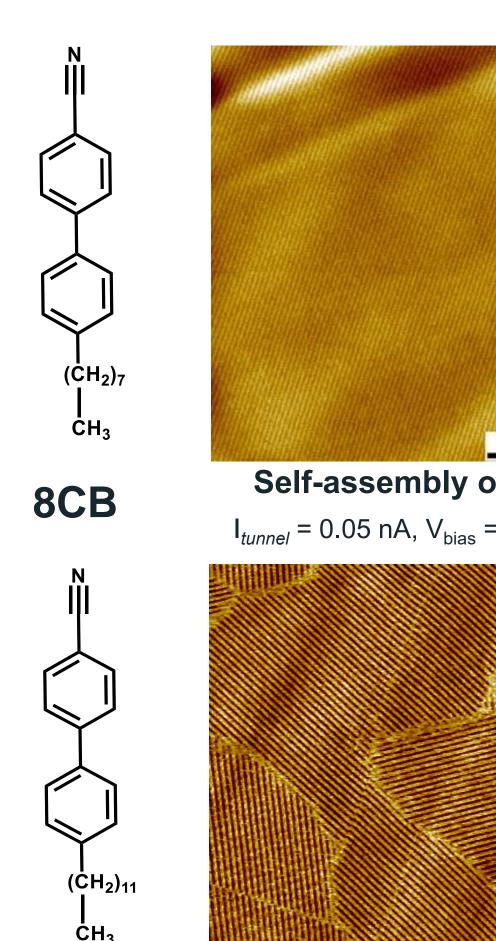




Cyanobiphenyl in ethanol

Assembly of 8CB and 12CB

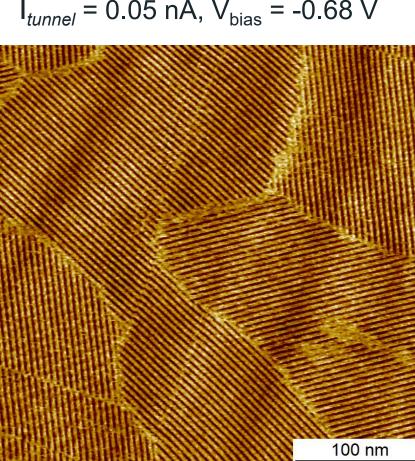
8CB and 12CB assembles in a similar fashion. However, 12CB forms smaller domains compared to 8CB. There is equal surface coverage of left-handed domains and right-handed domains.



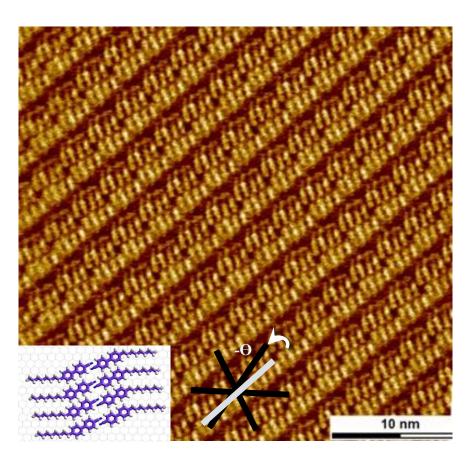
12CB

100 nm

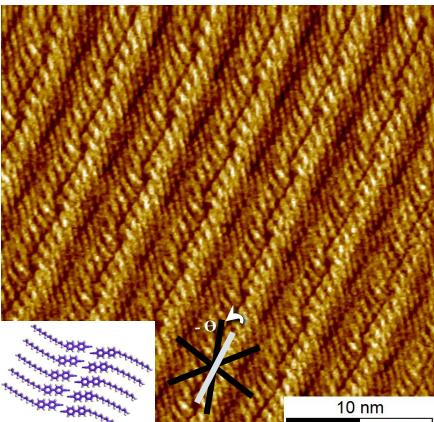
Self-assembly of 8CB $I_{tunnel} = 0.05 \text{ nA}, V_{bias} = -0.68 \text{ V}$



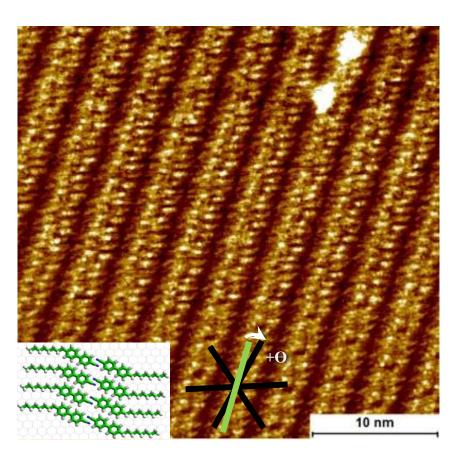
Self-assembly of 12CB 0.05 nA ,0.650V



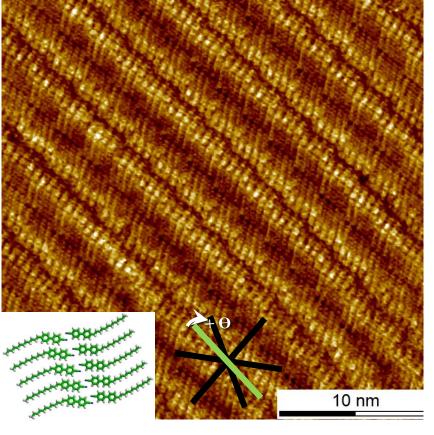
Left-handed domain 0.06 nA, 0.69 V



Left-handed domain 0.03 nA ,0.69 V

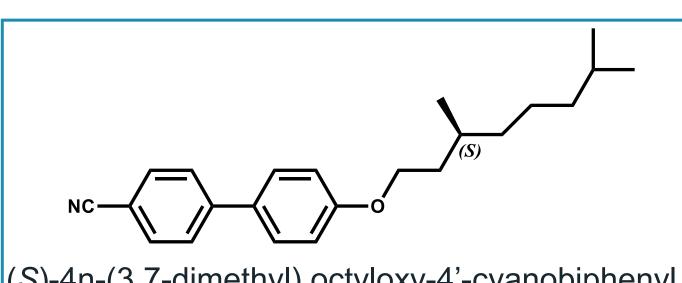


Right-handed domain 0.10 nA, 0.65 V

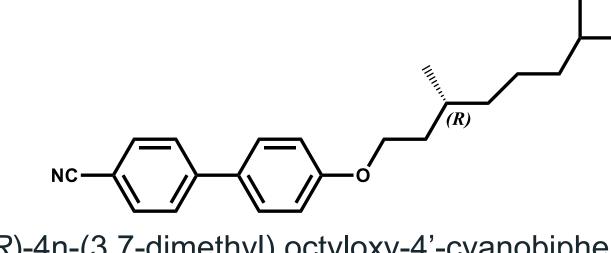


Right-handed domain 0.04 nA ,0.70 V

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



(R)-DM8OCB

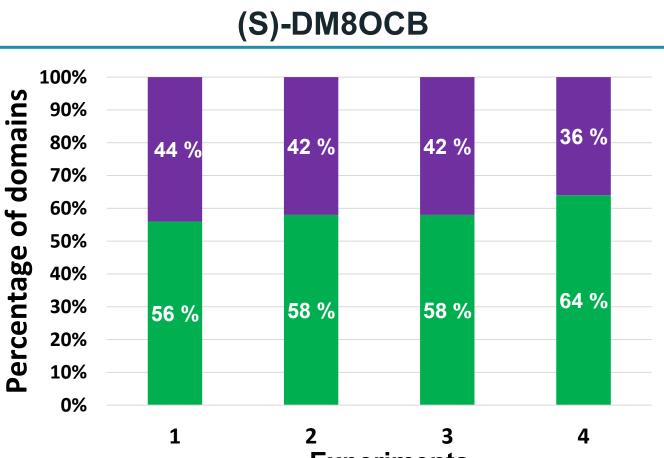
3:1 mixture of 12CB and (S)-DM8OCB

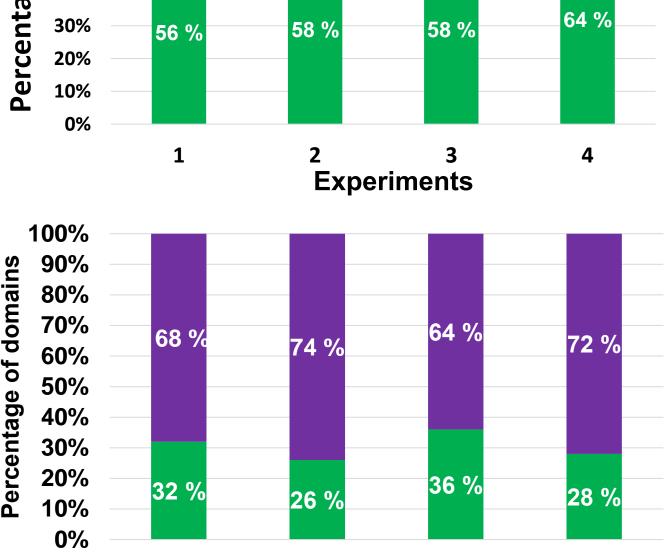
In 3:1 mixture of 12CB and (S)-

DM8OCB, of 4 sessions with 50

domains each, (59 \pm 2) % were

right-handed domains.





Experiments

Left-handed domains Right-handed domains

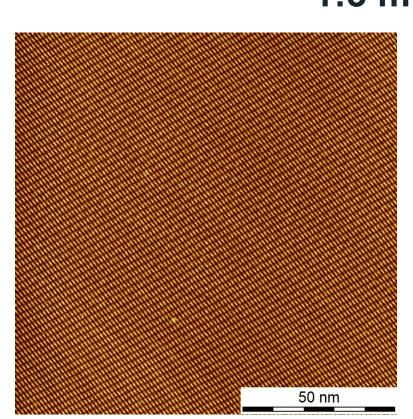
In 3:1 mixture of 12CB and (R)-DM8OCB, of 4 sessions with 50 domains each, (69 \pm 2) % were

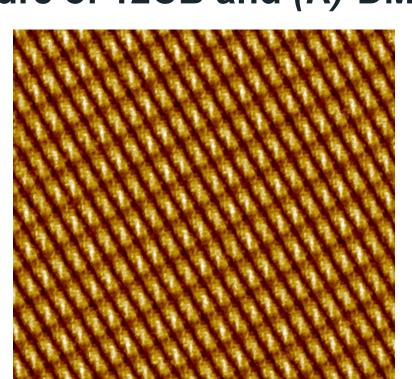
left-handed domains.

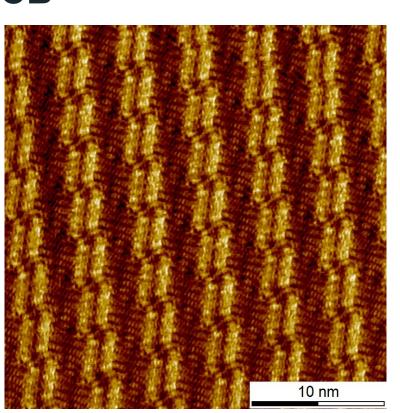
3:1 mixture of 12CB and (R)-DM8OCB

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

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





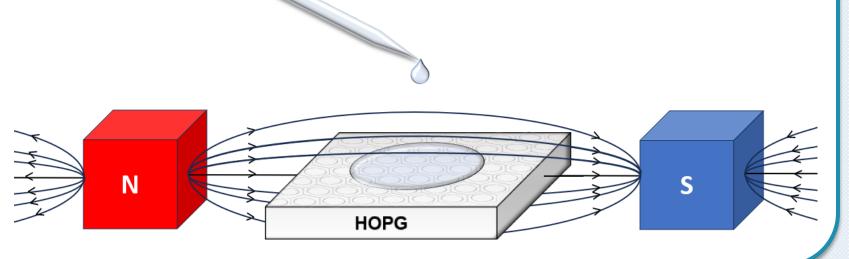


Phase separation of the chiral auxiliary and 12CB was observed.

Conclusion and Outlook

- 12CB forms smaller domains compared to 8CB and they self-assemble into left- and right-handed domains in equal probability.
- Addition of chiral auxiliaries to 12CB influences the supramolecular chirality of self-assembled molecular network 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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References

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