Poster

Self-assembly of 4-heptadecylcatechol: thermal symmetry breaking

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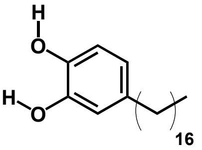
The self-assembly of organic molecules has been widely employed to produce well-defined two dimensional networks on surfaces. These self-assembled monolayers (SAMs) have potential applications in many fields, being of special interest the expression, control and transmission of chirality in these two-dimensional patterns. STM at the solid-liquid interface is a powerful technique in this kind of studies, since it allows the obtaining of submolecular resolution, and therefore, the exact molecular orientation on a given surface.

In this work, the behaviour of 4-heptadecylcatechol (Scheme 1) at the nonanoic acid/ HOPG interface has been studied. Two catechol units form a hydrogen-bonded dimmeric structure that in turn self-assembles onto the graphite surface as rows. Most SAMs described in literature are chiral, even when they are generated from prochiral, non-prochiral or non-chiral molecules. Unlike this, the pro-chiral molecule described in this contribution tends to form domains mostly racemic, where every dimmer is followed in the row by its non-superimposable mirror image (see Figure 1a, α phase).



Scheme 1 Structure of 4-heptadecylcatechol

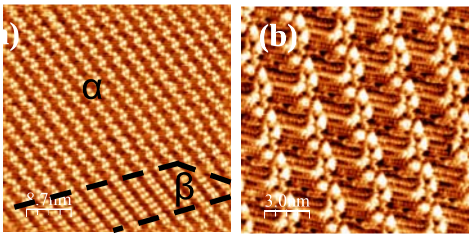


Figure 1 (a) STM image of 4-heptadecylcatechol at the nonanoic acid/ HOPG interface, showing both types of domains, racemic (α) and chiral (β). (b) Zoom area of α phase

Indeed, first experiments carried out at room temperature (20 to 25 ºC) and over a wide concentration range lead to the formation in all the cases of the racemate that covers most of the surface as checked over different substrate areas. By contrast with the kinetic control that leads to the unusual formation of the racemic structure, and to favour the formation of chiral domains, which are supposed to be thermodynamically more stable due to a more compact coverage of the surface, the samples were heated from room temperature up to 80ºC. As expected, no domains were observed at such temperatures until the system was cooled down to 25 ºC. Now, the whole surface was covered by only one enantiomer, giving rise to chiral domains that spread in one direction rows beyond the scan window (see Figure 2). In this way, we have been able to induce for the first time a thermal chiral transition on a racemic 2D pattern that generates spontaneously at room temperature (Scheme 2).

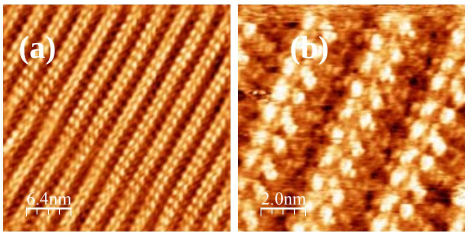
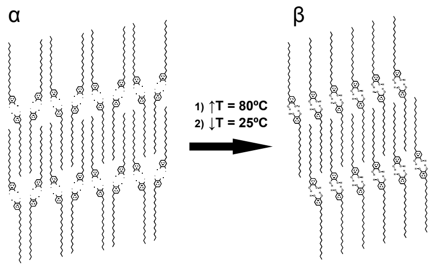


Figure 2 (a) STM image of 4-heptadecylcatechol at the nonanoic acid/ HOPG interface showing the chiral domains obtained after annealing. (b) Zoom area of the same domain.



Scheme 2 Thermal induce phase transition.

References

1. *Molecular chirality at fluid/solid interfaces: expression of asymmetry in self-organised monolayers*, N. Katsonis, E. Lacaze, B. L. Feringa, *Journal of Materials Chemisty* **2008**, *18*, 2065-2073.
2. *A thermal-induced chiral transition in self-assembled monolayers*, J. Saiz-Poseu, F. Busqué, D. Ruiz-Molina, *to be submitted.*