Up-standing Chiral Architectures through Topological Self-Assembly of Enantiopure Allenes

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Abstract

Materials capable or rotating light are of great interest in optics and photonic logics. We have at hand chiral systems presenting among the strongest chiroptical responses within organic molecules.[1] Those responses are very sensitive to conformational changes. Herein we present the first study of chiral allenes on STM. These enantiomerically pure molecules present a very densely packed topological self-assembly on Ag(111).

The flexibility and chirality of (*P,P*)-**1** (Figure 1), enable the topological self-assembly on a Ag[1,1,1] as ascertain by the combination of experimental ultra-high vacuum scanning tunneling microscopy (UHV-STM) and molecular dynamics (Figure 2).[2] We achieved the construction of up-standing complex chiral architectures from enantipure allenes. Topological self-assembly was found to have a crucial role in the formation of these novel chiral surfaces as ascertained by a combination of computational modeling, mass spectrometry and molecular manipulation studies. Careful analysis of high-resolution STM images confirm the transfer of chirality from single molecules to 2D networks. The use of enantiopure allenes with strong chiroptical responses along with their up-standing organization opens great possibilities for the construction of new smart materials that could be implemented into devises like sensors, catalysts, or logic gates. We expect to obtain chiral amplification due to the ordering of the chiral molecules as well as to control of the chiroptical responses by a tunable applied electric filed.

References

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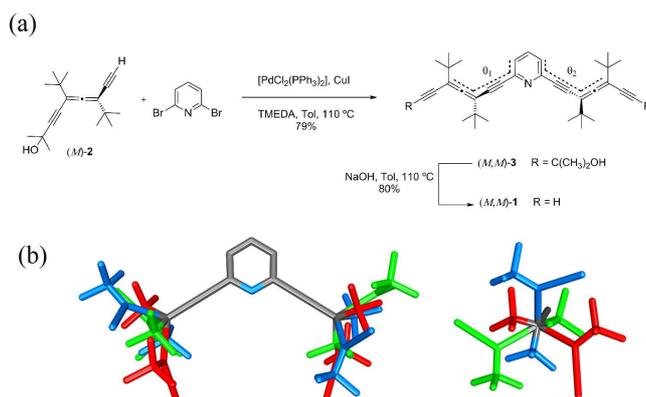
Figure 1. (a) Synthesis of (*M,M*)-**1** (Tol: Toluene) - *N,N,N´,N´*-Tetramethylethylenediamine (TMEDA). (b) Left: Three different conformations (blue, green, red) of (*M,M*)-**1** by rotation about θ_1 and θ_2. Right: View of the allene unit along the axis of rotation.

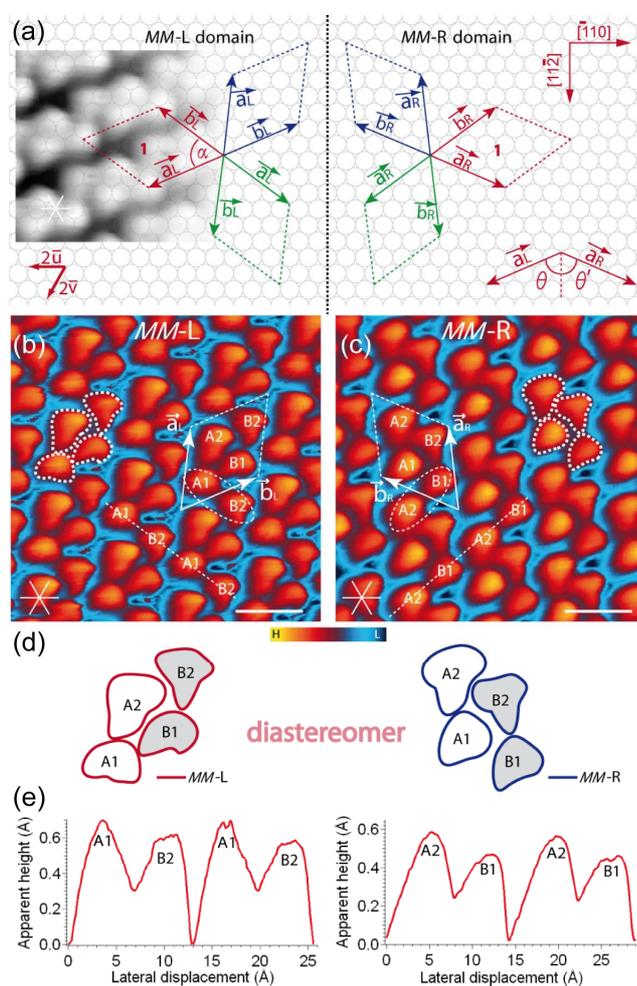

Figure 2. (a) Model of the molecular network unit-cells with proposed registry. Inset shows STM image in the same scale (Ub = −0.5 V, It = 0.1 nA). The unit-cell vectors aL and bL enclose the angle α. The angles θ, θ' are defined between the [11−2] direction and vector aL and aR, respectively. The primitive vectors of the Ag(111) surface are u and v. All six domains are experimentally observed (see Figure S3). High-resolution STM images of diastereomeric domains: (b) MM-L (Ub = −0.3 V, It = 0.1 nA) and (c) MM-R (Ub = −0.35 V, It = 0.05 nA). Dashed circles are contours of each single-molecule feature. Scale bars denote 10 Å. (d) Comparison of the outlines of MM-L and MM-R units. (e) The profiles of MM-L and MM-R domains are compared.