Hierarchical Chiral Expression from the Nano- to Mesoscale in Synthetic Supramolecular Helical Fibers of a Nonamphiphilic C-3-Symmetrical pi-Functional Molecule

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Résumé en anglais	The controlled preparation of chiral structures is a contemporary challenge for supramolecular science because of the interesting properties that can arise from the resulting materials, and here we show that a synthetic nonamphiphilic C-3 compound containing pi-functional tetrathiafulvalene units can form this kind of object. We describe the synthesis, characterization, and self-assembly properties in solution and in the solid state of the enantiopure materials. Circular dichroism (CD) measurements show optical activity resulting from the presence of twisted stacks of preferential helicity and also reveal the critical importance of fiber nucleation in their formation. Molecular mechanics (MM) and molecular dynamics (MD) simulations combined with CD theoretical calculations demonstrate that the (5) enantiomer provides the (M) helix, which is more stable than the (P) helix for this enantiomer. This relationship is for the first time established in this family of C-3 symmetric compounds. In addition, we show that introduction of the wrong enantiomer in a stack decreases the helical reversal barrier in a nonlinear manner, which very probably accounts for the absence of a majority rules effect. Mesoscopic chiral fibers, which show inverted helicity, i.e. (P) for the (S) enantiomer and (M) for the (R) one, have been obtained upon reprecipitation from dioxane and analyzed by optical and electronic microscopy. The fibers obtained with the racemic mixture present, as a remarkable feature, opposite homochiral domains within the same fiber, separated by points of helical reversal. Their formation can be explained through an oscillating crystallization mechanism. Although C-3 symmetric disk-shaped molecules containing a central benzene core substituted in the 1,3,5 positions with 3,3-diamido-2,2-bipyridine based wedges have shown peculiar self-assembly properties for amphiphilic derivatives, the present result shows the benefits of reducing the nonfunctional part of the molecule, in our case with short chiral isopentyl chains. The research reported herein represents an important step toward the preparation of functional mesostructures with controlled helical architectures.
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