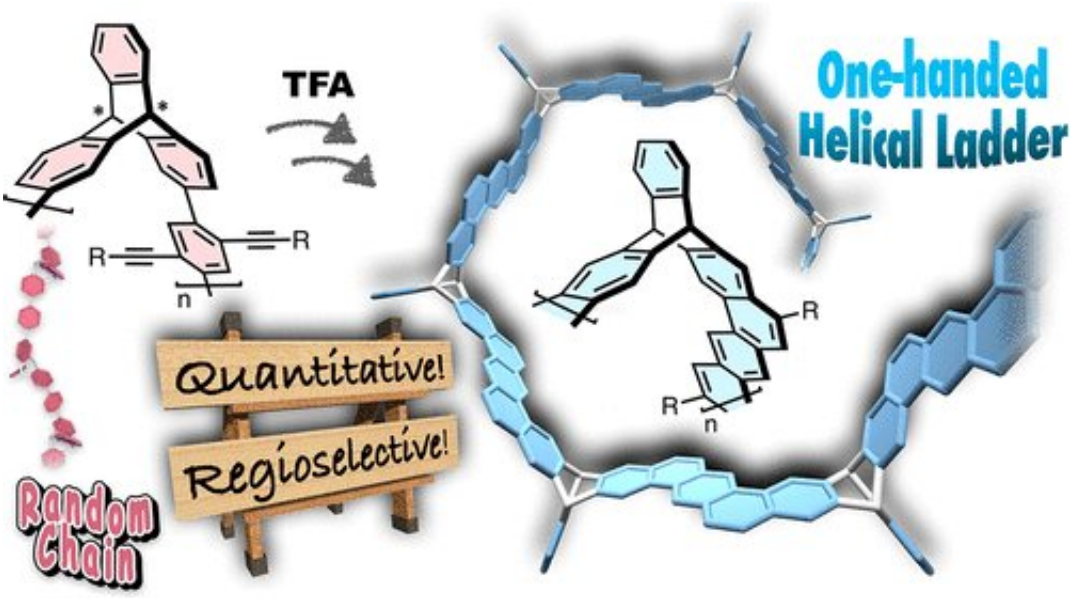
Synthesis of helical ladder polymers

May 16 2019



Report: An efficient synthesis of optically active ladder-type molecules and polymers through intramolecular cyclization of chiral triptycenes containing bis[2-(4-alkoxyphenyl)ethynyl]phenylene units. The electrophile-induced cyclization reactions are directed away from the bridgehead carbon atoms of triptycene by steric factors, thereby producing one-handed twisted ladder units without any detectable byproducts. Moreover, the quantitative and regioselective nature of this intramolecular cyclization allowed us to synthesize optically active ladder polymers with a well-defined one-handed helical geometry in which homoconjugated dibenzo[a,h]anthracene units are helically arranged along the main chain. This synthesis route enables the construction of a variety of nanoscale helical ladder architectures and provides an entry into new chiroptical materials.

Researchers at Kanazawa University synthesized helical ladder polymers with a well-defined cyclic repeating unit and one-handed helical geometry, as they reported in the *Journal of the American Chemical Society*.

Ladder polymers—molecules made of adjacent rings sharing two or more atoms—are challenging to synthesize, because they require highly selective, quantitative reactions to avoid the formation of branching structures or of interruptions in the ring sequence in the polymer chain. Moreover, most existing strategies for the synthesis of ladder polymers suffer from severe limitations in terms of selectivity and quantitativity. Another important type of molecules are molecules with a helical structure (such as DNA and proteins), which play an important role in molecular recognition and catalysis. Thus, the fabrication of molecules that possess both a ladder and a helical structure could open up new applications of polymeric materials.

Tomoyuki Ikai, Timothy M. Swager and colleagues from an international collaboration started from triptycene, an aromatic hydrocarbon that is an achiral molecule, but from which chiral derivatives can be obtained by introducing substituents in the benzene rings in an asymmetric manner. Optically active triptycenes have practical uses as chiral materials, for example for chiral separation and circularly polarized luminescent materials. The researchers then used the chiral triptycenes as a framework to efficiently form single-handed helical ladder polymers using electrophilic aromatic substitution. Steric repulsion in the system resulted in the formation of one-handed twisted ladder units. The reactions were quantitative and regioselective (that is, there is a preferred direction of chemical bonding), which enabled the synthesis of optically active ladder polymers with well-defined helical geometry. No byproducts were detected.

Several techniques, including spectroscopy and microscopy techniques,

were used to characterize the reaction products during synthesis, and molecular dynamics simulations were employed to understand the structure of the resulting molecules, confirming the right-handed helical ladder geometry. The researchers also measured the optical activity of the molecules.

The newly reported synthesis route will open up the synthesis of nanoscale helical ladder architectures and optically active chiral materials. "We believe that these ladder polymers, which can fall into a new category of helical polymers, represent a promising class of advanced materials for use as nanochannels for molecular/ion transport, organic electronics, specific reaction fields, and functional hosts through further modification of the backbone and pendant units," commented the authors in the paper.

Chirality

A chiral system is an asymmetric system that cannot be superimposed on its mirror image (the word comes from the Greek for hands, because hands are a good example of a chiral system). Most biomolecules and molecules used in pharmaceutical compounds are chiral. Two molecules with opposite chirality have the same composition and structure, but mirror shapes, and they have different properties when they interact with other chiral molecules.

Electrophilic aromatic substitution

Electrophilic aromatic substitution is an organic reaction in which one atom attached to an aromatic system is replaced by an atom that is an electron acceptor (an electrophile). It is an important class of reactions, usually involving a benzene ring.

Steric repulsion

Steric repulsion is an effect that results from repulsive forces kicking in when atoms get too close to each other, so that their electron clouds overlap.

More information: Tomoyuki Ikai et al. Triptycene-Based Ladder Polymers with One-Handed Helical Geometry, *Journal of the American Chemical Society* (2019). DOI: 10.1021/jacs.8b13865

Provided by Kanazawa University