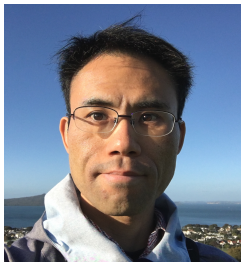
Chemistry of Multi-Layered Helicenes



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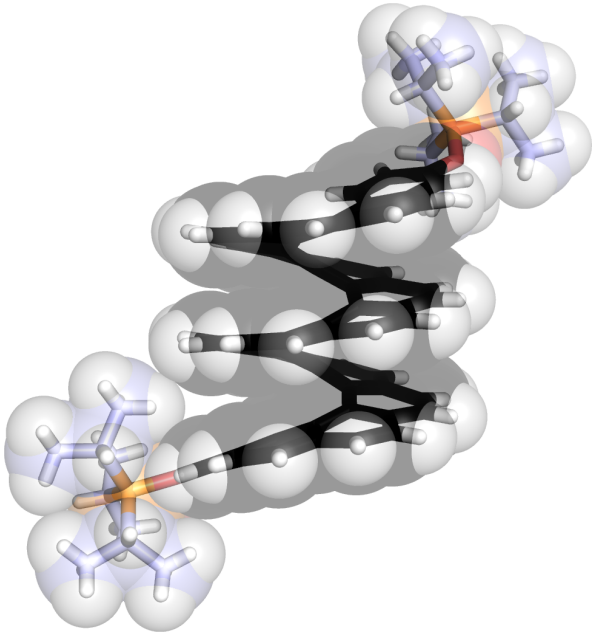
Research impact at a glance

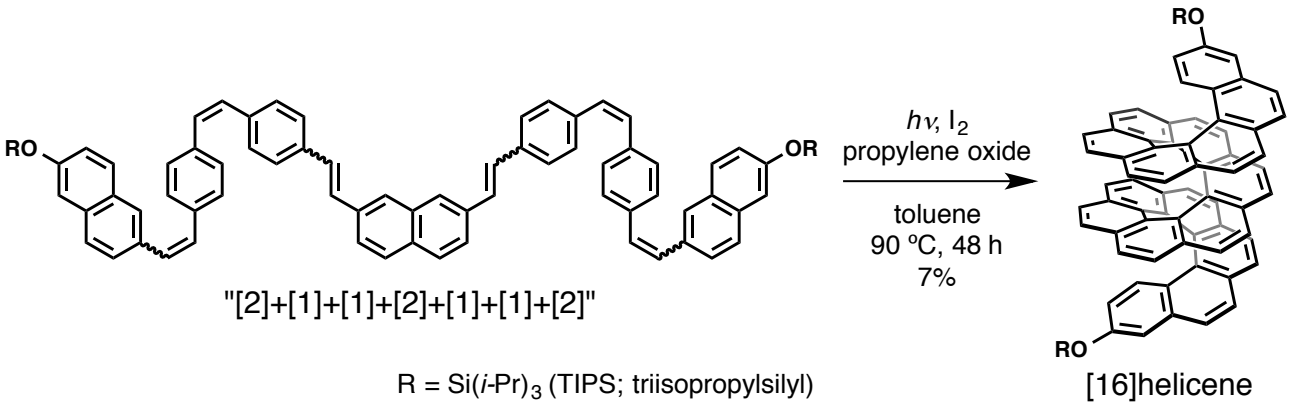
[*n*]Helicenes are helical polyaromatic compounds formed by *n* number of *ortho*-fused aromatic rings. With increasing *n* number, the π electrons start to form additional layers; a double layer at *n* = 7 and a triple layer at *n* = 13. The right figure is the X-ray crystal structure of [16]helicene, which is the longest [*n*]helicene that has been synthesized to date (C gray/blue, O red, Si yellow). As expected, the *i*, *i*+6, *i*+12 benzene rings (*i* = 1, 2, 3, or 4) are forced to form the triple-layered structure. The middle layer is tightly compressed by the upper and lower layers.



Detailed description of the research

Background:

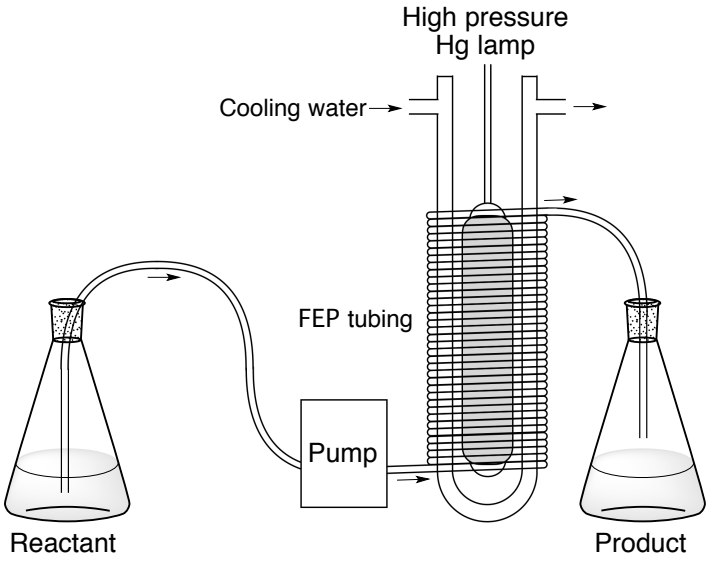
Our synthetic strategy toward [16]helicene is multiple photocyclization of a single-strand oligo(arylene–vinylene) precursor, in which the simple aromatic subunits [1] and [2] (namely, benzene and naphthalene units) are precisely arranged so as to avoid unfavorable side reactions under photoirradiation (see the next page). Actually, a [16]helicene with bulky triisopropylsilylether (TIPSO) protection was prepared by six-fold photocyclization of the precursor with a [2]+[1]+[1]+[2]+[1]+[1]+[2] sequence (where "+" denotes vinylene linkers). Finally, the TIPSO-[16]helicene was converted to unsubstituted [16]helicene in further three steps. We presume that the judiciously-designed precursor has an intrinsic propensity to exhibit spontaneous helical folding under photoirradiation, which may help the formation of helicene skeletons.



On-going research:

1. Continuous flow photoreaction

A more efficient synthetic strategy toward [16]helicene is necessary to investigate the physical properties and functions. In order to overcome the drawbacks of conventional batch photoreactions, which should decompose [16]helicene during prolonged photoirradiation, we try to develop a continuous flow technique for the synthesis of [16]helicene.



2. Partially-fluorinated helicenes

In double-layered helicenes, interlayer interactions between the overlapped aromatic rings are generated. If aromatic rings at the second layer are polyfluorinated to be electron-deficient, favorable arene–perfluoroarene stacking interactions become possible. Expecting unusual properties derived from the electron-deficient second layer, we try to synthesize terminally-tetrafluorinated [7]helicene.

Selected publications

Original papers:

1. T. Murase, T. Suto, H. Suzuki, “Azahelicenes from the Oxidative Photocyclization of Boron Hydroxamate Complexes”, *Chem. Asian J.* **2017**, *12*, 726–729.
2. K. Mori, T. Murase, M. Fujita, “One-Step Synthesis of [16]Helicene”, *Angew. Chem. Int. Ed*. **2015**, *54*, 6847–6851.