Synthesis of π-Extended Helicenes Through Cyclization of *p*-Terphenyl-based Precursors

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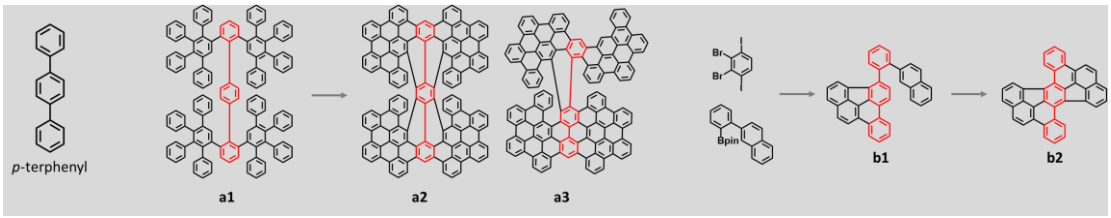
Helicenes, a class of polycyclic aromatic hydrocarbons with non-planar, helical structures, have attracted significant attention for their unique chiroptical properties and potential applications in optoelectronics, enantioselective catalysis, and nanotechnology.[1] Incorporating helicenes into nanographene frameworks presents a promising avenue for creating π-extended helicenes with enhanced electronic and structural properties.[2] The *p*-terphenyl backbone, with its rigid and extended conjugated structure, serves as an excellent platform for creating oligoarylene precursors for this aim.[3]

We have explored the synthesis of unprecedented π-extended helicenes through the oxidative cyclodehydrogenation of oligophenylene precursors having the *p*-terphenyl backbone. By utilizing Diels–Alder cycloaddition and Scholl reaction as key steps, we obtained π-extended double [9]helicene (**a2**) along with its isomer [7][9]helicene (**a3**) as a byproduct through aryl migration. Compared to **a3**, **a2** exhibits a higher photoluminescence quantum yield Φ of 18% in the NIR region and an increased circular dichroism dissymmetry factor g_{CD} of 0.019 in the visible region, rendering it an excellent near-infrared emissive chiral PAH. We further investigated the impact of acid and temperature on the formation of the two main products. Moreover, we have also synthesized unprecedented double [5]helicene **b2** with five-membered rings, via an unexpected domino Suzuki coupling and cyclization reactions in a mild condition, demonstrating a new approach to achieve π-extended helicenes with five-membered rings.



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