

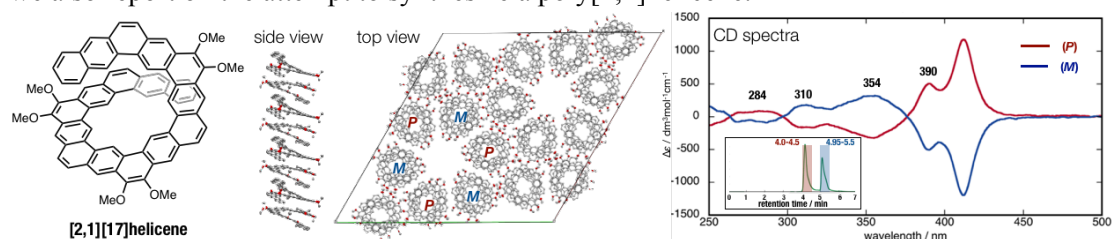
Synthesis, Structure and Properties of π -Expanded Carbohelicenes

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Helicene represents one of the non-planar aromatics with a helical structure. The development of helicene chemistry has diversified by elongation, conjugation of multi-helicene, and laterally π -elongation of the helicene structure.¹ In particular, expanded helicenes with a larger diameter of the shaft are one of great interests in this field and materials science.² They are expected to exhibit the molecular encapsulation ability taken advantage of their vacancies, and larger π -conjugation and π - π overlapping between helical pitches than conventional helicenes, resulting in novel electrical, optical, and chiroptical properties. Particularly, [2,1]helicenes, kekulene-like-shaped expanded helicenes, have attracted much attention due to those simple and beautiful structures and unique physical and electronic properties.^{2a,b,c} However, the chemistry of [2,1]helicenes are still in its infancy and only shorter racemic analogues with 13 benzene rings were reported so far.

Herein, we report the synthesis of novel expanded [2,1]carbohelicenes composed of 15 and 17 benzene rings. The stepwise Wittig elongation of dibromo phenanthrene units having aldehyde and phosphonium salt and subsequent ring closure by Yamamoto coupling successfully afforded up to [2,1][17]helicene. The structural and photophysical evaluations by NMR and X-ray crystallographic analyses and conventional spectroscopic analyses were also performed. Furthermore, we succeeded in the optical resolution of right- and left-handed helicenes for the first time in the related molecules, and clarified those chiroptical properties by circular dichroism (CD). The racemization process and photophysical properties were also estimated by computational studies. In the presentation, we also report on the attempt to synthesize a poly[2,1]helicene.



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