Synthesis of π-Extended [2*n* + 1]Helicenes: Helically Twisted Wire Molecules with Large Effective Conjugation Length

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π-Conjugated aromatic molecules with helically twisted geometry are fascinating materials with potential applications in inductors, springs, and pressure sensors working on the nanometer scale. In this work, we synthesized π-extended [5], [7], and [9]helicene derivatives **1**–**3** (Figure 1a).

The homogeneously π-extended helicenes showed the lowest-energy absorption bands at 500−1100 nm (i.e., $\lambda_{max,abs}$ = 529, 675, 809 nm for **1**, **2**, and **3**, respectively), which were attributed to the HOMO→LUMO transitions by DFT calculations. Given that the excitation energy of the original [*n*]helicenes is largely independent of the length of the helical structure, the prominent red shift of **1**–**3** in the absorption bands is likely attributed to significant orbital interactions between phenanthrene subunits in the π-extended helicene framework. Enantiomers of **1**–**3**, isolated by HPLC with a chiral column, exhibited Cotton effects with dissymmetry factors of g_{CD} = 0.2–3.0 × 10^{-2} (Figure 1b). Interestingly, π-extended helicenes **1**–**3** were not emissive due to their ultrafast nonradiative decay dynamics in the $S_1 \rightarrow S_0$ transition with time constants of about 1 ps, which is marked contrast to emissive planar molecules such as rylenes[1] and carbon-bridged oligo(phenylene vinylene) molecules[2].

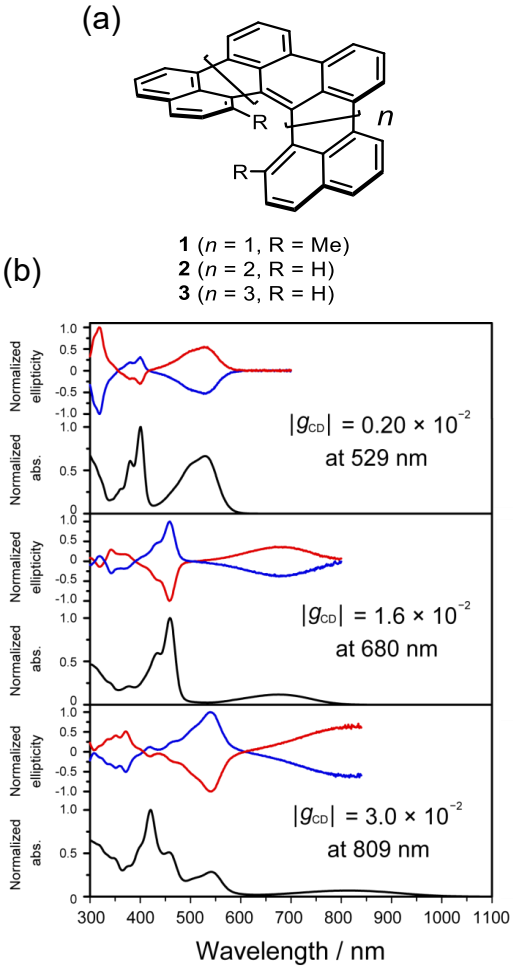

Figure 1. (a) Molecular structures of π-extended helicenes **1**–**3** (b) Absorption and circular dichroism (CD) spectra of **1** (top), **2** (middle), **3** (bottom). Red and blue lines denote the (*P*)- and (*M*)-isomers.

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