Sub-Expanded Heterohelicenes as Stimuli-Controlled Soft Molecular Springs

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Helicenes, by virtue of their unique screw-type structures, were proposed as functional models for molecular springs; however, experimental realization has remained an elusive and unmet task until now, because of the lack of appropriate helicene molecules consisting of backbone-decorated dynamic architectures. Aiming to explore this unearthed direction, we relied on our '*rollover annulation*' chemistry,[1] to access a novel class of modular flexible heterohelicenes with stimuli (acid/base and light)-responsive core and peripheral modules.[2] By applying pH (at core-embedded free imidazole sites) and light (at backbone-tethered dithienylethene units) stimuli, we demonstrate that these flexible heterohelicenes exhibit spring-like movement, with the reversible contraction/extension of the helical pitch. The uniquely functionalized structure of these molecules played a critical role in bestowing such capability, as revealed by crystallographic, spectroscopic and computational data. Careful assessment disclosed that the protonation/deprotonation-induced reversible generation and delocalization of positive charge throughout the π-conjugated helical rim switch the operative interactions between the π clouds of the terminal overlapping arene rings of the helicenes between repulsive and attractive, leading to extension/contraction of the helical pitch. On the other hand, in the case of the light stimulus, it was analyzed that the light-induced ring-closure of the photoactive dithienylethene units created a geometric distortion causing the helicenic wings to bend outward from the helicene rim, which resulted in extension of the helical pitch. The photo-assisted (or thermal) reverse ring-opening reaction converted the system to its original conformation, thus enabling the helicene molecule to display spring-like reversible extension/contraction motion. The new insights on the reversible dynamic features of this class of heterohelicenes under the influence of external stress would guide crucial design principles of helicene-based molecular springs for potential applications**.**

1. (a) Ghorai, D.; Dutta, C.; Choudhury, J. *ACS Catal.* **2016**, *6*, 709–713. (b) Karak, P.; Dutta, C.; Dutta, T.; Koner, A. L.; Choudhury, J. *Chem. Commun.* **2019**, *55*, 6791–6794. (c) Karak, P.; Rana, S. S.; Choudhury, J. *Chem. Commun.* **2022**, *58*, 133–154.
2. Karak, P.; Choudhury, J. *Chem. Sci.* **2022**, *13*, 11163–11173.