

# Intramolecular cyclization of helicenes towards non-benzenoid nanographenes via formation of radicals

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On-surface synthesis has recently become a leading tool for controllable C-C bond formation that would otherwise hardly be accessible by conventional solution chemistry. It enables reliable and predictable preparation of atomically precise low-dimensional materials with unprecedented properties via targeted precursor design. [1–3] The advancement of on-surface synthesis gave rise to a novel class of magnetic materials, namely open-shell magnetic nanographenes. The magnetism here mostly stems from the formation of unpaired electrons (radicals) due to a sublattice imbalance, topological frustration or aromatic stabilization. [3] Such carbon-based spin systems are often considered promising candidates for spintronics applications due to their weak spin–orbit coupling and hyperfine interaction, allowing for long spin-lifetime and spin diffusion lengths. [4,5]

Here we demonstrate that the radical formation within the non-planar hydrocarbons such as helicenes leads to intramolecular bond formation and reorganization on Au(111) substrate resulting in non-benzenoid nanographenes. The products are identified using ToF-SIMS, STM and nc-AFM, corroborating the proposed radical-induced cyclization mechanism. Such mechanism contrasts with the Diels-Alder cycloaddition and cyclodehydrogenation mechanisms previously reported for helicenes on surfaces. [6,7]

## Reference

- [1] J. Björk, et al. *Chem. Eur. J.* **20**, 928 (2014).
- [2] S. Clair, et al. *Chem. Rev.* **119**, 4717 (2019).
- [3] S. Song, et al. *Chem. Soc. Rev.* **50**, 3238 (2021).
- [4] M. Slota, et al. *Nature* **557**, 691 (2018).
- [5] H. Min, et al. *Phys. Rev. B.* **74**, 165310 (2006).
- [6] O. Stetsovych, et al. *Nat. Chem.* **10**, 213 (2017).
- [7] A. Mairena, et al. *Chem. Sci.* **10**, 2998 (2019).