Substrate-dependent magnetic properties of a non-hexagonal low-bandgap nanographene

W. Xu[1], Q. Huang[2], C Zhao[1], C. Pignedoli[1], R. Fasel[1], X Feng[2] and P Ruffieux[1]

[1] *Nanotech@surfaces Laboratory, Empa - Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland*

[2] *Center for Advancing Electronics Dresden, Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Mommsenstrasse 4, Dresden 01062, Germany*

Wangwei.xu@empa.ch

Recent advances in on-surface synthesis have provided a breakthrough in the production of magnetic nanographenes (NGs), which hold great promise as building blocks for constructing one-dimensional spin chains or two-dimensional spin lattices. Open-shell NGs are commonly achieved through zigzag edges, sublattice imbalance, or topological frustration [1-3]. However, an unexplored method to introduce magnetism in NG involves incorporating a non-hexagonal structure, thereby breaking its sublattice symmetry.

Here, we report the on-surface synthesis of an open-shell non-hexagonal NG. The strain induced by the non-hexagonal structure leads to the loss of two methyl groups in the precursor during cyclodehydrogenation. This process results in the predominant formation of **3**, which is characterized by a free-standing triplet ground state with a gap of less than 200 meV. The characterization of **3** was conducted using scanning tunneling microscopy, scanning tunneling spectroscopy, and atomic force microscopy. Our results demonstrate that **3** exhibits a charged singlet ground state on Au(111), which was further validated through hydrogen passivation and step-by-step tip activation of the radicals. The observed energy shift of **3**'s molecular orbital on Ag(111) and $TbAu_2$ suggests that **3** is a charge of -2e on these surfaces. In addition to the methyl-based synthesis of non-hexagonal NGs, we will present a synthesis approach allowing to achieve periodic pentagon-heptagon structures in graphene nanoribbons (GNRs). Starting from a precursor with hexagonal rings only, we achieve a periodic pentagon-heptagon arrangement through substrate-assisted polymerization and subsequent dehydrogenative formation of non-hexagonal rings. Furthermore, we will describe the critical competition between halogen-dependent polymerization and cyclodehydrogenation to achieve the final target structure.

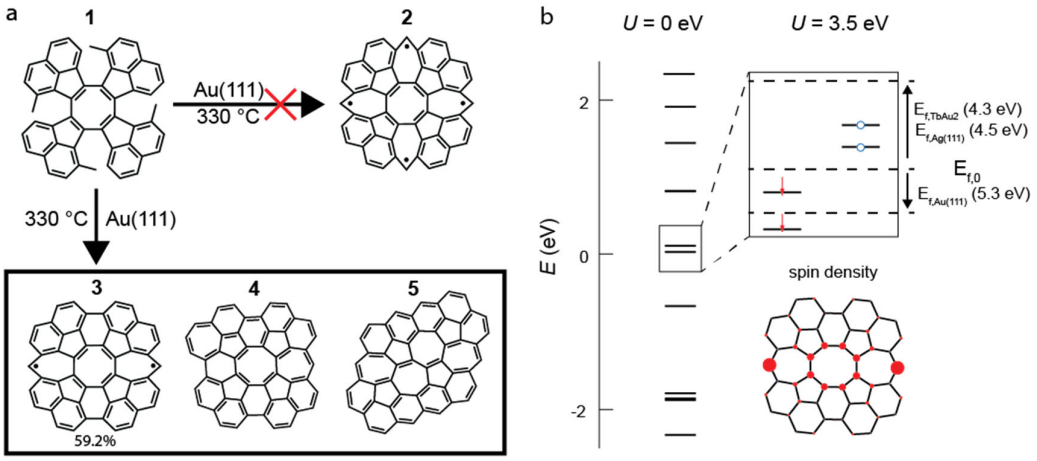

Fig. 1. Schematic diagram of the on-surface synthesis approach and the substrate-dependent electronic properties of **3**.

References :

[1] Morita, Y., *et al.* Nature Chem, **3**, 197–204 (2011)

[2] Blackwell, R.E., et al. Nature, **600**, 647–652 (2021).

[3] Mishra, S., *et al.* Nat. Nanotechnol. **15**, 22–28 (2020).