On-Surface Synthesis and Single-Molecule Manipulation for the Atomically Precise Fabrication of Carbon Nanomaterials

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Recent advancements of on-surface synthesis techniques enable the fabrication and precise characterization of carbon-based nanomaterials with atomic-scale accuracy. These materials often exhibit novel (opto-)electronic and magnetic properties, which are partly derived from the inherent characteristics of the precursor molecules and partly emerge from the unique structures formed during synthesis. Therefore, on-surface synthesis presents a highly versatile alternative to conventional solution-phase chemistry, leading to novel products not obtainable by conventional chemical methods.

Specifically, the quest for nonbenzenoid sp^2 carbon allotropes has stimulated substantial research efforts because of their predicted unique mechanical, electronic, and transport properties. However, synthesis of these carbon networks remains challenging due to the lack of reliable protocols for generating nonhexagonal rings. We have developed various on-surface synthesis strategies by which polymer chains are linked to form nonbenzenoid carbon networks. In this way, we synthesized biphenylene network, a carbon allotrope with 4-6-8-membered rings (Figure 1a), which is metallic already at very small dimensions [1], and other carbon networks.

Acenes are another important class of carbon materials with potential for use in organic electronics. We synthesized tridecacene (13ac) [2] and pentadecacene (15ac) [3], the longest acenes known to date, via multistep single-molecule manipulation (Figure 1b). We find antiferromagnetic open-shell ground state electron configurations for both acenes. Notably, 15ac shows a low-bias spin-excitation feature, indicating a singlet-triplet gap of around 124 meV. Investigation of 15ac complexes with up to 6 gold atoms suggest considerable multiradical contributions to the electronic ground state of 15ac.

Doping with heteroatoms alters the electronic and magnetic properties of carbon-based nanomaterials. We present a variety of nitrogen-containing carbon nanostructures including planar and curved cycloarenes (Figure 1c) as well as N-doped graphene nanoribbons.

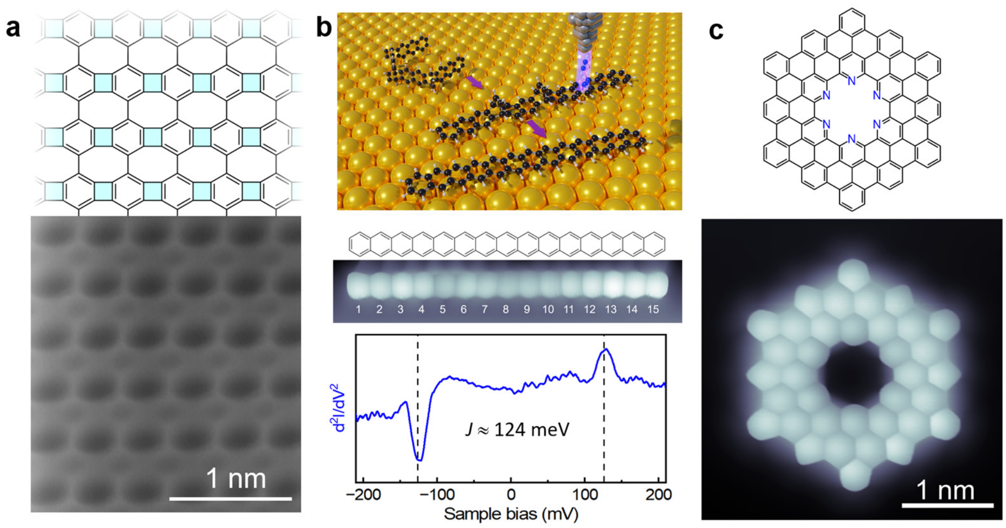

Figure 1. (a) Biphenylene network, (b) long acenes by single-molecule manipulation, (c) N-doped cycloarene.

References:

[1] Q.T. Fan et al., J.M. Gottfried, Science **372**, 852-856 (2021).

[2] Z. Ruan et al., J.M. Gottfried, J. Am. Chem. Soc. **146**, 3700-3709 (2024).

[3] Z. Ruan et al., J.M. Gottfried, J. Am. Chem. Soc. **147**, 4862–4870 (2025).