

## On-surface synthesis of organic nanostructures and molecules via scanning probe manipulation

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Constructing low-dimensional covalent assemblies with tailored size and connectivity is challenging yet often key for applications in molecular electronics where optical and electronic properties of the quantum materials are highly structure dependent. We present a versatile approach for building such structures block by block on bilayer sodium chloride (NaCl) films on Cu(111) with the tip of an atomic force microscope, while tracking the structural changes with single-bond resolution [1]. Covalent homo-dimers in *cis* and *trans* configurations and homo-/hetero-trimers were selectively synthesized by a sequence of dehalogenation, translational manipulation and intermolecular coupling of halogenated precursors. Further demonstrations of structural build-up include complex bonding motifs, like carbon-iodine-carbon bonds and fused carbon pentagons. Using scanning probe manipulation, we were also able to synthesize the structurally elusive molecule P<sub>3</sub>N<sub>3</sub>, an inorganic aromatic benzene analogue, which is difficult to obtain via traditional synthetic methods due to its high reactivity [2]. This work shows ways for synthesizing elusive molecules and organic nanoarchitectures, studying structural modifications and revealing pathways of intermolecular reactions.

[1] Q. Zhong et al. *Nature Chemistry* **13**, 1133 (2021)

[2] Q. Zhong et al. (under review) preprint <https://doi.org/10.21203/rs.3.rs-2169632/v1>