

On-surface synthesis of planar π -extended [12]cycloparaphenylene

[*n*]cycloparaphenylenes feature extensive *para*-conjugation that leads to useful electronic and optoelectronic properties, but their strained topology prevents their conversion into planar macrocycles. Now, on-surface coupling of cleverly designed precursors affords planar π -extended [12]cycloparaphenylene.

The bottom-up, atomically precise synthesis of carbon nanostructures enables the tailoring of their electronic properties at a molecular level. [*n*]cycloparaphenylenes ([*n*]CPPs)—closed rings of phenylenes linked in the *para* position—possess desirable π -electron delocalization along the carbon backbone, but the high strain in these systems prevents their π -extension into either larger or planar structures. Now, a collaboration led by Sabine Maier and Andreas Görling at Friedrich-Alexander-Universität Erlangen-Nürnberg and Konstantin Amsharov at Martin-Luther-Universität Halle-Wittenberg in Germany describes the on-surface synthesis of planar π -extended [12]CPP, featuring an all-armchair edge topology, whereby the peripheral phenylene units are solely *para*-conjugated (<https://doi.org/10.1038/s41557-022-00968-3>)¹.

Planarizing CPPs requires the introduction of a strong in-plane bend in what would otherwise be a straight edge. The team achieved this by designing bowl-shaped dibrominated indacenopicene precursors that contain the appropriate curvature for the paraphenylene backbone. These precursors were covalently

coupled on a Au(111) surface—where the surface acts as both a support and a catalyst—via an Ullmann-type dehalogenative coupling followed by cyclodehydrogenation. Trimers, tetramers ([12]CPP) and pentamers form *via cis* coupling, while dominant *trans* coupling leads to chain structures (Fig. 1).

“The exclusive *para*-conjugation at the periphery of planar π -extended [12]CPP yields delocalized electronic states and facilitates a strong electronic communication along an extended π -system.”, explains Maier. Furthermore, planarization maximizes *p*-orbital overlap, contributing to a reduced electronic bandgap in comparison to conventional CPPs. Density functional theory calculations additionally find that [12]CPP features ring currents in its doubly charge configuration, affording global aromaticity.

Looking to the future, Maier hopes to experimentally characterize the unique electronic properties of such systems: “Synthesis strategies on insulating surfaces should be explored to decouple the molecular systems from the metal substrate electronically. Scanning probe measurements in the presence of a magnetic field could then

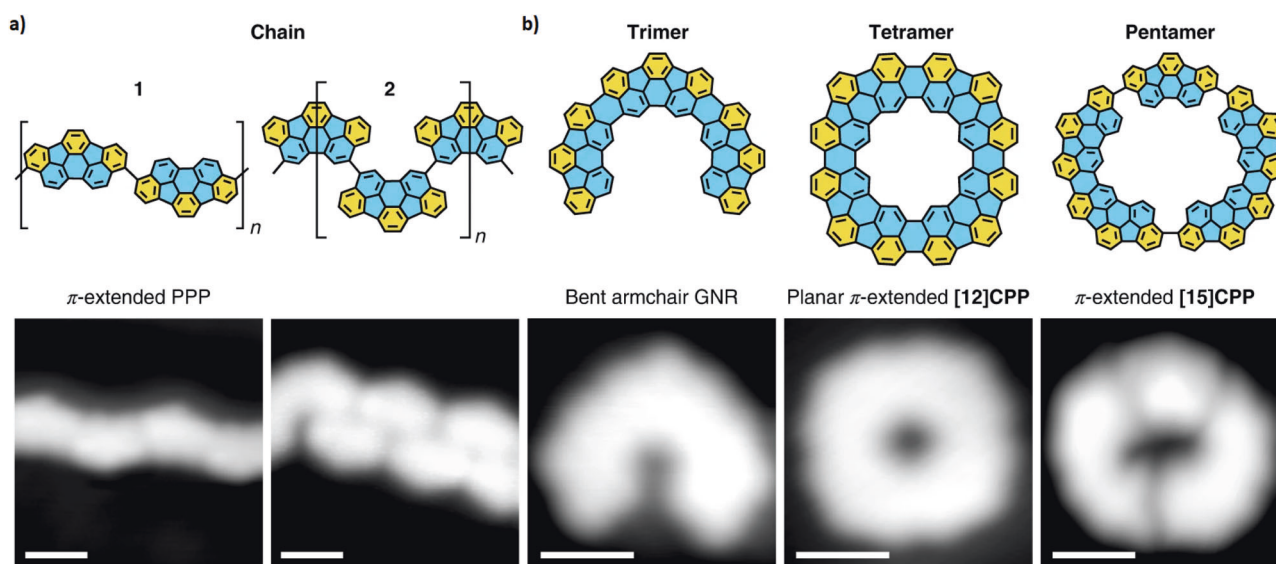



Fig. 1 Atomically precise carbon nanostructures formed by Ullmann-type coupling of dibrominated indacenopicene precursors followed by cyclodehydrogenation on Au(111). *Trans* coupling leads to π -extended polyparaphenylene chains (a), while *cis* coupling affords bent armchair graphene nanoribbons (trimers), planar π -extended [12]CPPs (tetramers) and π -extended [15]CPP (pentamers) (b). Micrographs are high-resolution scanning tunneling microscopy images, with scale bars 1 nm. Reprinted by permission from Springer Nature: Nat. Chem., copyright 2022.

facilitate the first direct visualization of ring currents at the atomic scale.” Furthermore, these properties could serve to make planar π -extended CPPs promising quantum materials.

Victoria Richards 

 email: victoria.richards@nature.com

Published online: 22 August 2022

Reference

1. Xiang, F. et al. Planar π -extended cycloparaphenylenes featuring an all-armchair edge topology. *Nat. Chem.* **14**, 871–876 (2022). <https://doi.org/10.1038/s41557-022-00968-3>.



Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit <http://creativecommons.org/licenses/by/4.0/>.

© Springer Nature Limited 2022