Synthesis of atomically precise porous graphene nanomaterials

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The bottom-up synthesis is a powerful approach for the creation of graphene-based nanomaterials (GNMs) with atomic precision. This approach relies on well-defined chemical reactions between specially designed molecular precursors that dictate the structure of the resulting GNMs. Preparation of a new GNM generally requires a design and synthesis of a new molecular precursor, which is often very challenging and laborious. We report a family of molecular precursors based on 7,10-dibromo-triphenylenes that can selectively produce different varieties of atomically precise GNMs – porous nanographenes (pNGs) and porous graphene nanoribbons (pGNRs) – through the use of different synthetic environments [1]. More specifically, we show that upon Yamamoto polymerization of these molecules in a solution environment, the free rotations of the triphenylene units around the C-C bonds result in the formation of cyclotrimers at high yields. In contrast, in the case of on-surface polymerization of the same molecules on Au(111), these rotations are impeded, and the coupling proceeds toward the formation of long polymer chains. These chains can then be converted into pGNRs by annealing. Correspondingly, the solution-synthesized cyclotrimers can also be deposited onto Au(111) and converted into pNGs via a thermal treatment. Thus, both processes start with the same molecular precursor and end with an atomically precise GNM on Au(111), but the type of the product, pNG or pGNR, depends on the specific coupling approach. We also produced extended nanoporous graphenes (NPGs) through the lateral fusion of highly aligned pGNRs at high coverage. All synthesized products were atomically precise, including the NPGs, which contained only [18]annulene nanopores. We demonstrate the generality of this approach by synthesizing two varieties of 7,10-dibromo-triphenylenes that produced six GNM products with different dimensionalities. The basic 7,10-dibromo-triphenylene is amenable to structural modifications potentially providing access to many new GNMs. We show that by constructing different GNMs from the same molecular building blocks it is possible to tune the band gap in a very wide range. Electronic properties of these and related GNM/GNR structures as well as their relevance to magnetic property engineering in nanographenes will also be discussed [2].
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References

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