Surface-confined Synthesis of 2D sp/sp^2 Graphdiynes

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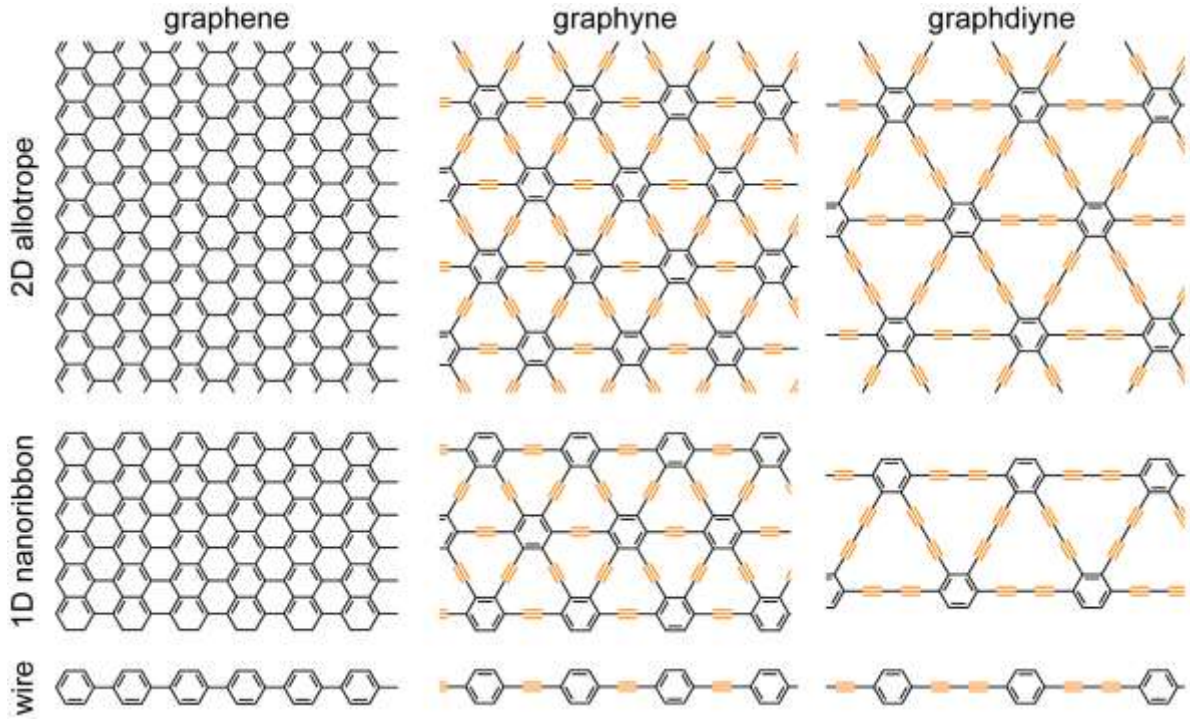
The development and understanding of carbonaceous compounds and carbon allotropes are topics of major interest for science and technology. Notably zero-, one- and two-dimensional species and architectures are currently explored to generate advanced materials for multiple application fields, including nanoelectronics, molecular separation and storage, nanomechanics, optoelectronics, or energy storage and conversion. An important aspect therein is the control of sp^2-hybridized ring and sp-hybridized chain motifs that can be combined to afford multitudinous scaffolds.[1,2] The most obvious two-dimensional (2D) materials contrivable from this combination are the allotropes known as graphyne (GY) and graphdiyne (GDY), depicted in Scheme 1, which are considered promising alternatives for graphene. The crystalline carbon sheets can also be regarded as ideal 2D polymers or covalent organic frameworks, which represent a topical domain in synthetic chemistry, though their fabrication faces great challenges. Moreover, various one-dimensional (1D) counterparts, such as nanoribbons or nanotubes, are achievable from the GY/GDY-related hydrocarbon materials, expanding the scope of carbyne, ideally being an infinite chain of exclusively sp-hybridized carbon. Also these systems are of high current interest, and substantial efforts were dedicated to their theoretical investigation, albeit limited achievements exist regarding their realization. Sophisticated solution-chemistry protocols allow the controlled synthesis of short polymeric strands or patches, however with increasing oligomer size, undesired side groups, interfering with the targeted material properties, are necessary to provide the required solubility. Additionally, the 3D-character inherent to the polymerization process in solution frequently counteracts the formation of regular low-dimensional structures. Overall, the synthesis of attractive atomically-defined carbon-rich materials of the GY/GDY family with conventional methods faces severe obstacles calling for innovative approaches. Surface-confined chemistry[3] has recently attracted interest in view of their potential to address the construction of nanometre-sized molecular nanomaterials and -devices by a bottom-up approach. Herein, we report herein on the controlled synthesis of novel 2D carbon allotrophes, which are supposed to exhibit conjugation on the base of interconnected sp/sp^2 carbon atoms (see figure).[4] The synthetic protocol involves C-C homo-coupling of taylor-made molecular precursors on a Ag(111) surface, which act both as catalysts and template. Gaseous H_2 evolves as the only by product avoiding (electronic) contamination of the 2D polymer with spurious dopants. In addition, we managed to graft non-covalently magnetic molecules, $TbPc_2$ Single-Molecule Magnets, on contacted graphene nanojunctions. The obtained supramolecular spintronic devices are investigated in view of their I-V-device characteristics showing the behaviour of multiple-field-effect nanotransistors.[5][6]



Scheme 1: Graphene, graphyne and graphdiyne

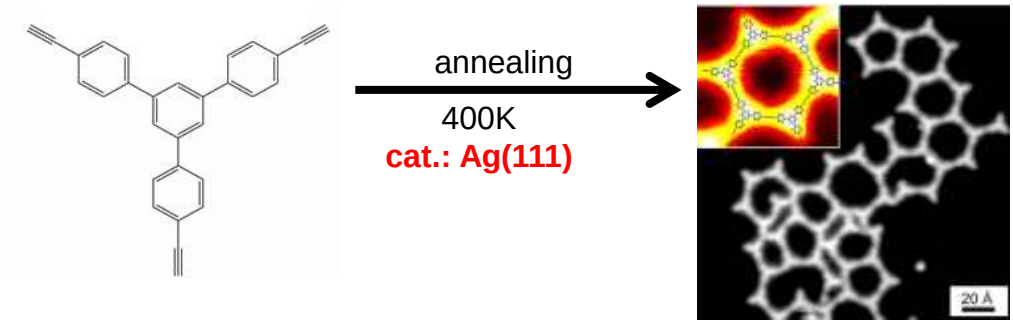


Figure 1: Surface-confined Synthesis of graphdiyne domains

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