

NOVEL NON-BENZENOID GRAPHENE ISOMERS BY ON-SURFACE SYNTHESIS

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The quest for planar sp^2 -hybridized carbon allotropes other than graphene, such as phagraphene, graphenylene, and biphenylene network, has stimulated substantial research efforts because of the materials' predicted unique mechanical, electronic, and transport properties. However, their syntheses remain challenging due to the lack of reliable protocols for generating non-hexagonal rings during the in-plane tiling of carbon atoms. We have developed an on-surface synthesis strategy by which we first generate straight polymer chains, which then link to form the non-benzenoid graphene isomers. Using this approach, we achieved the bottom-up growth of ultraflat biphenylene network with periodically arranged four-, six-, and eight-membered rings of sp^2 -hybridized carbon atoms, through on-surface inter-polymer dehydrofluorination (HF-zipping) reaction (Figure 1a). Apart from graphene, biphenylene network is the only experimentally known planar sp^2 carbon so far. Its characterization by scanning probe methods (STM, AFM, STS) confirms the non-benzenoid nature and reveals that it is metallic rather than a dielectric already at very small dimensions. While HF-zipping generates the four- and eight-membered rings during the on-surface reaction, the non-benzenoid structural elements may already be contained in the precursor: using an azulene-based precursor, we achieved sp^2 carbon nanostructures with odd-numbered rings, such as phagraphene nanoribbons containing five-, six- and seven-membered rings (Figure 1b). Additional non-benzenoid four- and seven-membered rings can be formed during dehydrogenative C-C coupling of the intermediate 2,6-polyazulene chains, resulting in tetra-penta-hepta(TPH)-graphene (Figure 1c) with metallic properties.

References

- [1] Q.T. Fan, L.H. Yan, M.W. Tripp, O. Krejčí, S. Dimosthenous, S.R. Kachel, M.Y. Chen, A.S. Foster, U. Koert, P. Liljeroth, and J.M. Gottfried, *Science*, 372 (2021), pp. 852-856.
[2] Q.T. Fan, D. Martin-Jimenez, D. Ebeling, C.K. Krug, L. Brechmann, C. Kohlmeyer, G. Hilt, W. Hieringer, A. Schirmeisen, and J.M. Gottfried, *J. Am. Chem. Soc.*, 141 (2019), pp. 17713-17720 (2019).

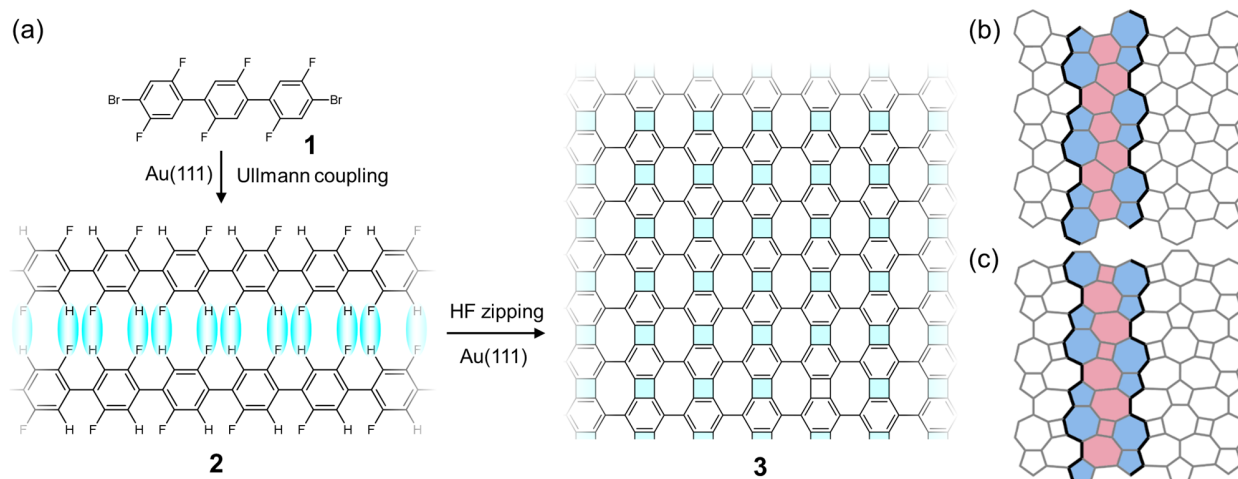


Figure 1: (a) On-surface synthesis of biphenylene network 3 from 4,4''-dibromo-2,2',2'',5,5',5''-hexafluoro-1,1':4',1''-terphenyl 1 by HF-zipping of the intermediate poly(*p*-phenylene) polymer 2. (b) Phagraphene and (c) tetra-penta-hepta(TPH)-graphene..