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Letter to the Editor

Synthesis of wide atomically precise graphene nanoribbons from *para*-oligophenylene based molecular precursor

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ABSTRACT

The exploration of graphene nanoribbons (GNRs) and understanding of the structure–property relationship requires the synthesis of GNRs with precisely controllable architecture. In this communication we report on bottom-up fabrication of wide armchair GNR from a *para*-oligophenylene based molecular precursor. The obtained GNR represents the widest rationally synthesized GNR up to now.

Graphene nanoribbons (GNRs) are polycyclic aromatic hydrocarbons (PAHs) infinitely extended in one dimension which can be considered as thin stripes of graphene. GNRs have been predicted to show interesting electronic properties that depend strongly on their width and edge structure [1]. Despite the many curious theoretical investigations demonstrating the particular properties of GNRs [2–4], the experimental verification is still challenging because the production of GNRs of well-defined structure is still limited [5]. Therefore, the further exploration of GNRs and understanding of the structure–property relationship requires the synthesis of GNRs with precisely controllable architecture. Although the investigation of polycyclic aromatic hydrocarbons has been restricted for a long time to low-mass molecular compounds, because the larger PAHs are usually highly insoluble materials, current progress indicates that GNRs can be produced in a controllable manner on metal surfaces [6]. Previously Grill and coworkers have demonstrated that one and two-dimensional PAHs frameworks can be obtained through highly selective surface assisted coupling [7]. The resulting structures can be precisely engineered by controlling the chemical structure of the precursor molecule. This so-called bottom-up methodology has been successfully extended to the synthesis of GNRs from the specially designed precursor, for which thermally induced cyclodehydrogenation on a Au substrate resulted in the formation of well-defined GNRs [8]. Since the structure of the synthesized GNRs is fully predefined by the precursor, the fabrication of a wide range of different GNRs with engineered chemical and electronic properties appears to be possible. In this communication we demonstrate that *p*-oligophenylene (POP) based precursors can be used for the facile synthesis of wide armchair nanoribbons with adjustable width. The potential is demonstrated by the synthesis of wide arm-chair

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GNR of width $N = 15$ (15 carbon atoms) utilizing dibromo-*p*-pentaphenyl (DBPPP) as a molecular precursor.

The general bottom-up strategy of GNR fabrication includes three subsequent steps: (1) deposition of the monomer unit bearing two latent active groups, (2) activation of the latent group (usually bromine) resulting in the formation of free radicals, which causes polymerization through radical recombination and (3) final cyclodehydrogenation to the desired GNR (Fig. 1). In a retrosynthetic approach the GNR molecules can be divided into small periodic structural units in many different ways, but only few of them will satisfy the requirements for suitable GNR monomers. As a first precondition the precursor molecule should be rather robust, since it should be stable during deposition and the activation of the latent group. This excludes the usage of high molecular PAHs, which undergo partial decomposition during evaporation onto the surface. Furthermore, the monomer units should possess two symmetrically equivalent active groups. In this case the possibility for different types of coupling is avoided and full control over the polymer structure can be achieved. For the cyclodehydrogenation step only one possible way should be open, which can be "programmed" into the precursor structure either by high symmetry or by special geometry. Many other factors such as mobility on the metal surface, possible side reactions and accessibility of radical centers for recombination also have to be taken into consideration.

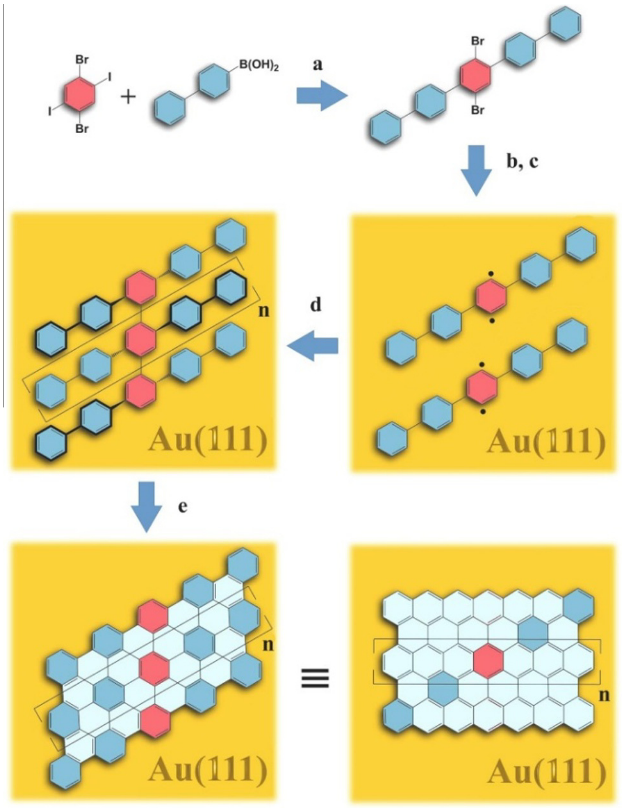

Fig. 1 – Synthetic route to the [15] armchair GNR. (a) Pd(PPh$_3$)$_4$, (b) UHV deposition, (c) thermal activation, (d) radical recombination (polymerization), (e) annealing (cyclodehydrogenation). The central ring and biphenyl fragments of DBPPP are coded by red and blue color, respectively, for clarity.

10,10′-Dibromo-9,9′-bianthryl was successfully demonstrated to be a suitable monomer for GNR fabrication fulfilling all the preconditions discussed above [5]. Due to the hindered rotation around the single bond connecting the adjacent anthracene units the molecule has a twisted conformation. This provides a good accessibility of the radical centers for recombination and increases the mobility of the precursors on the surface. Moreover, the high molecular symmetry allows only one possible way for polymerization and subsequent cyclodehydrogenation into a GNR. On the other hand, the examples of pure acene-type (linearly-fused benzene rings) based precursors are probably limited to the dianthryl molecule since higher homologues such as heptacene are rather reactive compounds.

para-Oligophenylenes (POPs) represent an alternative simple motive which can be used for the GNR synthesis. In contrast to acenes, the stability of POPs is almost independent of the molecule size that allows using higher homologues and fabricate wide ribbons. Although on the surface the POP molecules have a planar conformation, which could hinder the direct radical recombination, the rotational barrier between adjacent benzene rings is sufficiently small to adopt a twisted conformation and induce polymerization. Importantly, the POP based precursors do not require precedent dimerization, thus keeping an acceptable molecular weight of the precursor even in the case of very wide ribbons.

In the present work dibromo-*p*-pentaphenyl was chosen as a POP-based precursor. The compound was synthesized by regioselective Suzuki coupling of biphenylboronic acid with dibromodiiodobenzene (for synthesis details see Supplementary data). Single-crystal X-ray diffraction data (Fig. 2) shows that the bromine substituents causes steric demands in the *peri*-position increasing the dihedral angle between the benzene fragments. This drastically reduces the conjugation along the main chain and leads to a considerable improvement of the solubility. In contrast to pristine *p*-pentaphenyl, DBPPP exhibits a moderate solubility in common organic solvent which is an important prerequisite for successful purification and characterization.

The DBPPP precursor molecules were deposited under ultra high vacuum condition onto an atomically clean Au(111) surface. STM measurements were performed using an Omicron Variable Temperature Scanning Tunneling Microscope (details see in Supplementary material). Fig. 3 summarizes our experimental findings of the GNR synthesis on the Au(111) surface according to the scheme presented in Fig. 1. In the first step, the molecules were deposited onto the Au(111) surface held at room temperature. The DBPPP molecules are very mobile on the surface and can only be imaged when the coverage is close to a full monolayer. Subsequently, intermolecular linking through radical recombination is achieved by annealing to 600 K, at which temperature the debrominated intermediates have sufficient thermal energy to diffuse along the surface and form single covalent C–C bonds with each other leading eventually to polymer chains. STM images of the conjugated monomers show protrusions with a periodicity of about 0.8 nm (Fig. 3a, b), in agreement with the expected periodicity of the pentaphenyl core of

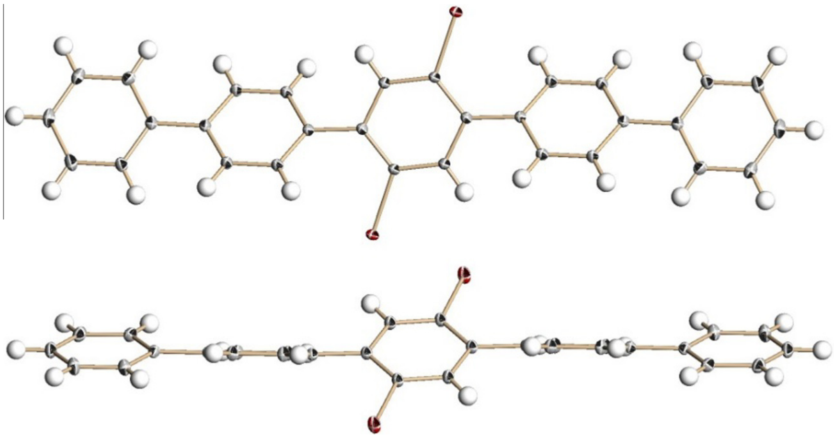

Fig. 2 – ORTEP projections of dibromo-*p*-pentaphenyl molecule (DBPPP) showing significant deviation from planarity due to steric hindrance between hydrogen and bromine atoms in the *peri*-positions. Displacement ellipsoids are drawn at 50% probability level. (A color version of this figure can be viewed online.)

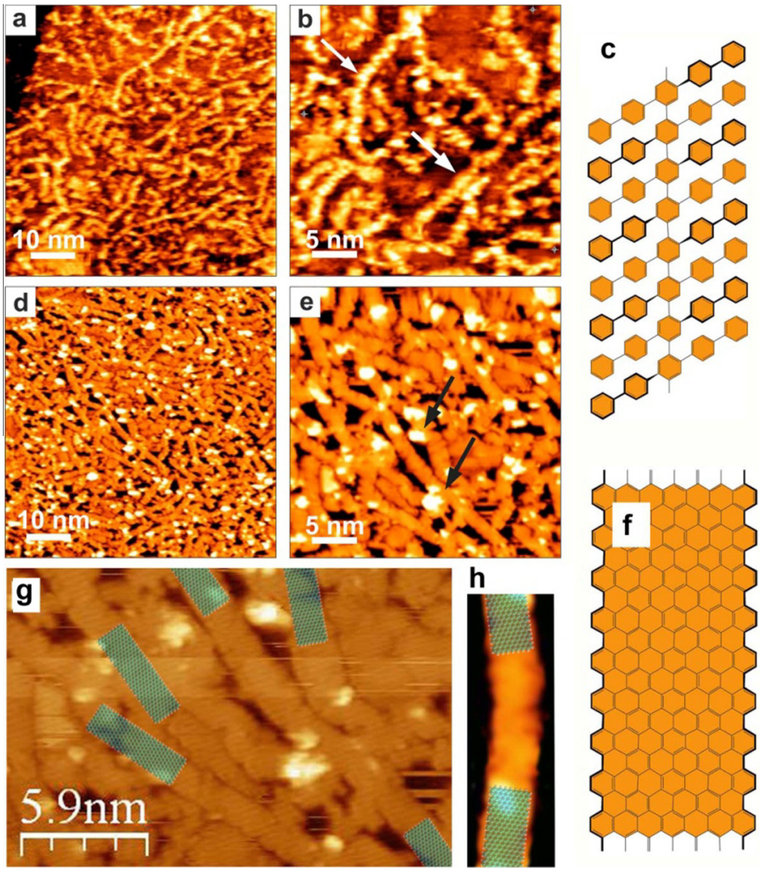

Fig. 3 – STM images of PPP polymer and [15] armchair GNRs obtained from the DBPPP molecules: (a) and (b) DBPPP molecules deposited onto the Au(111) and annealed to 600 K, individual polymers can be identified as indicated by the white arrows (image size $30 \times 30\ \mathrm{nm}^2$); (c) schematic representation of the polymer; (d) and (e) the same surface after annealing to 780 K. The cyclodehydrogenation results in the GNR formation (black arrows); (f) schematic representation of GNR from (d) and (e). (g) and (h) Structural models of a [15] armchair GNR overlaid onto the STM image.

about 0.6 nm. Moreover, the polymer is imaged with a width of 1.75 nm in agreement with the structural model (1.8 nm). To obtain a fully condenced system the sample was annealed in a third step to 720 K, which induces intramolecular cyclodehydrogenation of the polymer chain and leads to the formation of armchair ribbons with a width of 15 carbon atoms (Fig. 3c, d) with 2.1 nm width and the apparent height of 0.14 nm. Fig. 3 shows that the obtained GNRs do not show a perfect structure and are not entirely defect-free. However, GNRs of relatively good quality can be formed at high precursor densities, where the coupling of the radicals appears to be more likely due to limited available space and favorable packing of the monomers. At lower precursor densities only very short GNRs along with single molecules were observed. The latter observation is most probably due to the formation of C–Au bonds with the surface since the pristine molecules show high mobility. Despite the imperfection of the final products, the polymer formation from the biradical of *p*-pentaphenyl is a very interesting finding. These radicals were found to react with each other rather effectively and form the desired polymers, in contrast to the previously reported observation for a phenyl biradical on the Cu(111) surface, where no C–C bond formation was found [9]. The question regarding defects could be answered by the following considerations. The first annealing step leads to debromination and formation of extremely active radicals. High precursor densities help in guiding the radical recombination and formation of the polymer chain but also enhances the probability of side reactions. This idea finds its support in the observation at low coverage. Here, the very short GNRs are found along with a disordered phase of molecules bonded to the Au(111) surface.

In summary, facile synthesis of wide GNR using a *p*-oligophenyl based precursor – DBPPP is reported. The rather effective polycondensation of DBPPP upon annealing is an interesting finding as it shows that biradicals formed are sufficiently mobile to cause further recombination. Further annealing of the polymers yields $N = 15$ armchair GNRs representing the widest rationally synthesized GNRs to date. Although the structure of the latter was found to have some defects our findings pave the way toward the synthesis of extra wide nanoribbons in a fully rational fashion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.06.010.

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