

**A study on the on-surface synthesis of novel
carbon-based nanoribbon structures**

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Chapter 1.

General Introduction

1-1. Graphene

The word “Graphene” is a combination of “graphite” and the suffix –ene, named by Hanns-Peter Boehm in 1962.^{1,2} It was first isolated in 2004, by Geim and Novoselov from University of Manchester, UK.³ They used Scotch tape to peel single-layer and few-layer graphene off from highly oriented pyrolytic graphite (HOPG) and transferred them onto substrate, where the thickness identified by the color contrast under optical microscope. This surprisingly simple method which referred as mechanical exfoliation enables rapid follow up studies throughout the world by other researchers.

Graphene is a two-dimensional (2D) single atomic layer of graphite. The lattice structure of graphene is sketched in Figure 1-1. The carbon atoms in graphene are covalently bonded to three adjacent atoms via strong σ -bonds (electron cloud along the bond axis) with bond length of ~ 1.42 Å and bond angle of 120° , forming a sp^2 hybridized orbital. The remaining electrons that occupy $2p_z$ orbitals resulting into delocalized π -bonds (electron cloud perpendicular to the bond axis) and are responsible for the current conduction in graphene. This lattice structure is generally referred to as the honeycomb lattice or on a more formal level, hexagonal lattice with two sites per unit cell. The lattice of graphene has been directly observed (Figure. 1-2) by scanning tunneling microscopy (STM)^{4,5} and tunneling electron microscopy (TEM).^{6,7}

Since its experimental realization in 2004, both the theoretical and experimental studies showed graphene exhibits series of favorable properties, such as quantum Hall effect at room temperature,^{8,9} high carrier mobilities ($> 200\,000\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at electron densities of $2 \times 10^{11}\text{ cm}^{-2}$),¹⁰ exceptional Young modulus values ($> 0.5\sim 1\text{ TPa}$), and large spring constants ($1\sim 5\text{ N m}^{-1}$).¹¹⁻¹³ In addition, the single atom thickness nature also revealed unique morphological properties, such as high specific surface areas (theoretically predicted $> 2500\text{ m}^2\text{g}^{-1}$ and experimentally measured as $400\sim 700\text{ m}^2\text{g}^{-1}$)¹⁴⁻¹⁷. All of above mentioned properties make graphene a promising candidate for practical applications in electronics,¹⁸⁻²⁰ sensing,^{21,22} catalysis,^{23,24} gas and energy storage,^{25,26} conversion,¹⁷ as well as

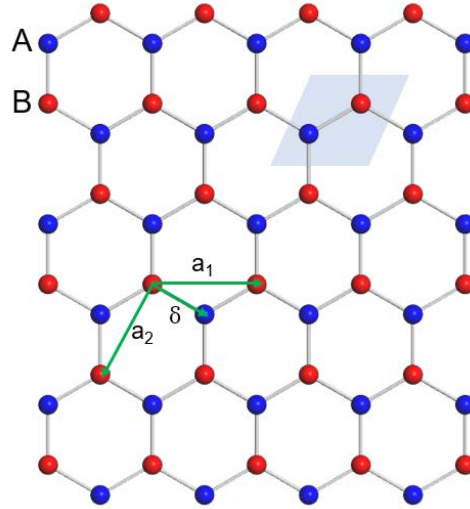


Figure 1-1. A sketch of honeycomb lattice structure: An unit cell is shadowed in light grey. The A sublattice sites are marked in red and the B sublattice sites in blue. The primitive lattice vectors a_1 and a_2 and basis vector δ are marked.

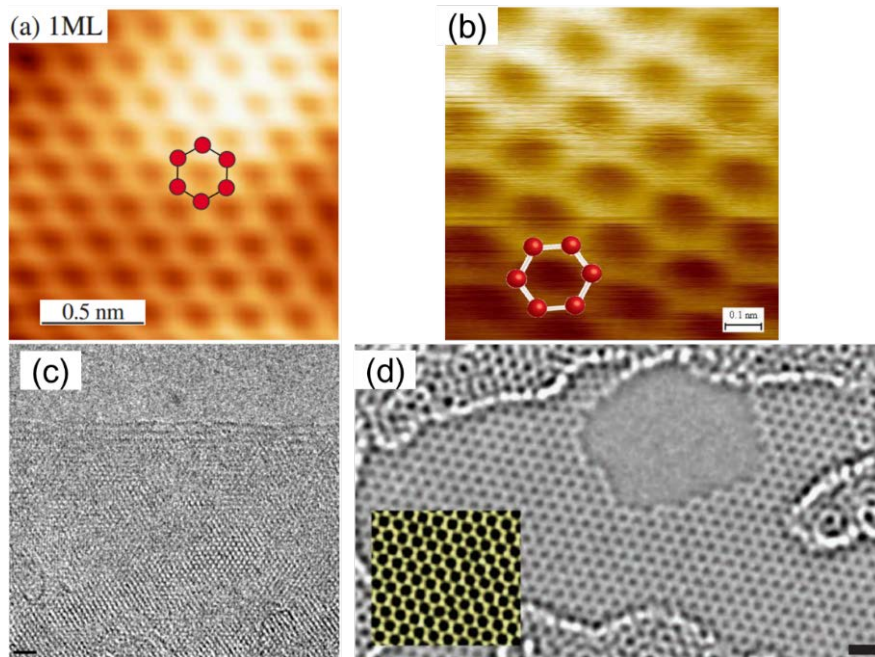


Figure 1-2. STM images (a⁴ and b⁵) and TEM images (c⁶ and d⁷) of single layer graphene indicating its lattice honeycomb structure. Ref. [4]; Copyright 2008 American physical society. Ref. [5]; Copyright 2007 National academy of sciences. Ref. [6]; Copyright 2007 Nature publishing group. Ref. [7]; Copyright 2009 The American association for the advancement of science.

With all the distinguished properties mentioned above, mass production of graphene became one of the most important research topics for its potential applications. The production of graphene can be basically classified into two categories, one is exfoliation of graphite and the other is growing graphene on a substrate with chemical feedstock. The mechanical exfoliation provides high-quality graphene and adequate amount for laboratory research, however, incapable of mass production for industrial production in large-scale. Several alternative exfoliation ways have been developed to overcome this obstacle. One of those methods is liquid-phase exfoliation of graphite with organic solvents such as *N*-methyl-pyrrolidone (NMP) and *N,N*-dimethylformamide (DMF).^{32,33} Sonication assisted exfoliation in tetrabutylammonium hydroxide (TBA) and oleum-intercalated graphite in DMF can also provide high-quality graphene sheets. Graphene dispersions can be produced in the presence of 1-pyrenecarboxylic acid in relatively high yields.³⁴ Ultrasonic energy act as an effective driving force for the exfoliation in the liquid-phase methods reported so far. However, the sonication led to decrease of the size of the produced graphene flakes. Several other approaches have also been reported besides sonication, such as negatively charged complexes in polycarbonate electrolytes,³⁵ and electrochemical exfoliation of HOPG in sulfuric acid. Reduced graphene oxide (rGO) is also a widely used graphene material. Graphene oxide (GO) is usually prepared by Hummers' method where strong acids (concentrated sulfuric) and oxidants such as potassium permanganate and sodium nitrate are used for the treatment of graphite.³⁶ GO can be easily dispersed in water or other high polar solvents in a single sheet form and subsequently reduced chemically or thermally to afford rGO.

Despite these various application potentials of graphene, the conduction in graphene cannot be turned off because of its zero bandgap nature, which significantly hinders its further application in field-effect transistor (FET) devices. Plenty of efforts have been made to open up a bandgap of graphene over the past decade. One way to open a bandgap is to vary the carrier concentration in bilayer graphene via a chemical doping approach³⁷⁻³⁸ or applying an electric field perpendicular to in-plane direction.³⁹⁻⁴⁰ By controlling the carrier density in a bilayer of graphene, the occupation of electronic states near fermi level (E_F) and the magnitude of gap between the valence band and conduction band can be manipulated. However, the preparation of bilayer graphene with precise AB stacking is an intriguing task which will limit the practicability.⁴¹ Application of uniaxial strain in a single layer graphene has been reported for bandgap tuning⁴²⁻⁴³ but a required global uniaxial strain of

over 20% seems impractical.⁴⁴ Several other methods have also been proposed to open the bandgap such as by water adsorption to the graphene surface⁴⁵ and by patterned adsorption of atomic hydrogen onto the Moiré superlattice positions of graphene.⁴⁶ However, currently the most promising method for opening and tunable bandgaps is structural confinement of graphene into nanometer wide ribbons^{41,47-49} or patterning graphene into a nanomesh.⁵⁰

Graphene nanomesh, can be opened up a bandgap in a large sheet of graphene to create a semiconducting thin film.⁵⁰ The nanomesh is prepared using block copolymer lithography and can have variable periodicities and the connecting neck width as low as 5 nm. FET devices based on graphene nanomesh can support currents nearly 100 times greater than individual GNR devices, and the current on/off ratio can be tuned by varying the neck width. However, this “top-down” approach has less control of the edge geometry. Moreover, the highest current on/off of ~100 is inadequate for practical application, because the high ratio devices require a reduction in the neck width through etching, which can lead to partial breakage of the graphene nanomesh current pathway.

1-2. Graphene Nanoribbons

Graphene nanoribbons (GNRs) are narrow stripes of graphene with widths on the nanometer scale. As mentioned above, GNRs preserve tunable bandgaps in contrast to infinite graphene. The electronic structure of GNRs is highly dependent on its geometry and chemical composition. The one-dimensional band structure of a GNR depends critically on its edge structure⁵¹ and the size of the bandgap depends inversely on the GNRs width.⁵²

The GNRs are generally classified into two types according to their edge structures, namely armchair type and zigzag type. The lattice structure of GNRs are depicted in Figure 1-3. The width of the armchair GNRs are characterized by the number of dimer lines (N-AGNR) across the ribbon width, whereas the zigzag GNRs are characterized by the number of zigzag chains (N-ZGNR) across the ribbon width. Theoretical investigation of GNRs could be traced back to 1996, when Nakada *et al.* first reported the edge effects in narrow GNRs.⁵¹ It has been predicted that armchair type GNRs exhibit semiconducting behaviors with a direct bandgap when especially narrower than 10 nm,⁵² and zigzag type GNRs preserve quasi-metallic properties with zero bandgap as well as strongly localized edge

state along the zigzag edge. The tunable bandgap of GNRs as a function of its width is depicted in Figure 1-4.⁵³ In addition, the GNRs can be further classified into more types due to its edge structure variety other than armchair and zigzag, such as acene type GNRs, which were predicted to possess high carrier mobility and also show semiconducting behaviors with open bandgaps.

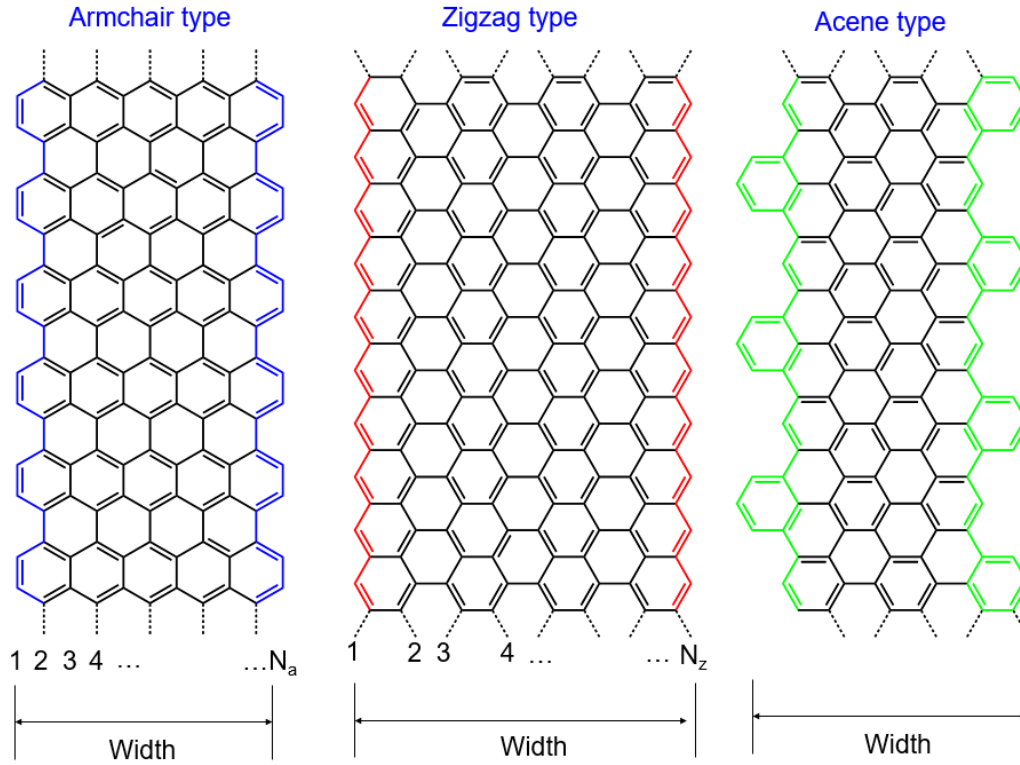


Figure1-3. Sketch of structures of armchair type, zigzag type, and acene-type GNRs.

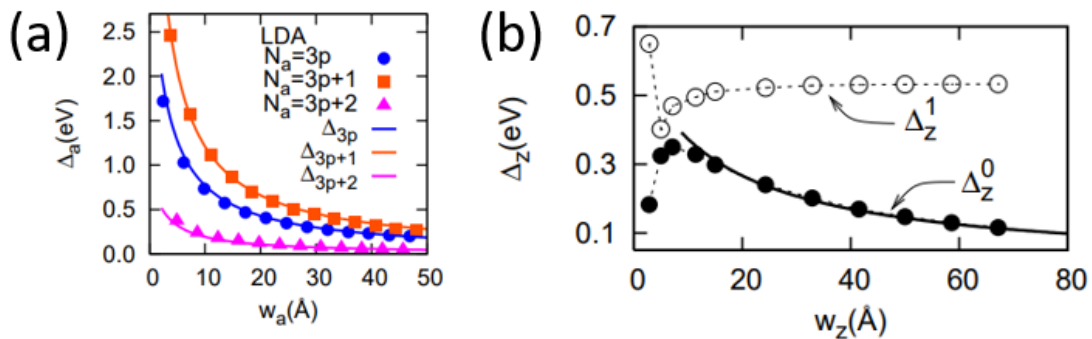


Figure 1-4. Bandgap of armchair-edged (a) and zigzag-edged GNRs (b) as a function of GNRs width obtained from first-principle calculation. Ref. [53]; Copyright 2006; American physical society.

1-3. Fabrication of GNRs via ‘top-down’ approaches

Top-down approaches mainly in principle consist of two strategies, i.e. first, E-beam lithography⁵⁴⁻⁵⁷ or metal-nanoparticle catalyzed cutting⁵⁸⁻⁵⁹ of graphene into one-dimensional narrow stripes; second, unzipping of carbon nanotube (CNT) along the longitudinal direction to GNRs by polymer-protected plasma etching or strong oxidant chemical reagent treatment.⁶⁰⁻⁶⁹

Huang *et al.*⁶⁶ utilized high quality large exfoliated graphene sheet, patterned narrow stripes of resist on top by electron beam lithography to protect the underlying graphene, and used oxygen plasma to etch away the unprotected part to obtain narrow GNRs. GNRs with width down to ~20 nm were obtained by using this method as shown in Figure 1-5.

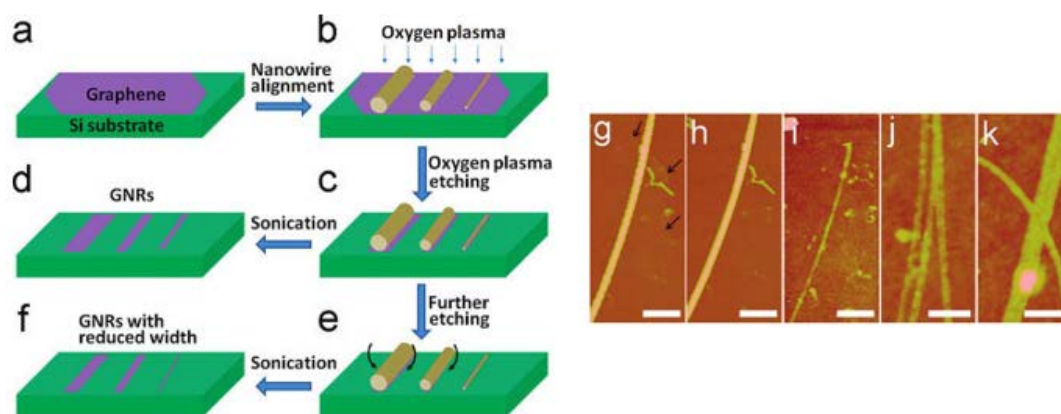


Figure 1-5. Fabrication process of GNRs by oxygen plasma etch with a nanowire etch mask (a-f). AFM images of a nanowire etch mask lying on top of a graphene flake before (g) and after (h) oxygen plasma etch. AFM images of the resulting GNR after sonication removing the mask nanowire (i). Branched and crossed graphene nanostructures from merged and crossed nanowire masks (j-k). The scale bar in (g-i) are 300 nm, and those in (j, k) are 100 nm. Ref. [66]; Copyright 2009; American Chemical Society.

Another chemical route was developed in solution to produce graphene nanoribbons with width below 10 nm by Dai *et al.*⁶⁰ First, graphite was treated with annealing at 1000 °C in H₂/Ar atmosphere, afterwards, the resulting exfoliated graphite was dispersed in a 1,2-dichloroethane solution of poly(*m*-phenylenevinylene-co2,5-dioctoxy-*p*-phenylenevinylene) (PmPV) by sonication to form a

homogeneous suspension. Centrifugation then removed large pieces leave GNRs which were characterized by AFM after deposited on substrates. By taking advantage of this method GNRs with various widths ranging from 50 nm down to sub-10 nm can be obtained. FET devices made from these GNRs show excellent semiconducting properties (Figure 1-6). The bandgaps of GNRs in different width estimated from current on/off ratio were consistent with theoretical calculation.

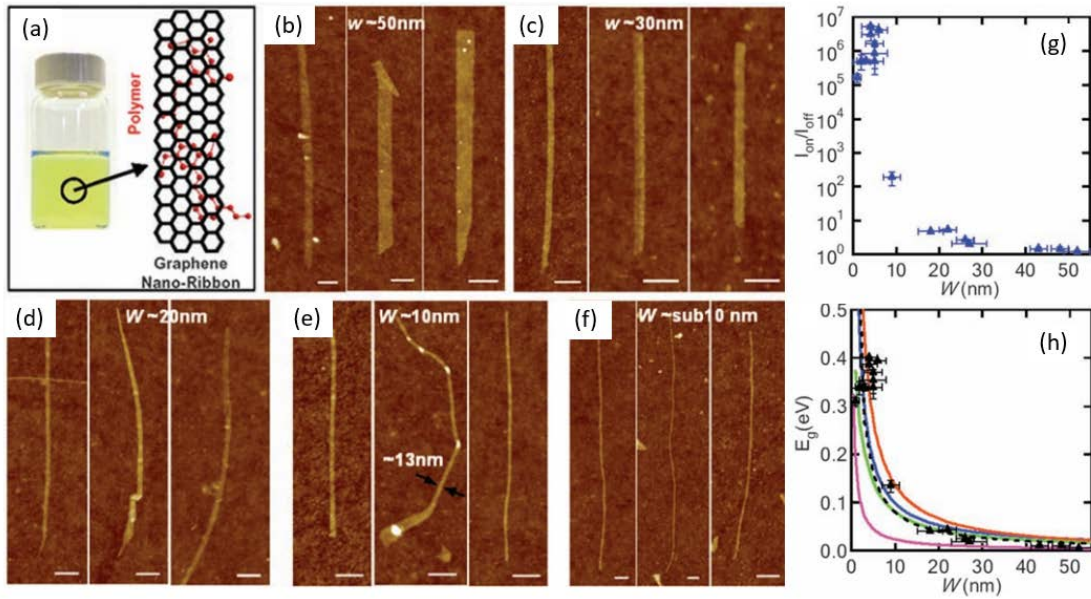


Figure 1-6. (a) Photograph of a polymer PmPC/DCE solution with GNRs stably suspended in the solution. (b-f) AFM images of GNRs in different width. (g) Current on/off ratios for GNRs in a function of width. (h) Bandgaps of GNRs in a function of width. All scal bar indicate 100 nm. Ref. [60]; Copyright 2008 The American association for the advancement of science.

Preparing GNRs from CNTs was also developed by Tour *et al.*⁶² and Dai *et al.*⁶³ with different methods, i.e., unzipping of CNTs with an oxidative solution and plasma etching. Oxidized GNRs were obtained by suspending multi-walled carbon nanotubes in concentrated sulfuric acid followed by potassium permanganate treatment (Figure.1-7). As-prepared GNRs were poor conductors due to large number of oxygen-containing functional groups and structural defects present on its surface because of the strong oxidative process. Hydrazine reduction was carried out to reduce the oxidized GNRs and partially recovered the conductivity.

An alternative process was carried out by Dai *et al.*⁶³ to unzip multiwalled CNTs (MWCNTs) by

Ar plasma etching. MWCNTs first embedded in a poly(methyl methacrylate) (PMMA) thin film as etching mask on a Si substrate (Figure 1-8). The unmasked areas of CNTs were etched faster than the areas protected by PMMA under the Ar plasma, leading to formation of GNRs with smooth edges. Single-, bi- and multilayer GNRs and GNRs with width ranging from 10 to 20 nm were produced depending on the starting materials and etching time. The current on/off ratio for the GNRs FETs could be as high as 100 at room temperature, which suggested a bandgap opening.

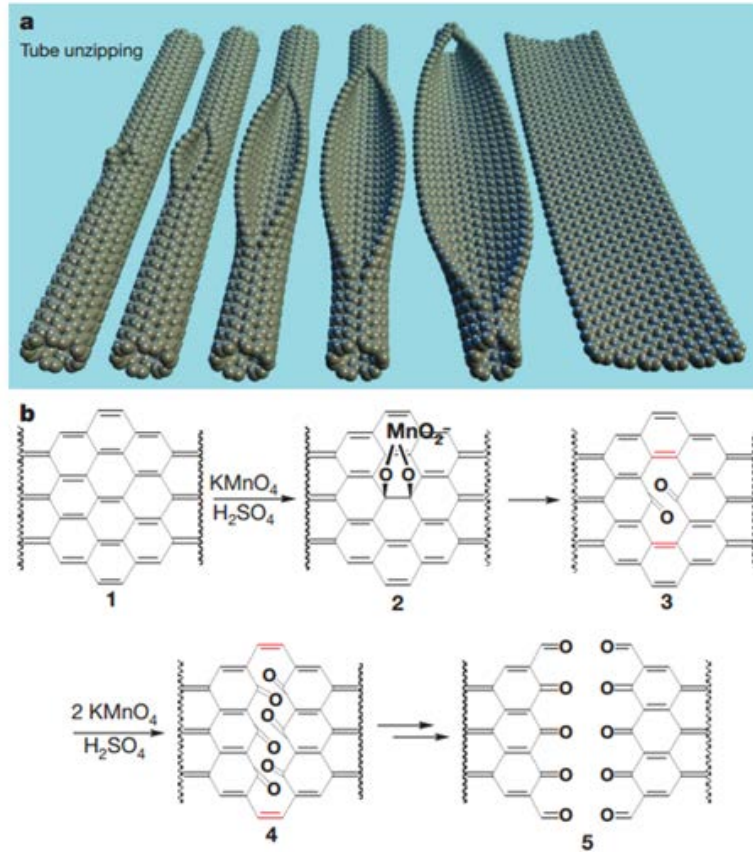


Figure 1-7. Schematic representation of fabrication of GNRs through oxidative unzipping of CNTs (a). The assumed mechanism of CNT unzipping (b). Ref. [62]; Copyright 2009 Nature publishing group.

In 2014, Magada, G. Z. *et al.*⁷⁰ developed a lithographic process based on STM that applied a bias voltage of 2.0-2.3 V between the tip and the graphene while the tip was slowly moved along the desired cutting direction. By utilization of this nanofabrication technique, both armchair- and zigzag-edged GNRs were obtained, and characterized their electronic properties (Figure 1-9). In contrast to

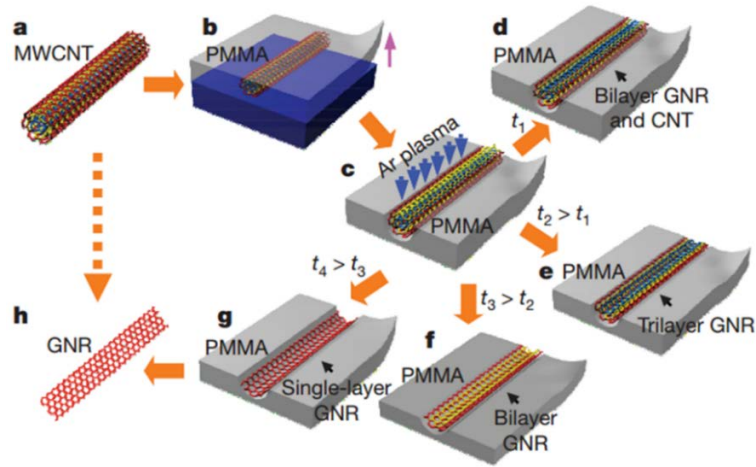


Figure 1-8. A pristine MWCNT (a) was deposited on a Si substrate as starting material and coated with a PMMA film (b). The PMMA-MWCNT film was peeled from the Si substrate, turned over and then exposed to an Ar plasma (c). Different products were generated after plasma etching for different times (d-g). The PMMA was removed to release the GNR. Ref. [63]; Copyright Nature publishing group.

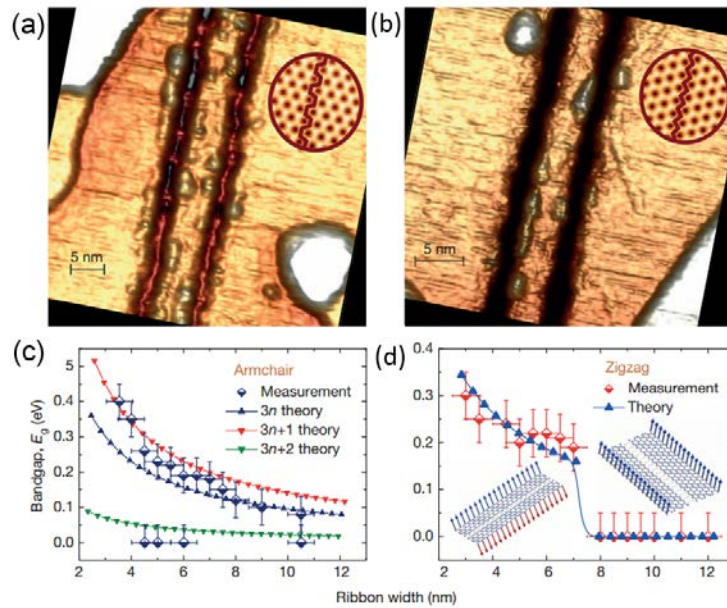


Figure 1-9. STM images of a 5-nm-wide GNR with armchair edge (a) and a 6.5-nm-wide GNR with zigzag edge (b) patterned by scanning tunneling lithography in a graphene sheet deposited on Au(111). The bandgaps measured by tunneling spectroscopy as a function of ribbon width in armchair (c) and zigzag (d) GNRs. Ref. [70]; Copyright Nature publishing group.

the armchair-edged GNR which display quantum confinement gaps, the zigzag-edged GNRs narrower than 7 nm exhibit bandgap of about 0.2-0.3 eV, which can be identified as a signature of interaction-induced spin ordering along their edges. Moreover, upon increasing the ribbon width, a semiconductor-to-metal transition was revealed, indicating the switching of the magnetic coupling between opposite ribbon edges from the antiferromagnetic to the ferromagnetic configuration.

Some of the above mentioned “top-down” fabricated GNRs prohibiting excellent semiconducting properties with high current on/off ratio and mobility. However, the drawbacks such as low yields or lack of precise width and edge structure control exist. These drawbacks hinder the practical applications on electronic devices. In addition, fabricating GNRs with width less than 10 nm is still challenging due to reasons such as electron beam focusing limitation. Therefore, an alternative approach is emerged: “bottom-up” method.

1-4. Fabrication of GNRs via ‘bottom-up’ approach

As mentioned above, the ‘bottom-up’ approaches fabricating GNRs have been widely developed in the decade to overcome the drawbacks of the ‘top-down’. The advantages of ‘bottom-up’ approaches include atomically precise control of the GNRs structure, narrow width (< 2 nm), and tunable bandgaps depending on GNRs’ structure enabled by the precursor design. The bottom-up approach can be realized through strategies including solution based and surface-assisted synthesis.

Solution based organic chemistry is a common method for the synthesis of various kinds of new organic compounds. For the synthesis of GNRs, however, is a daunting task, because its large size suffer from a poor solubility. Recently, the organic chemist dealt with this problem by introducing flexible alkyl chains⁷¹⁻⁷³ or edge chlorination⁷⁴ to produce GNRs with high quality.

Besides the solution-based approaches, surface-assisted synthesis has also been widely developed in recently. This approach possess advantages of synthesis GNRs with atomically precise which can be directly visualized by scanning probing microscopy. The first attempt to fabricate GNRs via the surface-assisted method was reported by Müllen and Fasel *et al.* in 2010 as shown in Figure 1-10.⁷⁵ This synthetic protocol consists of three steps under ultrahigh vacuum (UHV). 1) Feed precursor molecules onto a clean metallic substrate by sublimation. 2) Polymerization of the precursors on the

surface. 3) Intramolecular dehydrogenation upon annealing to afford the GNRs. Later its electronic structure and edge state were well studied.⁷⁶⁻⁷⁹

After this pioneering work by Müllen and Fasel *et al.*, surface-assisted bottom-up synthesis of GNRs has become a hot topic. Many researchers started to fabricate novel GNRs to investigate the properties of them as well as application on electronic devices.⁸⁰

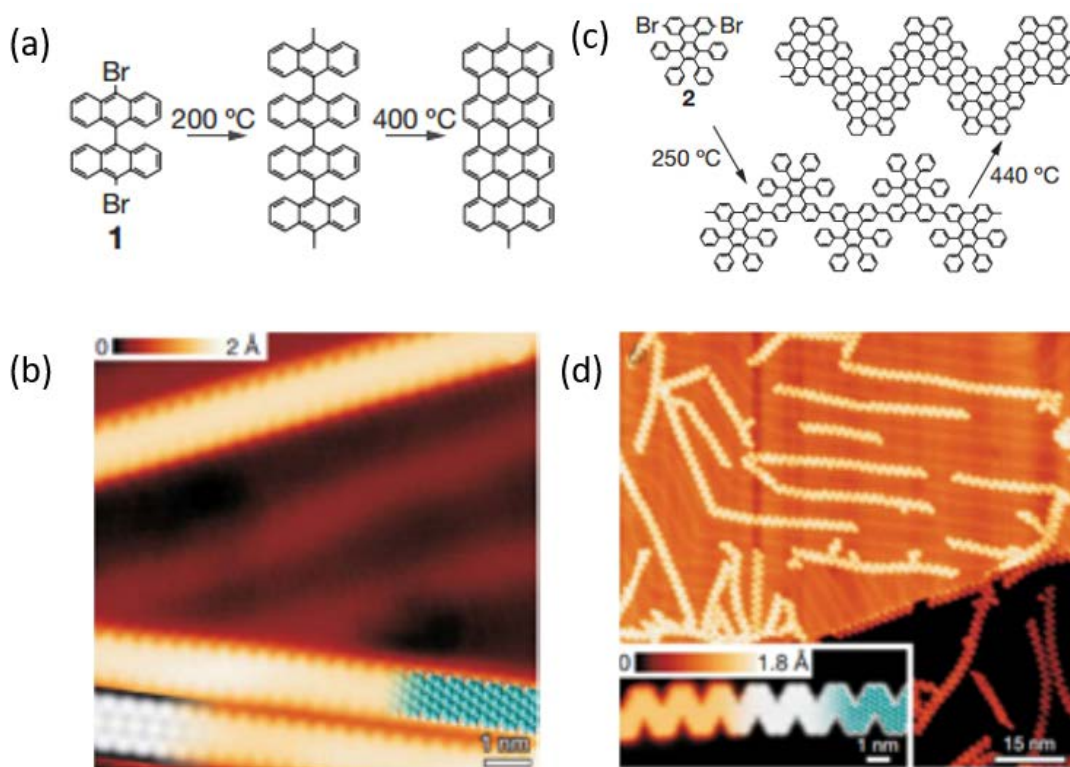


Figure 1-10. (a) Reaction scheme from 10,10'-dibromo-9,9'-bianthryl to 7-AGNRs. (b) STM image with partly overlaid molecular model of the ribbon. (c) Reaction scheme from 6,11-dibromo-1,2,3,4-tetraphenyltriphenylene to chevron-type GNRs. (d) Overview STM image of chevron-type GNRs, inset shows a high-resolution STM image. Ref. [75]; Copyright Nature publishing group.

Various armchair-edged GNRs have been synthesized except 7-AGNR via different precursor molecule designs. As illustrated in Figure 1-11 (a) 5-, (b) 9- and (c) 13-AGNRs were synthesized using different precursor design strategies.⁸¹⁻⁸³ The width of GNRs are usually determined by the width of precursor molecule such as in the case of 5-, 7-, and 13-AGNRs as shown in Figure1-11 (a), Figure1-10 (a), and Figure1-11 (c), respectively. An exceptional case of the 9-AGNR is the one synthesized

using a smaller precursor that the center of the polymer is two alternating orientations as shown in Figure1-11(b). This study of these GNRs revealed that their bandgaps change inversely with the lateral width, which is in agreement with the theoretical predictions.⁵¹⁻⁵²

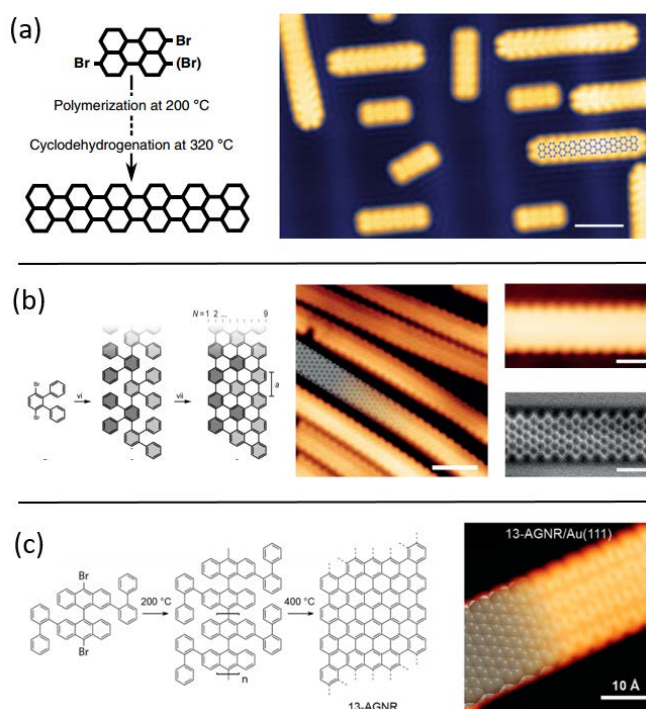


Figure 1-11. Schematic synthetic strategies of armchair edged GNRs with different width from different precursor molecules, including width $N = 5$ (a), 9 (b) and 13 (c). The scale bar in (a) is 2 nm, and those in (b) are 1 nm. Ref. [82]; Copyright 2017 American Chemical Society. Ref. [83]; Copyright 2013 American Chemical Society.

The novel GNRs synthesis via surface-assisted bottom-up route is not limited to armchair-edged GNRs. Figure1-12 shows a cove-edged GNR and chair-edged GNR. The cove-edged GNR containing a unique cove-type periphery based on 11,11'-dibromo-5,5'-bischrysene as a precursor. It was synthesized via the Ullmann coupling reaction of the precursor followed by intramolecular dehydrogenation. Both the experimental spectroscopic data and DFT calculations show it possess smaller bandgaps than AGNRs of similar width.⁸⁴ Chiral-edged GNRs has been first synthesized on a Cu(111) surface by Han *et al.*⁸⁵⁻⁸⁶ using 10,10'-dibromo-9,9'-bianthryl which would produce armchair-edged GNRs on both Au(111) and Ag(111).⁸⁷ Later, Liljeroth *et al.* further studied the effects of the substrate, precursor shape, and molecule-molecule interactions on determining the reaction pathway.⁸⁷

Their results shown that the irrespective of the bianthryl precursor (dibromo-, dichloro-, or halogen-free bianthryl), the Ullman coupling route is inactive on Cu(111), instead, chair-edged GNRs formed.

Doping is a powerful tool for bandgap tuning in semiconductors, while the precise control of the doping sites is still a challenging task so far. Taking the advantage of the bottom-up synthetic technique, precisely doped GNRs can be fabricated by introducing the heteroatoms into the precursors in advance. Bronner⁸⁸ and Sinitskii *et al.*⁸⁹ have performed this process by synthesize nitrogen doping chevron-type GNRs and observed bandgap shift by a high-resolution electron energy loss spectroscopy and photoelectron spectroscopy. Following studies have been conducted by Shixuan *et al.*⁹⁰ using rationally selected nitrogen substituted oligophenylene precursors. They took the direct imaging of the nitrogen-doped GNRs Figure 1-13(a) as well as the characterization of the band structure by STS.

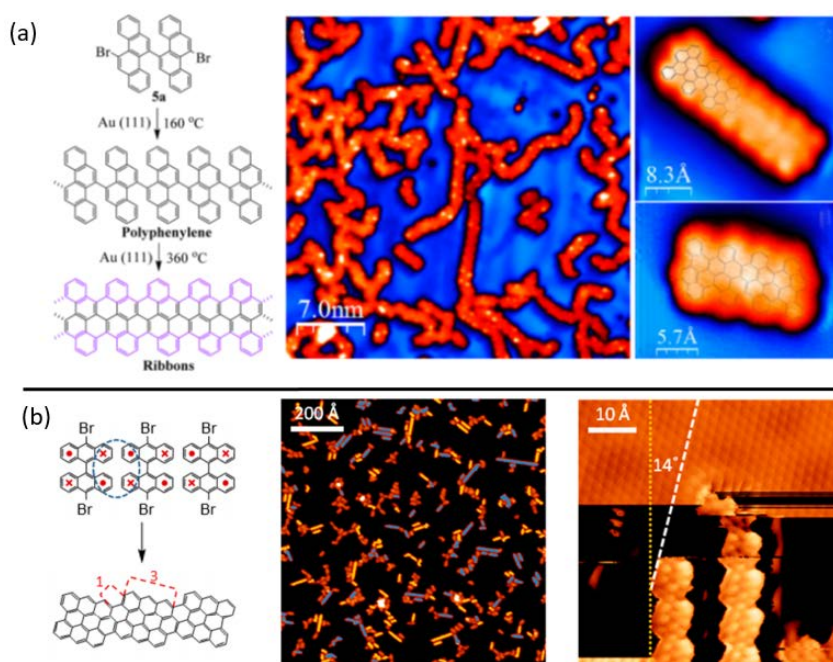


Figure 1-12. Schematic synthetic strategies and STM images of cove-edged GNR (a) and chiral GNR (b). Ref. [85]; Copyright 2014 American chemical society.

Boron-doped GNR has been synthesized by Kawai *et al.*⁹¹ and Crommie *et al.*⁹² by an identical precursor as shown in Figure 1-13(b). The concept of precursor molecule 5,10-bis(10-bromoanthracene-9-yl)-5,10-dihydroboranthrene design is similar with 10,10'-dibromo-9,9'-bisanthracene for the 7-AGNR synthesis featuring a regioregular pattern of Boron atoms along the central backbone of the ribbon. DFT calculations reveal that B-7AGNRs have a deep acceptor band at

energies within the gap of undoped 7-AGNRs, which is localized along the backbone of a B-7AGNR and verified experimentally through dI/dV imaging.

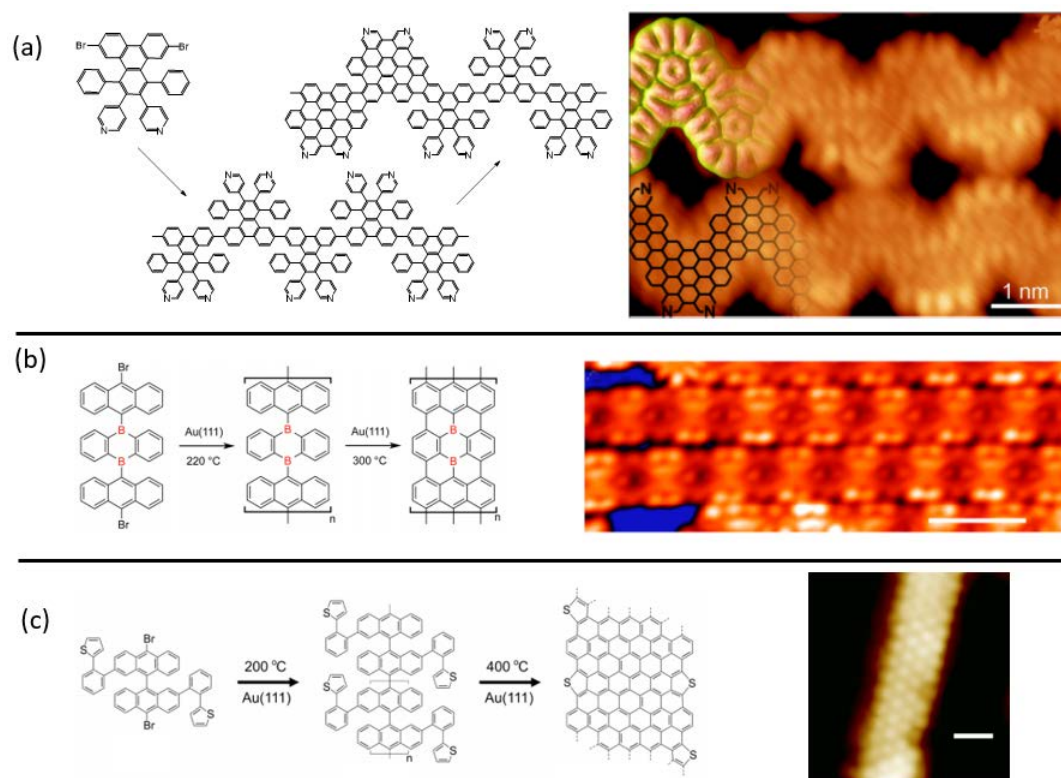


Figure 1-13. Schematic synthetic strategies and STM images of N-doped (a) B-doped (b) and S-doped GNR (c). The scale bar in (b) and (c) indicate 2 nm and 1 nm, respectively. Ref. [90]; Copyright 2015 American chemical society. Ref. [92]; Copyright 2015 American chemical society. Ref. [93]; Copyright 2016 American chemical society.

M. F. Crommie *et al.*⁹³ reported a sulfur doped 13-AGNR by a precursor which was derived from 10,10'-dibromo-9,9'-bisanthracene and (2-phenyl)thiophene substituents (Figure 1-13c). Compared to undoped 13-AGNRs, the molecular orbitals associated with the LUMO in the sulfur doped ones span a significantly broader energy range. The results are consistent with simulations that sulfur dopant will increase the energy separation between CB and CB+1 as well as between the VB and VB-1 band edges. (CB refers to the conduction band, and VB refers to the valence band)

Bandgap engineering has also been realized by creating heterostructures of GNRs. Feael and Müllen *et al.* first brought this idea to reality by synthesizing an isostructure but partially nitrogen

doped graphene nanoribbon heterojunctions (Figure 1-14a).⁹⁴ They designed a nitrogen-containing precursor based on the hydrocarbon pristine one that two of the phenyl rings are replaced by pyrimidinyl rings. The four nitrogen atoms at its periphery did not interfere in the polymerization and cyclodehydrogenation reactions. The two pristine and nitrogen doped GNR segments are highlighted in translucent grey and blue, respectively. A differential conductance dI/dV maps taken at different bias voltages can clearly distinct the two chemically different ribbon segments, which shows a band shift of 0.5 eV, behave similarly to traditional p-n junctions.

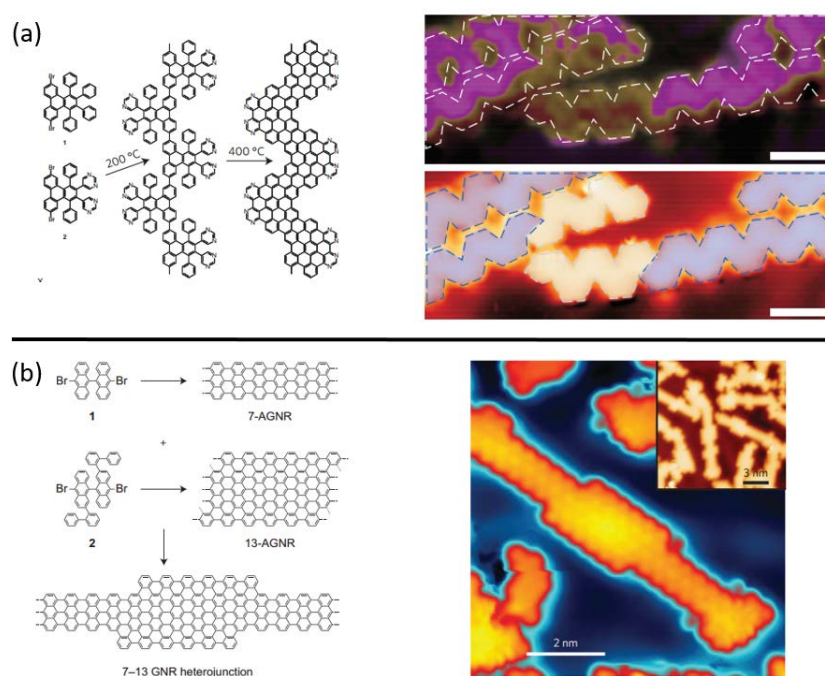


Figure 1-14. Schematic synthetic strategies and STM images of chevron-type GNRs heterojunctions (a) and junctions of different widths (b). The scale bars in (a) indicate 2 nm. Ref. [94]; Copyright 2014 Nature publishing group. Ref. [95]; Copyright 2015 Nature publishing group.

Crommie *et al.*⁹⁵ fabricated a different heterojunction by the molecular building blocks 10,10'-dibromo-9,9'-bianthracene and 2,2'-di((1,1'-biphenyl)-2-yl)-10,10'-dibromo-9,9'-bianthracene which are precursors of 7-AGNR and 13-AGNR, respectively (Figure 1-14b). The heterojunctions are well characterized by STM and the local electronic structure taken by tunneling conductance dI/dV spectra mapping demonstrated molecular-scale bandgap engineering.

After six years of the first surface-assisted bottom-up fabrication of AGNRs, Fasel and Müllen *et*

al. fabricated zigzag-edged GNR by using a U-shape precursor in 2016.⁹⁶ The STS investigation shows the existence of edge-localized states with large energy splittings. But the spin-related properties, such as spin confinement and filtering have not been explored yet.

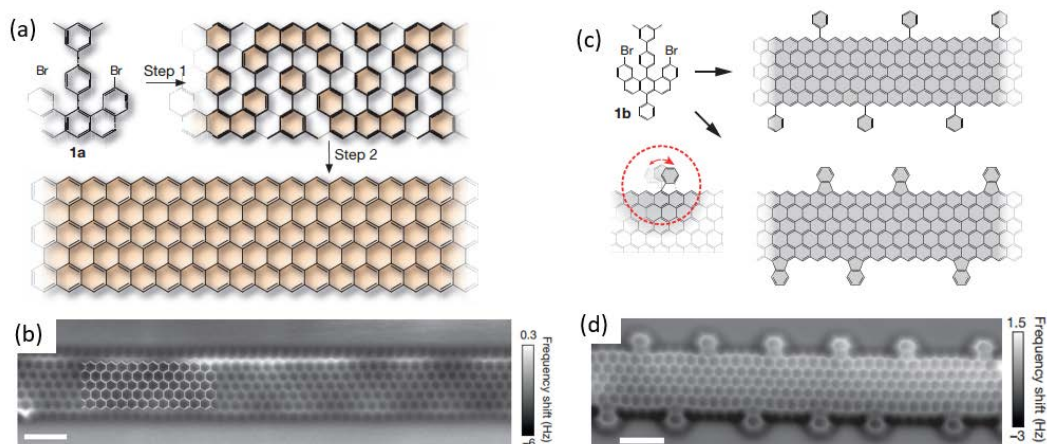


Figure 1-15. Schematic synthetic strategies and nc-AFM image of 6-ZGNR (a,b) and edge-modified 6-ZGNR. Scale bars in (b) and (d) indicate 1 nm. Ref. [96]; Copyright 2016 Nature publishing group.

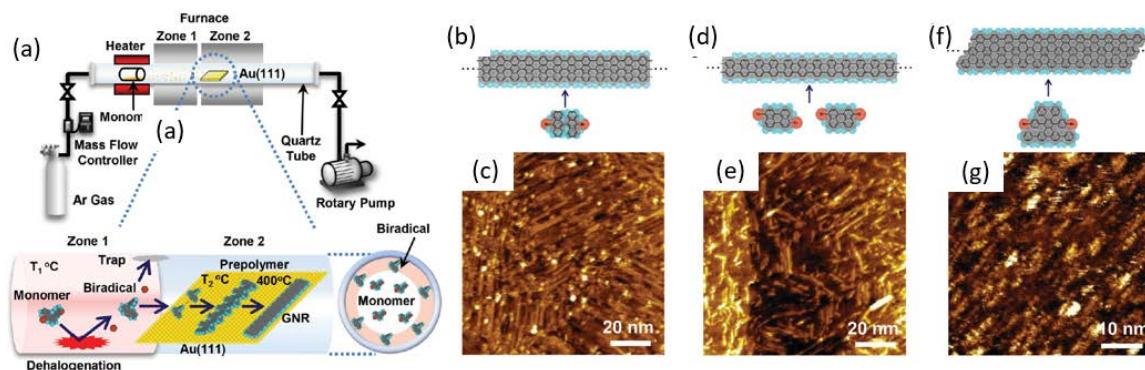


Figure 1-16. Experimental setup of 2Z-CVD with an illustration of the presumed GNR growth mechanism (a). Chemical structures of GNRs in different width (b, d and f). STM images of GNRs in different width (c, e and g). Ref. [97]; Copyright 2014 John Wiley and Sons.

Although the bottom-up route can produce GNRs with defined edges and controllable widths, the methods suffer from the large scale productions because of the low solubility of GNRs and the need for special environments and instruments (UHV). Therefore, a simple bottom-up synthetic method for large-scale production is required not only for complete characterization of the material but also for use in bulk-film devices such as transistors and photovoltaic cells. To this end, Sakaguchi et al. have

developed a two-zone chemical vapor deposition (2Z-CVD) method (Figure 1-16a),⁹⁷ which enabled large-scale growth of all types of armchair-edged GNRs ($3p$, $3p+1$, and $3p+2$; where p is carbon atom number along the width) (Figure 1-16 b-g) in extremely low-vacuum conditions (1 Torr). The GNRs thin film on Au(111) can be successfully transferred to an insulating substrate for device fabrication. FET devices thus were fabricated to measure bandgaps of the GNRs from Tauc plots of the optical absorption, which shows good agreement with the theoretical value.

1-5. Motivation and objectives

As described in the previous sections, GNR, with a 1D graphitic structure, are of great interest in materials science not only for their fundamental aspects but also for their potential applications. One of the main topics of research in this field is the fabrication of new GNRs with the desired edge structures and widths to study the unknown characteristics. Surface-assisted synthesis of GNRs has attracted much attention because it enables the fabrication of GNRs from designed precursors with structural control.

The aim of this thesis is to fabricate novel GNRs and study the GNRs growth mechanisms by chemically designing and synthesizing new precursors and perform the on-surface bottom-up syntheses on Au(111) via 2Z-CVD. The growth mechanisms of the GNRs were also studied in detail. Moreover, the fabricated GNRs on Au(111) could be transferred to insulating substrate by a gold etching process for making field-effect transistors (FETs) and characterize their properties.

In chapter 3, the objective is to fabricate an acene-type GNR on Au(111) with a 'Z-bar-linkage' precursor. It proposed a new 'conformation-controlled surface catalysis' methodology for the efficient production of organized acene-type GNRs. This concept is driven by the chiral transformation on surface of designed 'Z-bar-linkage' precursor having both flexibility and rigidity, followed by homochiral polymerization and conformation controlled dehydrogenation into acene-type GNR. Because this mechanism is analogous to enzymatic catalysis, a new concept of 'biomimetic surface reactions' was built. Additionally, these findings will be useful for the fabrication of new nanocarbon materials.

In chapter 4, the objective is to fabricate wide GNRs on Au(111). A densely packed PPP chain

array was fabricated by the polymerization of DBTP on Au(111) via 2Z-CVD. Because the 2Z-CVD can dramatically reduce the interchain space down to 0.1 nm, wide GNRs can be efficiently produced by interchain fusion of densely packed PPP chains upon further annealing. The FET device based on the wide GNRs exhibits an average current on/off ratio of $1.6 \pm 0.6 \times 10^3$.

In chapter 5, the objective is to fabricate covalently interchain-linked GNRs by a stepwise growth process. First, prepolymer arrays were grown on-surface polymerization of a precursor, 1,9-dibromodibenzo[*g,p*]chrysene at 250 °C. Further annealing of the prepolymer at 450 °C converted the prepolymers into interchain-linked GNRs via intramolecular and intermolecular dehydrogenation reactions.

In chapter 6, the thesis is summarized and future prospective is given.

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Chapter 2.

Experimental

2-1. General information

2-1-1. Materials

All chemicals and reagents were purchased from Sigma-Aldrich Co., Ltd, TCI Co., Ltd, Nacalai Co., Ltd, and other commercial suppliers and used as received unless otherwise specified.

2-1-2. Methods

All manipulations of organic synthesis were performed under nitrogen using standard Schlenk techniques. Dry THF, DCM, and toluene was transferred via cannula under argon. Elemental analyses were performed on a Yanako CHN Corder MT-5 system. Mass spectra was recorded by JEOL JNM-MS700v for EI and a KRATOS analytical AXIMA-LNR mass spectrometer for MALDI. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and silica gel 60N (Kanto Chemical Co., Ltd), respectively. Gel permeation chromatography (GPC) was performed on an LC-9210NEXT or LC-9201 system (Japan Analytical Industry Co., Ltd) with JAIGEL 1H and 2H polystyrene columns (eluent: CHCl_3 , flow: 3.5 mL/min).

Solution-state NMR spectra were recorded on JEOL JNM-ECP300 (300 MHz for ^1H), Varian Unity (300 MHz for ^1H , 75 MHz, for ^{13}C), JEOL JNM-ALS400 (400 MHz for ^1H , 100 MHz for ^{13}C), and JEOL JNM-ECA600 (600 MHz for ^1H , 150 MHz for ^{13}C) instruments. NMR spectra were reported in parts per million using tetramethylsilane (δ 0.00 ppm for chloroform-d) or residual solvent (δ 7.26 ppm for chloroform-d) as the internal standard for ^1H NMR, and from the solvent carbon (δ 77.00 ppm for chloroform-d) for ^{13}C NMR. Abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, m = multiplet, br = broad.

2-1-3. Au(111) substrates

Au(111) on glass and Au(111) on mica substrates were prepared using an e-beam vacuum-deposition system. Evaporated gold was deposited on the mica or glass substrate, which was heated at 350°C under a vacuum of 2×10^{-8} Torr. Deposition was performed at a rate of 0.5 Ås^{-1} , up to a thickness of 30 nm.

2-1-4. Two-zone chemical vapor deposition (2Z-CVD)

The main equipment for fabricating GNRs is a 2Z-CVD (Figure 2-1). The 2Z-CVD system consisted of a quartz tube (26 mm ϕ , 86 cm) as the reactor, a rotary pump, which can evacuate the system to below 7×10^{-4} Torr, a two-zone electric furnace with a temperature controller, an Ar gas flow system with a mass-flow controller, and a mantle heater for evaporating the monomer. The quartz tube was cleaned by annealing at 1000 °C for 20 min, followed by immersion in conc. nitric acid for 20 min for removing impurities, which deactivate radicals. The precursor was casted in a quartz boat which was placed in the upstream of the quartz tube. An Au(111)-deposited mica or glass substrate were placed in the quartz tube. Ar gas was fed into the quartz tube at a flow rate of 500 sccm, resulting in a vacuum of 1 Torr. GNRs were synthesized in two stages: In the first stage, the temperature of the quartz tube (zone 2) was set to 250 °C, with the subsequent evaporation of the precursors by heating to approximately 240 °C using the mantle heater. The path of the monomers through the quartz tube (zone 1) was heated to 350 °C.; in the second stage, the temperature of zone 2 was increased to a given temperature for converting the polymers into GNRs by dehydrogenation.

The basic principle of CVD is to expose a substrate to a vapor of precursor molecules, which react on the surface, often facilitated by supplying energy to the system in the form of heat or using a substrate which is catalytically active.

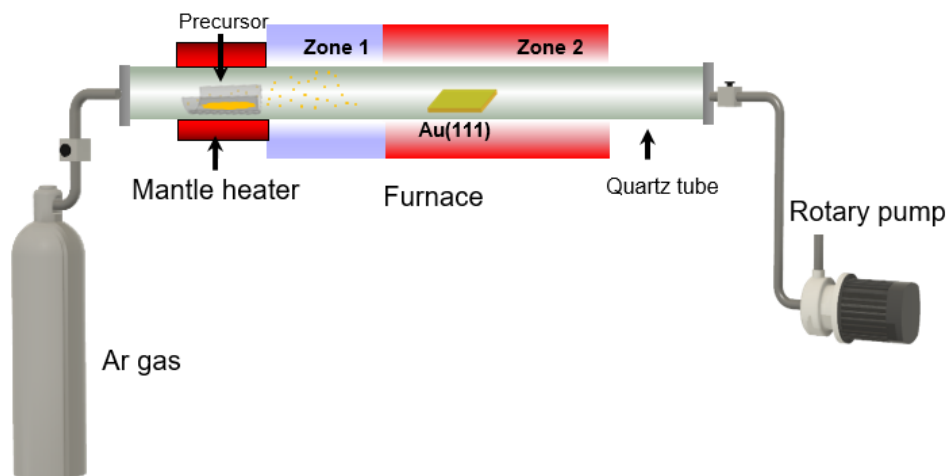


Figure 2-1. Experimental setup of two-zone chemical vapor deposition (2Z-CVD).

2-1-5. Raman spectroscopy

Raman spectroscopy was performed using a laser Raman microscope (LV-RAM500/532; Lambda Vision Co., Ltd) with a 532 nm laser. A 0.75/50 $\times$ microscope objective was used. The diameter of the laser spot is in the order of 1 μ m. Raman spectrum was taken from the different spots of the same sample annealed at different temperatures. Overall, each spectrum was recorded three times for each sample at different positions. The typical Raman integration time was 10 s.

2-1-6. Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS)

STM measurements were performed under the current-constant mode using a commercial instrument (PicoSPM; Keysight Technologies Inc., formerly Molecular Imaging) under Ar at room temperature. All STM images were acquired at a tip bias of 0.2 V under a constant current of 5–20 pA. An electrochemically etched Pt–Ir (80:20) wire was used as the tip.

STS measurements were performed as follows: (1) STM imaging with a tunneling current of 5–20 pA, (2) movement of the tip to the desired position, (3) changing the constant current corresponding to change in the tip-to-sample distance, (4) acquisition of I–V curves, averaged by 10 sweeps. Each sweep was accomplished within 1.0 s. The feedback loop was off during voltage sweep. These

conditions can prevent possible damage of the tip during measurements. Typically, STS data was acquired by measurement at five different positions on the same sample.

Preparation of hydrophobic SiO₂/Si substrate

To enhance the transfer yield, heavily doped n⁺⁺ silicon substrates with a 300 nm thick SiO₂ gate insulator (SiO₂/Si) was converted into hydrophobic surface by as follows: First, SiO₂/Si substrates were immersed in a mixture of ammonia solution (1.0 mL, 28 w/w% in water), hydrogen peroxide (1.0 mL, 30w/w% in water), and 5 mL deionized water at 80 °C for 20 min, rinsed with deionized water, dried at 150 °C for 20 min, and irradiated by deep UV light for 15 min. Second, the substrates were immersed in an anhydrous toluene (4.0 mL) solution of chlorotrimethylsilane (40 μL) at 60 °C for 2 h in a glove box, rinsed with toluene (4 mL × 3), and dried at 150 °C for 10 min.

GNR transfer process

The GNR/Au(111) glass substrate was immersed in water for separating the GNR/Au(111) film from the glass. Next, the GNR/Au(111) film was placed on the surface of a gold-etchant aqueous solution (10 mL), which contains KI (1.8 g) and I₂ (120 mg). Most of the gold film disappeared after 2 min, and SiO₂/Si was attached to the floating GNRs film. Another 4 min was required for completely etching gold, the GNR-transferred SiO₂/Si was withdrawn from the etchant solution, rinsed with deionized water, a saturated Na₂SO₃ aqueous solution (10.0 g Na₂SO₃ dissolved in 9.0 mL deionized water), and deionized water, followed by drying on a hot plate at 120 °C for 20 min. Finally, GNRs on the SiO₂/Si substrate were annealed in a UHV chamber at 200 °C under a pressure of <10⁻⁸ Torr for 1 h to strengthen the adhesion of GNRs to the substrate.

FET fabrication

FETs were fabricated by electron-beam lithography using a JEOL JSM-7001 system equipped with BEAM DRAW (Tokyo Technology) at an acceleration voltage of 30 keV. Alignment mark patterns on GNRs-transferred substrate were made by electron beam lithography on a spin-coated positive resist (ZEP520A), the palladium metal deposition (10.0 nm), and lift-off by immersing in *N*-methyl-2-pyrrolidone (NMP). The GNRs film on SiO₂/Si was scratched off by an electrochemically

sharpened Pt–Ir (80%:20%) needle to make isolated channels. The insulating mask pattern except channel to avoid the current leakage was made by electron beam lithography on a negative resist (4-methyl-1-acetoxycalix[6]arene, 2 wt% chlorobenzene solution) and development by chlorobenzene. Source and drain electrodes were made by electron beam lithography on a positive resist (ZEP520A), the palladium metal deposition (10.0 nm), and lift-off by immersing in NMP. A set of source and drain electrodes was isolated from the others by scratch using a sharpened Pt–Ir needle.

I–V Measurements

FET devices were set in the vacuum chamber (5×10^{-6} Torr) of a three-terminal probe station. All electrical measurements were performed using a semiconductor characterization system (4200-SCS; Keithley Instruments Inc.) at room temperature. Carrier mobilities were calculated according to the equation used for transconductance measurements.¹

$$\mu = \left(\frac{L}{W} \right) \frac{1}{C} \frac{1}{V_{DS}} \left(\frac{\partial I_{DS}}{\partial V_{GS}} \right)$$

Here, L and W denote the length (250 nm) and width (500 nm) of the source and drain electrodes, respectively. C denotes the capacitance of 300 nm thick SiO₂ dielectrics (11.6 n F cm^{-2}).² V_{DS} denotes the drain–source voltage. I_{DS} denotes the drain-source current. V_{GS} denotes the gate-source voltage. Measurements were performed on four substrates having at least four sets of SD electrodes each.

2-2. Calculations

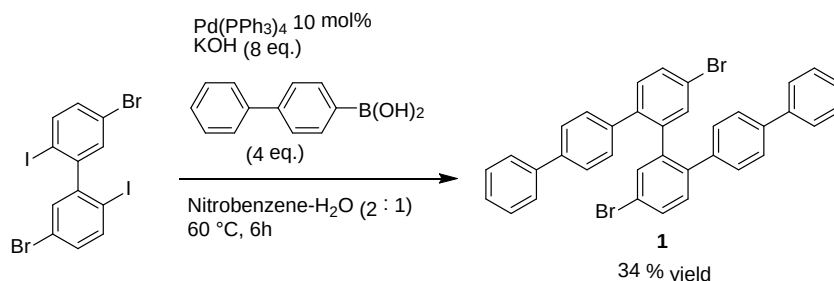
Calculations were conducted using the Materials Studio software suite (BIOVIA Co., Ltd.).

2-3. Synthetic procedures

2-3-1. Synthesis of ‘Z-bar-linkage’ precursors for acene-type GNR.

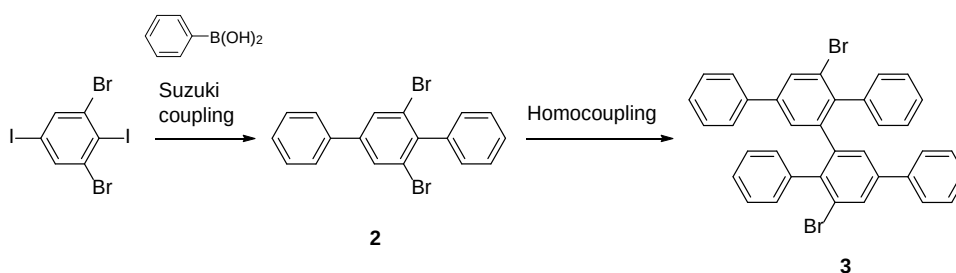
5,5'-Dibromo-2,2'-diiodo-1,1'-biphenyl,³ 4-bromo-1-iodo-2-nitrobenzene,⁴ and 1,4-dibromo-2,6-diiodobenzene⁵ were prepared according to the literature.

4'',5'''-Dibromo-1,1':4',1'':2'',1''':4''',1''''-sexiphenyl: (1)



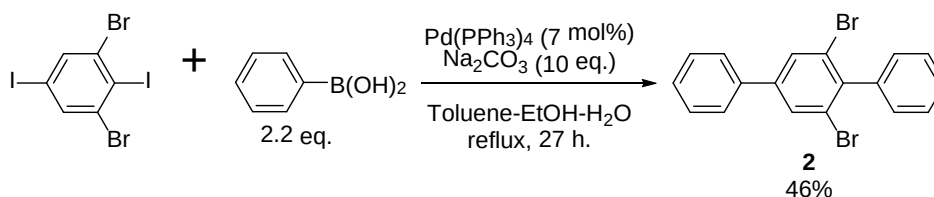
First, [1,1'-biphenyl]-4-ylboronic acid (280 mg, 1.41 mmol, 4 equiv) and KOH (160 mg, 2.85 mmol, 8 equiv) were added to a solution of 5,5'-dibromo-2,2'-diiodo-1,1'-biphenyl (200 mg, 0.35 mmol, 1 equiv) in nitrobenzene (20 mL) and H_2O (10 mL). Second, $\text{Pd(PPh}_3)_4$ (41.0 mg, 35 μmol , 0.1 equiv) was added to the solution after degassing. Third, the mixture was heated to 60 °C for 6 h under N_2 . Next, the biphasic mixture was diluted with chloroform. Then, the organic layer was collected, washed with brine (100 mL), passed through a short silica gel pad, and then concentrated in vacuo. Finally, the mixture was purified by GPC and recrystallized using hexane. **1** was obtained in 37.0 mg (34% yield). ^1H NMR (600 MHz, 20 °C, CDCl_3) δ 7.54 (d, J = 6.82 Hz, 4H), 7.50 (d, J = 8.24 Hz, 2H), 7.43 (dd, J = 7.38, 7.38 Hz, 4H), 7.34 (t, J = 6.91 Hz, 2H), 7.21 (d, J = 8.06 Hz, 4H), 7.03 (d, J = 8.11 Hz, 2H), 6.54 (d, J = 8.03 Hz, 4H); ^{13}C NMR (125 MHz, 20 °C, CDCl_3) δ 140.65, 140.53, 139.52, 139.17, 138.29, 134.00, 131.45, 131.15, 129.22, 128.79, 127.32, 126.90, 126.32, 121.30.

2-3-2. Synthesis of 'H-bar-linkage' precursors.



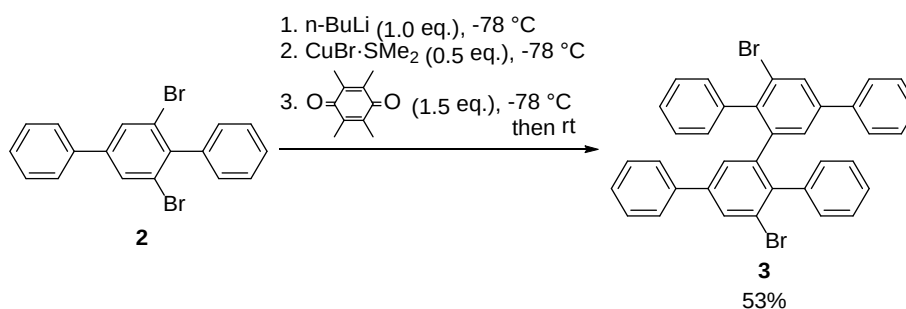
Scheme 1. Synthetic route of 3'',6''-Dibromo-4',5''-diphenyl-1,1':2'',1''':4''',1''''-quaterphenyl: (**3**)

2',6'-Dibromo-1,1':4',1''-terphenyl: (2)



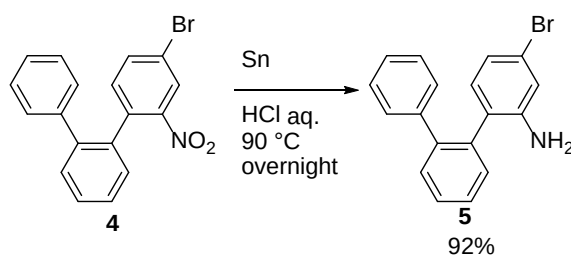
First, 1,4-dibromo-2,6-diiodobenzene (2.43 g, 5.00 mmol), phenylboronic acid (1.34 g, 11.0 mmol), Na_2CO_3 (5.42 g, 51.1 mmol), toluene (160 mL), ethanol (80 mL), and deionized water (50 mL) were added into a 500 mL three-neck flask. Second, the flask was equipped with a magnetic stirring bar, a stopcock, three-way stopcock, and a condenser with a three-way stopcock. Third, the mixture was degassed by bubbling N_2 for 1 h. Next, $\text{Pd(PPh}_3)_4$ (0.420 g, 0.362 mmol) was added to the mixture under N_2 . Then, the resulting mixture was stirred and refluxed for 27 h at 120 °C. After cooling to room temperature, the reaction mixture was diluted using water (50 mL) and toluene (50 mL). Next, the organic layer was extracted using toluene (50 mL $\times$ 3), washed with brine (50 mL), and dried over Na_2SO_4 (ca. 10 g); the desiccant was filtered and concentrated in vacuo. Finally, the resulting crude solid was purified by silica-gel column chromatography (eluent: hexane). **2** (899 mg, 46%) was obtained as a white powder. mp. 123–127 °C; ^1H NMR (400 MHz, 20 °C, CDCl_3) δ 7.83 (s, 2H), 7.56 (d, J = 7.56 Hz, 2H), 7.51–7.34 (m, 6H), 7.24 (d, J = 6.59 Hz, 2H); ^{13}C NMR (100 MHz, 20 °C, CD_2Cl_2): δ 143.0, 141.3, 140.8, 137.8, 130.2, 129.2, 128.9, 128.3, 128.1, 128.0, 126.9, 124.6; Anal. calcd for $\text{C}_{18}\text{H}_{12}\text{Br}_2$: C, 55.71; H, 3.12; found: C, 55.80; H, 3.15.

3'',6'-Dibromo-4',5''-diphenyl-1,1':2',1'':2'',1'''-quaterphenyl: (3)



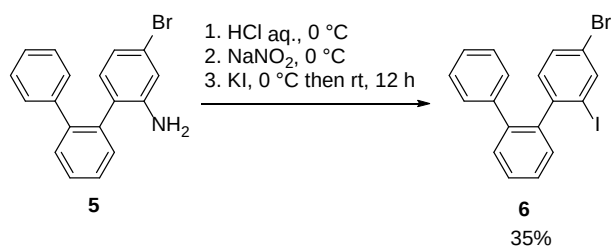
First, [1,1'-biphenyl]-2-ylboronic acid (2.42 g, 12.19 mmol, 2 equiv) and K₂CO₃ (5.06 g, 36.59 mmol, 6 equiv) were added to a solution of 4-bromo-1-iodo-2-nitrobenzene (2 g, 6.09 mmol, 1 equiv) in toluene (6.0 mL) and H₂O (3.0 mL). Second, Pd(PPh₃)₄ (0.7 g, 0.60 mmol, 0.1 equiv) was added to the solution after degassing. Third, the reaction mixture was heated to 90 °C for 9 h under N₂. Next, the product was extracted using CH₂Cl₂. After concentrating the resulting solution in vacuo, **4** (1.17 g, 54% yield) was obtained by column chromatography (11:1 hexane/toluene). ¹H NMR (300 MHz, 20 °C, CDCl₃) δ 7.93 (d, *J* = 1.95 Hz, 1H), 7.59 (dd, *J* = 8.25, 1.95 Hz, 1H), 7.51–7.39 (m, 3H), 7.23–7.20 (m, 3H), 7.18–7.16 (m, 1H), 7.12–7.08 (m, 3H).

4-Bromo-[1,1':2',1''-terphenyl]-2-amine: (**5**)



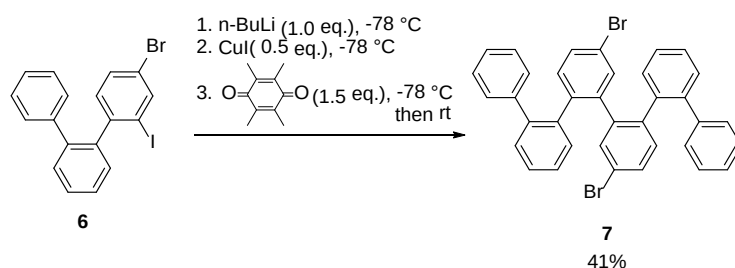
First, conc. HCl (6.3 mL) was added to a solution of **4** (1.17 g, 3.30 mmol) in 12.6 mL of ethanol. Second, tin powder (0.7826 g, 6.6 mmol) was added, and the reaction mixture was heated overnight to 90 °C. Third, after cooling, the mixture was poured into ice water (24 mL) and then made alkaline using an aqueous NaOH solution (pH 14.0). Next, the precipitate was collected by filtration and dried under vacuum. Finally, **5** (965 mg, 90% yield) was purified by alumina column chromatography (hexane: CH₂Cl₂ = 10:1 + triethylamine 1%). ¹H NMR (300 MHz, 20 °C, CDCl₃) δ 7.52–7.40 (m, 3H), 7.37–7.34 (m, 1H), 7.27–7.19 (m, 5H), 6.80 (m, 2H), 6.74 (d, *J* = 1.05 Hz, 1H), 3.52 (br, 2H).

4-Bromo-2-iodo-1,1':2',1''-terphenyl: (**6**)



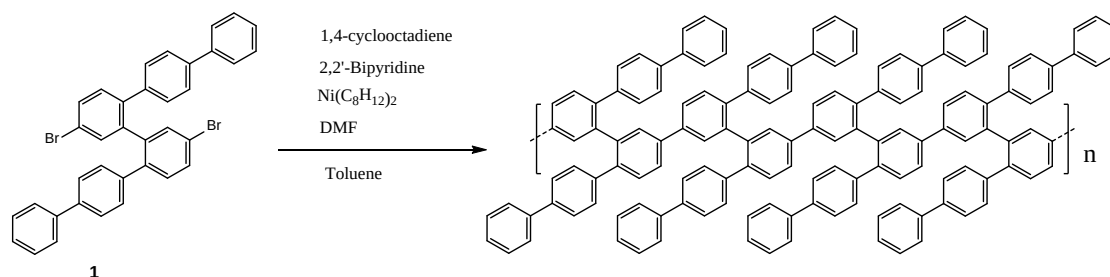
First, an aqueous solution of sodium nitrite (237 mg 3.57 mmol) was carefully added to a suspension of **5** (963 mg 2.97 mmol) in conc. HCl (0.57 mL) cooled at 0 °C in 5 min. Second, the yellow mixture was stirred at 0 °C for 50 min and carefully added to an aqueous solution of KI (0.67 g 4.0 mmol) in 5 min. Third, the mixture was stirred at room temperature for 12 h, followed by quenching using an aqueous solution of saturated sodium sulfite. Next, the product was extracted using diethyl ether and washed with 1 M HCl, brine, water, and dried using Na₂SO₄. Finally, the title product **6** (452 mg, 35% yield) was purified by column chromatography (9:1 hexane/ethyl acetate). ¹H NMR (300 MHz, 20 °C, CDCl₃) δ 8.76 (d, *J* = 2.01 Hz, 1H), 8.66–8.63 (m, 4H), 8.51 (d, *J* = 8.82 Hz, 1H), 7.75–7.63 (m, 6H), 6.74 (m, 1H).

4'',5'''-Dibromo-1,1':2',1'':2'',1''':2''',1''':2''',1''':2'''-sexiphenyl: (7)



First, *n*-BuLi (0.15 mL 0.23 mmol, 1.6 M in hexane) at -78 °C was added to a solution of **6** (100 mg 0.23 mmol) in anhydrous THF (2.1 mL). Second, the mixture was stirred for 30 min at -78 °C, and CuI (22.0 mg 0.12 mmol) was added under nitrogen. Third, tetramethyl-*p*-benzoquinone (57.0 g, 0.35 mmol) was added after another 5 min. Next, the mixture was stirred overnight at room temperature. The product was then extracted using CH₂Cl₂, washed with 1 M HCl, dried over Na₂SO₄, and passed through a silica gel pad (eluent: hexane). After purification by recycling GPC, **7** (58.7 mg, 41% yield) was obtained. ¹H NMR (300 MHz, 20 °C, CDCl₃) δ 7.96 (d, 2H), 7.38–7.50 (m, 8H), 7.31 (dd, 2H), 7.21–7.25 (m, 6H), 7.11–7.18 (m, 4H), 6.93 (d, 2H); ¹³C NMR (75 MHz, 20 °C, CDCl₃) δ 145.32, 141.57, 140.85, 140.69, 140.57, 132.00, 130.69, 130.65, 130.25, 129.58, 128.46, 127.85, 126.99, 126.75, 121.00, 100.76.

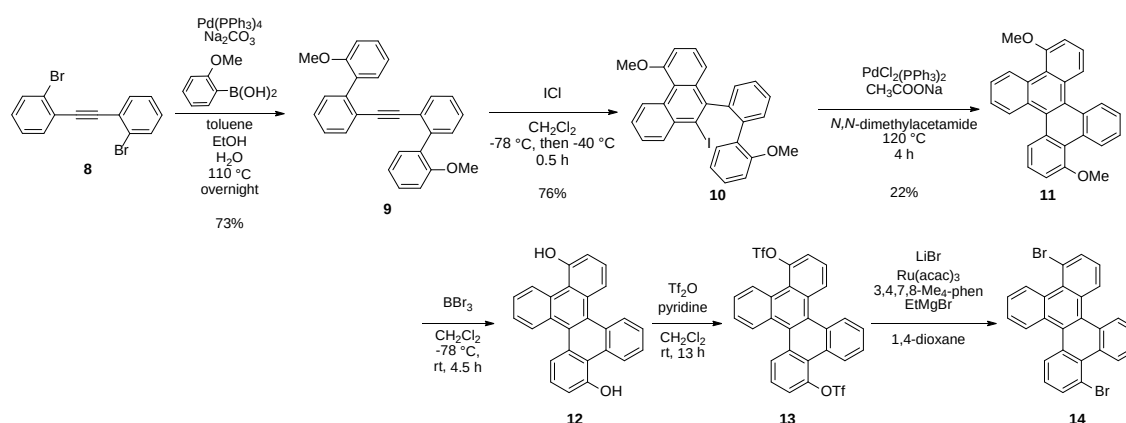
2-3-4. Synthesis of polymer from ‘Z-bar-linkage’ precursors.



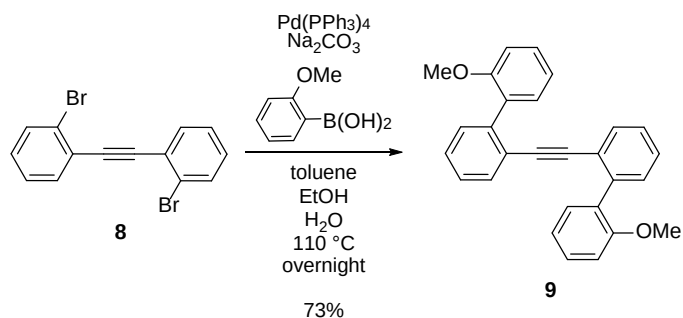
First, in a glove box, bis(1,4-cyclooctadiene)nickel(0) complex (8.50 mg, 3.09 μmol), 2,2'-bipyridyl (4.83 mg, 3.09 mmol), and 1,4-cyclooctadiene (4.0 μL , 3.34 mg, 3.09 μmol) were added to 2.0 mL of DMF (anhydrous and degassed) in a 9 mL glass vial. Second, the reaction mixture was heated to 50 $^{\circ}\text{C}$ and kept for 30 min. Third, the toluene solution of the precursor **1** (15.2 mg, 24.7 μmol in 2.0 mL of toluene (anhydrous and degassed)) was added to the catalyst solution in the vial. Next, the reaction mixture was stirred at 80 $^{\circ}\text{C}$ for 5 days. The polymer was then precipitated by adding methanol, filtered, and washed with methanol, conc. HCl, water, a 0.5 M NaOH solution, and water. Finally, the product was obtained as a white powder (1.80 mg, 3.94 μmol , 16% yield).

2-3-5. Synthesis of 1,9-dibromodibenzo[*g,p*]chrysene for interchain-linked GNRs.

1,2-Bis(2-bromophenyl)ethyne was prepared according to the literature.⁶

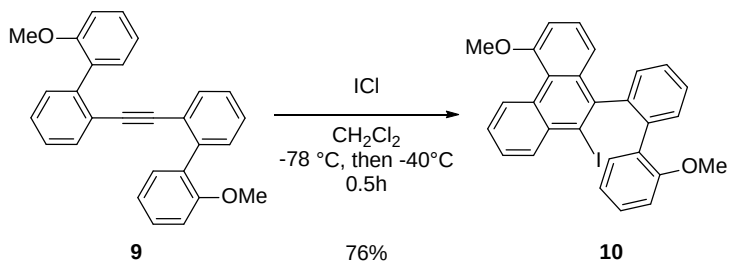


1,2-bis(2'-methoxybiphenyl-2-yl)ethyne (**9**)



A three-necked 1 L flask equipped with a magnetic stirrer, condenser, and glass stopcock was added **8** (13.0 g, 38.7 mmol), Na_2CO_3 (90.1 g, 85.0 mmol), and 2-methoxyphenylboronic acid (12.7 g, 83.6 mmol). The flask was replaced by nitrogen atmosphere, added toluene (326 mL), water (208 mL), and ethanol (204 mL). The reaction mixture was degassed by freeze-vacuum technique repeated three times, then added $\text{Pd(PPh}_3)_4$ (3.88 g, 3.36 mmol, 8.7 eq.) over the frozen reaction mixture under nitrogen flow. The reaction mixture was stirred at 110°C in oil bath to maintain reflux overnight. After cooling to r.t., the reaction mixture was diluted with chloroform. The organic layer was collected and combined with further extraction of aqueous layer by using chloroform. Combined organic layer was dried over anhydrous Na_2SO_4 , and concentrated by evaporation. The crude material was purified by silica gel chromatography (eluent hexane: CH_2Cl_2 = 1:1). Collected product washed with hexane gave **9** as a white solid (10.5 g, 26.8 mmol, 69% yield). Melting point $153.3\text{--}154.1^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.45–7.11 (m, 12H), 7.05–7.89 (m, 4H), 3.73 (s, 6H, OMe); ^{13}C NMR (100 MHz, CDCl_3): δ 156.74, 140.62, 132.18, 131.44, 130.16, 129.67, 128.90, 127.54, 126.73, 123.39, 120.09, 110.92, 91.51, 55.51; MS(EI): m/z 390 $[\text{M}^+]$.

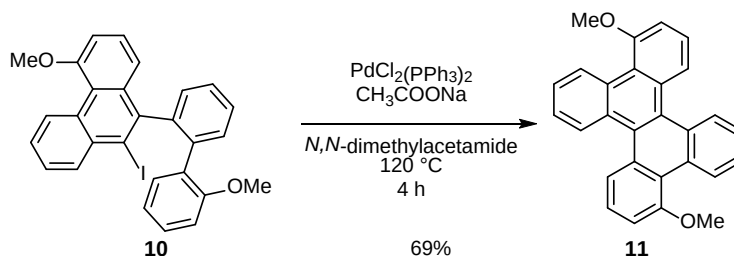
10-(2'-methoxybiphenyl)-5-methoxy-9-iodophenanthrene (**10**)



A three-necked 500 mL flask equipped with a magnetic stirrer, condenser, and glass stopcock was

added **9** (1.40 g, 3.58 mmol). The flask was replaced by nitrogen atmosphere, added CH₂Cl₂ (anhydrous, 300 mL) at r.t. to dissolve completely, and cooling to -78 °C. The reaction mixture was added ICl (0.783 g, 4.82 mmol) slowly via syringe. After the addition, the reaction mixture was stirred at -40 °C for 30 min. The reaction was quenched by the addition of saturated Na₂SO₃ aqueous solution, the organic layer was collected and combined with further extraction of aqueous layer by using CH₂Cl₂. Combined organic layer was washed with saturated NaHCO₃ aqueous solution, water, and brine, dried over anhydrous Na₂SO₄, and concentrated by evaporation. Obtained yellow viscous solid washed with hexane gave **10** as a white solid (1.41 g, 2.73 mmol, 76% yield). Melting point: 165.1–167.2 °C; ¹H NMR(400 MHz, CDCl₃): δ 9.59(d, 1H), 8.41(d, 1H), 7.63–7.42(m, 5H), 7.35–6.87(m, 6H), 6.57–6.45(m, 2H), 4.08(s, 3H, OMe), 3.41(s, 3H, OMe); ¹³C NMR(100 MHz, CDCl₃): δ 157.95, 156.20, 144.83, 144.74, 137.96, 134.58, 134.17, 132.52, 131.77, 131.36, 130.88, 130.32, 129.13, 128.36, 128.23, 127.43, 127.14, 126.97, 126.92, 125.99, 122.29, 120.59, 119.44, 110.01, 109.59, 108.77, 55.75, 54.66 (28 peaks); MS(EI): *m/z* 516[M⁺].

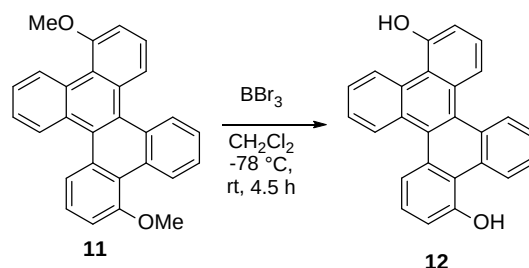
1,9-dimethoxydibenzo[*g,p*]chrysene (**11**)



A three-necked 1 L flask equipped with a magnetic stirrer, condenser, and glass stopcock was added **10** (1.31 g, 2.53 mmol), PdCl₂(PPh₃)₂ (98.7 mg, 14.1 mmol), and CH₃COONa (3.83 g, 46.7 mmol). The flask was replaced by nitrogen atmosphere, added *N,N*-dimethylacetamide (anhydrous grade, degassed, 50 ml). The reaction mixture was degassed by freeze-vacuum technique repeated three times, then added Pd(PPh₃)₄ (3.88 g, 3.36 mmol, 8.7 eq.) over the frozen reaction mixture under nitrogen flow. The reaction mixture was stirred at 120 °C for 4 h. After cooling to r.t., the reaction was quenched by adding 1 M HCl aqueous solution and diluted with CH₂Cl₂. The organic layer was collected and combined with further extraction from aqueous layer by using CH₂Cl₂. Combined

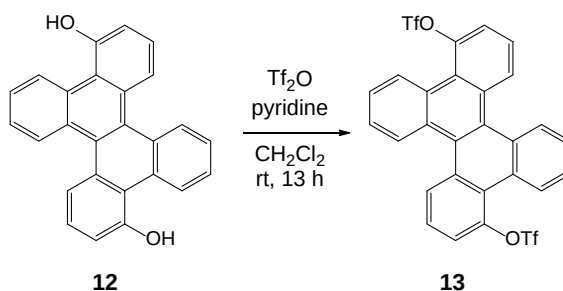
organic layer was dried over anhydrous Na_2SO_4 , and concentrated by evaporation. The crude material was purified by silica gel chromatography (eluent hexane: CH_2Cl_2 = 1:1). Recrystallization of collected product from chloroform gave **11** as a white solid (0.700 g, 1.80 mmol, 69% yield). Melting Point: 242.1-246.8 °C; ^1H NMR(400 MHz, CDCl_3): δ 9.40–9.36(m, 2H), 8.60–8.55(m, 2H), 8.25(d, 2H, J = 7.68 Hz), 7.61–7.43(m, 6H), 7.17(d, 2H, J = 7.62 Hz), 4.12(s, 6H); ^{13}C NMR(100 MHz, CDCl_3): δ 157.71, 131.41, 130.01, 129.37, 128.64, 128.20, 128.05, 126.78, 126.10, 125.52, 121.39, 120.94, 108.66, 55.89 (14 peaks); MS(EI $^+$): m/z 388[M $^+$].

Dibenzo[*g,p*]chrysene-1,9-diol (**12**)



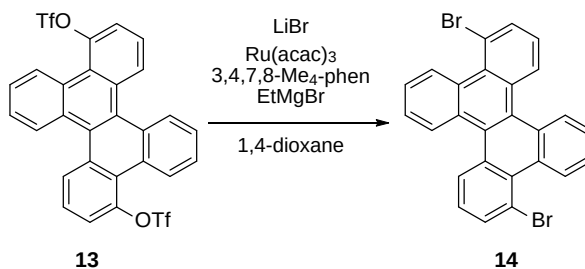
A three-necked 300 mL flask equipped with a magnetic stirrer, condenser, and glass stopcock was added **11** (1.65 g, 4.25 mmol). The flask was filled by nitrogen atmosphere, added CH_2Cl_2 (anhydrous grade, degassed, 130 mL), and cooled to -78 °C. The reaction mixture was added BBr_3 (1 M in dichloromethane 28 mmol, 28.0 mL) slowly via syringe for 10 min. After the addition, the reaction mixture was warmed and stirred at r.t. for 4.5 h, then quenched by adding water and diluted with CH_2Cl_2 . The organic layer was collected and combined with further extraction from aqueous layer by using CH_2Cl_2 . Combined organic layer was dried over anhydrous Na_2SO_4 , and concentrated by evaporation. CH_2Cl_2 was poured over the crude material, and filtered to remove the insoluble solid. The light yellow solid was obtained by removal of the solvent and rinsing with hexane (1.01 g, 2.79 mmol, 66% yield). Thus the obtained yellow-white solid product **12** was used for next step without further purification. ^1H NMR(400 MHz, CDCl_3): δ 9.31 (dd, J = 7.93 Hz, 1.28 Hz, 2H), 8.60 (d, J = 7.93 Hz, 1.28 Hz, 2H), 8.25(d, J = 8.35 Hz, 2H), 7.64–7.54(m, 4H), 7.45(t, J = 7.93 Hz, 2H), 7.05(d, J = 7.5 Hz, 2H), 5.63(brs, 2H, OH); MS(EI): m/z 360[M $^+$].

Dibenzo[*g,p*]chrysene-1,9-diyl bis(trifluoromethanesulfonate) (**13**)



12 (1.01 g, 2.79 mmol) was put in a 25 mL Schrenk flask equipped with a magnetic stirrer and glass stopcock. After the flask was replaced by nitrogen atmosphere, CH_2Cl_2 (anhydrous grade, degassed, 13.0 mL) and pyridine (0.55 mL) was poured, and cooled to 0 °C. Trifluoromethane sulfonate anhydride (1.0 mL, 5.94 mmol) was added into the reaction mixture slowly via syringe for 10 min. After the addition, the reaction mixture was warmed and stirred at r.t. for 13 h. The reaction was quenched by adding water and diluted with CH_2Cl_2 . The organic layer was collected and combined with further extraction from aqueous layer by using CH_2Cl_2 . Combined organic layer was dried over anhydrous Na_2SO_4 , and concentrated by evaporation. The crude material was purified by alumina column chromatography (eluent: toluene), and recrystallized using chloroform. **13** was obtained as light yellow solid (0.699 g, 1.12 mmol, 40% yield). Melting point: 221.9 °C; ^1H NMR(400 MHz, CDCl_3): δ 8.98–8.94(m, 2H), 8.73(d, J = 7.99 Hz, 2H), 8.53–8.48(m, 2H), 7.73–7.57(m, 8H); ^{13}C NMR(100 MHz, CDCl_3): δ 147.02, 147.00, 131.82, 129.89, 129.02, 128.30, 128.23, 128.13, 127.87, 127.08, 127.00, 126.71, 124.42, 120.98 (14 peaks); MS(EI $^+$): m/z 624[M^+].

1,9-dibromodibenzo[*g,p*]chrysene (**14**)



A 30 mL oven-dried Schrenk flask equipped with a magnetic stirrer, condenser, and glass stopcock was set and LiBr (grained, 171.7 mg, 1.98 mmol, 19 eq.) was put into it. The flask was heated by heat gun (400 °C) for 20 min. After cooling down to r.t., Ru(acac)₃ (13.9 mg, 0.0349 mmol, 0.33 eq.), and 3,4,7,8-Me₄Phen (9.60 mg, 0.0406 mmol, 0.38 eq.) were added into the flask, then replaced with nitrogen. 1,4-Dioxane (5.0 mL) and EtMgBr (0.25 mL, 1.0M in THF) were added into the flask dropwise, followed by addition of a 1,4-dioxane solution of **13** (66.9 mg, 0.107 mmol, 1.0 mL) dropwise. The reaction mixture was refluxed for 4 days (at 120 °C in oil bath). TLC analysis indicated starting material remains. The reaction mixture was worked up by filtration using a cerite pad, extract with chloroform. Organic layer was washed with water and concentrated. The mixture of starting material and brominated product was roughly separated by silica gel chromatography (eluent hexane:dichloromethane = 5:1). The recovered mixture was subjected under the same reaction condition. After 5 days under the reflux condition, TLC analysis indicated disappearance of the starting materials. The reaction mixture was worked up by the same protocol by filtration using a cerite pad, extract with chloroform. Organic layer was washed with water, and concentrated. The product was purified by silica gel chromatography (eluent hexane:dichloromethane = 5:1), and washed with hexane. **14** was obtained as a yellow solid (10.7 mg, 0.0220 mmol, 21% yield). Melting point: 226.8-228.8 °C; ¹H NMR(600 MHz, CDCl₃): δ 9.39(d, *J* = 7.6 Hz, 2H), 8.60(d, *J* = 8.17 Hz, 2H), 8.45(d, *J* = 7.56 Hz, 2H), 7.95(d, *J* = 7.56 Hz, 2H) 7.71–7.55(m, 4H), 7.44(t, *J* = 7.87 Hz, 2H); ¹³C NMR(600 MHz, CDCl₃): δ 133.98, 131.68, 130.29, 130.10, 129.61, 128.46, 128.04, 127.89, 127.80, 127.63, 124.66, 120.71 (12 peaks); MS(EI⁺): *m/z* 486[M⁺], 406[M-Br]⁺, 326[M-2Br-2]⁺.

2-4. Reference

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Chapter 3

Homochiral polymerization driven selective growth of acene-type graphene nanoribbon

3-1. Introduction

GNRs have been successfully fabricated on metal substrates using techniques such as ultra-high vacuum (UHV) deposition¹⁻⁷ and chemical vapor deposition (CVD).⁸ The mechanism underlying these processes is believed to involve heterogeneous catalysis based on the electronic interactions between the reactants and the metal surface.^{9, 10} Although Au(111) surfaces have been reported to assist the dehydrogenation of prepolymers to afford GNRs,^{11,13} the detail mechanism of such catalysis, especially the role of metal surface, is unclear whether it is due to the electronic effect on the prepolymers or the conformational effect on the prepolymers. In addition, acene-type GNRs,^{14,15} which have the same chiral vector as zigzag-edged GNRs,¹⁶ have been predicted to show high carrier mobility by theory.¹⁷ Thus, the precursor design to produce well organized acene-type GNRs on surface is desired.

In this chapter, a new 'conformation-controlled surface catalysis' methodology for efficient production of organized acene-type GNRs, which is driven by the conformation-adaptation of precursor on the surface, analogous to enzymatic catalysis is proposed.^{18,19} To realize this concept, a precursor with a 'Z-bar-linkage' was designed, which represents as two terphenyl units are linked like a 'Z', exhibiting flexible geometry that allows it to adopt optimized conformation on Au(111) which can promote the conformationally controlled chemical reactions led to acene-type GNRs.

3-2 Results and discussion

3-2-1. Selective growth of acene-type graphene nanoribbons.

Figure. 3-1 shows the experimental setup of 2Z-CVD and the stepwise growth process. Z-bar-linkage precursor (4'',5'''-dibromo-1,1':4',1'':2'',1''':2''',1''':4''',1''''-sexiphenyl) was synthesized

according to procedures detailed in the chapter 2. The precursor was sublimed so that it could be supplied to the Au(111) substrate in zone 2 by passing through zone 1 in a quartz tube equipped with two furnaces. 2Z-CVD is advantageous because it permits the independent control of temperature in the two separated zones 1 and 2. This technique successfully afforded a series of armchair-edged GNRs in high yield using a conventional apparatus⁸. Although it is difficult to analyze the radicals in situ in the CVD system, the existence of prepolymers as an intermediate of GNRs similar to those of UHV deposition¹⁻⁷ strongly indicates the existence of biradicals in the fabrication process of GNRs. The generation of a high density of radicals has been hypothesized to occur in zone 1 by the collision of precursors with the hot wall. The polymerization of the radicals supplied to the Au(111) substrate has been assumed to occur in zone 2, followed by dehydrogenation, affording GNRs. Similar to the results obtained for armchair-edged GNRs,⁸ the 2Z-CVD of the precursor exhibited the temperature dependence of zone 1 and the height dependence of the substrate from the hot wall on the Raman intensity (Figure 3-2). These results significantly suggest that the biradicals of precursor are possibly produced by the collision with the hot wall in zone 1.

The material grown by 2Z-CVD at 250 °C on Au(111) supplied with 50 µg of the precursor and annealed at the given temperatures (250, 375, 450, and 500 °C) in zone 2 were examined by STM at room temperature under Ar. Height profiles were measured for evaluating periodicity in the lateral direction. As shown in Figures 3-3 (a, b), and Figure 3-4 (a, c), a densely packed array of straight 1D chains with a maximum length of 22.5 nm was observed in the STM images of the material grown at 250 °C. A periodicity of 0.80 nm was observed along the chain axis (Figure 3-3c), indicating the formation of polymers with a well-aligned planar conformation on Au(111) with polyphenylene moieties lying on the surface, as indicated by an overlaid space-filling model (Figure 3-3b). The STM images were in good agreement with the STM simulation (Figure 3-5a). Based on molecular mechanics (MM) calculations, the polymer was determined to be flexible and could adopt several random conformations because of its zigzag backbone, where benzene rings could rotate around the C–C single bonds, and the C–C bonds could bend. Nevertheless, the 2Z-CVD-grown polymers adopted a planar conformation on Au(111).

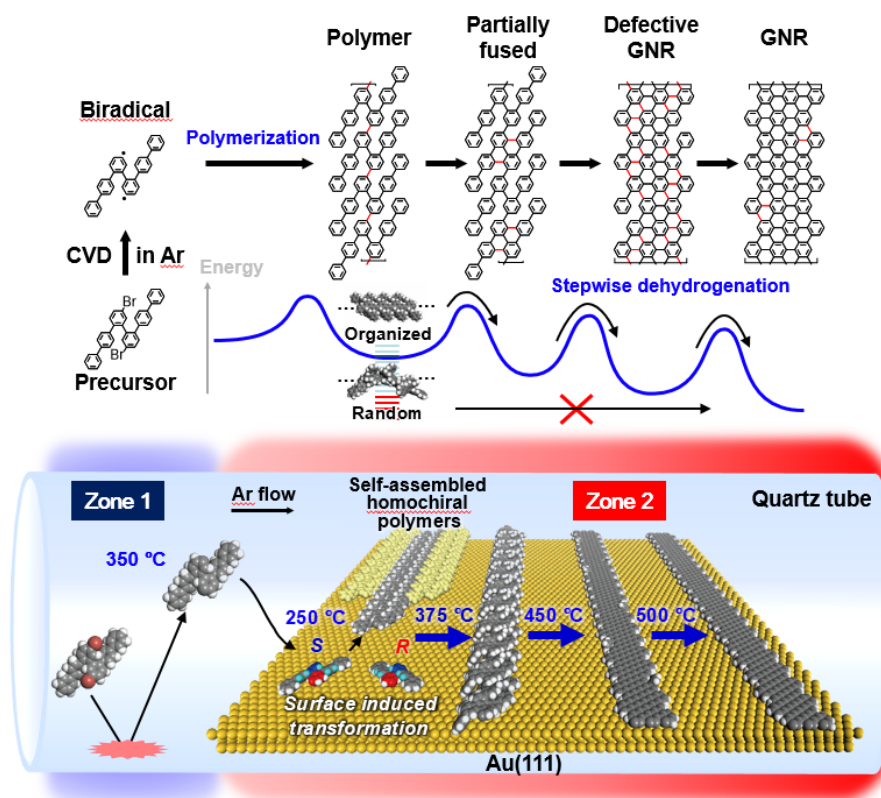


Figure 3-1. Schematic representation of growth of acene-type GNRs from Z-bar-linkage precursor by two-zone chemical vapor deposition (2Z-CVD). 3D illustration shows an example for the growth of GNRs from precursor by the surface-induced chirality of left-handedness (S). Energy diagrams for each reaction are also shown. Colors of the benzene rings in the precursor in the space-filling view indicate the relative heights from the Au(111) surface; red, near the surface; blue, far from the surface.

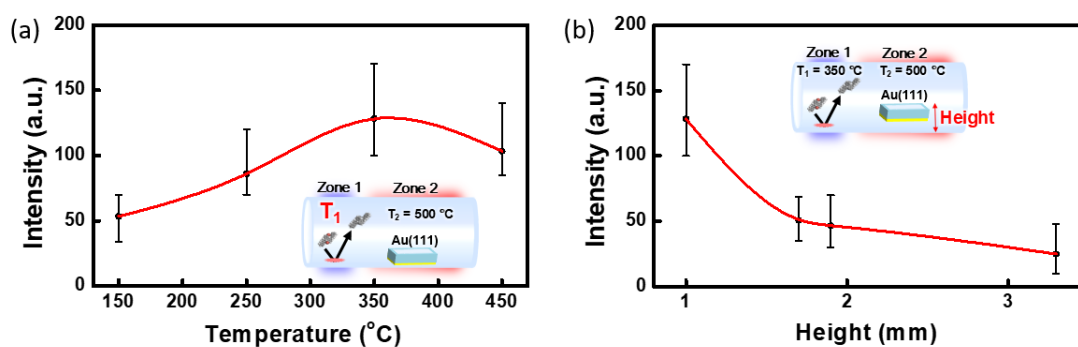


Figure 3-2. Temperature and height dependence on Raman intensity of GNRs using Z-bar-linkage precursors. (a), Temperature dependence of zone 1 (T_1) on the G-band Raman intensity of GNRs. (b), Height dependence of the Au(111) substrate located in zone 2 on Raman intensity. GNRs were produced by 2Z-CVD at the temperature of $T_2 = 250$ °C, followed by $T_2 = 500$ °C in zone 2.

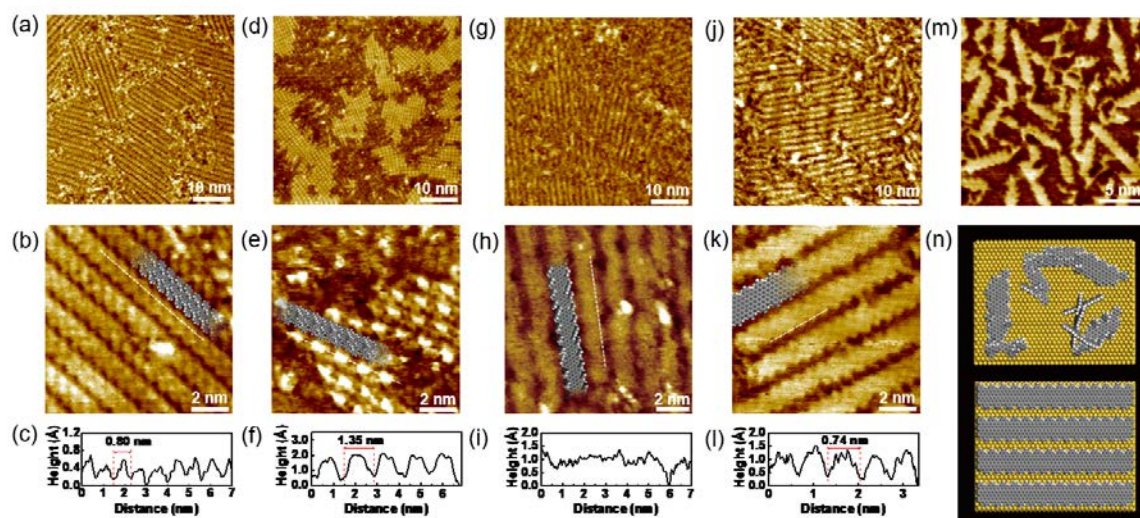


Figure 3-3. (a, b), The Au(111) substrate grown at 250 °C by 2Z-CVD supplied with a 50 g precursor. (d, e), followed by annealing at 375 °C for 10 min. (g, h), 450 °C for 10 min. (j, k), 500 °C for 10 min. (m), The Au(111) substrate grown at 250 °C supplied with 25 g precursor, followed by annealing at 500 °C for 10 min. (n), illustration of the conformation-controlled dehydrogenation mechanism with low- and high-density GNRs. (c, f, i, l), Cross-sectional analysis of lines in (b), (e), (h), and (k), respectively. All STM images were recorded under Ar at room temperature.

The sample annealed at 375 °C formed a structure, in which dots were spaced at a distance of 1.35 nm along the chain axis (Figures 3-3d–f). This unique structure was in good agreement with the model, in which dehydrogenation in the inner core occurred at alternate monomer units along a chain (Figure 3-1), as shown in the overlaid space-filling model (Figure 3-3e). Because the stress originating from dehydrogenation at one monomer site might be released at the neighboring polyphenylene unit, dehydrogenation at alternate monomer units was presumed to proceed sequentially. These results indicated that the dot structure in the STM images is a 'partially fused polymer' (Figure 3-1), which was well reproduced by the STM simulation (Figure 3-5). Annealing at 450 °C resulted in the formation of wavy chains in the STM images (Figures 3-3g, h). Because no periodicity appeared at the edges of the chain (Figure 3-3i), these structures were estimated to be 'defective GNRs' (Figure 3-1), which were completely fused at the inner core and partially at the outer core, as shown in the overlaid space-filling model (Figure 3-3h).

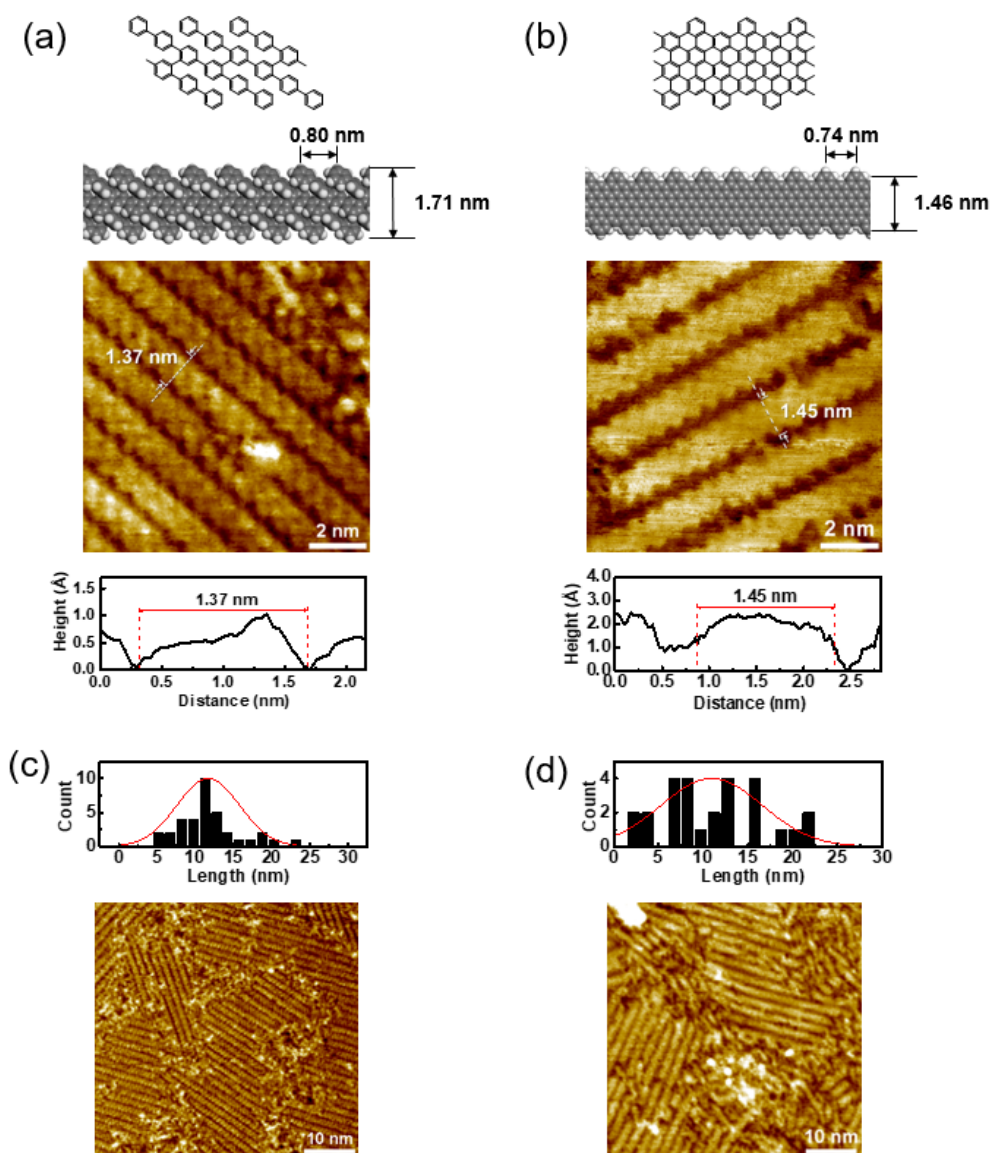


Figure 3-4. (a, b), Cross-sectional analysis of lines in STM images of polymers (a) and GNRs (b). (c, d), Length histogram with a distribution fit obtained from the STM images of polymers (c) and GNRs (d).

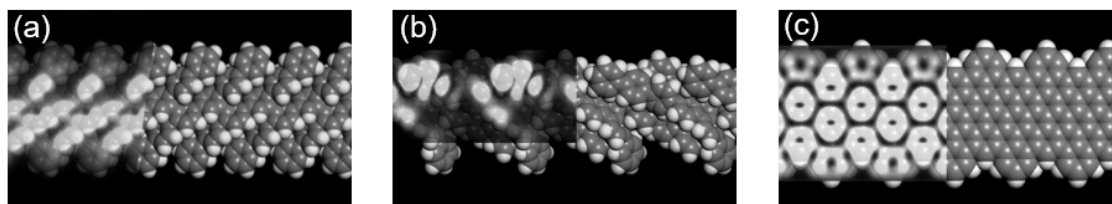


Figure 3-5. STM simulation of 2Z-CVD-grown chains from the Z-bar-linkage precursor. (a), Polymer, (b), Partially fused polymer and (c), GNR.

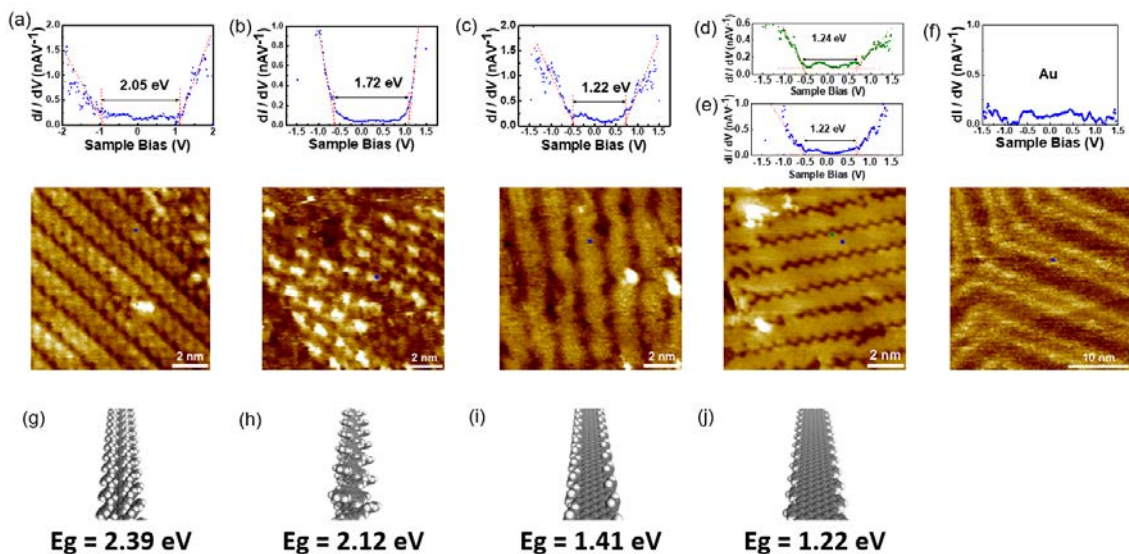


Figure 3-6. Experimental and theoretical bandgaps. (a-f), dI/dV curves of polymer (a), partially fused polymer (b), defective GNR (c), GNR measured at the edge (d), GNR measured at the center (e) and Au(111) (f), were measured by STS at the location marked by blue or green dot in STM images. The reconstructed herringbone structure was seen in Au(111). (g-j), The bandgaps of polymer (g), partially fused polymer (h), defective GNR (i) and GNR (j) were predicted by DFT calculations.

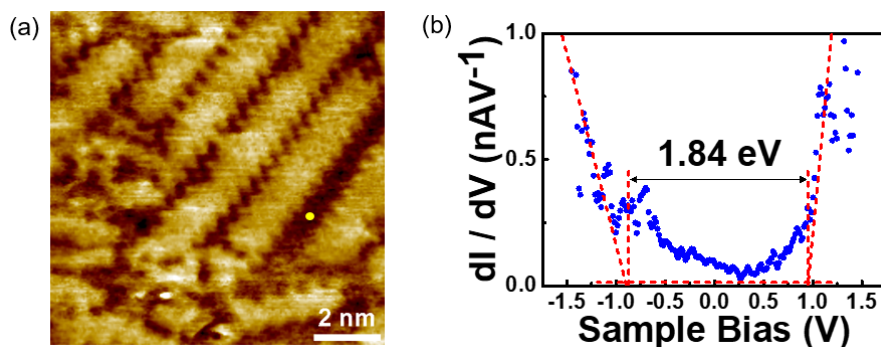


Figure 3-7. Bandgap of GNRs background. (a, b), The dI/dV curve (b) was measured at the background (a) marked as yellow dot.

Moreover, annealing at 500 °C resulted in an array of almost straight chains with a maximum length of 21.3 nm and a width of 1.45 nm (Figures 3-3j, k and Figure 3-4b). Perfectly fused acene-type GNRs were observed because the edges of chains exhibited protrusions with a periodic spacing of 0.74 nm, corresponding to the benzene rings of cove edges (Figure 3-3l). Bandgaps obtained from scanning tunneling spectroscopy (STS) were estimated by taking into account the major peaks without

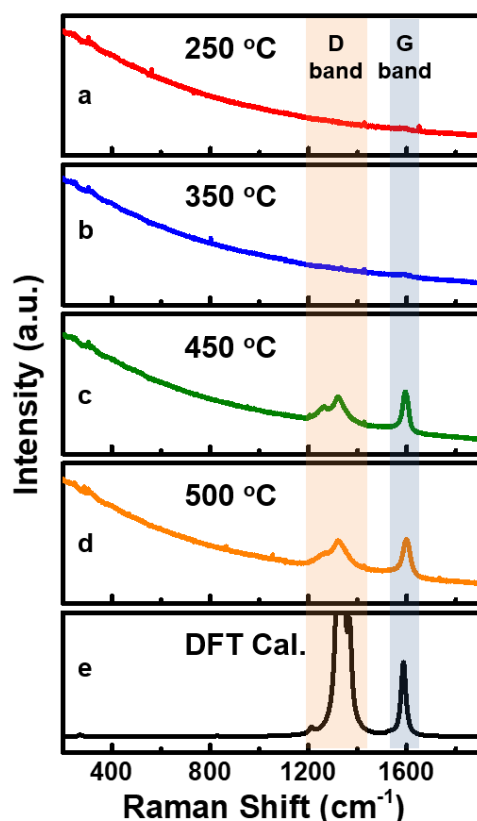


Figure 3-8. Raman spectra of the 2Z-CVD-grown samples from the Z-bar-linkage precursor. (a-e), Experimental spectra of samples grown at 250 °C (a), annealed at 350 °C (b), 450 °C (c), 500 °C (d), and DFT calculations (e). Intensities of a–d are comparable.

detailed sub-levels in dI/dV curves. Experimental results were in agreement with the results obtained from the density functional theory (DFT) calculations for each model (Figure 3-6); this agreement between experiments conducted on Au(111) and theory in the gas phase might originate from the weak interaction between the molecular chains and surface. The polymer and partially fused polymers are supposed to exhibit less interaction with Au(111), attributed to the bulky polyphenylene moiety. Although GNRs with a flat geometry are in general expected to interact with Au(111), the STS measurement of the background, except GNR chains, suggested the existence of underlayers, which are supposedly short partially fused chains, from the bandgap value (Figure 3-7). Figure 3-3 (a) shows the STM images of the polymers. As the objects observed at the boundary were supposed to be short random polymer chains, the annealing of polymers might result in them being submerged under GNRs during dehydrogenation, thereby resulting in low interaction between GNRs and Au(111). The reason

for this submergence is not currently known. The Raman spectrum of the sample annealed at 500 °C exhibited a G-band at 1598 cm^{-1} and D-bands at 1324 cm^{-1} and 1270 cm^{-1} . Although the observed intensities differed from the calculations, the peak positions were in agreement with those calculated by DFT (Figure 3-8). The observed pathway for stepwise dehydrogenation (Figure 3-1) was supported by energy calculations using DFT, indicating that dehydrogenation starting from the inner core of the chain, rather than from the outer core, was energetically favored for avoiding strained macrocycles (Figure 3-9). Although these calculations did not account for the interaction with Au(111), they provided useful information about the reaction paths from the polymer.

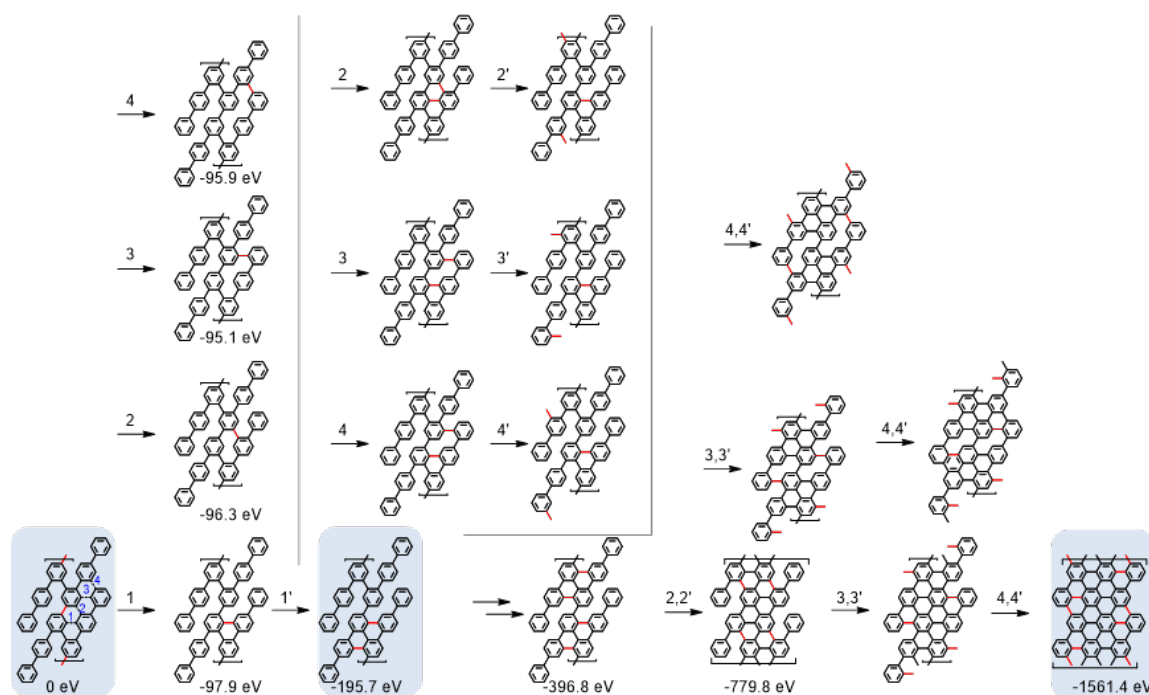


Figure 3-9. Plausible reaction pathway from polymer to GNR. Total free energies of a single strand in the gas phase were calculated by CASTEP with GGA-PBE. Relative energies were corrected by the energy of abstracted hydrogen molecules and standardized by the energy of starting polymer.

3-2-2. Conformation-controlled dehydrogenation.

When the 2Z-CVD-grown samples supplied with 25 μg of the precursor were annealed at 500 °C, low-density short GNRs were observed, though exhibiting position dependence on STM images (Figure 3-3m). However, some chains exhibited irregular structures with winding chains and non-

uniform width (Figure 3-3m). The observed low-density GNRs exhibiting irregular structures suggest imperfect dehydrogenation, while almost perfect dehydrogenation was achieved for the self-assembled high-density GNRs (Figure 3-3n). These remarkable results demonstrate the direct evidence of the concept of 'conformation-controlled dehydrogenation'. Hence, the optimized pathway of dehydrogenation occurs via the planar conformation of polymers on Au(111). Another interesting aspect is that the self-assembly of polymers on Au(111) forming densely packed chains assists perfect dehydrogenation; hence, it stabilizes a planar conformation suitable for fusion. A similar phenomenon in which self-assembly promotes the reaction has been reported for self-assembled protein complexes in biology.²⁰

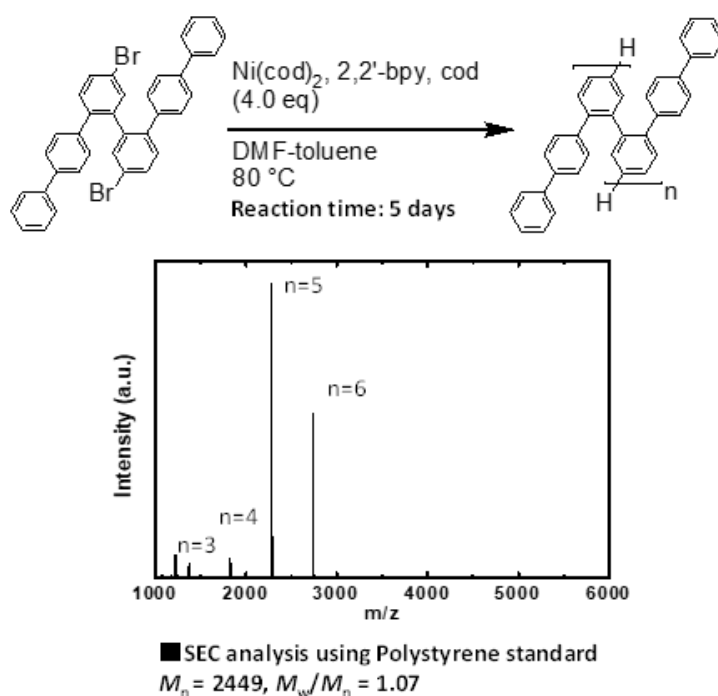


Figure 3-10. Molecular weight distribution of the synthetic polymers from the Z-bar-linkage precursors, as measured by MALDI-TOF MS.

For supporting this new concept of conformation-controlled dehydrogenation, synthetic polymers were prepared from the same precursor for investigating the conformational effects on the growth of GNRs (Figure 3-10). Synthetic polymers with a maximum of six repeat units, corresponding to a chain length of 5 nm, were deposited on Au(111) by spin-coating, followed by annealing at the given temperatures. As shown in Figure 3-11, short winding chains were observed in the STM images of

samples annealed at 250 °C and 470 °C, rather than straight long-chain arrays produced by 2Z-CVD. This result indicates that random conformations of synthetic polymers prevent dehydrogenation. These results also support the above new concept.

Armchair-edged GNRs have been reported to be formed from the 10,10'-dibromo-9,9'-bianthryl precursor. Because the prepolymer synthesized from this precursor has a rigid linear backbone, it leads to a limited dehydrogenation pathway. In contrast, as the polymer built from the precursor contains a flexible zigzag backbone (Figure 3-1), it leads to a wide variety of pathways for dehydrogenation to GNR (Figure 3-9). If only one polyphenylene segment inverts in the polymer, it prevents dehydrogenation. These considerations indicate the difficulty in principle for the precursor to reach the final state (GNR) of the dehydrogenation pathway. Nevertheless, it is surprising that the planar conformation of polymers on Au(111) successfully selects an optimized pathway into GNRs.

3-2-3. Surface-induced homochiral polymerization in a chain.

For clarifying the growth mechanism of the polymer, conformations of the biradicals of the precursor on Au(111) were investigated by the quantum mechanics/molecular mechanics (QM/MM) approach. QM/MM is based on the hybrid method of DFT and MM, which allows us to perform the geometry optimization of molecules adsorbed on surface by taking into account electronic interactions with the surface. This protocol consisted of two stages: (i) the conformation screening of the precursor (dibrominated form), and (ii) the geometry optimization of the biradical form of the precursor. At the first stage of conformation screening, adsorption simulations using MM were performed by loading a single precursor onto Au(111), as traditional MM only supports neutral or charged atoms, except radical species. Although these MM calculations were performed using the dibrominated form of the precursor, these calculations provided useful information for deducing the conformations of the biradical form of the precursor on Au(111). These calculations predicted four conformations of precursor on Au(111), as specified by parameters such as 'surface chirality' and 'height symmetry' (Figure 3-12a). Surface chirality originates from enantiomers with right (*R*)- or left (*S*)-handedness when molecules are placed on a 2D surface.²¹⁻²³ Not only chiral molecules, but also achiral ones, have been reported to afford surface chirality as measured by STM.²⁴⁻²⁶ Height symmetry corresponded to

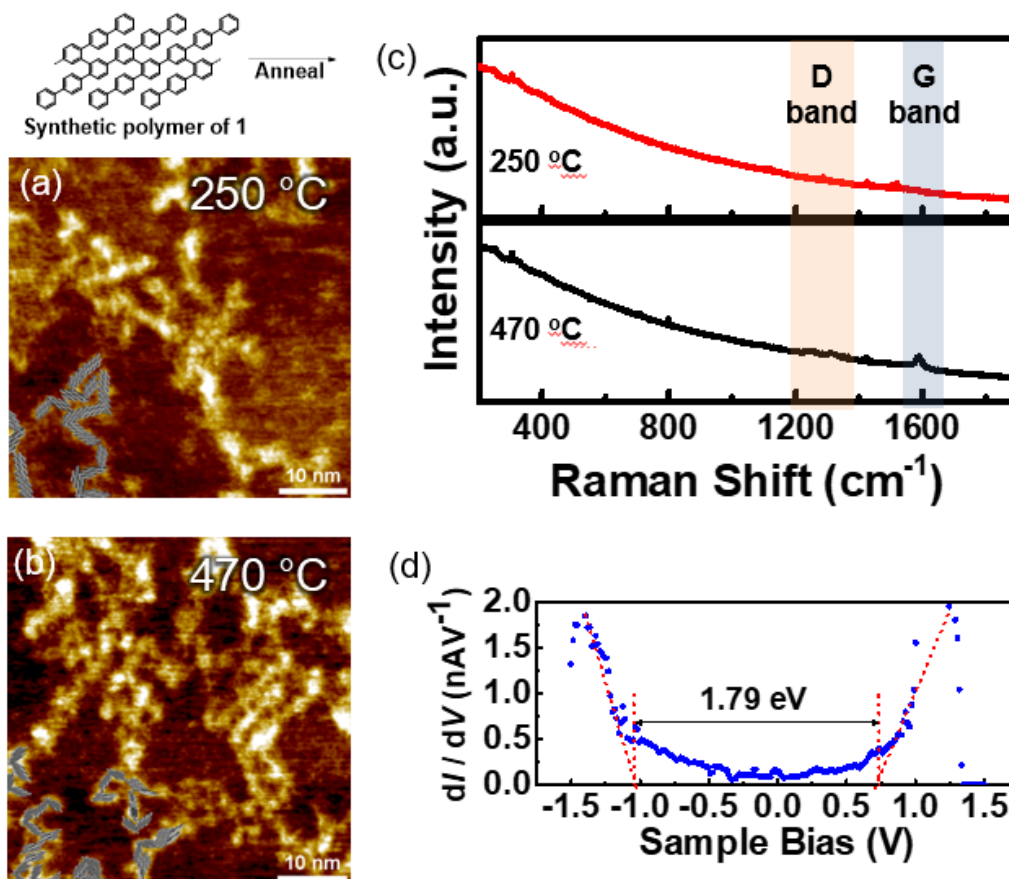


Figure 3-11. Characterization of spin-coated synthetic polymers from the Z-bar-linkage precursors. (a, b), The STM images of spin-coated (2000 rpm.) synthetic polymers on Au(111)/mica using 20 μL polymer solution (0.1 $\mu\text{g/mL}$ o-dichlorobenzene) followed by annealing at 250 $^{\circ}\text{C}$ for 10 min (a) and using 20 μL polymer solution (1.0 $\mu\text{g/mL}$ tetrachloromethane) followed by annealing at 470 $^{\circ}\text{C}$ for 10 min (b) using CVD apparatus. c, Raman spectra of spin-coated synthetic polymers on Au(111) annealed at 250 $^{\circ}\text{C}$ and 470 $^{\circ}\text{C}$. d, dI/dV curve of the sample annealed at 470 $^{\circ}\text{C}$, as measured by STS.

the relative height from the Au(111) surface of two bromine (Br)-substituted benzene rings in the central biphenyl moiety (Figure 3-12a). Two structures could be considered: a height-symmetrical structure, denoted as ' dd ' (down-down), in which two Br-substituted benzene rings could be located near the surface, and a height-asymmetrical structure denoted as ' ud ' (up-down), in which these benzene rings could be at different heights from the surface. Because the dd and ud structures have (R) and (S) enantiomers, four conformers identified by symbols R_{dd} , S_{dd} , R_{ud} , and S_{ud} possibly exist (Figure 3-12a). Conformers R_{ud} and S_{ud} exhibit height-asymmetrical chirality (C_1 chirality), whereas

conformers R_{dd} and S_{dd} exhibit height-symmetrical chirality (C_2 chirality). At the second stage for the geometry optimization of the adsorbed biradical forms, R_{ud} and R_{dd} on Au(111) were calculated by QM/MM. Input geometries of radical forms were obtained by removing bromine atoms from the results of the MM adsorption simulation of dibrominated forms at the first stage. Then, the biradical form and the adjacent two layers of Au (98 atoms) were treated by the QM level.

The calculation results indicated that the height-asymmetrical conformer R_{ud} exhibits a significantly lower formation energy in singlet state as compared with that of the height-symmetrical conformer R_{dd} by $77.5 \text{ kcal}\cdot\text{mol}^{-1}$ (Figure 3-12a and Table 3-1). Such a remarkable difference in the formation energies is hypothesized to stabilize R_{ud} on Au(111) as the dominant species. For considering the reason for the stabilization of R_{ud} , the strain of each of the conformers R_{ud} and R_{dd} on Au(111) was evaluated from the optimized geometry. The distortion of each terphenyl branch from linearity was measured (Figure 3-12b). R_{ud} has three carbon atoms exhibiting a deviation greater than $0.2 \text{ \AA}$, while R_{dd} has eight atoms over the same threshold. R_{dd} adopting a possible 'double arch' structure of two terphenyl branches was remarkably distorted as compared to R_{ud} . This result indicates that the remarkably lower formation energy of R_{ud} possibly originates from lower molecular torsion. If the two radical sites contact with Au(111) to form the R_{dd} conformer, they affect two terphenyl branches to be distorted. In contrast, if only one radical site contacts with Au(111) to form R_{ud} , the asymmetrical structure results in less distortion on two terphenyl branches. Thus, the geometry of the Z-bar-linkage precursor possibly adopts asymmetrical structures as the most stabilized form on the Au(111) surface.

Each radical form of the precursor having the same chiral conformation with height-asymmetry of R_{ud} or S_{ud} was proposed to be exclusively polymerized to form a homochiral polymer in a chain because the head-to-tail coupling could be achieved for conformers with the same chirality (Figure 3-12c). The periodically tilted lines, which appeared perpendicular to the chain axis, correspond to chirality observed in the STM images (Figure 3-3b); these results showed good agreement with the directionally aligned polyphenylene in the STM simulation by DFT calculations (Figure 3-5). In the square of 20 nm STM image, periodically tilted lines were clearly observed with (R)- and (S)-handedness, demonstrating homochirality in a chain (Figure 3-12d). These surprising results indicate that the surface-assisted homochiral polymerization spontaneously occurs among the precursor radicals with the same chirality, excluding those with opposite chirality (Figure 3-12c and Figure 3-).

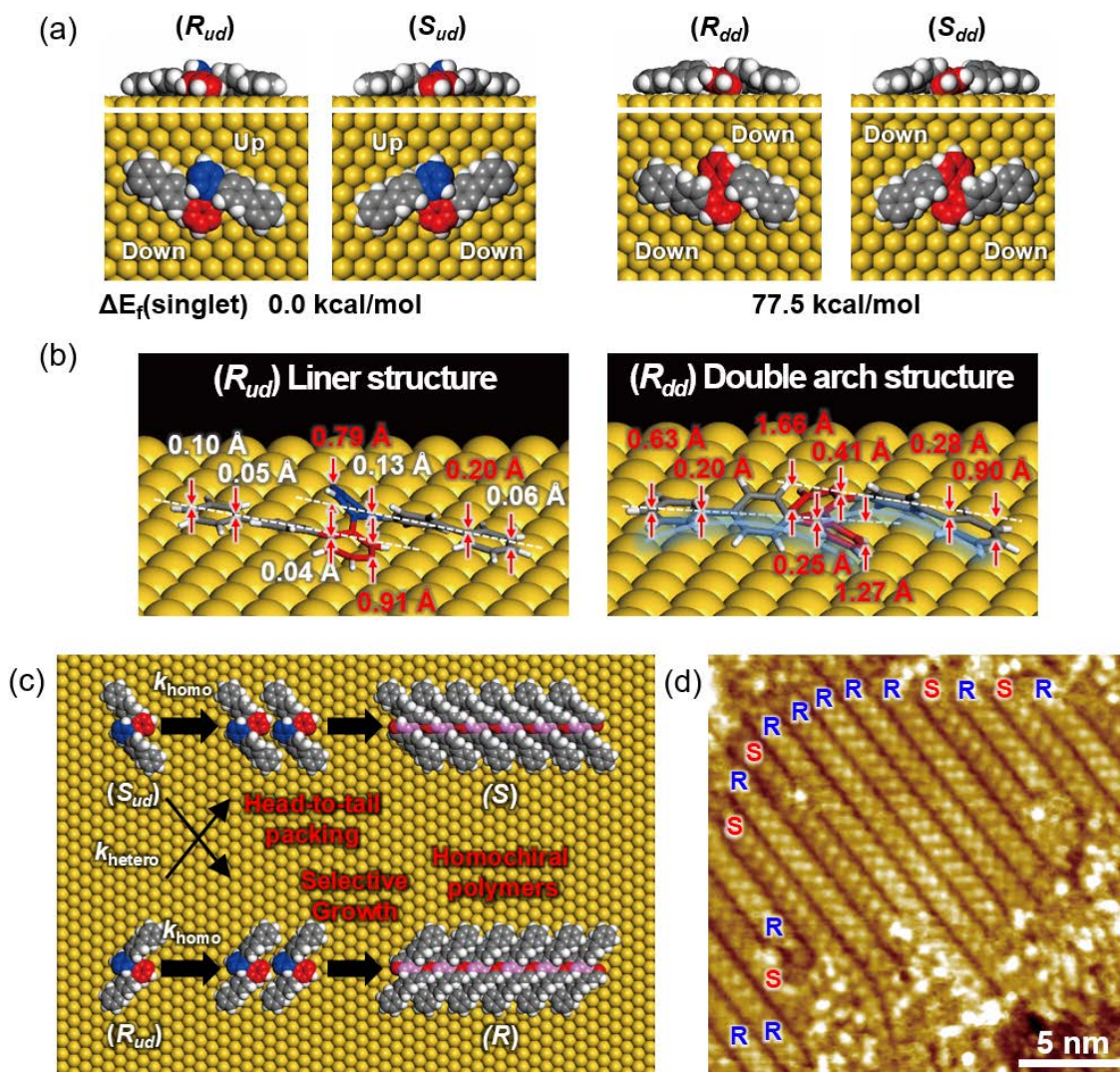
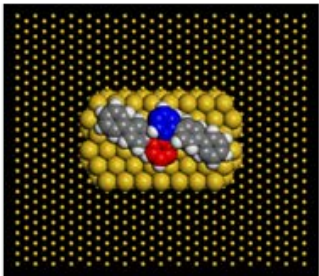
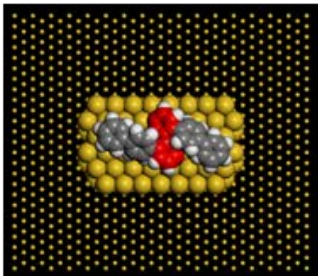
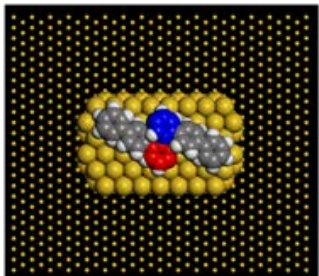
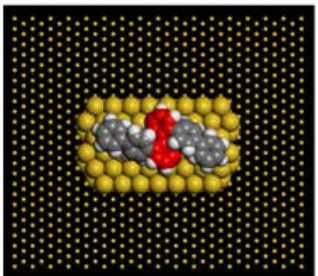


Figure 3-12. (a), Optimized geometries of the biradical form of Z-bar-linkage precursor on Au(111) with relative formation energies (ΔE_f) in singlet state calculated by QM/MM method. Symbols 'R' and 'S' denote right- and left- handedness for chirality, respectively. Symbols 'u' and 'd' denote up and down, respectively, and indicate the relative height of the benzene rings with radical from Au(111) and are identified by colors blue (up) and red (down). (b), Deviations from linearity for each terphenyl branch in optimized geometries (R_{ud} and R_{dd}). The distortion of each carbon atoms greater than 0.2 Å shows the red font while that smaller than the threshold shows the white font. (c), Mechanism of homochiral polymerization in a chain. The rate of polymerization for conformers with the same chirality (k_{homo}) was presumed to be significantly greater than that for conformers with different chiralities (k_{hetero}). (d), The square of 20 nm STM image of homochiral polymers in a chain, grown on Au(111) at 250 °C by 2Z-CVD, with symbols denoted (R) or (S) indicating chirality.

Table 3-1. Formation energy difference of conformers of the biradical forms on Au(111) at the optimized geometry obtained by QM/MM calculations. The singlet-state energy of R_{ud} was set as zero. The biradical form and near two-layered Au atoms (98 atoms) indicating the space-filling model were treated as the QM layer. The remaining 670 Au atoms, indicating small dots, were treated as the MM layer.

Geometry	(R_{ud})	(R_{dd})
$\Delta E_f(\text{singlet})$ (Kcal/mol)	 0.00	 77.51
$\Delta E_f(\text{triplet})$ (Kcal/mol)	 0.83	 78.24

14a) Typically, chiral polymers have been known to form in solution only when homogeneous catalysts or chiral monomers are used.²⁷⁻²⁹ Despite the absence of a chiral catalyst or chiral monomers, homochiral polymerization in a chain successfully proceeded. These results suggested that precursor radicals with the same chirality can react during the lifetime of radicals, which diffuse on the surface owing to strong conformational interaction (Figure 3-12c). This proposed mechanism for surface homochiral polymerization of Z-bar-linkage precursor is based on the concept of head-to-tail polymerization, where the monomers can directionally react with one another (Figure 3-12c). An analogy has been reported on homogeneous-catalyst assisted polymerization, such as the stereoselective polymerization of isotactic polymers^{30, 31} and the regioregular polymerization of 3-

hexylthiophene, affording poly(3-hexylthiophene).^{32, 33} The results obtained in this chapter on this surface system provide a unique model for understanding the mechanism of homochiral polymerization.

For comparison, H-bar-linkage precursor (3'',6'-dibromo-4',5''-diphenyl-1,1':2',1'':2'',1''':-quaterphenyl) and W-bar-linkage precursor (4'',5'''-dibromo-1,1':2',1'':2'',1''':2''',1''':2''''-sexiphenyl) were also synthesized to evaluate the required geometry to produce GNRs. The geometry of these precursors would facilitate the formation of the same acene-type GNRs as like the Z-bar-linkage precursor if those could be successfully polymerized and perfectly dehydrogenated on Au(111).

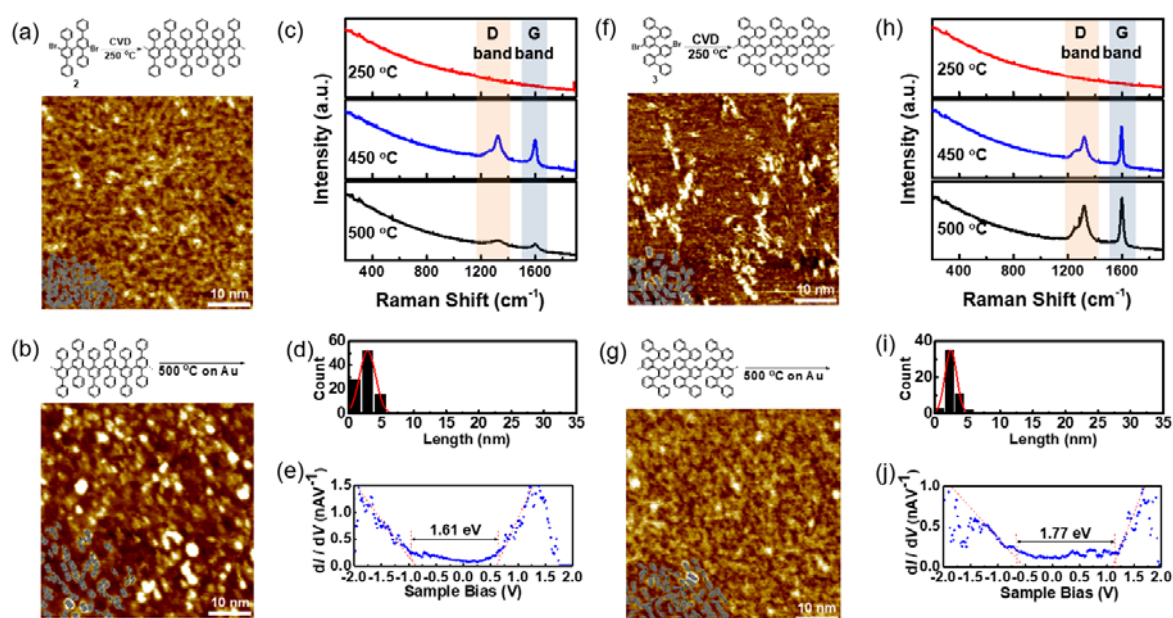


Figure 3-13. Characterization of 2Z-CVD-grown chains from H- and W-bar-linkages. a, f, b, g, STM image of samples annealed at 250 °C (a and f) and 500 °C (b and g). (d, i), Length histogram obtained from the STM images of polymers (b) and (g), respectively. e, j, dI/dV curves of H- (e) and W-bar-linkages (j) annealed at 500 °C, respectively. c, h, Raman spectra for H- (c) and W-bar-linkage (h).

However, STM images of materials grown by 2Z-CVD on Au(111) at 250 °C for these precursors exhibited short winding chains with random orientation, which were presumed to be polymers (Figure 3-13). Short winding chains were observed in the STM images of samples annealed up to 500 °C. From these results, H-bar-linkage and W-bar-linkage precursors could not afford organized polymers and GNRs, but rather short, disordered, and partially fused GNRs. Due to the steric hindrance among

the precursors as well as the ease of deformation to unfavorable conformations, these might disturb polymerization of these precursors (Figure 3-14). These results suggest that the Z-bar-linkage precursor has a specific geometry suitable for homochiral polymerization.

3-2-4. Mechanism of enantioselectivity in homochiral polymerization.

Supramolecular polymers are known to form stacked monomers by noncovalent interactions, such as hydrogen bonding.³⁴ Chiral monomers have been reported so far to form homochiral stacked chains via multiple hydrogen bonding.³⁵⁻³⁸ Such chiral aggregation is based on an 'error-tolerant'

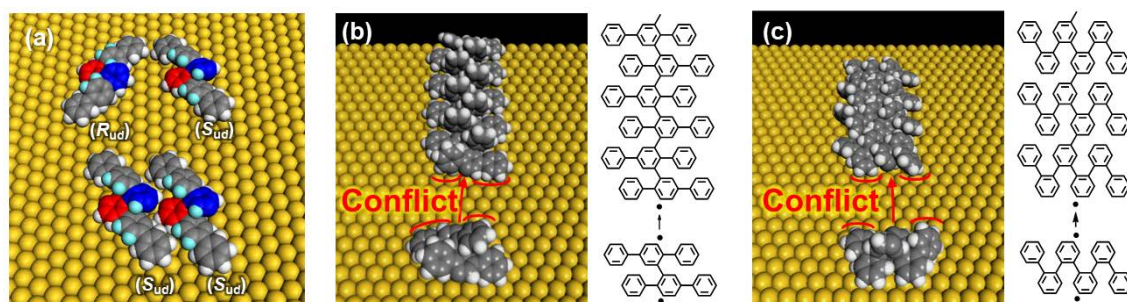


Figure 3-14. Mechanism of polymer growth. (a), Comparison of the bimolecular reactions between (Rud)-(Sud) and (Sud)-(Sud). (b), Stereo view of polymerization of the H-bar-linkage precursors. (c), Stereo view of the polymerization of the W-bar-linkage precursors.

thermodynamic equilibrium process, suggesting that if mismatch aggregation occurs with monomers of different chiralities, it can be repaired by equilibrium to an aggregate with matching chirality. Another example is the formation of chiral GNRs by annealing of enantioselectively assembled 10,10'-dibromo-9,9'-bianthryl on Cu(111).³⁹ Such enantioselectivity is also derived from surface equilibrium in self-assembling process at room temperature, which is similar to the case of supramolecular polymers. The mechanistic details of enantioselectivity have been reported by the direct observation of chiral recognition events of diphenylalanine adsorbed on Cu(110) by dynamic STM measurements.⁴⁰ This study indicated that at the single-molecule level, chiral recognition is dynamic, involving mutually induced conformational adjustments.

In contrast, the observed homochiral polymerization in a chain by us is a rare example of a

surface-induced enantioselective chemical reaction. The lifetime of the precursor radicals is considered to be an important parameter for determining whether the mechanism is controlled by kinetics or thermodynamics; the short lifetime likely favors a kinetic-controlled mechanism, while the long lifetime likely leads to a thermodynamic mechanism. The lifetime of radicals has been reported to vary from several tens of picoseconds⁴¹ to seconds⁴² depending on the environments. Although there is no evidence of the lifetime of biradicals herein, it might not be long because the radical polymerization occurs under the condition of a high biradical concentration of precursors. It is hypothesized that if a mismatch reaction among precursors with different chiralities occurs within the lifetime, a homochiral polymer might not form. Hence, the growth of polymers herein is possibly not based on thermodynamic equilibrium but on kinetically controlled polymerization, resulting in the formation of 'covalently bonded precursors'. In addition, the enantioselectivity might be caused by the mechanism of a 'surface-assisted shape-discriminating reaction'. Such a mechanism is analogous to the lock-and-key mechanism of enzymatic reactions in biology, which exploits conformational matching between the reactant and enzyme.¹⁹ The surface chirality of polymers produced with a low supply amount of precursors is very useful to understand about the more detailed mechanism of enantioselective polymerization. Although position dependence on the STM images was observed, most of those of polymers produced from a low supply amount (20 μg) of precursors annealed at 250 °C exhibited an array of polymers surrounded by several disordered short chains (Figure 3-15). The annealing of these samples at 500 °C resulted in the mixture of GNR arrays surrounded by short irregular chains (Figure 3-15). These results indicate that the surrounding disordered short chains at 250 °C possibly convert to irregular GNRs, while polymer arrays convert to GNR arrays. Currently, the growth mechanism for random short chains at the boundary area is not clear with respect to whether these chains could be formed by the conversion of homochiral into disordered ones or by the heterochiral coupling.

Acene-type GNRs grown on Au(111) were successfully transferred to a surface-oxidized Si substrate by gold etching. Detail of the transfer process is described in chapter 2. A field-effect transistor (FET) was fabricated by electron-beam lithography via the deposition of Pd metal on the GNR-transferred Si substrate with a defined channel length of 500 nm and channel width of 250 nm (Figures 3-16a and b). Before metal deposition, the sample surface, except for the channel, was masked

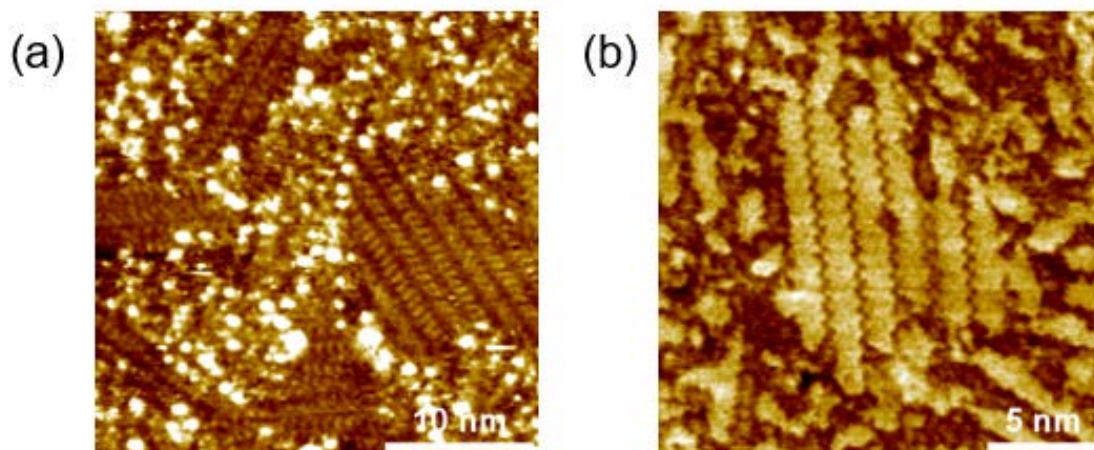


Figure 3-15. STM images of low-density wires produced from a low supply amount of Z-bar-linkage precursors (20 μg). (a, b), Samples were grown on Au(111) at 250 $^{\circ}\text{C}$ for polymerization (a) and 500 $^{\circ}\text{C}$ for dehydrogenation (b) by 2Z-CVD.

3-2-5. GNR transistor characteristics.

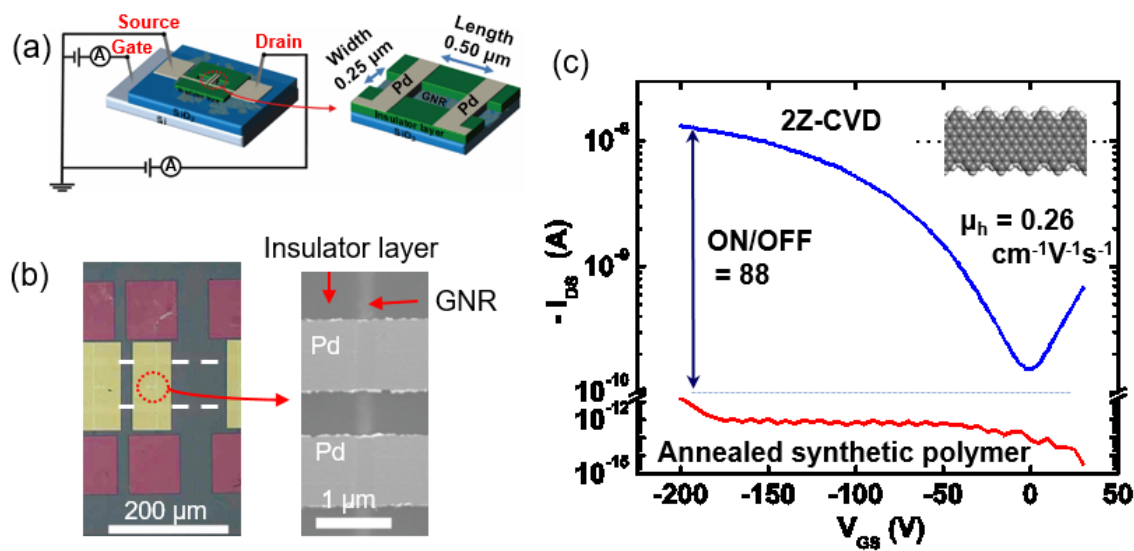


Figure 3-16. (a), Layout of the FET device. (b), Optical (left) and electron (right) microscope views of FET. (c), Transfer characteristics of acene-type GNRs grown by 2Z-CVD (blue) and of the annealed spin-coated polymers (red).

by an electron-beam-radiated calixarene resist for insulating it against the leakage of current from the

drain and source electrodes (Figures 3-16b). As shown in Figures 3-16c, the transfer characteristics of the GNR-based FETs prepared by 2Z-CVD using the Z-bar-linkage precursor and those of the annealed spin-coated synthetic polymers (Figure 3-11) were compared. The FETs produced from 2Z-CVD exhibited excellent ambipolar semiconductor characteristics with a hole mobility of $0.26 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and an on/off ratio of 88, whereas those prepared from spin-coating exhibited a negligible current (Figure 3-16c). A remarkable contrast in transistor characteristics might be attributed to the actual conjugated length of GNRs synthesized from different processes. The observed on/off ratio is comparable to those of GNRs fabricated by the top-down approaches,⁴³⁻⁴⁵ and also within a range of those of GNRs fabricated by the bottom-up approaches.^{46, 47} Because our FETs are based on the macroscopic film, the further improvement on on/off ratio might be achieved by the measurement on single molecular level. In addition, the observed carrier mobility is believed to be the highest for the bottom-up fabricated GNRs reported so far.^{46, 47} The results indicated that bottom-up fabricated GNRs are excellent semiconductor materials for bulk organic FET devices.

3-3. Conclusions

In conclusion, a precursor with a geometry of 'Z-bar-linkage' was designed, and efficiently converted into organized acene-type GNRs with a width of 1.45 nm grown on Au(111) by 2Z-CVD. This study provided a new concept of 'conformation-controlled surface catalysis', where the conformational adaptation of precursors and prepolymers on Au(111) could lead to the optimized reaction pathway to produce acene-type GNRs. The Z-bar-linkage precursor was considered to adopt the chiral conformations with height-asymmetry on Au(111), thereby forming self-assembled homochiral polymers in a chain with a planar conformation, followed by efficient stepwise dehydrogenation into GNRs via a conformation-controlled mechanism. In addition, high-density self-assembled homochiral polymers stabilized the planar conformation could promote dehydrogenation, while randomly oriented short chains resulted in irregular-shaped GNRs. Finally, the FET devices fabricated using acene-type GNRs showed excellent semiconducting properties. These findings will pave the way for the fabrication of new nanocarbon materials, which can be applied to electronics, as well as for the understanding of shape-dependent reactions on the surface

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Chapter 4

Wide graphene nanoribbons produced by intermolecular fusion of poly(*p*-phenylene) via 2Z-CVD

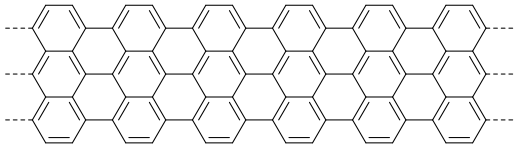
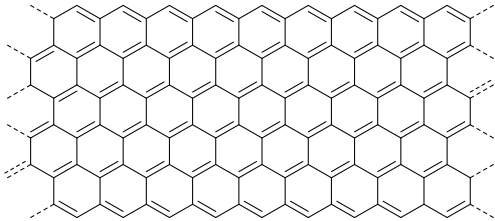
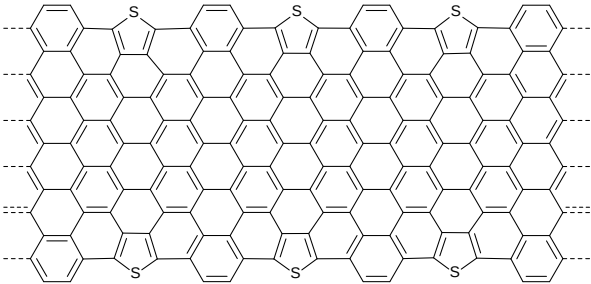
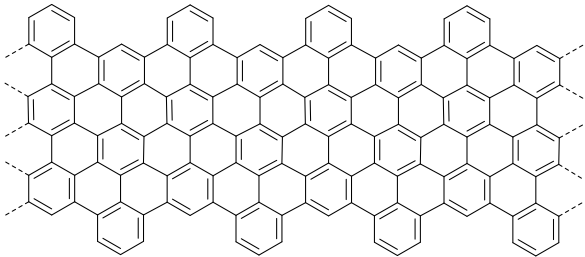
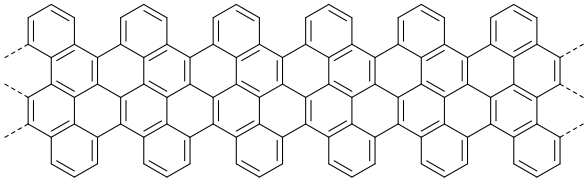
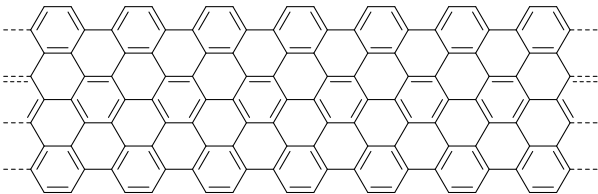
4-1. Introduction

Most of the GNRs prepared by the bottom-up synthesis so far have widths of less than 2 nm (Table 4-1).¹⁻⁶ Because, in general, the fabrication of wide GNRs by a bottom-up method requires high-molecular-weight precursors. However, these precursors exhibit disadvantages of high sublimation temperatures and low solubility. Moreover, it is difficult to produce GNRs with a width of less than 10 nm by top-down approaches, because of limitations of electron beam focusing in the lithography processes.⁷ For these reasons, fabrication of GNRs with widths ranging between 2 and 10 nm by bottom-up and top-down approaches remains a challenge.

It has been reported that wide GNRs can be formed by side-by-side interchain fusion via dehydrogenation reaction in case of 7-AGNR from 10,10'-dibromo-9,9'-bianthryl (DBBA)⁸ (Figure 4-1) and those containing boron (Figure 4-2).⁹ These results are reflective of the important approaches for producing GNRs with widths ranging from 2 to 10 nm. However, interchain reactions typically occur occasionally due to low density. Therefore, densely packed chains are assumed to be imperative to fabricate wide GNRs.

Recently, Basagni et al. have reported ordered and extended poly(*p*-phenylene) (PPP) on Au(111), oriented side by side, which can be converted into GNRs by thermal annealing as shown in Figure 4-3.¹⁰ They utilized Ullmann coupling of the precursor 4,4''-dibromo-*p*-terphenyl (DBTP), affording a sparsely packed PPP chain array with an interchain spacing of 0.7 nm, where the width of the PPP chain is 0.5 nm. With further annealing of the PPP, GNRs form mainly by interchain fusion of two, three, and four PPP chains. The widest fused structure (~3.3 nm) is formed of multiple interconnected GNRs containing six fused PPP chains. The limitation in the GNR width is assumed to be related to a large spacing of 0.7 nm between the chains, preventing the efficient interchain fusion. Hence, the reduction in the interchain spacing is considered the key to obtain wide GNRs.

Table 4-1. Calculated width of the reported GNRs fabricated by the bottom-up routes. Copyright 2017; Royal Society of Chemistry.

<i>Chemical Structure</i>	<i>Calcd. width</i>
	$\sim 1.19 \text{ nm}^1$
	$\sim 1.64 \text{ nm}^2$
	$\sim 1.91 \text{ nm}^3$
	$\sim 1.82 \text{ nm}^4$
	$\sim 1.41 \text{ nm}^5$
	$\sim 1.43 \text{ nm}^6$

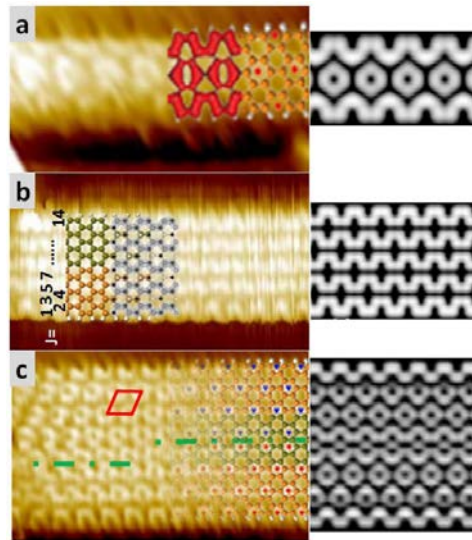


Figure 4-1. STM images of 7-, 14-, and 21-AGNRs (left column) synthesized from DBBA and corresponding DFT simulations (right column). Ref. [8]; Copyright 2015 Nature publishing group.

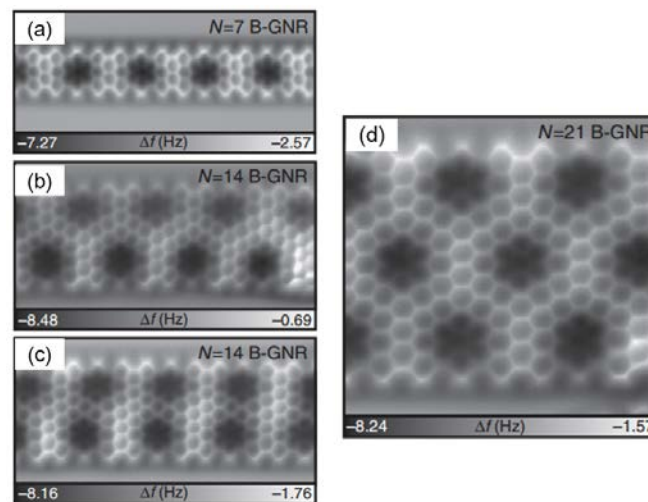


Figure 4-2. nc-AFM images of boron doped 7B-GNRs (a), 14B-GNRs (b) and 21B-GNRs (c), where the 14B-GNRs 21B-GNRs are produced from interchain fusion of 7B-GNRs. Ref. [9]; Copyright 2015 Nature publishing group.

In this chapter, wide GNRs were fabricated by 2Z-CVD using 4,4''-dibromo-*p*-terphenyl as the precursor. Densely packed arrays of poly(*p*-phenylene) (PPP) produced on Au(111) by this method could be converted into wide GNRs via interchain fusion by thermal annealing as shown in Figure 4-4. The FET prepared from these wide GNRs exhibited an excellent on/off current ratio of $1.6 \pm 0.6 \times 10^3$.

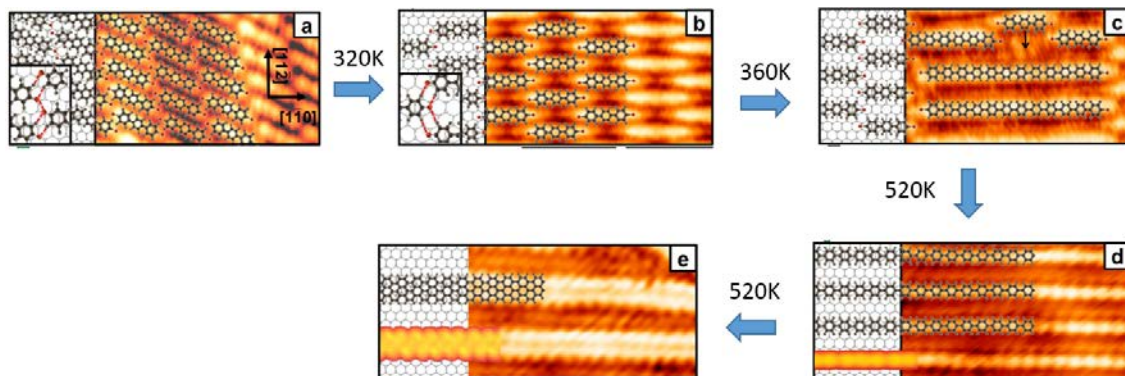


Figure 4-3. Diagrammatic representation of the different structures obtained during the synthesis of GNRs from 4,4''-dibromo-*p*-terphenyl. Oligomers (c) and poly(*p*-phenylene) polymers (d) are formed by 4,4''-dibromo-*p*-terphenyl polymerization at different temperature. GNRs (e) are formed by interchain fusion of the poly(*p*-phenylene). Ref. [10]; Copyright 2015 American chemical society.

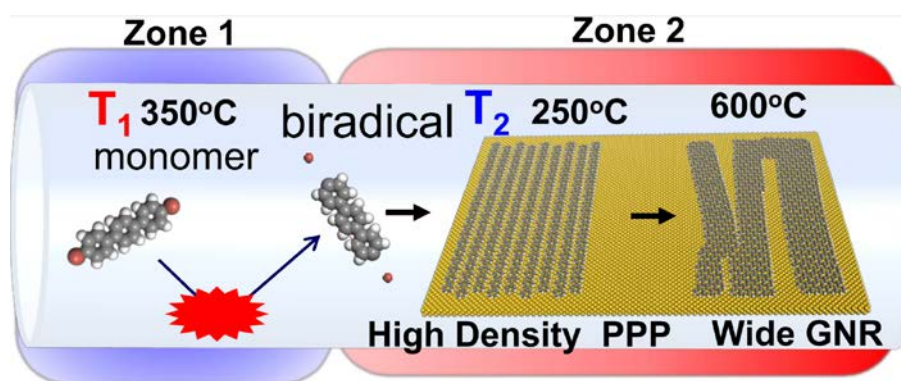


Figure 4-4. Concept of the GNR growth mechanism through polymerization of the precursor DBTP and intermolecular fusion of the densely packed PPP. Copyright 2017; Royal Society of Chemistry.

4-2. Results and discussion

4-2-1. Fabrication of densely packed poly(*p*-phenylene)

For growing PPP chains, DBTP (40 μg) was subjected to sublimation at 245°C ; hence, it can pass through the hot quartz tube (zone 1) heated to 350°C , followed by deposition on Au(111) at 250°C (zone 2). The products thus obtained were examined by STM, which, as shown in Figure 4-5, were parallel, densely packed PPP chains with a long-range order. The statistical analysis of the products showed that the majority of the PPP chains had a length ranging from 20 to 50 nm, while the

longest one measured ~ 90 nm (Figure 4-6). Cross-sectional analysis indicated that the width of PPP is 0.8 nm, with an interchain spacing of 0.1 nm. In contrast to those fabricated by UHV deposition on Au(111) reported before (Figure 4-3),¹⁰ the interchain spacing is reduced from 0.7 nm to 0.1 nm. On surface polymerization of PPP on Cu(111)^{11,12} and Au(887)¹³ was reported to afford a narrower spacing near 0.1 nm, due to the strongly adsorbing surface and uniaxial lattice, respectively. Regardless of using Au(111) which corresponds to a weakly adsorbing surface, our densely packed PPP chains with high yield revealed the advantage of 2Z-CVD. These results might originate from the generation of high-density biradicals via debromination of the precursor by collision with the hot quartz tube wall of zone 1.

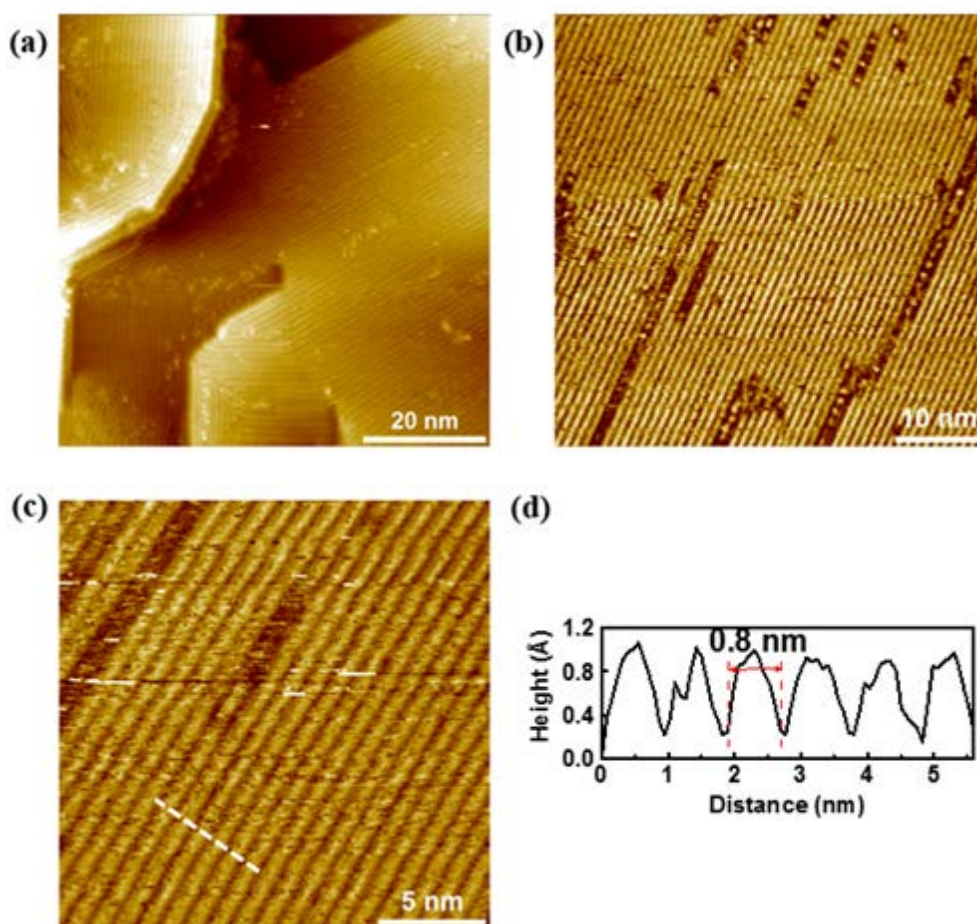


Figure 4-5. (a) Room temperature STM overview image of densely packed PPP chain arrays under Ar shows the length of the chain is ~ 80 nm. (b) and (c) Close inspection of the PPP indicates its densely packed and (d) cross sectional analysis of the line in (c) suggests the width of the chain is 0.8 nm and interchain spacing is ~ 0.1 nm. Copyright 2017; Royal Society of Chemistry.

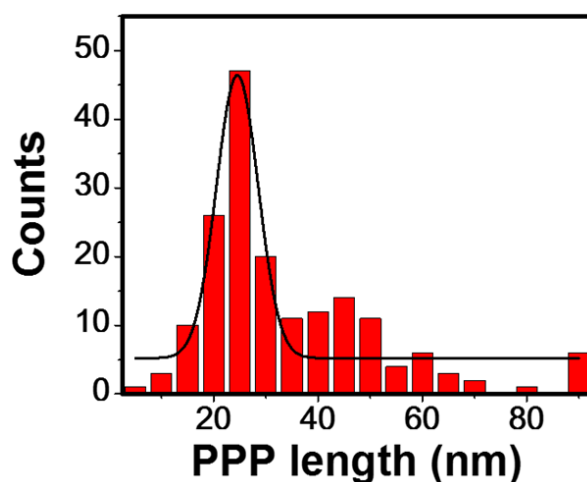


Figure 4-6. Histogram of PPP chains length distribution from two different samples including Figure 4-5 (a). Copyright 2017; Royal Society of Chemistry.

4-2-2. Fabrication of wide GNRs

The PPP chains on Au(111) were further annealed at different temperatures (500, 550, and 600 °C). After annealing, STM observation revealed the formation of wide chains with different widths (Figure 4-7, 4-8 and 4-10). It is assumed that there are two fusion reaction mechanisms depending on different annealing temperatures. At ~500 °C, the fused PPP chains were still aligned parallel after the annealing process (Figure 4-10 a, b). This process is referred to as ‘static fusion’ which is considered to be the interchain reaction of the ‘frozen’ parallel-aligned PPP. As shown in the cross-sectional analysis of the statically fused chains in Figure 4-10 (b) two, three, four, and five fused PPP chains were produced at this stage. The number of fused PPP chains increased from two to five compared with the previous results.¹⁰ This is believed to be benefitted from the smaller interchain spacing. On the other hand, upon higher annealing temperatures (over 550 °C), wide GNRs with a random orientation formed on Au (111) by interchain reactions of the statically formed GNRs driven by a random diffusional process (Figure 4-10 c, d). This process can be referred to as ‘dynamic fusion’. Cross-sectional profiles (Figure 4-7) perpendicular to the fused chains axes (at 600 °C) revealed that the chain widths of 1.0, 1.2, 1.9, and 7.2 nm correspond to two, three, five, and nineteen fused PPP chains, respectively. The width distribution of the chains was obtained (Figure 4-9a) by a statistical analysis of six STM images from two samples (Figure 4-7 a, c and 4-8). The ordinate shows the

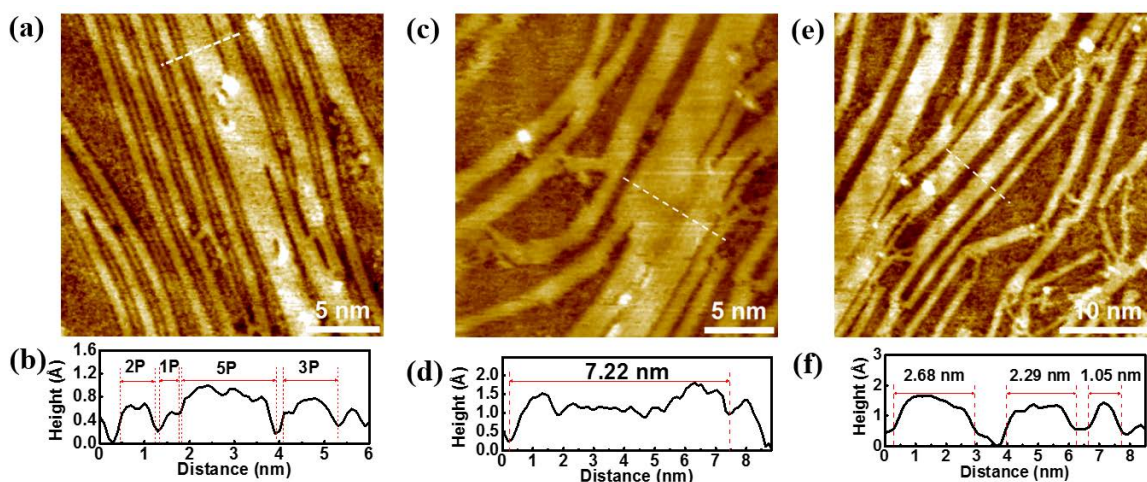


Figure 4-7. Room temperature STM images of GNRs obtained after annealing at 600 °C suggest GNRs in different width. (b) Cross sectional analysis of the line in (a) indicates the number of fused PPP chains. (nP denotes the number of fused PPP chains). (d) Cross sectional analysis of the line in (c) indicates the width of the widest fused chain is 7.22 nm. (f) Cross sectional analysis of the line in (e) indicates the three GNRs aligned parallel with width of 2.68 nm, 2.29 nm and 1.05 nm, respectively. Copyright 2017; Royal Society of Chemistry.

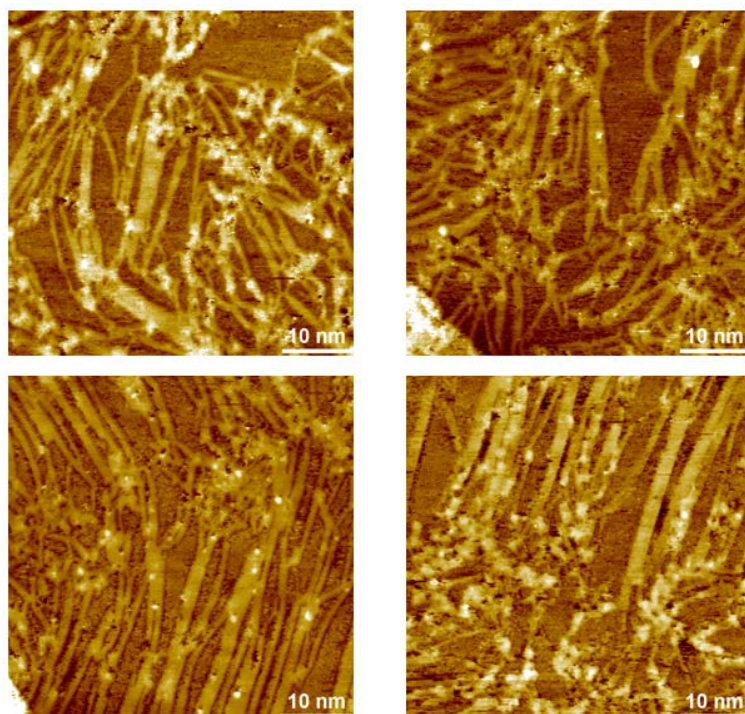


Figure 4-8. STM images of GNRs on Au(111) at different position after annealing at 600 °C which are used for statistical analysis in Figure 4-9a. Copyright 2017; Royal Society of Chemistry.

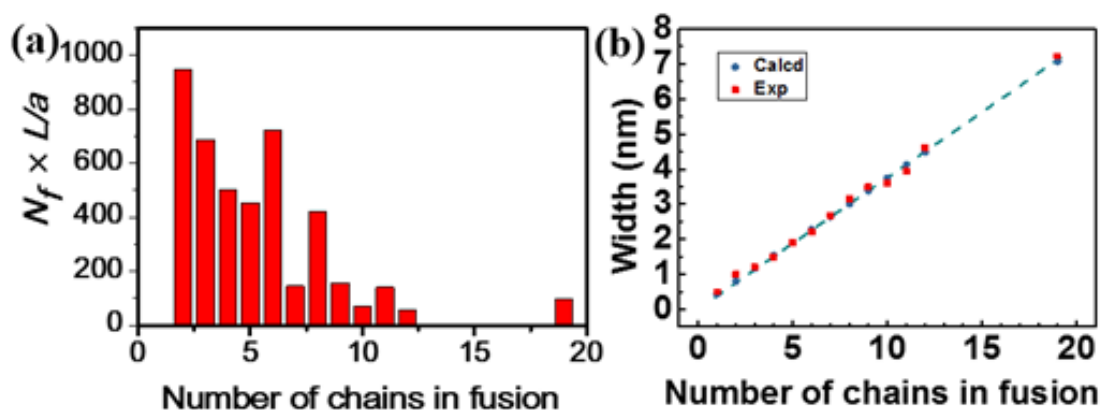


Figure 4-9. (a) Histogram of chains in fusion distribution. (b) Widths of the GNRs as a function of the number of PPP chains in fusion. Copyright 2017; Royal Society of Chemistry.

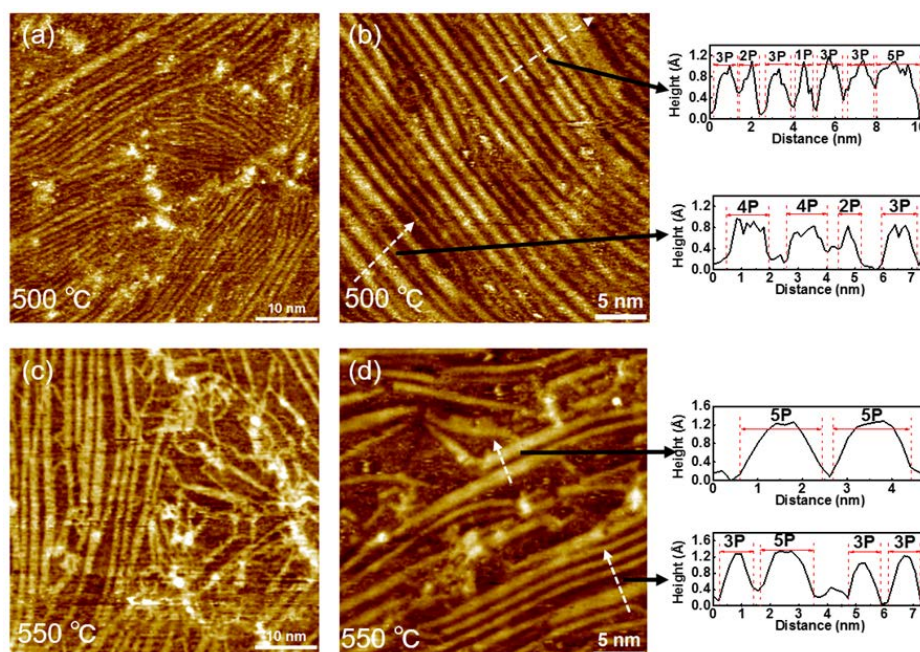


Figure 4-10. STM images of PPP annealed at 500 °C (a and b) and 550 °C (c and d). Cross sectional analysis of the line in (b and d) indicating the number of fused PPP chains (denoted by nP). Copyright 2017; Royal Society of Chemistry.

number of fused monomer units, $N_f \times L/a$, where N_f refers to the number of fused PPP chains with a length L (nm), and a corresponds to the precursor unit length of 1.3 nm.

The distribution indicates a varying number of fused chains. Observed widths of chains involved in interchain fusion were in a good agreement with the calculated ones (Figure 4-9b). Moreover, Raman spectroscopic measurements of the PPP and fused chains after annealing (Figure 4-11) were

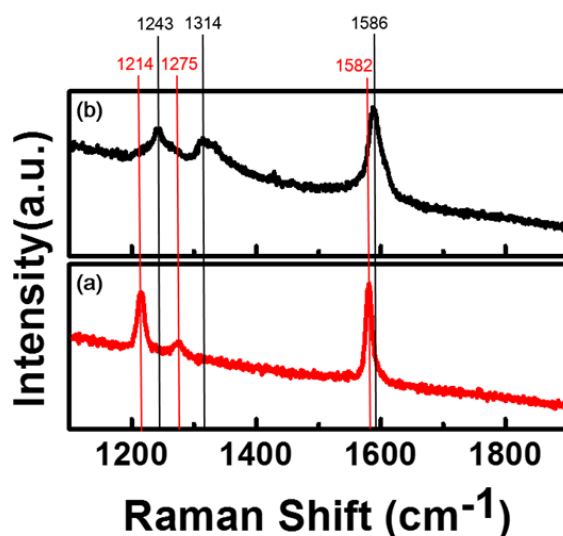


Figure 4-11. Raman spectra of the materials grown by 2Z-CVD on Au(111) supplied with 40 μg of the DBTP precursor. (a) PPP chains produced at 250 $^{\circ}\text{C}$. (b) GNRs annealed at 600 $^{\circ}\text{C}$ on Au(111). The three intense peaks between 1200 and 1600 cm^{-1} are associated with the edge C-H in-plane bending mode ($\sim 1220 \text{ cm}^{-1}$), the inter-ring C-C stretching mode ($\sim 1280 \text{ cm}^{-1}$) and the ring C-C stretching mode ($\sim 1600 \text{ cm}^{-1}$). Copyright 2017; Royal Society of Chemistry.

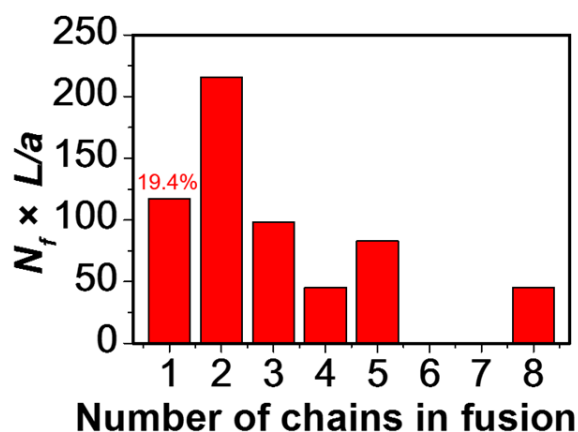


Figure 4-12. Histogram of chains in fusion distribution based on Figure. 2d, which indicate 19.4% PPP chains remain after annealing at 600 $^{\circ}\text{C}$. Copyright 2017; Royal Society of Chemistry.

in good agreement with previously reported results.¹⁰ Therefore, it can be concluded that GNRs were indeed produced by the thermal annealing process. Statistical analysis of Figure 4-7 (a) suggests 19.4% PPP chains remained unfused after the annealing process (Figure 4-12). In addition, other geometries

such as wider ribbons splitting into two branches, presumably in the middle of zipping up of two GNR chains, were observed (Figure 4-7). These structures might originate from imperfect fusion of GNRs during diffusion at high temperature. In the direct synthesis of GNR from precursors, such a structure has never been obtained.

4-2-3. Electrical characterization on wide GNR based field-effect transistors

GNRs grown on Au(111) were successfully transferred to a silicon substrates with a 300 nm thick surface oxide gate insulator (SiO_2/Si). Details have been described in the chapter 2 (GNR transfer process). A field-effect transistor (FET) based on the transferred GNR film was fabricated by electron-beam lithography, followed by the deposition of Pd metal on the GNR-transferred SiO_2/Si substrate with a channel length of 1 μm and a width of 250 nm (Figure 4-13a). Before metal deposition, the sample surface, except for the channel, was masked by an e-beam-irradiated calixarene resist to insulate it against the leakage of current from the drain and source electrodes. Measurements were carried out under vacuum (5×10^{-6} Torr). The device exhibits an average current on/off ratio (from five devices) of $1.6 \pm 0.6 \times 10^3$ (Figure 4-13b). The value is of the same order as that of the DBBA-based thin-film FET devices prepared by a bottom-up synthesis.¹⁴⁻¹⁶ The average hole mobility of $3.6 \pm 1.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ also indicates good semiconductor characteristics. The hole mobility of a FET based on PPP chains could not be measured, because it showed a 10^5 times lower current than that based on GNRs. Therefore, the carrier transport in the FET must completely originate from the GNRs.

4-3. Conclusion

In summary, a densely packed PPP chain array was fabricated by the polymerization of DBTP on Au(111) via 2Z-CVD. 2Z-CVD dramatically reduced the interchain spacing from 0.7 nm to 0.1 nm in contrast to previously reported result. In addition, further annealing of the PPP chains afforded fused structures with a width of up to 7.2 nm, resulting in efficient interchain fusion. The GNRs thus produced exhibited good semiconducting properties in FET devices.

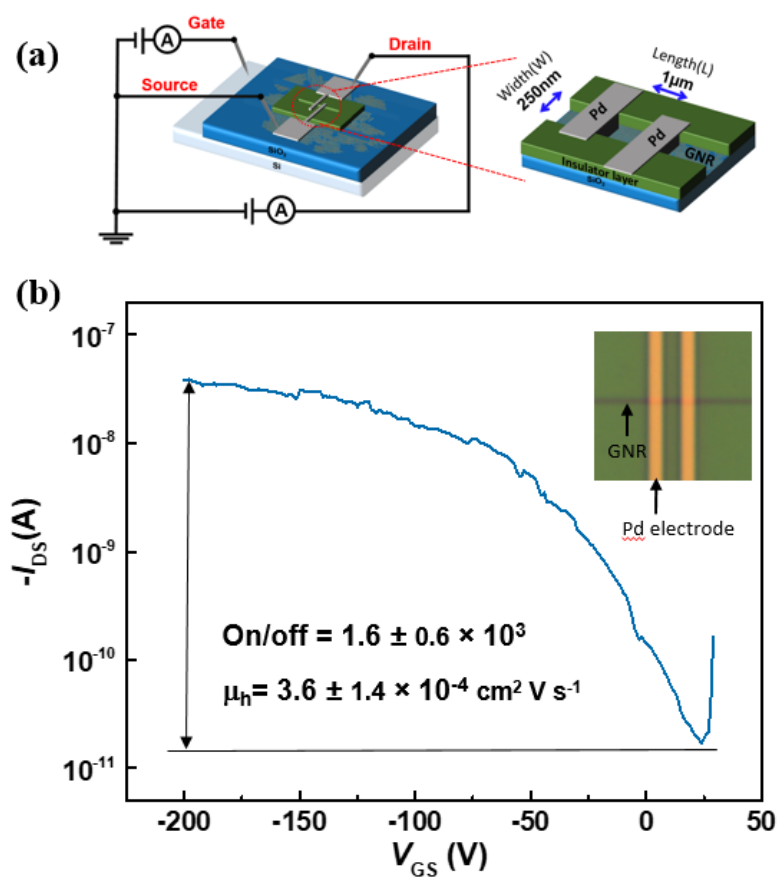


Figure 4-13. (a) Layout of the FET device. (b) FET properties of the GNRs annealed at 600 °C with an inset showing the optical microscope image of a FET device. Copyright 2017; Royal Society of Chemistry.

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Chapter 5

Interchain-linked Graphene Nanoribbons from Dibenzo[*g,p*]chrysene via 2Z-CVD

5-1. Introduction

It has been reported that the GNRs could be interchain linked (Figure 5-1 and 5-2) via cross-dehydrogenative coupling.^{1,2} These phenomena will be applicable to produce the covalently-bonded π -conjugated 2D structures. However, the linked GNRs reported so far have low density resulting in the undeveloped 2D structures. Because the UHV deposition methods might generate the low-density radicals of precursors due to the inseparable processes of radical generation from precursors, and GNR growth, resulting in an inefficient inter-ribbon connection.

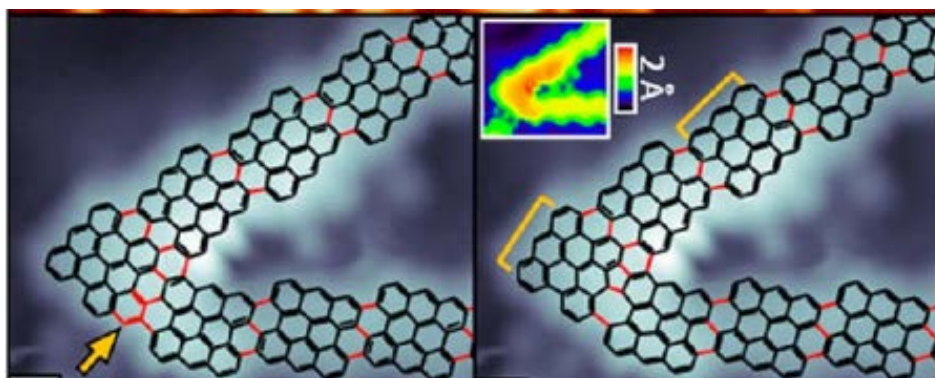


Figure 5-1. Connected chair-edged GNRs from 10,10'- dibromo-9,9'-bianthryl on Cu(111). The black (red) lines indicate the monomer units (bonds formed between the monomers). Ref. [1]; Copyright 2015 American chemical society.

In this chapter, high density of sp^2 -covalently linked chiral GNRs were fabricated from a precursor 1,9-dibromodibenzo[*g,p*]chrysene. Prepolymer arrays were grown by surface-assisted polymerization of the precursor at 250 °C. Further annealing of the prepolymer at 450 °C converted the prepolymers into interchain-linked graphene nanoribbons via intramolecular and intermolecular dehydrogenation reactions.

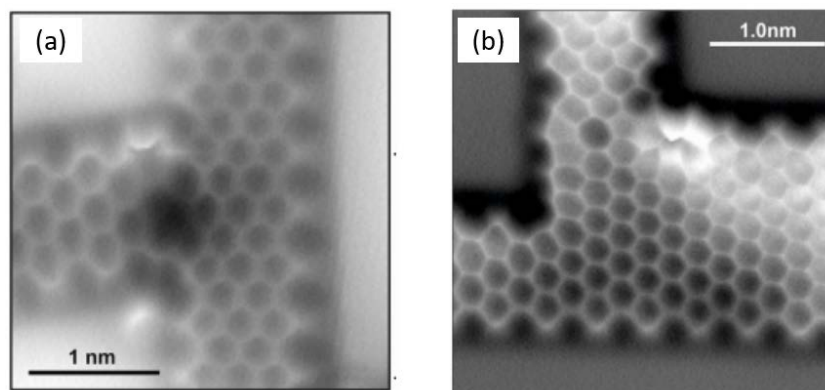
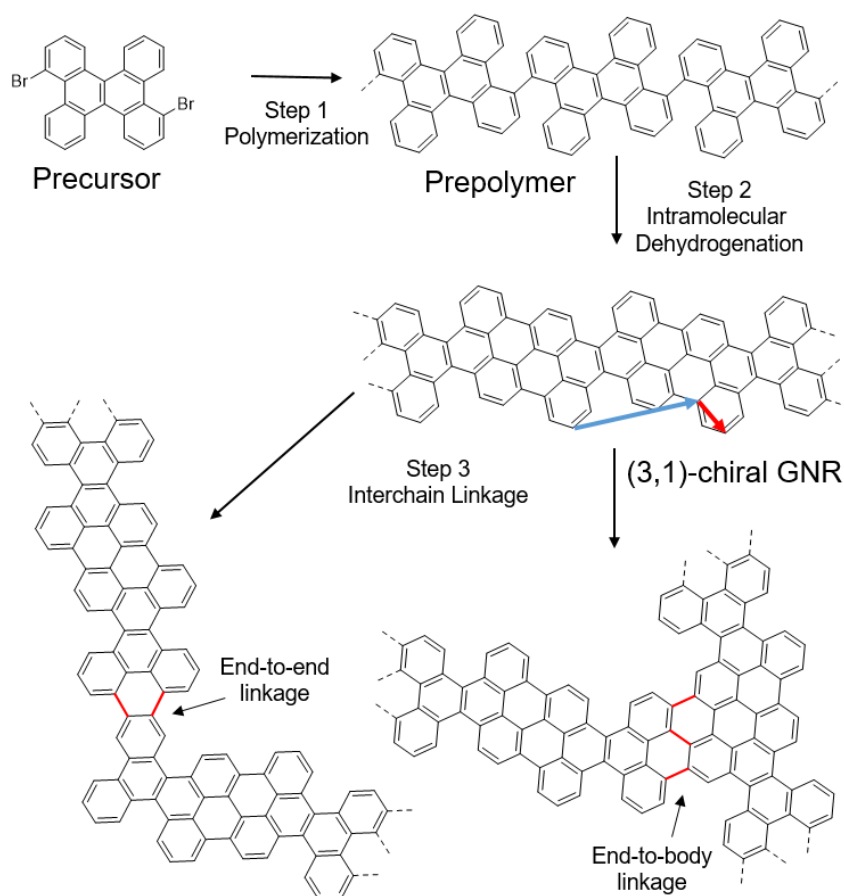


Figure 5-2. nc-AFM images of armchair-edged GNR junctions from 10,10'- dibromo-9,9'-bianthryl on Au(111). Ref. [2]; Copyright 2015 American chemical society.

5-2. Results and discussion

5-2-1. Synthesis of prepolymer via 2Z-CVD

Scheme 5-1 depicts the growth process of the linked GNRs on Au(111). First, for the growth of prepolymer, a precursor solution ($100\ \mu\text{L}$ of $0.20\ \text{mg} \cdot \text{mL}^{-1}$ in CHCl_3) was cast in a quartz boat, which was placed at the upstream of the quartz tube. The precursor was subjected to sublimate at $325\ ^\circ\text{C}$ so that it can pass through the hot quartz tube (zone 1) heated to $350\ ^\circ\text{C}$, followed by deposition on Au(111) at $250\ ^\circ\text{C}$ (zone 2). The sample was studied by scanning tunneling microscopy (STM). The alternatively-aligned bright and dark dots were seen as shown in Figure 5-3 (a, b). Magnified image (Figure 5-3c) shows the periodicity of pair of bright and dark dots to be $1.25\ \text{nm}$, the length of the dot-pair to be $1.02\ \text{nm}$, and width of dots to be $0.91\ \text{nm}$. These results indicate that the aligned dots correspond to the prepolymers of polydibenzo[*g,p*]chrysene where the dot-pairs correspond to the precursor units of dibenzo[*g,p*]chrysene, because these are in a good agreement with the molecular model (Figure 5-3d). Length histogram of polymer chains in Figure 5-3 (a) suggests the length in average to be $3.08\ \text{nm}$ as shown in Figure 5-3 (e).



Scheme 5-1. Reaction scheme of surface-assisted bottom-up synthesis of linked GNRs through a three-step process via 2Z-CVD. Step 1: polymerization of the precursor to form prepolymer at 250 °C, Step 2: intramolecular dehydrogenation to form GNR at 450 °C, Step 3: intermolecular dehydrogenation to form linked GNRs via two ways which are referred to as ‘end-to-end’ and ‘end-to-body’ linkage. Copyright 2017; The Chemical Society of Japan.

5-2-2. Synthesis of linked GNRs via 2Z-CVD

The prepolymers on Au(111) were then further annealed at 450 °C. STM images after annealing reveal that the aligned dots are converted into the winding chains (Figure 5-4a, b). Magnified STM image of chains (Figure 5-4c) reveals a width of ~0.95 nm and an edge periodicity of 1.21 nm. Because the observed width and periodicity of chains are in a good agreement with those of model of chiral GNR (Figure 5-4d), we conclude that the GNRs were formed via intramolecular dehydrogenation of prepolymers by thermal annealing. Additionally, STM images of Figure 5-4 (a, b) show that the high-density linked GNRs were formed on Au(111) via intermolecular dehydrogenation, resulting in a well-

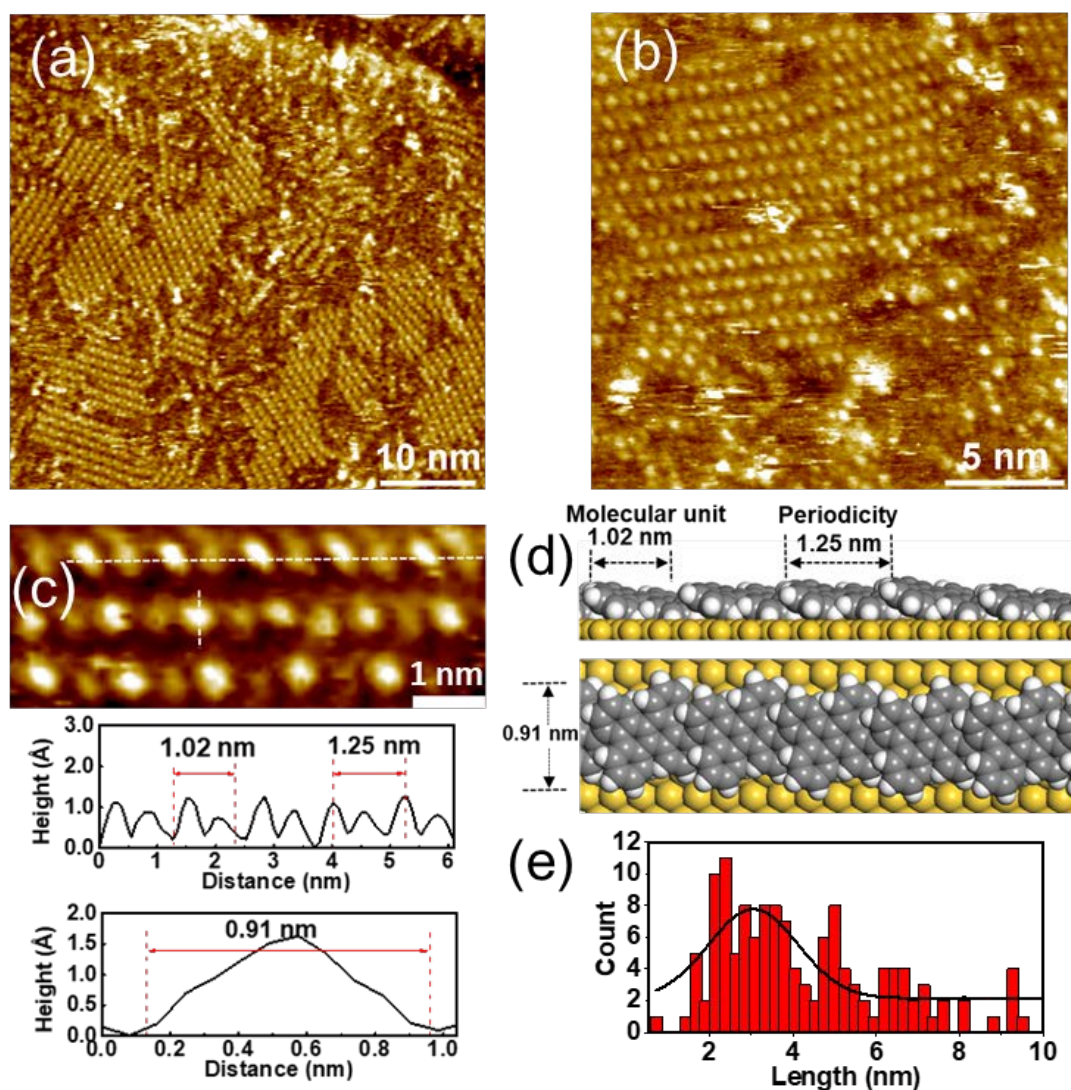


Figure 5-3. (a) and (b) STM images of prepolymers on Au(111) grown at 250 °C. (c) Magnified STM image and cross-sectional analysis of horizontal line (upper) and vertical line (lower). (d) Molecular model of prepolymers on Au(111). (e) Length histogram obtained from the STM image of (a). Copyright 2017; The Chemical Society of Japan.

developed 2D structure. Magnified STM images of linked GNRs as shown in Figure 5-4 (e) shows that there are two kinds of GNRs linkage modes of ‘end-to-body’ and ‘end-to-end’ linkage. Along the edges of chiral GNR, ‘bay regions’ are supposed to be the suitable geometries for interchain coupling. These well-developed 2D linked structures might be produced by a 2Z-CVD in which the high-density biradicals were generated via debromination of the precursor by collisions with the hot quartz tube wall of zone 1. Raman spectra of the annealed sample at 450 °C showing the pronounced peaks of a

G band ($\sim 1588\text{ cm}^{-1}$), a D band ($\sim 1317\text{ cm}^{-1}$), and a D' band ($\sim 1638\text{ cm}^{-1}$) as shown in Figure 5-5 (a), also support the formation of chiral GNRs, while negligible weak peaks were observed in those grown at $250\text{ }^{\circ}\text{C}$ (Figure 5-5b). These results are in a good agreement with previous reports.¹

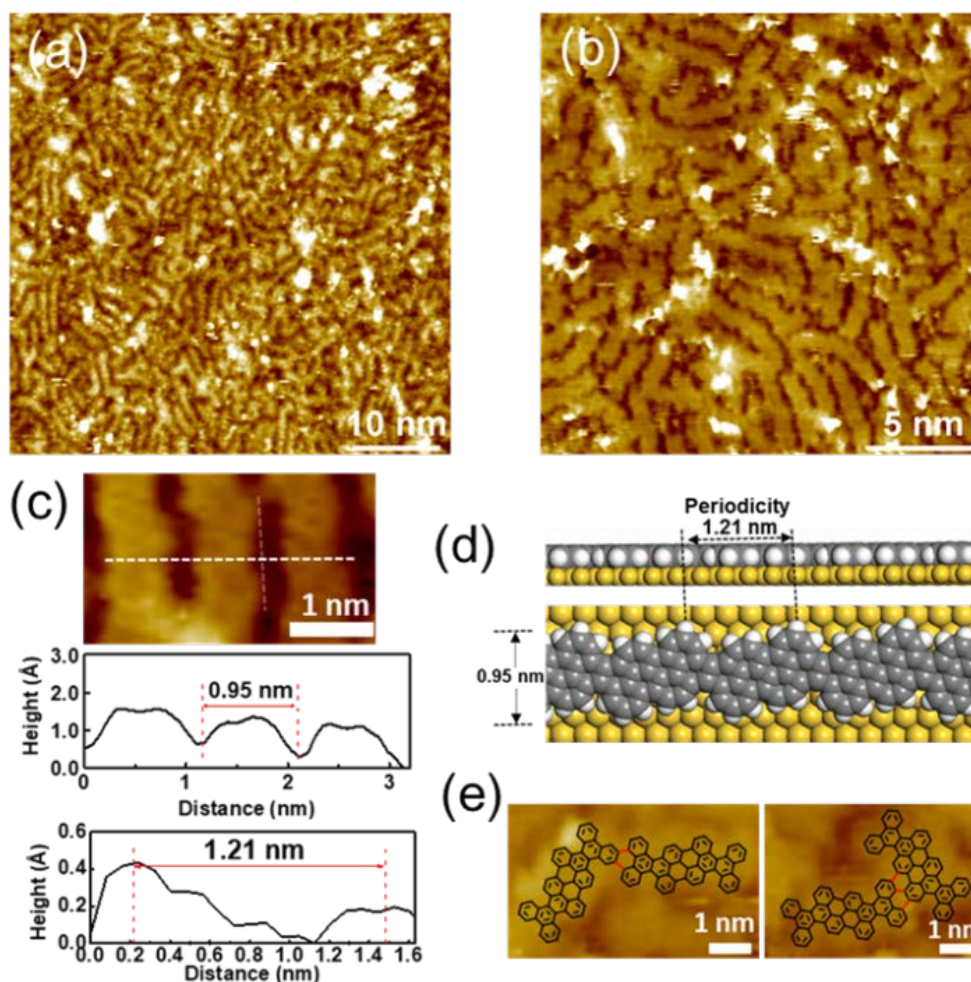


Figure 5-4. (a) and (b) STM images of linked GNRs on Au(111) annealed at $450\text{ }^{\circ}\text{C}$ of prepolymers. (c) Magnified STM image and cross-sectional analysis of horizontal line (upper) and vertical line (lower). (d) Molecular model of GNR. (e) STM images with overlaid molecular model of linked GNRs in end-to-end and end-to-body manners. Copyright 2017; The Chemical Society of Japan.

5-3. Conclusion

In summary, high-density interchain-linked GNRs from a precursor 1,9-dibromodibenzo[*g,p*]chrysene were fabricated via 2Z-CVD. The fabrication process consists of the

polymerization, intramolecular-, and intermolecular-dehydrogenation. The sp^2 covalent bonding linkage of GNRs will provide the potential applications for electronic devices.

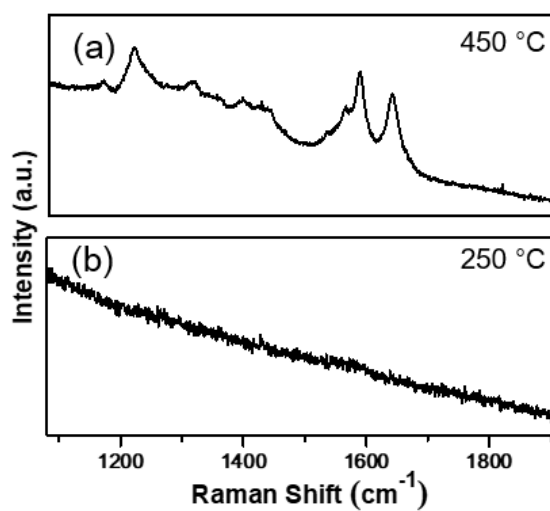


Figure 5-5. Raman spectra of linked GNRs (a) annealed at 450 °C and prepolymer (b) grown at 250 °C. Copyright 2017; The Chemical Society of Japan.

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Chapter 6

General Conclusion

The thesis mainly focused on synthesizing GNRs with novel structures such as acene-type GNR, wide GNRs, and a chiral GNR, and their growth mechanisms from a precursor. The results of the research could be concluded as follows:

In chapter 2, materials, apparatus, and methods required for their syntheses and handling are described. Synthetic procedures of the precursors that used in this thesis are given.

In chapter 3, a new principle of surface-assisted GNR synthesis, which termed as “conformation-controlled heterogeneous catalysis” was demonstrated. The chemical designed and synthesized flexible “Z-bar-linkage” precursor molecule can transform into a special chiral conformation on a metal surface, and can afford self-assembled homochiral polymers with a special planar conformation by chemical vapor deposition, followed by efficient step-wise dehydrogenation to form acene-type GNRs. These unprecedented results for the “conformation-driven dehydrogenation reactions” and “surface-induced homochiral polymerization” present a new concept that has never been reported.

(1) “Z-bar-linkage” molecular design: A precursor with novel geometry was proposed that can transform into a height-asymmetrical chiral conformation (head-to-tail structure) on a surface via out-of-plane-deformation, resulting in efficient homochiral polymerization on the surface.

(2) Homochiral polymerization on surface: Chemical vapor deposition of the Z-bar-linkage precursor successfully led to homochiral polymerization in a chain on the surface, even in the absence of a chiral catalyst or chiral monomers. This is the first example of surface-assisted homochiral polymerization, with an interesting mechanism of “shape-discriminated reaction”. Similar to the “lock and key” mechanism in enzymatic catalysis, this extremely exclusive polymerization among precursors having the same chirality is triggered by head-to-tail interaction within the precursors. Such an extraordinary exclusive radical polymerization on a surface has never been reported before.

(3) New dehydrogenation mechanism: A special planar conformation of homochiral polymers was found on the surface induced the most efficient step-wise dehydrogenations, via annealing and conversion into acene-type GNRs; this process is called “evolutionary growth.” This is similar to the

“optimization algorithm” in nature, which selects the most optimized pathway from many options. Also, such a planar conformation of homochiral polymers optimized for dehydrogenation leading to GNRs was stabilized by polymer self-assembly, which is similar to protein complexes in biology. Additionally, during the step-wise dehydrogenations, a novel structure made of alternately fused polymers was observed. Thus, a new mechanism of dehydrogenation was proposed, which has not been reported before and which has been termed the “conformation-controlled mechanism.”

In chapter 4, series of wide GNRs were fabricated by interchain fusion of densely packed poly(*p*-phenylene) chains, which were produced by the polymerization of 4,4''-dibromo-*p*-terphenyl (DBTP) on Au(111). In great contrast to the previous reported methods, the 2Z-CVD is advantageous because it allows to provide the highly concentrated radicals via independent temperature control of the two zones 1 and 2, which are hypothesized for radical generation and efficient GNR growth, respectively. As a result, the interchain spacing was reduced from 0.7 nm to 0.1 nm, which dramatically increased the efficient interchain fusion reaction. The widest structure obtained show a width of up to 7.2 nm. This strategy successfully overcame the width limit of direct on-surface bottom-up fabrication of GNRs, usually within ~2 nm, due to low solubility and high sublimation temperature of big precursor molecules. The wide GNRs thus produced in this chapter exhibited good semiconducting properties in FET devices.

In chapter 5, covalently interchain-linked chiral GNRs were fabricated by a stepwise growth process. First, prepolymer arrays were obtained by surface-assisted polymerization of dibromodibenzo[*g,p*]chrysene. Further annealing of the prepolymer produced the interchain-linked GNRs via intramolecular and intermolecular dehydrogenation reactions. The specially designed precursor formed ‘bay regions’ along the edges of chiral GNRs, which are supposed to be the suitable geometries for interchain coupling. As a result, sp²-covalently linked chiral GNRs with high density were produced after annealing at high temperature.

Compared to the “top-down” approaches such as unzipping CNT and e-beam lithography, the surface-assisted “bottom-up” method, like UHV deposition, can produce GNR with atomically precise and well-controlled width. The 2Z-CVD method, utilized in this thesis, further improved the fabrication of GNRs, because it doesn’t need the elaborate and costly UHV equipment and it can produce GNRs with high yield. It also makes possible to fabricate electronic devices by transfer the

GNR film to insulating substrate through a gold etching process.

List of Publications

1. Homochiral polymerization-driven selective growth of graphene nanoribbons

Hiroshi Sakaguchi, Shaotang Song, Takahiro Kojima, and Takahiro Nakae

Nature Chemistry **9**, 57-63 (2017)

(Chapter 3)

2. Wide Graphene Nanoribbons Produced by Intermolecular Fusion of Poly(*p*-phenylene) via Two-zone Chemical Vapor Deposition

Shaotang Song, Takahiro Kojima, Takahiro Nakae, and Hiroshi Sakaguchi

Chemical Communications **53**, 7034-7036 (2017)

(Chapter 4)

3. Interchain-linked Graphene Nanoribbons from Dibenzo[*g,p*]chrysene via Two-Zone Chemical Vapor Deposition

Shaotang Song, Guanbo Huang, Takahiro Kojima, Takahiro Nakae, Hiroshi Uno, and Hiroshi Sakaguchi.

Chemistry Letters, DOI: 10.1246/cl.170614 (2017)

(Chapter 5)

List of Presentations

International Conference

1. Edge structure controlled synthesis of graphene nanoribbons

S. Song, T. Nakae, T. Kojima, and H. Sakaguchi

The 2015 International Chemical Congress of Pacific Basin Societies, 2015.12.15-20, Honolulu, Hawaii, USA

2. Bottom-up Growth Mechanism of Graphene Nanoribbon on Au(111) Surface

S. Song, T. Nakae, T. Kojima, and H. Sakaguchi

The 2nd International Symposium on π -System Figuration, 2016.4.14-15, Saitama, Japan

3. Novel Nanographene Material Synthesized via Chemical Vapor Deposition

S. Song, T. Nakae, T. Kojima, and H. Sakaguchi

The 2nd International Symposium on Synthetic Two-Dimensional Polymers (S2DP-2), 2016.6.2-4, Nara, Japan

4. CVD Synthesis of Acene-Type Graphene Nanoribbons by Surface-Conformation-Driven Mechanism

T. Nakae, S. Song, T. Kojima, and H. Sakaguchi

The 2nd International Symposium on Synthetic Two-Dimensional Polymers (S2DP-2), 2016.6.2-4, Nara, Japan

Domestic Conference

1. Structure-controlled surface synthesis of molecular-width graphene nanoribbons by radical polymerization-chemical vapor deposition

S. Song, S. Fujita, T. Nakae, and H. Sakaguchi

The 95th CSJ Annual Meeting, 2015.3.26-29, Nihon University, Tokyo, Japan

2. Synthesis novel Graphene Nanoribbon via Two-Zone Chemical Vapor Deposition

T. Nakae, T. Iruka, S. Fujita, S. Song, H. Sakaguchi

The 95th CSJ Annual Meeting, 2015.3.26-29, Nihon University, Tokyo, Japan

3. Bottom-up On-surface Synthesis of Acene-type GNR

T. Kojima, T. Nakae, S. Song, M. Yano, H. Sakaguchi

26th Symposium on Physical Organic Chemistry, 2015.9.24-26, Ehime, Japan

4. Surface Synthesis of Acene-type Graphene Nanoribbon Driven by Self-Assembly of a Flexible Monomer Molecule

T. Nakae, T. Kojima, S. Song, M. Yano, H. Sakaguchi

6th symposium of Molecular Architectonics, 2015.10.23-24, Kyoto, Japan

5. Acene-type Graphene Nanoribbons Fabrication by Radical Polymerization-chemical vapor deposition

S. Song, T. Nakae, T. Kojima, H. Sakaguchi

6th symposium of Molecular Architectonics, 2015.10.23-24, Kyoto, Japan

6. Surface Synthesis of Acene-type Graphene Nanoribbon

T. Nakae, S. Song, T. Kojima, and H. Sakaguchi

50th Symposium of Fullerene, Nanotube, and Graphene, 2016.2.20-22, Tokyo, Japan

7. Direct Observation of Homochiral Polymerization-Leading Growth of Graphene Nanoribbon on Au(111) Surface

S. Song, T. Nakae, T. Kojima, and H. Sakaguchi

Institute for Chemical Research International Symposium 2016, 2016.3.7-8, Kyoto, Japan

8. Novel Acene-type Graphene Nanoribbon Synthesized from A Surface Transformable Molecule,
and Its Mechanism of Polymerization and Dehydrogenation
T. Nakae, S. Song, T. Kojima, H. Sakaguchi
The 96th CSJ Annual Meeting, 2016.3.24-27, Kyoto, Japan
9. Synthesis of Acene-Type Graphene Nanoribbon by Surface-Induced Homochiral Polymerization
S. Song, T. Nakae, T. Kojima, H. Sakaguchi
The 96th CSJ Annual Meeting, 2016.3.24-27, Kyoto, Japan
10. Surface Synthesis of Acene-type Graphene Nanoribbon
T. Nakae, T. Kojima, S. Song, H. Sakaguchi
7th symposium of Molecular Architectonics, 2016.10.20-21, Kyushu, Japan
11. Development of a Biomimetic Catalytic Process for Acene-type GNR
T. Kojima, S. Song, T. Nakae, H. Sakaguchi
Scientific Research on Innovative Areas [π -system figuration: control of Electron and Structure
Dynamism for Innovative Functions] 3rd Open Symposium, 2016.10.20-21, Sendai, Japan
12. Fabrication of Acene-Type Graphene Nanoribbons on Au(111)
S. Song, T. Kojima, T. Nakae, and H. Sakaguchi
Symposium on Surface Science and Nanotechnology Kansai, 2017.1.24-25, Kyoto, Japan
13. Surface-assisted Bottom-up Synthesis of Width-controlled Graphene Nanoribbon
T. Kojima, S. Song, T. Nakae, H. Sakaguchi
The 97th CSJ Annual Meeting, 2017.3.16-19, Tokyo, Japan

List of Honors

1. Young Researcher Award

The Surface Science Society of Japan

Symposium on Surface Science and Nanotechnology Kansai

“Fabrication of Acene-type Graphene Nanoribbons on Au(111)”

S. Song, T. Kojima, T. Nakae, and H. Sakaguchi

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