

**A study on the on-surface synthesis of
polar graphene nanoribbons toward energy applications**

XIE CONG

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Content

Content	I
Chapter 1 General Introduction	1
1.1 Carbon-based materials for energy applications.....	1
1.2 Graphene nanoribbons	1
1.3 Fabrication of graphene nanoribbons	4
1.4 Edge functionalization of graphene nanoribbons	7
1.5 Asymmetric graphene nanoribbons	9
1.6 Motivation and objectives.....	19
References.....	24
Chapter 2 Experimental	28
2.1 General information.....	28
2.1.1 Chemical	28
2.1.2 Two-zone chemical vapor deposition	28
2.1.3 Molecular-vapor-assisted low-temperature growth.....	29
2.2 Organic synthesis	30
2.3 Characterization	35

2.3.1	Scanning tunneling microscopy / scanning tunneling spectroscopy.....	35
2.3.2	Raman spectroscopy	36
2.3.3	X-ray photoelectron spectroscopy	36
2.4	Calculation	36
2.4.1	Raman simulation	36
2.4.2	Bandgap simulation	37
	References.....	38
Chapter 3 Vectorial On-surface Synthesis of Polar 2D Polymer Crystals .		39
3.1	Introduction.....	39
3.2	Experimental.....	41
3.2.1	General information.....	41
3.2.2	Scanning tunneling microscopy image simulation.....	41
3.2.3	Adsorption simulation on Au(111)	41
3.2.4	Electrostatic potential mapping calculation.....	42
3.2.5	Calculation of polymer inter-chain interaction energy.....	42
3.3	Results and discussion	43
3.3.1	Design strategy of 3-vectorial building blocks.....	43

3.3.2	Stereoregular on-surface polymerization.....	44
3.3.3	Mechanism of stereoselective on-surface polymerization	50
3.3.4	UHV on-surface synthesis of [3, 2-BuO] polymers	54
3.3.5	Polar 2D polymer crystals	61
3.4	Conclusion	63
	References.....	64
Chapter 4 Molecular-Vapor-Assisted Low-Temperature Growth of		
	Graphene Nanoribbons	67
4.1	Introduction.....	67
4.2	Experimental.....	70
4.2.1	General information.....	70
4.2.2	Kinetic studies.....	70
4.3	Results and discussion	75
4.3.1	Demonstration of molecular-vapor-assisted low-temperature growth of GNRs.....	75
4.3.2	Mechanism of molecular-vapor-assisted dehydrogenation	83
4.3.3	Edge functionalization at low temperature	97
4.4	Conclusions.....	107
	References.....	108

Chapter 5	Aryl Shift Rearrangement in Scholl-type Reaction toward Nanographene	113
5.1	Introduction.....	113
5.2	Experimental.....	118
5.2.1	Organic synthesis procedure	118
5.2.2	X-ray crystallographic analysis	128
5.2.3	Mass spectrum analysis	129
5.2.4	Rearrangement calculations.....	129
5.3	Results and discussion	130
5.3.1	Organic synthesis of precursor	130
5.3.2	Scholl reaction toward rearranged product.....	132
5.3.3	Mechanism of aryl shifts in Scholl reaction	137
5.4	Conclusions.....	151
	References.....	153
Chapter 6	General Conclusions	158
Appendix		160
	Crystal data for compound 15.....	160
	Rearrangement computational results.....	166

List of publications	199
Acknowledgement	200

Chapter 1

General Introduction

1.1 Carbon-based materials for energy applications

Carbon-based materials—including graphene, carbon nanotubes (CNTs), graphene nanoribbons, and porous carbons—play pivotal roles in advancing energy technologies due to their exceptional conductivity, tunable surface chemistry, and structural versatility.^[1] In energy storage, they enable high-power supercapacitors and enhance lithium-ion battery electrodes by improving ion diffusion and stability. For energy conversion, they serve as efficient catalysts (e.g., for oxygen reduction or hydrogen evolution reactions) and as critical components in fuel cells and solar cells.^[2] Their nanoscale engineering further enables capabilities in emerging fields such as mechanical / thermal energy harvesting and green hydrogen production.^[3–5] By tailoring atomic structures and defects, carbon materials offer sustainable solutions for next-generation energy systems. This thesis focuses on polar graphene nanoribbons achieved through edge functionalization, which is a promising platform for next-generation energy-related technologies.

1.2 Graphene nanoribbons

The discovery of graphene in 2004 marked a significant shift in materials science, revealing its extraordinary electronic, thermal, and mechanical properties arising from its two-dimensional honeycomb lattice.^[6,7] However, the zero bandgap of pristine graphene limits its direct application in

semiconductor devices, thus driving intensive research on its one-dimensional counterpart, graphene nanoribbons (GNRs).^[8] These quasi-1D nanostructures, typically under 100 nm wide, exhibit tunable bandgaps as well as other electronic properties controlled by quantum confinement and edge topology.^[9]

GNRs are atomically thin strips of graphene whose edges critically determine their electronic behavior,^[10,11] making them versatile candidates for semiconductor applications. (Figure 1-1) Armchair GNRs (AGNRs) are usually semiconductor materials with a bandgap inversely proportional to their width (e.g., a ~ 1.3 eV gap for a 1-nm-wide AGNR).^[12–15] Zigzag GNRs (ZGNRs) usually exhibit metallic or semi-metallic properties due to spin-polarized edge states, showing promise in spin electronics.^[16,17] Chiral GNRs can achieve near-infrared optical responses through intermediate properties regulated by the edge tilt angle.^[18,19]

Theoretical studies further predict that heteroatom doping (e.g., nitrogen, boron) or asymmetric functionalization could introduce magnetic moments, ferroelectricity, or topological states, thereby expanding their applications beyond conventional electronics.^[20,21] However, realizing these predictions requires precise atomic-level control during synthesis, a challenge that has driven innovations in GNRs manufacturing techniques over the past decade.

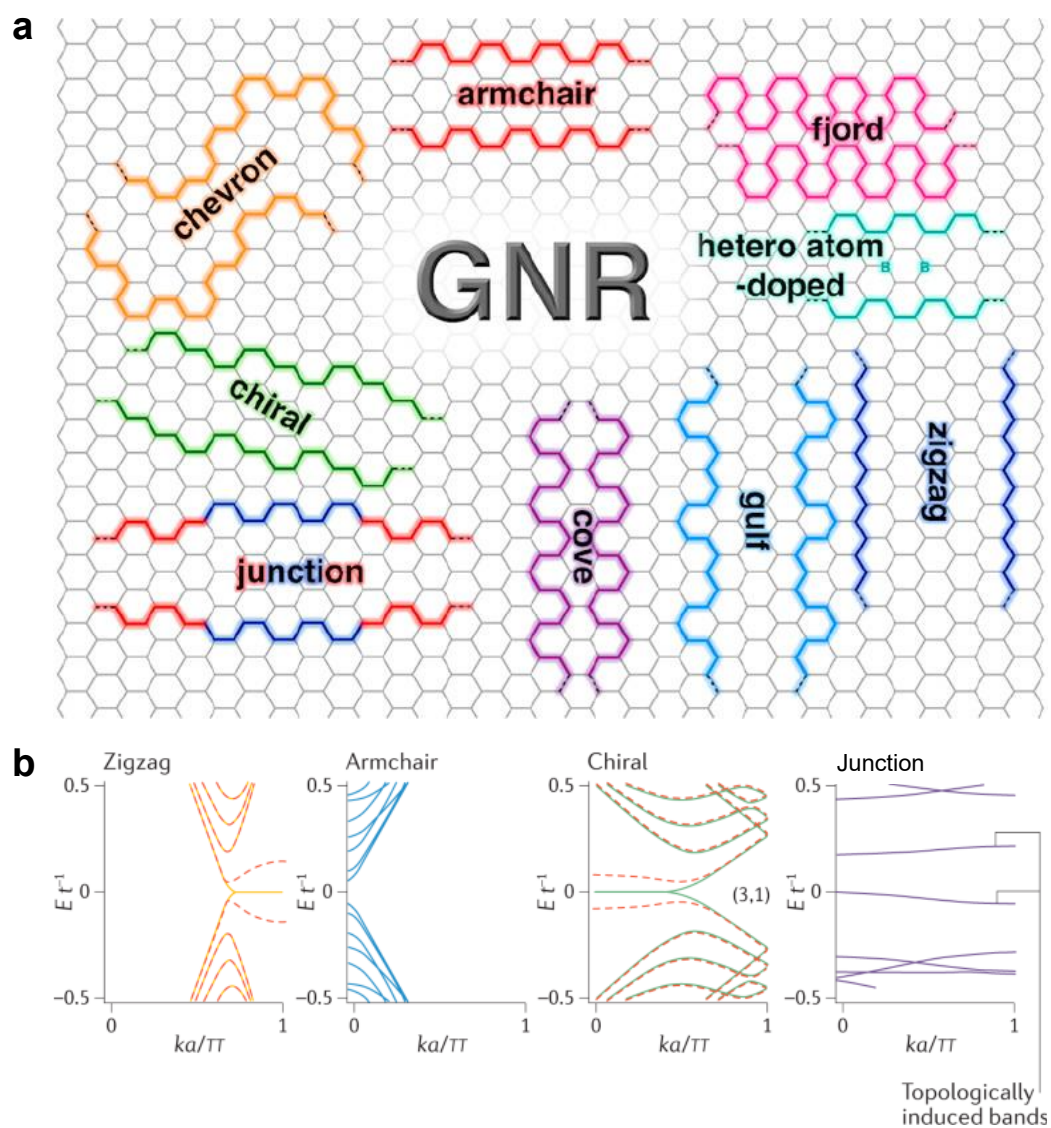


Figure 1-1. (a) Structures and (b) electric properties of graphene nanoribbons. Ref. [22] Copyright © 2019 American Chemical Society;
Ref. [6], Copyright © 2021, Springer Nature Limited.

1.3 Fabrication of graphene nanoribbons

The pursuit of GNRs has led to two broad synthetic pathways: top-down and bottom-up (Figure 1-2), each with distinct advantages and limitations.^[23]

Top-down strategies involve patterning or cutting pristine graphene or carbon nanotubes (CNTs) into GNRs. Such approaches are scalable, but they struggle to achieve atomic-level precision and often introduce defects that degrade electronic performance.^[24]

Bottom-up synthesis, especially on-surface synthesis (Figure 1-3), enables atomic-level control over GNR width and edge topology.^[12] This method typically involves metal-catalyzed coupling, such as polymerization of halogenated aromatic precursors (e.g., DBBA) on metal substrates Au(111) under ultrahigh vacuum (UHV), followed by thermally activated dehydrogenation (usually $>400\text{ }^{\circ}\text{C}$) to form GNRs.^[25,26] This approach has produced AGNRs as narrow as 0.8 nm with band gaps consistent with density functional theory (DFT) predictions, along with various structurally diverse GNRs. In-solution synthesis, such as Suzuki-Miyaura coupling of polyphenylene precursors,^[27] enables solution-synthesized GNRs, although there are challenges in alignment and defect control.^[28]

While conventional on-surface bottom-up methods offer high precision, the required high dehydrogenation temperatures ($>400\text{ }^{\circ}\text{C}$) often degrade functional groups at the GNR edges.^[29]

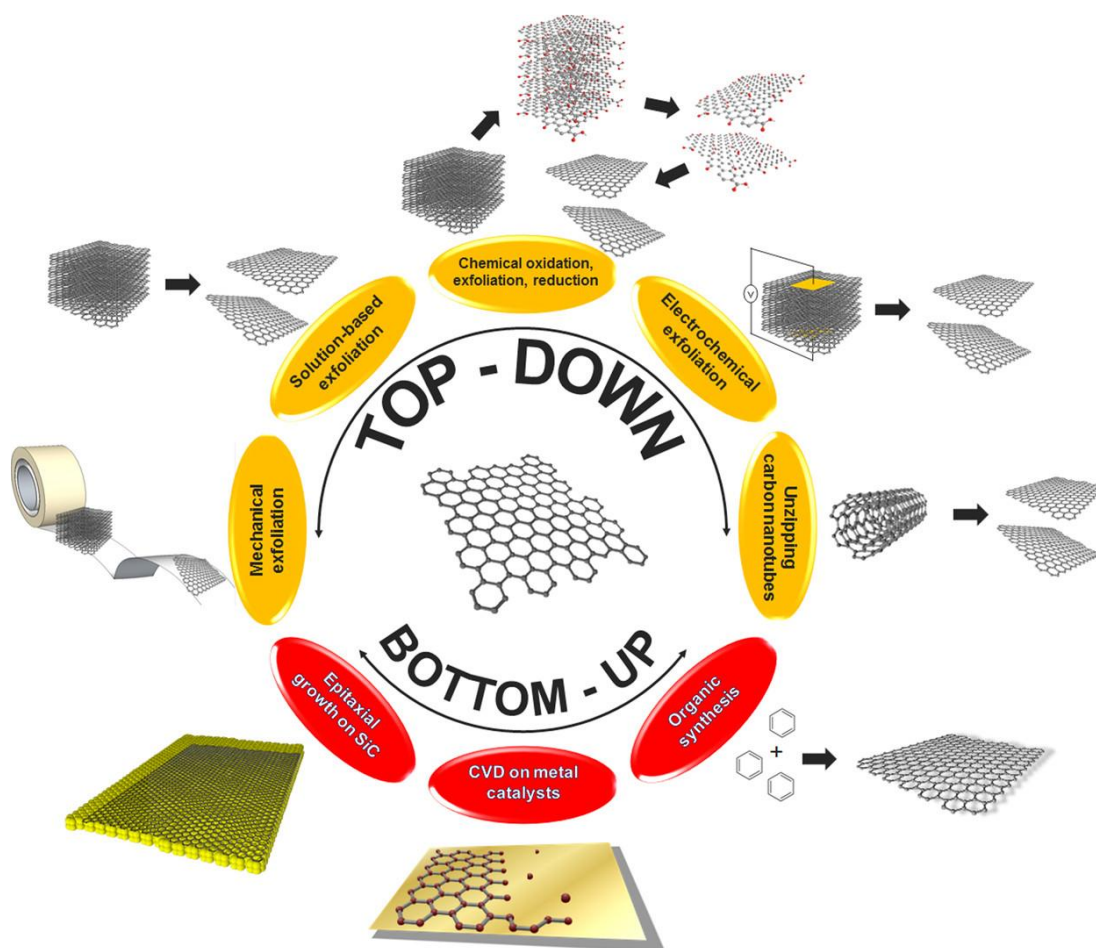


Figure 1-2. Top down and bottom-up preparation methods for graphene and graphene-related materials. Ref. [30], Copyright © 2014 American Chemical Society.

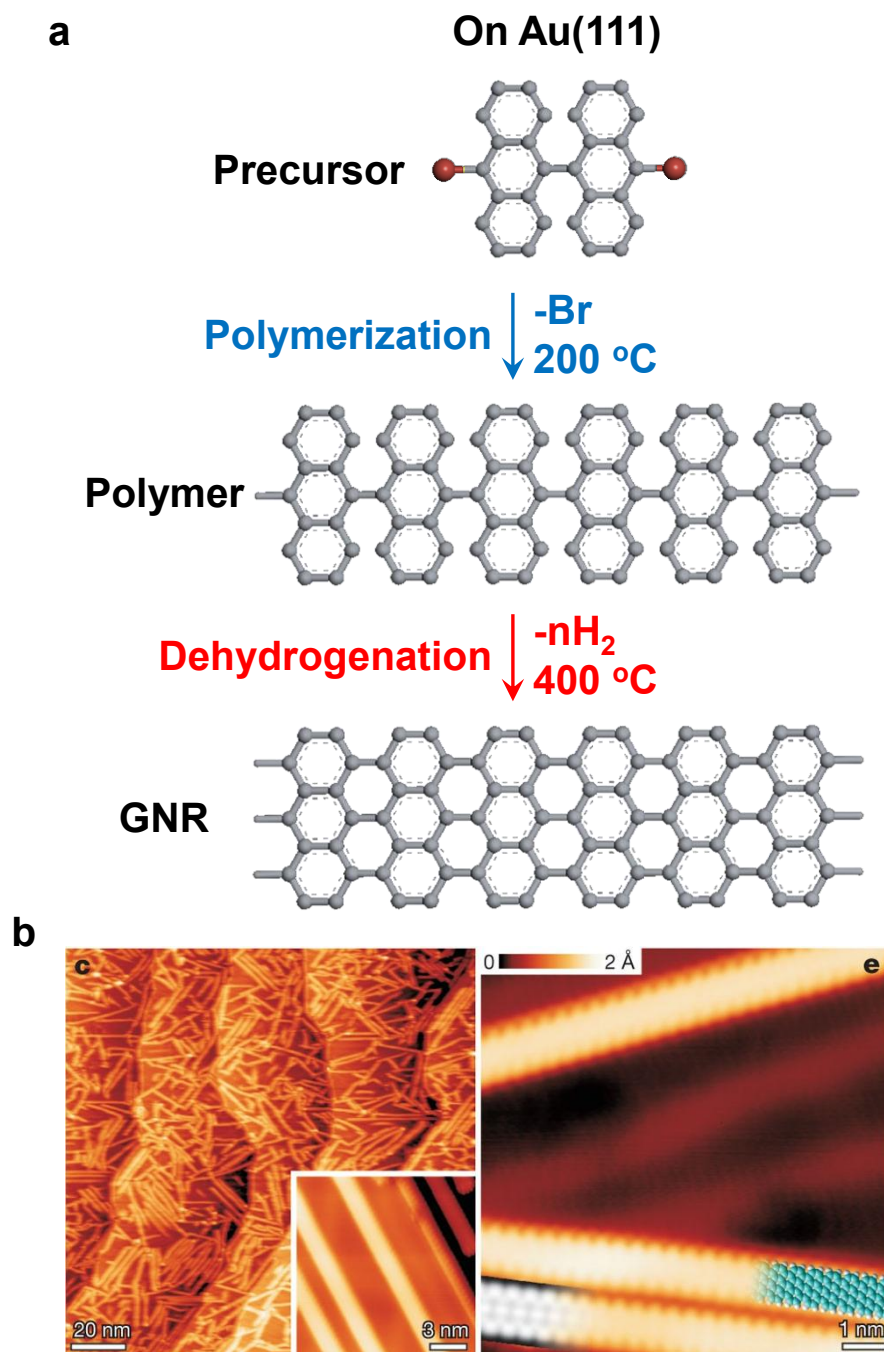


Figure 1-3. (a) Principle and (b) STM images of on-surface synthesized GNRs from precursor DBBA. Ref. [12], Copyright © 2010, Springer Nature Limited.

1.4 Edge functionalization of graphene nanoribbons

Edge functionalization (Figure 1-4a) is a key strategy for tuning the electronic, magnetic, and interfacial properties of GNRs. By covalently modifying reactive edge sites, this approach enables precise bandgap engineering, spin polarization, and charge carrier control,^[29] representing a crucial step towards translating GNRs from laboratory synthesis to multifunctional energy applications.

Edge fluorination significantly enhances the GNR work function. However, conventional high-temperature dehydrogenation ($>400^{\circ}\text{C}$) triggers C–F bond cleavage.^[31] Key breakthroughs have stabilized the fluorinated edges. Strategic molecular engineering minimizes steric clashes between fluorine atoms and residual hydrogen atoms, resulting in C-F bond retention during cyclodehydrogenation reactions on Au(111) at $350\text{--}400^{\circ}\text{C}$.^[32] In situ X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) confirm fluorinated GNR stability below 400°C .^[32]

Cyano ($-\text{CN}$) functionalization facilitates n-type doping, significantly downshifts GNR bands. However, it is easily decomposed during conventional on-surface synthesis. (Figure 1-4b) Only about 60% to 70% of the $-\text{CN}$ groups are retained after high-temperature Au(111) surface-assisted polymerization, and the remaining sites undergo cyclization to generate pyridinic nitrogen.^[33] Scanning tunneling spectroscopy (STS) and density functional theory (DFT) reveal that conjugated $-\text{CN}$ groups reduce the GNR bandgap by extending its π -network. This demonstrates the potential of

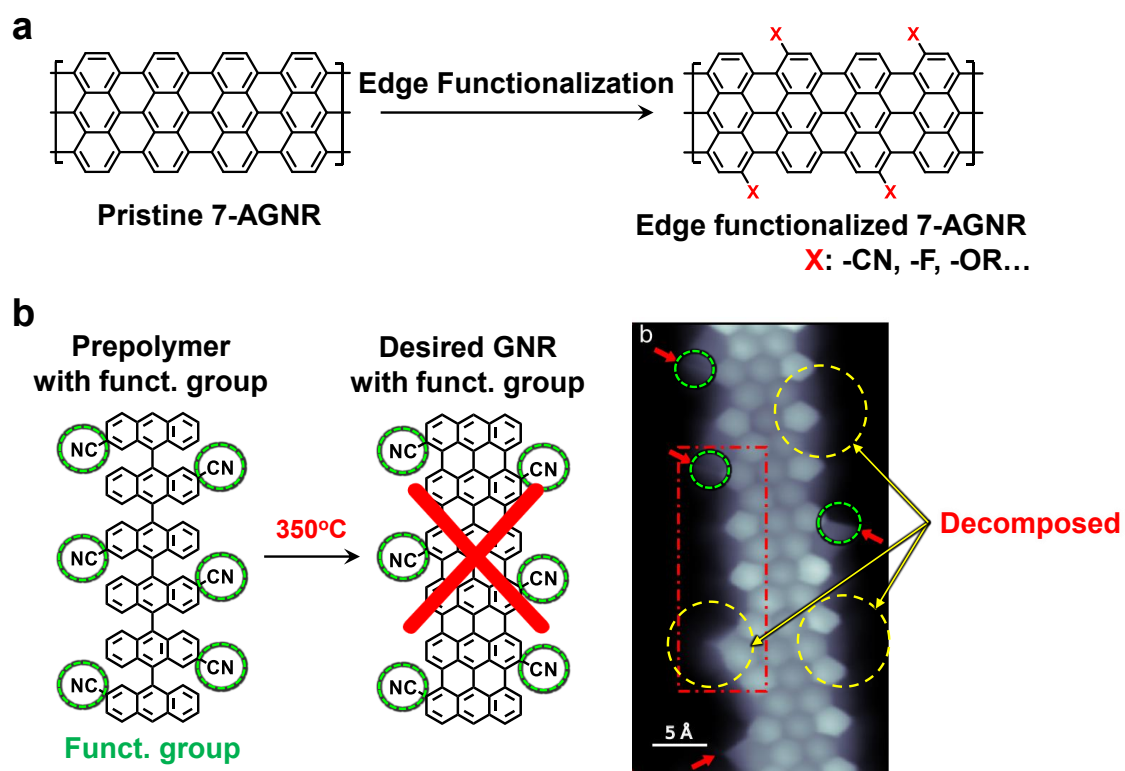


Figure 1-4. (a) Concept of GNR edge functionalization and (b) the challenge of functional group decomposition via traditional high temperature on-surface synthesis method. Ref. [33], Copyright © 2017 American Chemical Society.

functional groups to modify GNR physicochemical properties, though stability requires further improvement.

Conventional on-surface synthesis relies on metal-catalyzed dehydrogenation at high temperatures (usually $>400^{\circ}\text{C}$), which fundamentally compromises edge functionalization - a core requirement for tailoring GNR performance. This approach inherently degrades key functional groups, resulting in bond breakage, uncontrolled catalysis, and topological defects. (Figure 1-4b) This undermines the core advantage of edge-functionalized GNRs, predictable property tuning. While conventional methods excel in preparing pristine GNRs, they are limited in advanced applications that require high-performance properties.^[34] Essentially, high-temperature metal catalysis sacrifices functional diversity for structural precision—an unacceptable outcome for next-generation GNR devices.

1.5 Asymmetric graphene nanoribbons

Asymmetric GNRs break through symmetric limitations through geometric design or chemical modification, unlocking unique properties across physical and chemical domains. For instance, ferroelectricity necessitates non-centrosymmetric electric dipole alignment, resulting in polar GNRs.^[20,21,29,35,36]

Conventional symmetric ZGNRs exhibit antiferromagnetic coupling between their two edges, resulting in zero net magnetization.^[16] To unlock ferromagnetism, theoretical studies propose asymmetric edge passivation as a critical strategy.^[16] For example, passivating one edge with CO_2 while leaving

the other edge pristine breaks structural symmetry and quenches magnetic moments on the passivated edge.(Figure 1-5a) This imbalance generates a ferrimagnetic state with a net magnetic moment of up to 2.00 μB per unit cell. Density functional theory (DFT) calculations confirm that CO_2 adsorption energy (-3.75 eV) stabilizes this configuration, while asymmetric hydrogenation or oxidation induces similar effects.^[20] The localized spins on the unpassivated edge shift the system from antiferromagnetic to long-range ferromagnetic order.

Beyond ferromagnetism, electronic asymmetry via doping or edge-selective functionalization can induce half-metallicity.^[21] Theoretical models (Figure 1-5b) show that asymmetric boron-nitrogen doping or edge-specific chemical modifications create an imbalanced density of states at the Fermi level. This splits spin-up and spin-down bands, enabling 100% spin-polarized conduction.^[21] For instance, DFT studies predict that asymmetric ZGNRs with one edge doped with nitrogen and the other with boron exhibit a half-metallic gap of ~ 0.5 eV, making them ideal for spin filters. Stability analyses confirm these states persist at room temperature, crucial for device applications.^[21]

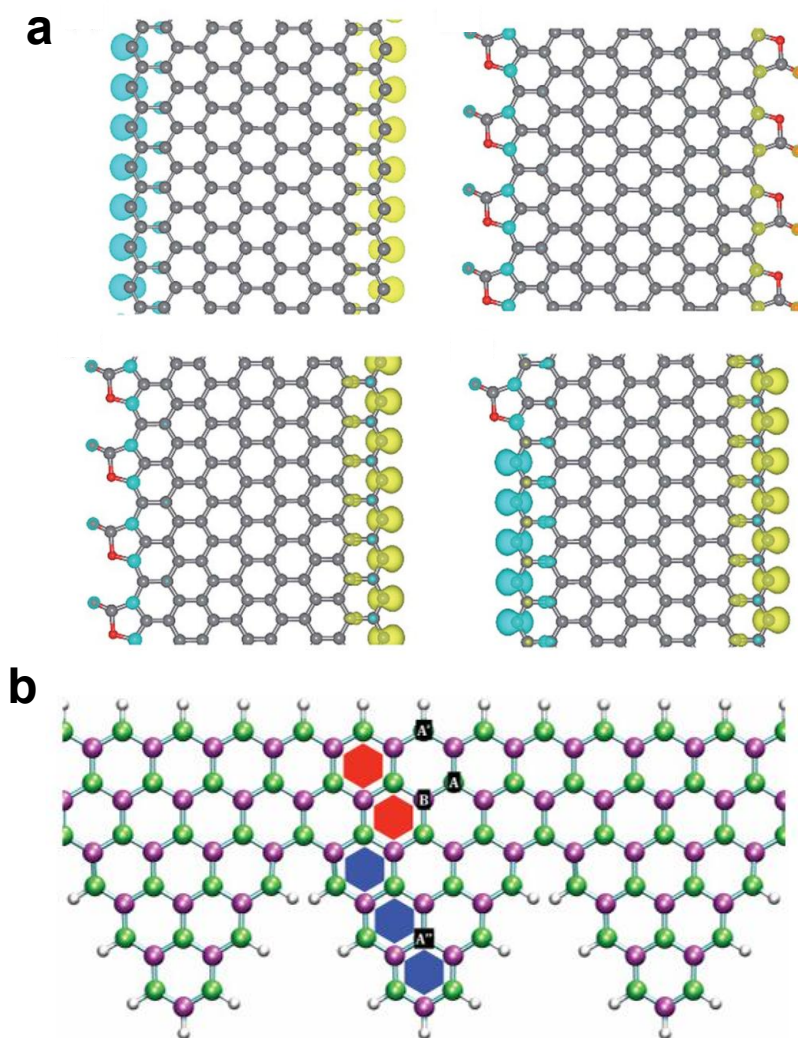


Figure 1-5. Theoretical studies of asymmetric graphene nanoribbons.

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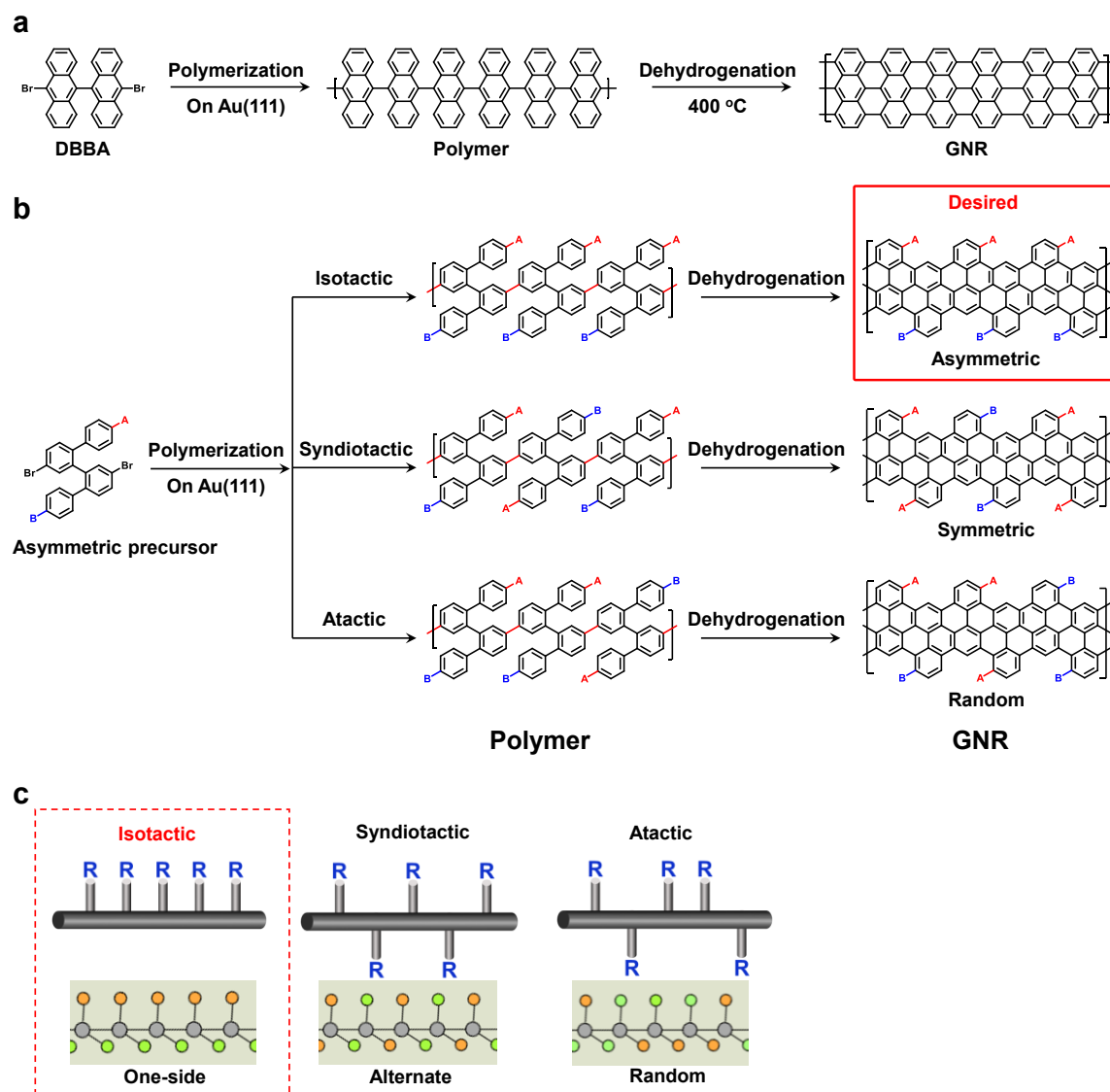


Figure 1-6. (a) Previous work of GNR on-surface synthesis from DBBA. (b) Challenge of stereoselective polymerization toward asymmetric GNRs (c) Definition of stereoselective polymers.

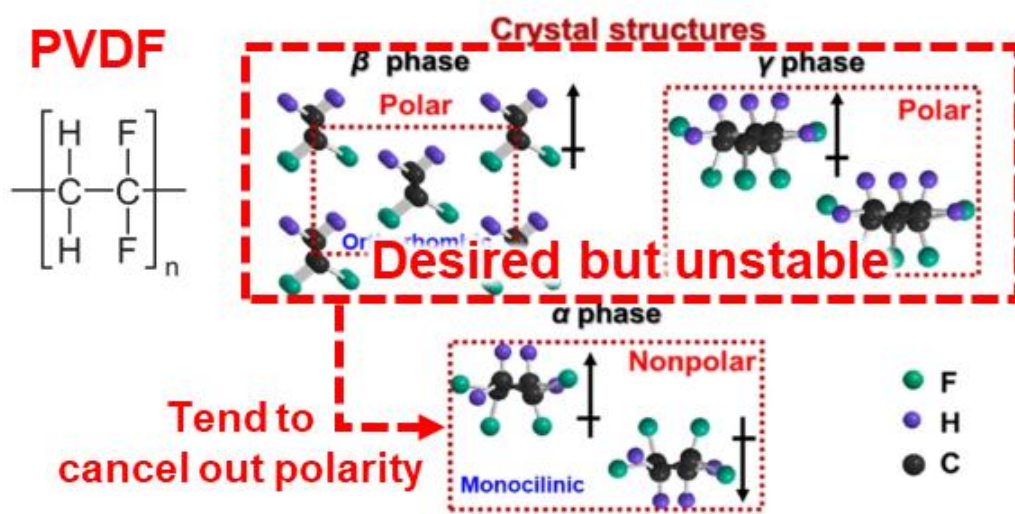


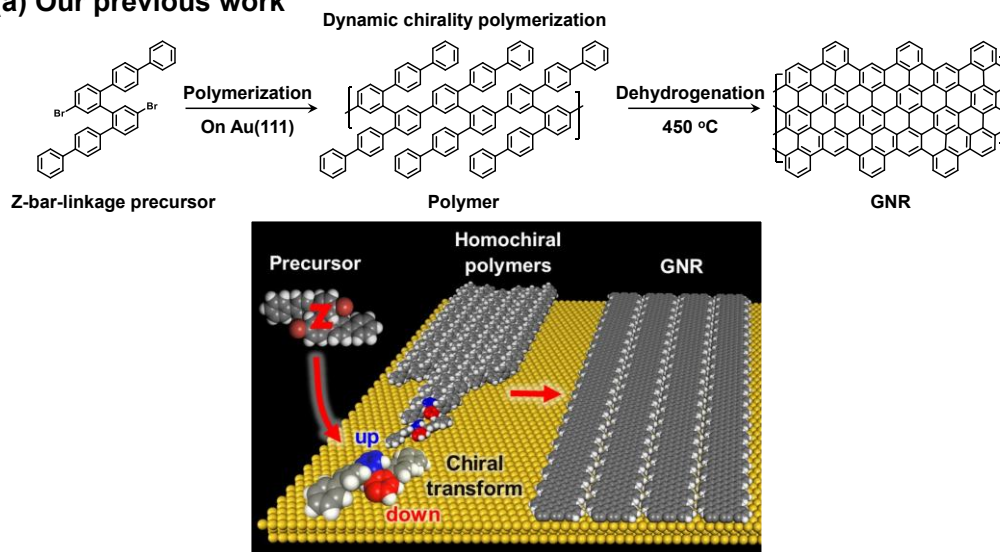
Figure 1-7. Problem of polarity cancellation during polar crystal formation.

The experimental preparation of polar GNRs (Figure 1-6) relies on stereoselective polymerization, a challenge that can force the unidirectional arrangement of asymmetric precursors.^[37] Furthermore, after synthesizing polar GNRs, we need the polar crystals. The desired polar phases are usually unstable, tend to cancel out the overall polarity, such as PVDF,^[38] making it a crucial challenge to polar crystal formation. (Figure 1-7)

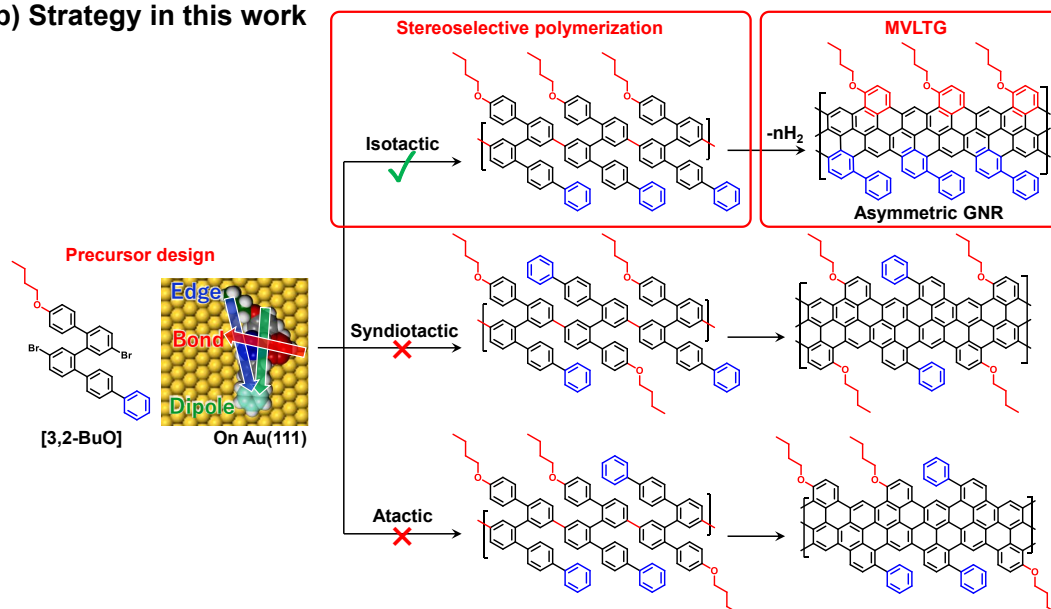
Our previous work introduced the concept of dynamic chirality polymerization to the on-surface synthesis of GNRs via two-zone CVD, (Figure 1-8a) which relies on the chiral deformation of the Z-bar-linkage precursors on Au(111).^[39] Inspired by this work, a compass-like precursor [3,2-BuO] possessing three vectors – dipole for introducing polar, bonding for dynamic polymerization, , and edge for inter-strand interaction - was designed to overcome the challenge of stereoselective polymerization. (Figure 1-8b and Figure 1-9a,b) The deformation of the precursor [3,2-BuO] on Au(111) forms a isotactic polymer, thereby forming a polar two-dimensional crystal via vectorial on-surface polymerization. Further MVLTG technology realized the dehydrogenation reaction of the polymer at a relatively low temperature without the decomposition of introduced functional substituents, thereby realizing GNR polar crystals.^[34] (Figure 1-8c and Figure 1-9c)

Recently, our group successfully realized asymmetric magnetism in Janus GNRs, featuring two distinct edge structures. (Figure 1-10) Achieved by the concept of vectorial on-surface synthesis of asymmetric Z-bar-linkage precursors, JGNRs exhibit ferromagnetism by spin splitting at one edge.^[17]

(a) Our previous work



(b) Strategy in this work



(c) Concept illustration of vectorial on-surface synthesis

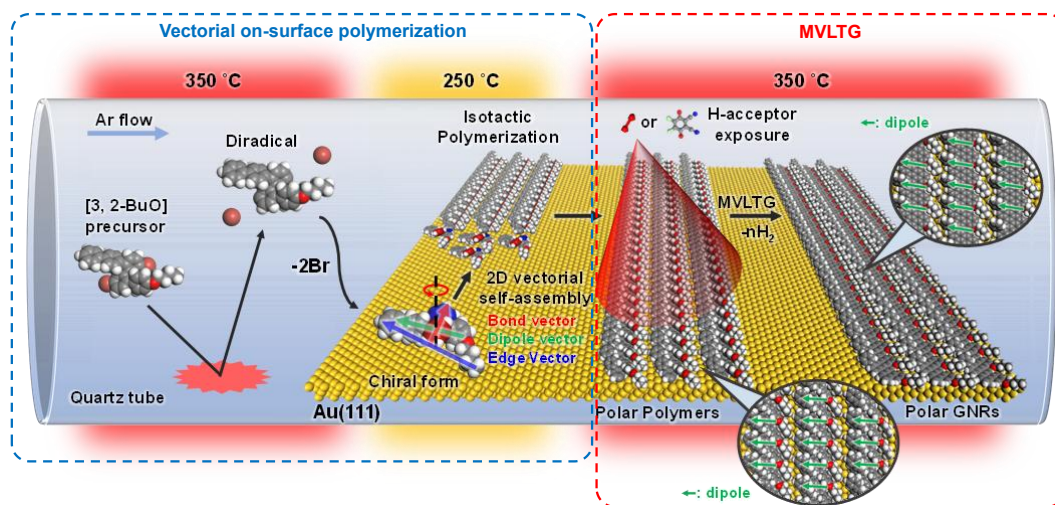


Figure 1-8. (a) Our previous work of GNR on-surface synthesis from Z-bar-linkage precursor via dynamic polymerization and dehydrogenation. (b) Strategy of asymmetric GNR on-surface synthesis via stereoselective polymerization and molecular vapor-assisted low-temperature growth (MVLTG). (c) Concept illustration of vectorial on-surface synthesis.

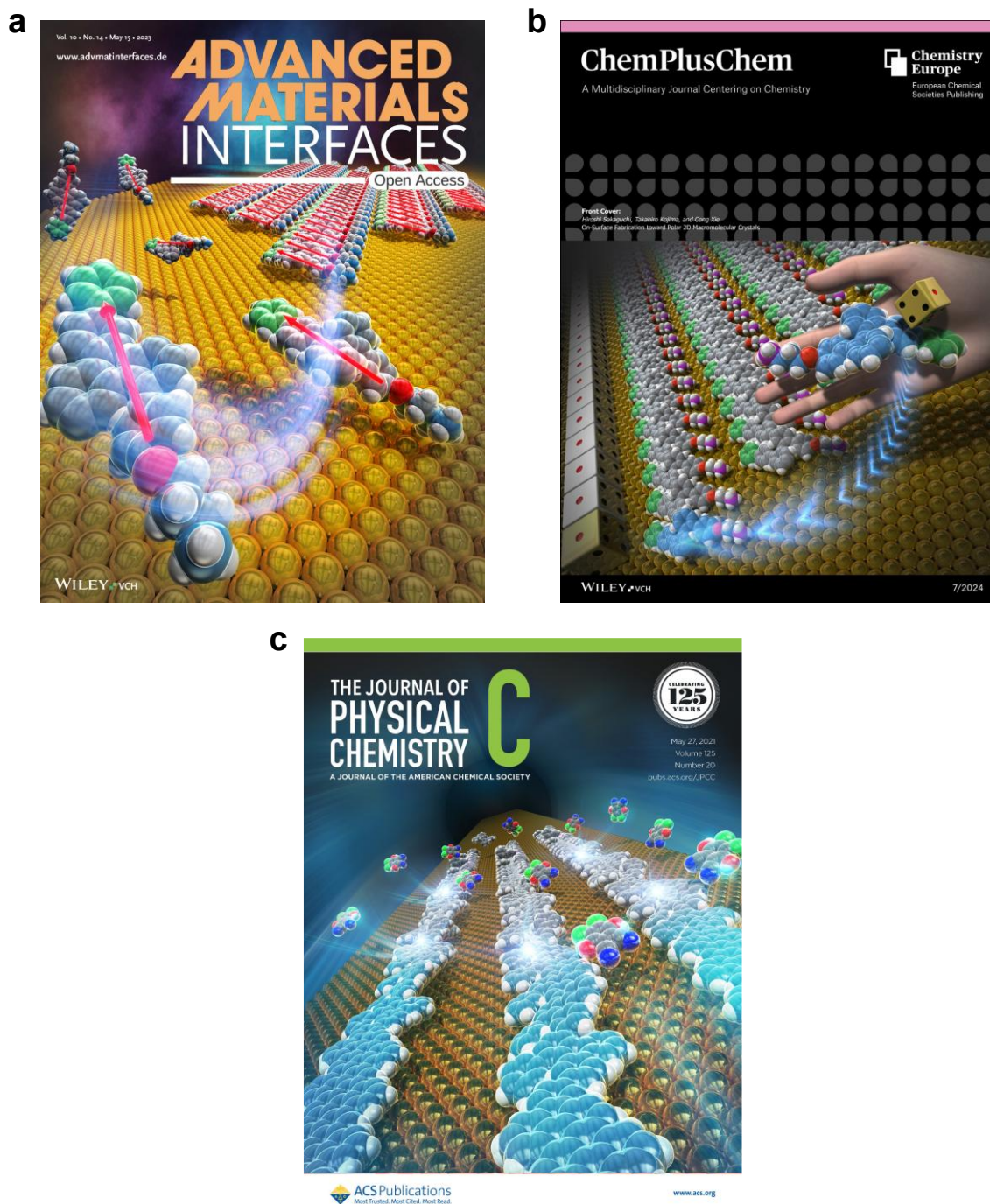


Figure 1-9. Concept illustrations selected as cover art in journals. (a), (b) vectorial on-surface polymerization and (c) molecular vapor-assisted low-temperature growth (MVLTG).

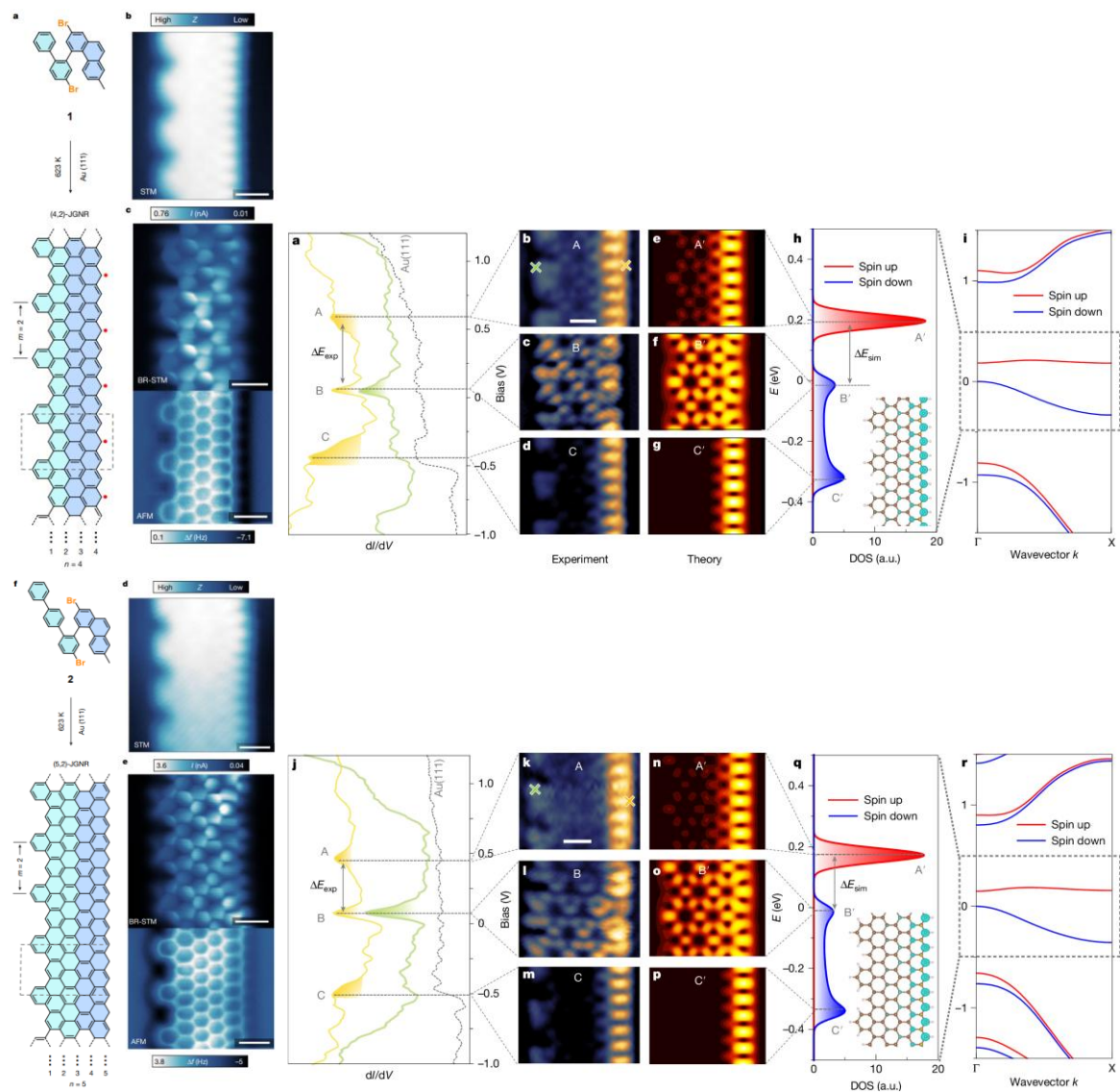


Figure 1-10. Ferromagnetic graphene nanoribbons synthesized by our group. Ref. [17]; Copyright © 2025, The Author(s), under exclusive licence to Springer Nature Limited.

1.6 Motivation and objectives

As mentioned above, polar graphene nanoribbons (GNRs) are one-dimensional graphene structures that have polar groups along one edge. They represent a promising platform for next-generation energy-related technologies, including energy harvesters. The realization of polar GNRs requires the synthesis of GNRs with asymmetric edge structures. To synthesize asymmetric GNRs, it is necessary to design asymmetric precursors by asymmetric introduction of functional groups and perform unidirectional on-surface polymerization. However, limited to the non-selective polymerization of conventional on-surface synthesis, asymmetric GNR precursors tend to polymerize randomly. Moreover, further high-temperature dehydrogenation required in conventional on-surface GNR synthesis always decomposes the introduced edge functional groups. Finally, even if we can obtain polar GNR, the polar crystal formation is still challenging, because of the overall polarity cancellation.

In this thesis, to achieve stereoselective polymerization, inspired by previous work of Z-bar-linkage precursor and dynamic chirality,^[39] a compass-like precursor possessing three bonding, edge, and dipole vectors was designed to undergo vectorial on-surface polymerization. the chirality deformation of the compass precursor on Au(111) forms polar polymers via stereoselective polymerization. Further, to solve the problem of high temperature decomposition at edge functional sites, molecular vapor-assisted low-temperature growth (MVLTG) technology was developed to enable the

dehydrogenation reaction of polar polymers at a relatively low temperature without decomposing the introduced edge functional substituents, thereby achieving polar GNRs. Finally, the polar GNR crystal formed via edge CH- π interaction.

In Chapter 1, a general background about GNRs was given. The current research progress and challenges in polar GNRs were discussed.

In Chapter 2, experimental and calculation details related to on-surface synthesis conducted in this thesis were described.

In Chapter 3, the functional groups were asymmetrically introduced to the edge of polar polymers. Polar crystals were successfully prepared on Au(111) surface by vectorial on-surface synthesis. The advantages of asymmetrically introducing functional groups into polymers are discussed. The challenge of stereoregular polymerization and the tendency for overall polarity cancellation during conventional on-surface bottom-up synthesis are reviewed. Enabled by the low halogen-contaminated metal surfaces provided by two-zone chemical vapor deposition, ‘compass’ precursors possessing three independent bonding, edge, and dipole vectors undergo isotactic polymerization via the vectorial self-assembly of chiral precursor diradicals without the need for chiral catalysts required in conventional in-solution polymerization. The isotactic polymers exhibit polar two-dimensional crystalline structures due to the hetero-edge CH- π interaction between the standing phenyl and butoxy groups, surpassing the homo-edge interactions of π - π and CH-CH. Our developed vectorial on-surface synthetic technique not only paves the way to the

realization of stereoregular control but also unlocks unprecedented crystal engineering.

In Chapter 4, a new low-temperature GNR growth method (molecular vapor-assisted low-temperature growth, abbreviated as MVLTG) was developed to enhance the dehydrogenation reaction from polar polymers to polar GNRs at a relatively low temperature. With the assistance of MVLTG, the polar GNR crystals were successfully achieved from polar polymer crystals. Conventional on-surface synthesis under ultra-high vacuum (UHV) deposition has been used to synthesize various types of GNRs. The dehydrogenation reaction from prepolymer to GNR requires catalysis with a metal substrate at high temperature, which suffers from undesired side reactions that decompose introduced functional substituents during conversion to GNRs. To overcome these drawbacks, we have developed a new method, molecular-vapor-assisted low-temperature growth, based on a massive excess of gaseous hydrogen-accepting molecules (DDQ, or oxygen) relative to the prepolymer on the metal surface. MVLTG reduces the GNR growth temperature of prepolymers with the Z-type precursor, 4',5"-dibromo-1,1':2,1':2"-quaterphenyl from 500 °C, used in conventional thermal annealing, to 350 °C. In order to investigate the reaction mechanism of MVLTG, a kinetic study using Raman spectroscopy to obtain GNR yields as a function of the hydrogen acceptor concentration and time, was in good agreement with a simulation based on the gas-2D solid-state reaction model. These studies suggest a successful “Scholl reaction” in the gas phase, in which gaseous hydrogen acceptors (DDQ and oxygen) efficiently extract hydrogens

from prepolymers at lower temperatures, converting them into GNRs. Additionally, MVLTG successfully synthesized polar GNRs from prepolymers made of the above-mentioned compass precursor in Chapter 3, suppressing decomposition of substituents. MVLTG not only realizes a new class of GNRs but also enables unprecedented on-surface synthesis.

In Chapter 5, we attempt to scale up GNR production via in-solution synthesis based on Z-bar-linkage precursor. Generally, the potential application of GNRs, such as electronic, photonic, and magnetic, requires large-amount fabrication of GNRs. The conventional GNR on-surface synthesis is always limited to less-amount production, which limits its energy application. On the other hand, in-solution synthesis, such as Scholl reaction, is an effective method to increase the production scale of GNRs. To achieve large-scale production of GNRs, we conducted in-solution synthesis using our originally designed Z-bar-linkage precursors. Even we didn't obtain the expected structure, we established the 1,4-aryl shift arrangement mechanism in the Scholl-type reaction. Oxidative dehydrogenation, known as Scholl reaction, is a powerful method for synthesizing many polycyclic aromatic hydrocarbons. Sometimes, unexpected rearrangements can lead to the formation of new structures that are usually difficult to obtain. Here, we discovered a novel Scholl-type reaction involving both 1,4-aryl- and 1,2-aryl shift rearrangements, resulting in the production of armchair nanographene. Additionally, we established the principle of the rearrangement mechanism through thermodynamic and kinetic studies using density functional theory. Theoretical studies indicated that the rearrangement reaction involves both

arenium cation- and radical cation mechanisms. The selection of arenium cation- or radical cation mechanisms depends on the sizes and positions of the shifting aryl groups. Large biphenyl or triphenylenyl groups undergo the arenium cation mechanism, while a small monophenyl group favors the radical cation mechanism. Our findings offer new insights into the controllable rearrangements in Scholl reaction and provide new synthetic methods for obtaining a variety of polycyclic aromatic hydrocarbons, which are typically challenging to design.

In chapter 6, a general conclusion and future perspective were given.

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Chapter 2

Experimental

2.1 General information

Experimental methodology related to on-surface synthesis conducted in Chapters 3 and 4 was described in this chapter. Experimental detail related to the rearranged Sholl-type reaction was described in Chapter 5.2.

2.1.1 Chemical

All reagents and solvents were obtained from commercial suppliers and used as received without purification. THF and CH₂Cl₂ were dried with a glasscontour solvent purification system.

2.1.2 Two-zone chemical vapor deposition

The two-zone CVD system (Figure 3-2 and Figure 4-2a) consists of a quartz tube (26 mm ϕ , 86 cm) as the reactor, a rotary pump, which can evacuate the system below 9.1×10^{-2} Pa, a two-zone electric furnace with two temperature controllers, 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 to remove impurities. The precursor (in a quartz boat) and the Au (111)-deposited mica 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 160 Pa. GNRs were synthesized in two stages: In the first stage, the T_{sub} temperature (quartz tube, zone 2) was set to 250 °C, with the subsequent evaporation of the precursors by heating to approximately

240 °C (T_{pre}) using the mantle heater. The path of the monomers through the quartz tube (zone 1) was heated up to 350 °C (T_{wall}).

Prepolymers were synthesized as follows. The T_{sub} temperature (quartz tube, zone 2) was set to 150 °C, with the subsequent evaporation of the precursors by heating to 190 °C (T_{pre}) using the mantle heater. The path of the precursors through the quartz tube (zone 1) was heated to 350 °C (T_{wall}), followed by formation of monomer biradicals and polymerization of prepolymers on Au(111).

2.1.3 Molecular-vapor-assisted low-temperature growth

MVLTG of GNRs was conducted as follows. The T_{sub} temperature (quartz tube, zone 2) was set to a given temperature (340 °C, 350 °C or 360 °C), followed by exposure cycles of hydrogen-acceptor vapors. For DDQ exposure, a quartz boat with a given amount of DDQ drop-cast was heated to 200 °C (T_{pre}) using the mantle heater, to form a molecular vapor carried by the continuing Ar flow at 500 sccm. Concentrations and exposure cycle times of DDQ were determined using a laser detector. For oxygen exposure, the aforementioned Ar flow was switched to an oxygen gas flow of a given pressure and exposure time. Then after each cycle of exposure of DDQ or oxygen, the degree of dehydrogenation was measured via STM and Raman spectroscopy. For comparison with traditional thermal synthesis, the T_{sub} temperature (quartz tube, zone 2) was set to 500 °C to convert polymers into GNRs without molecular vapors.

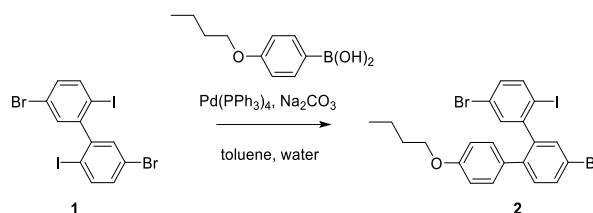
2.2 Organic synthesis

NMR spectra were reported in parts per million using tetramethylsilane (δ 0.00 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 recorded on JEOL JNM-ECP300 (300 MHz for ^1H) instruments. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and silica gel 60N (Kanto Chemical Co.), respectively. Gel permeation chromatography (GPC) was performed using a LC-9201 system (Japan Analytical Industry) with JAIGEL 1H and 2H polystyrene columns (eluent: CHCl_3 , flow: 10 mL/min). Column chromatography and TLC were performed with silica gel (70-230 mesh) and precoated silica gel plates, respectively.

4',5''-Dibromo-1,1':2',1'':2'',1'''-quaterphenyl (abbreviated to [2, 2] in Chapter 4) was synthesized according to our previous procedure.^[1]

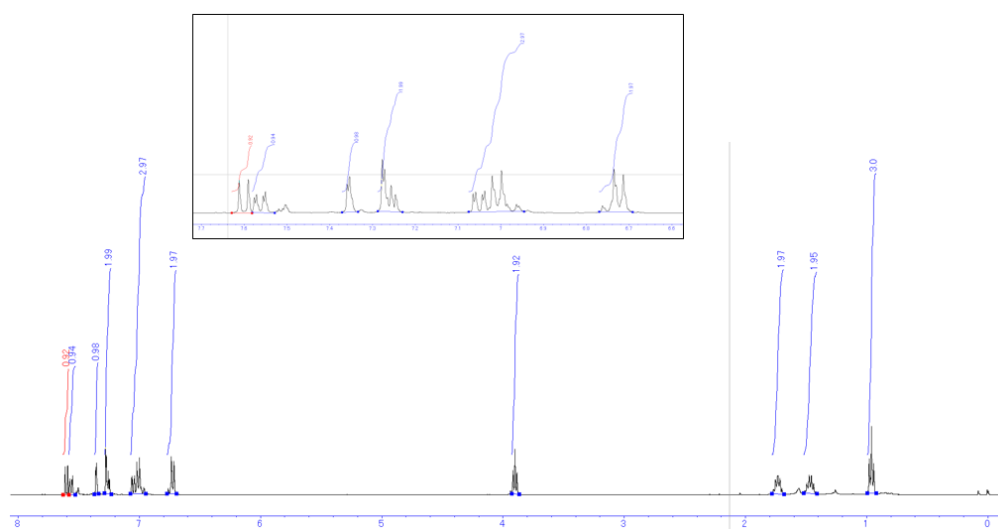
5,5'-Dibromo-2,2'-diiodo-1,1'-biphenyl, **1** was prepared according to procedures mentioned in literature.^[2]

5,5'-dibromo-2-iodo-4"-methoxy-1,1':2',1"-terphenyl: (**2**)

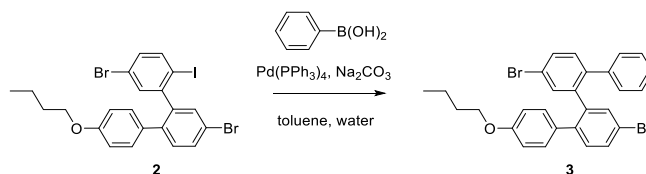


Toluene (5 mL) and water (2.5 mL) were added to a mixture of **1** (400 mg, 0.710 mmol), 4-butoxyphenylboronic acid (119 mg, 0.780 mmol), $\text{Pd(PPh}_3)_4$ (82.0 mg, 0.0710 mmol) and Na_2CO_3 (752 mg, 7.09 mmol). After overnight heating at 60 °C under a nitrogen atmosphere, the reaction mixture was diluted with water and extracted with CH_2Cl_2 . After evaporation of the solvent, the residue was purified by chromatography (silica gel, hexane : CH_2Cl_2 = 2 : 1) to afford **2** (180 mg, 47% yield) as a white solid.

^1H NMR (300 MHz, CDCl_3) δ 7.60 (d, J = 8.4 Hz, 1H), 7.56 (dd, J = 8.4, 2.0 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 7.28-7.25 (m, 2H), 7.06-7.00 (m, 3H), 6.76-6.70 (m, 2H), 3.90 (t, J = 6.4 Hz, 2H), 1.75-1.72 (m, 2H), 1.49-1.44 (m, 2H), 0.96 (t, J = 6.8 Hz, 3H).

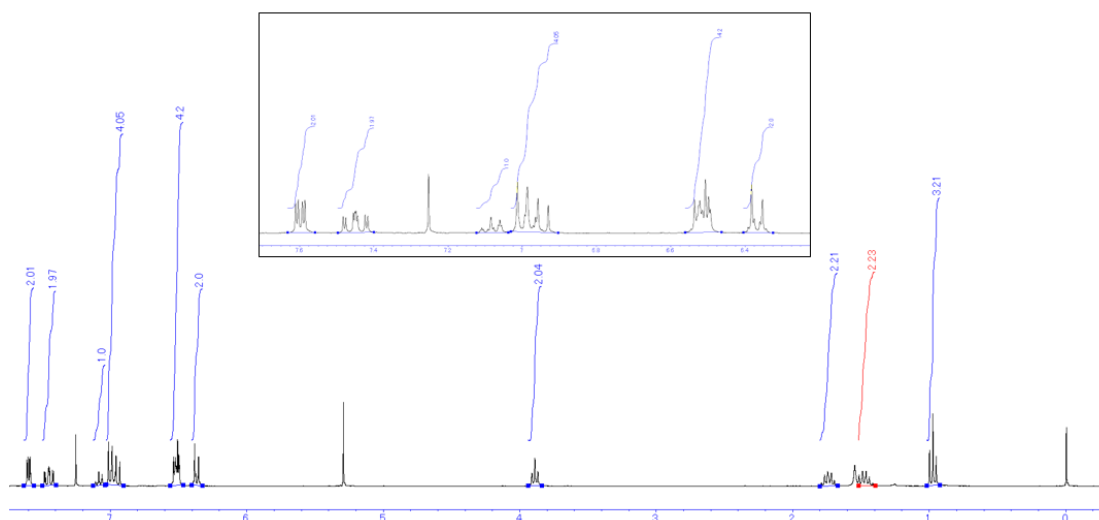


4',5''-dibromo-4-butoxy-1,1':2',1'':2'',1'''-quaterphenyl: (**3**)

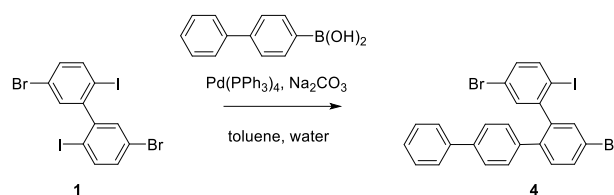


Toluene (2 mL) and water (1 mL) were added to a mixture of **2** (90 mg, 0.16 mmol), phenylboronic acid (22.2 mg, 0.182 mmol), Pd(PPh₃)₄ (19.1 g 0.0165 mmol) and Na₂CO₃ (106 mg, 0.993 mmol). After overnight heating at 60 °C under a nitrogen atmosphere, the reaction mixture was diluted with water and extracted with CH₂Cl₂. After evaporation of the solvent, the residue was purified by GPC (CHCl₃) followed by recrystallization from EtOH to afford **3** (23.6 mg, 29% yield) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.59 (dd, *J* = 7.2, 2.8 Hz, 2H), 7.48-7.42 (m, 2H), 7.11-7.06 (m, 1H), 7.10-6.93 (m, 4H), 6.54-6.49 (m, 4H), 6.36 (d, *J* = 8.1 Hz, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 1.79-1.70 (m, 2H), 1.55-1.42 (m 2H), 0.97 (t, *J* = 6.9 Hz, 3H).

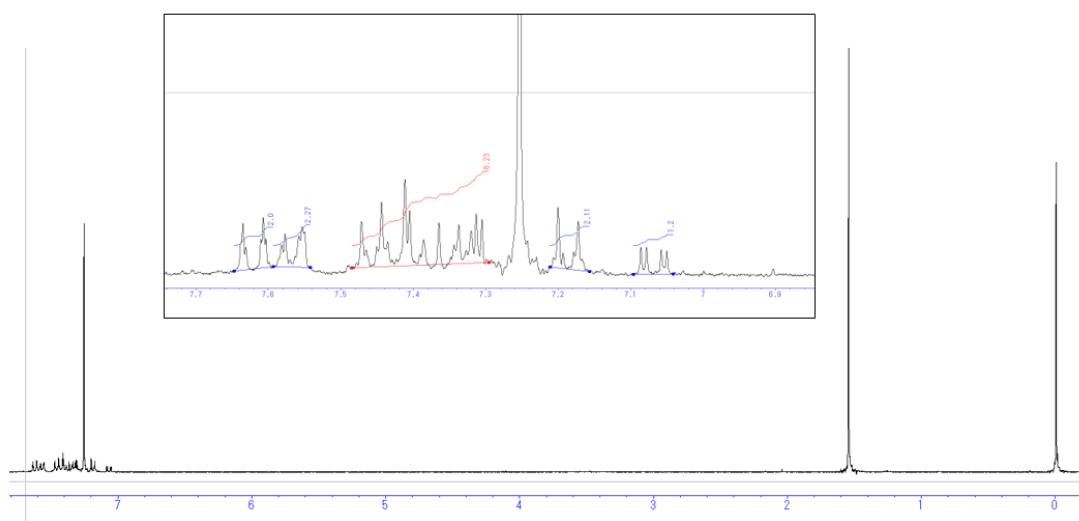


5,5'-dibromo-2-iodo-1,1':2',1'':4'',1'''-quaterphenyl: (**4**)

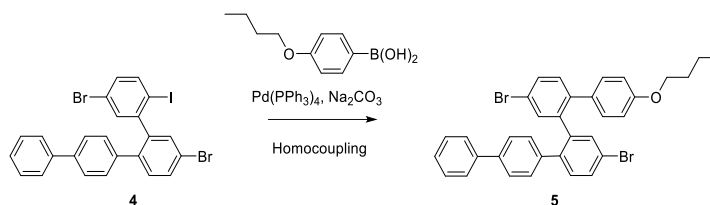


Toluene (5 mL) and water (2.5 mL) were added to a mixture of **1** (200 mg, 0.355 mmol), 4-biphenylboronic acid (77.3 mg, 0.390 mmol), $\text{Pd(PPh}_3)_4$ (20.5 mg, 0.0177 mmol) and Na_2CO_3 (226 mg, 2.13 mmol). After overnight heating at 90 °C under a nitrogen atmosphere, the reaction mixture was diluted with water and extracted with CH_2Cl_2 . After evaporation of the solvent, the residue was purified by chromatography (silica gel, hexane : CH_2Cl_2 = 5 : 1) followed by GPC (CHCl_3) to afford **4** (50 mg, 24% yield) as a white solid.

^1H NMR (300 MHz, CDCl_3) δ 7.62 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.5 Hz, 2H), 7.47-7.30 (m, 8H), 7.18 (d, J = 8.4 Hz, 2H), 7.07 (dd, J = 8.4, 2.4 Hz, 1H).

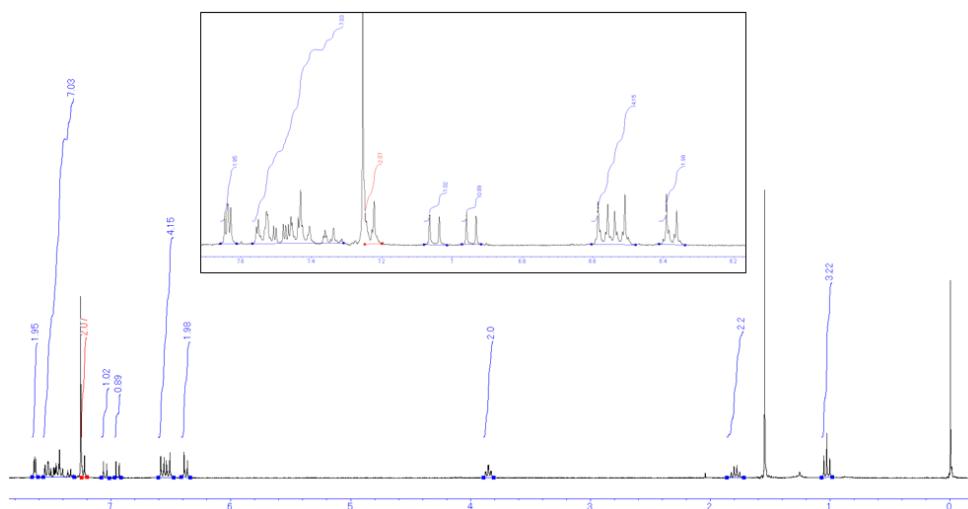


4',5''-dibromo-4-butoxy-1,1':2',1'':2'',1''':4''',1'''-quinquephenyl: (**5**)



Toluene (2 mL) and water (1 mL) were added to a mixture of **4** (25 mg, 0.0427 mmol), 4-butoxyphenylboronic acid (10.6 mg, 0.0427 mmol), Pd(PPh₃)₄ (4.9 mg, 0.0042 mmol) and Na₂CO₃ (26.9 mg, 0.254 mmol). After overnight heating at 60 °C under a nitrogen atmosphere, the reaction mixture was diluted with water and extracted with CH₂Cl₂. After evaporation of the solvent, the residue was purified by GPC (CHCl₃) followed by recrystallization from EtOH to afford **5** (8.1 mg, 29% yield) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 7.65-7.63 (m, 2H), 7.56-7.31 (m, 7H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.52 (d, *J* = 9.0 Hz, 2H), 6.38 (d, *J* = 9.0 Hz, 2H), 3.85 (t, *J* = 6.6 Hz, 2H), 1.85-1.73 (m, 2H), 1.03 (t, *J* = 6.6 Hz, 3H).



2.3 Characterization

2.3.1 Scanning tunneling microscopy / scanning tunneling spectroscopy

STM measurements in this thesis except Figure 3-7 were performed under the constant-current mode with a commercially available UNISOKU low temperature scanning tunneling microscopy system (USM-1100SA-2C) at 77 K. An electrochemically etched tungsten wire was used as the tip. STS (dI/dV) spectra were acquired using the following conditions; $V_{\text{sample}} = -0.5$ V, $I = 200$ pA under the reduced feedback loop during voltage sweep. Additionally, STM measurements for Figure 3-7 were performed with commercially available Omicron low temperature scanning tunneling microscopy and a homemade STM system, operating in ultra-high vacuum at temperatures below 5 K. High-resolution dI/dV imaging was performed with a CO terminated tip, the differential conductance map was recorded by a digital lock-in amplifier with a modulation frequency of 510 Hz and an AC voltage of 10 mV. Obtained images were analyzed using the SPIP software. Images were analyzed using SPIP software.

Au(111) substrates for two-zone CVD were made using a homemade e-beam vacuum-deposition system. Evaporated gold was deposited on 2.8×2.8 cm² mica substrates which were heated at 350 °C under a vacuum of 2.6×10^{-6} Pa. Samples up to 40 nm thick were deposited at a rate of $0.5 \text{ \AA s}^{-1}$. For UHV on-surface synthesis; clean Au(111) surfaces were prepared in-situ by repeated cycles of standard Ar⁺ sputtering (3×10^{-4} Pa, 1000 eV, 15 min) and annealing at 457 and 477 °C.

2.3.2 Raman spectroscopy

Raman spectroscopy was performed using a laser Raman microscope (LVRAM500/532; Lambda Vision Inc.) with a 532-nm excitation laser. After each cycle of DDQ or oxygen exposure, samples were immediately transferred via ambient conditions to the Raman experiment, to prevent water vapor deposition on Au(111).

2.3.3 X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) were acquired using a spectrometer (JEOL, JPS-9010TRX) with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6$ eV). The spectrometer was calibrated with the peaks of Au $4f_{7/2}$ (84.0 eV), Ag $3d_{5/2}$ (368.3 eV), and Cu $2p_{3/2}$ (932.7 eV). Fitting of spectra was performed with Voigt profiles.

2.4 Calculation

Calculations except kinetic study in Chapter 4 were performed using the BIOVIA Materials Studio software suite (Dassault Systèmes SE.).

2.4.1 Raman simulation

The CASTEP module was used for Raman simulations. The GNR structures for input were obtained from DFT structural optimization. Norm-conserving pseudopotentials were used with $16 \times 4 \times 1$ k-points. The plane-wave cutoff energy was set to 830 eV. Maximum thresholds for force and

displacement tolerances during structural optimization were $0.1 \text{ eV}\text{\AA}^{-1}$ and $0.0005 \text{ \AA}$, respectively. For the simulation in Figure 4-23, methoxy groups were used instead of butoxy groups because the length of the alkyl chains did not appear to affect the results of Raman simulations.

2.4.2 Bandgap simulation

The CASTEP module in BIOVIA Materials Studio software suite (Dassault Systèmes SE.) was used for DFT structural optimization and density of state calculations, the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE) was used as the exchange correlation functional employing on-the-fly-generated (OTFG) ultrasoft pseudopotentials.

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Chapter 3

Vectorial On-surface Synthesis of Polar 2D Polymer Crystals

3.1 Introduction

Asymmetric structures play crucial roles in producing particular properties and functionalities in various scopes of physics, chemistry and biology.^[1-4] For example, ferroelectrics require the non-centrosymmetric alignment of electric dipoles, and ferromagnetism needs spins to be coupled nominally in the same direction.^[2-3] One-dimensional carbon-based nanostructures have attracted a lot of attention because their electronic or magnetic properties can in principle be controlled by introduction of functional groups.^[5,6] Although on-surface synthetic techniques based on chemical reactions taking place on metal surfaces under ultrahigh vacuum (UHV) conditions have succeeded in creating various types of polymers, all those reported so far are limited to nonpolar structures.^[7-11] To create the novel class of electronically asymmetric polymers, predicted to bear promising functionality for new applications,^[1-4] brand new synthetic methods are required since conventional on-surface synthesis techniques suffer from the difficulties of stereoregular polymerization of the precursors and the polar inter-strand order of the polymers. To overcome these challenges, we designed compass precursors which, due to their dipole, bonding and edge vectors, (Figure 3-1a) are capable of aligning their reaction intermediates in the same 2D vectorial direction which leads to isotactic polymers with the polar 2D crystalline structures under two-zone chemical vapor deposition (CVD). (Figure 3-1b)

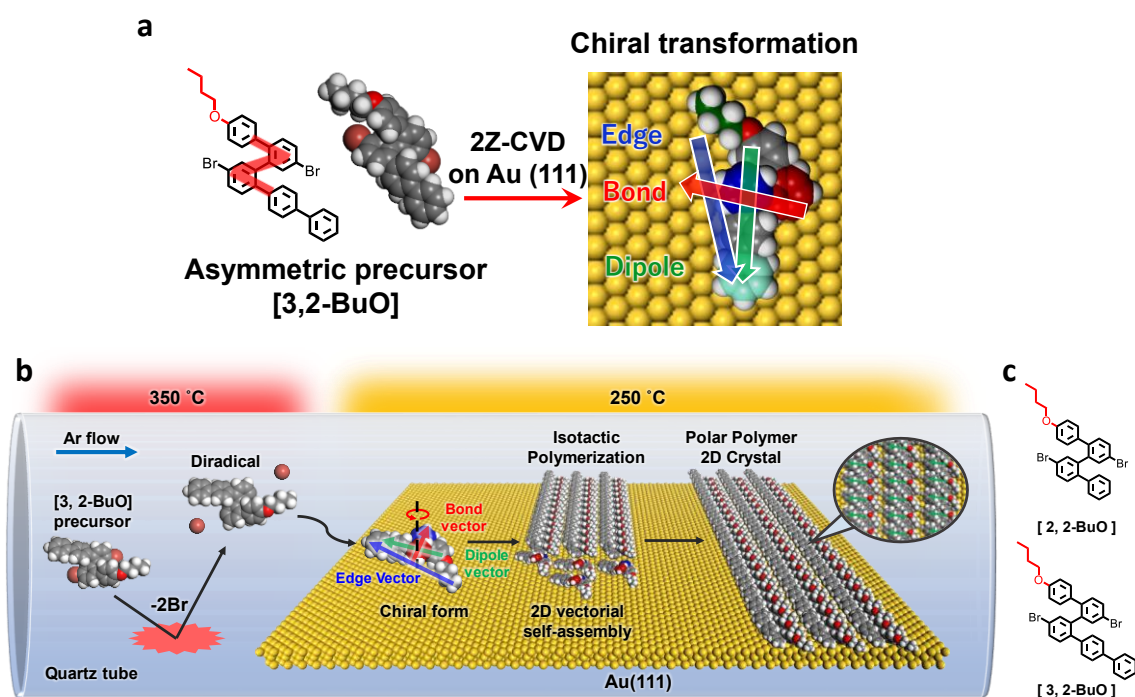


Figure 3-1. (a) New designed asymmetric Z-bar-linkage precursor [3,2-BuO] with 3 vectors. (b) Concept illustration of the vectorial on-surface synthesis of polar 2D polymer crystals. (c) Illustrations of the chemical compounds utilized in this study.

3.2 Experimental

3.2.1 General information

The experimental details of this chapter have been described in Chapter 2. Calculations in this chapter were performed using the BIOVIA Materials Studio software suite (Dassault Systèmes SE.).

3.2.2 Scanning tunneling microscopy image simulation

The STM image simulations were performed on crystal systems. The structure was optimized by molecular mechanics (MM) prior to DFT calculation. The Forcite module was used for the MM calculation with the COMPASS II force field. The CASTEP module was used for DFT structural optimization and STM calculations, the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE) was used as the exchange correlation functional employing on-the-fly-generated (OTFG) Ultrasoft pseudopotentials.

3.2.3 Adsorption simulation on Au(111)

100 different adsorption structures were calculated by the Monte Carlo method with a unit cell (46.24 x 40.05 x 49.72 Å) containing a three-layer gold substrate and a vacuum layer of 45 Å. The adsorption simulation was performed with the Adsorption Locator module based on the MM method, and COMPASS III was used for the force field. The precursor molecule was used as the initial structure. The obtained 100 structures were classified into four types, "ud", "du", "dd", and "uu", according to the difference in height between

the two benzene rings at the molecule's hinge. One of each of the four structure types was optimized by the quantum mechanics / molecular mechanics (QM/MM) method (with the QMERA module). The DMol3 module and GGA-PBE exchange correlation functional were used to calculate the properties of the QM atoms and GULP was used to calculate the properties of the MM volumes employing the ReaxFF 6.0 force field.

3.2.4 Electrostatic potential mapping calculation

Electrostatic Potential (ESP) mapping calculation was conducted on hydrogen-terminated polymer 5mer models, using for the charge density and dipole estimation calculations. In the DMol3 module, a hybrid B3LYP functional with an all-electron core DN basis set was used. The grid interval was set to 0.25 Å, the orbital cutoff distance was set to 3 Å and the multipolar expansion was set to hexadecapole.

3.2.5 Calculation of polymer inter-chain interaction energy

A unit cell (7.40 x 80.00 x 30.00 Å) was prepared, and two GNR strands were placed. Fine structural optimization calculation was performed by CASTEP module. DFT structural optimization and STM calculations, the Perdew-Burke-Ernzerhof generalized-gradient approximation (GGA-PBE) was used as the exchange correlation functional employing on-the-fly-generated (OTFG) Ultrasoft pseudopotentials. The energy landscapes were constructed from the energy calculations performed at each polymer strand coordinate. Inter-strand distance was set as the defined position of X and Y.

3.3 Results and discussion

3.3.1 Design strategy of 3-vectorial building blocks

Z-bar-linkage type precursors (molecules possessing two polyphenylene branches linked at hinge positions that look like the letter ‘z’) were used in this study. The backbone of these precursors allows them to adopt various conformations due to their flexibility at the hinge position while simultaneously holding rigid polyphenylene branches. Our previous work found that two-zone CVD of the symmetric z-bar-linkage precursor 4'',5'''-dibromo-1,1':4',1'':2'',1''':2''',1''':4''',1''':6'''-sexiphenyl resulted in the formation of homochiral polymers and their following conversion into covalently edge graphene nanoribbons (GNRs).^[12] The key to the success of this process is believed to be the dynamic chirality of the precursor's diradical in which the achiral (C_{2h}) forms in the gas phase might be transformed into chiral (C_1) forms when deposited on the metal surface. In this study, 3-vectorial; C_s symmetry z-bar-linkage precursors with three vectors (dynamic chirality-driven bond (polymerization) vector, unidirectional intermolecular force-inducing edge vector and electronic asymmetry-inducing dipole vector) are designed to create polar polymers. The two strategies implemented in designing the asymmetric precursors are the length control of the polyphenylene branches and the introduction of the electronic asymmetry-inducing butoxy (abbreviated to -BuO) functional group. The n in the $[n, m]$ notation refers to the number of benzene units in the z-bar-linkage precursor's aryl branch and the m refers to the number of benzene units in the modifier

functional group branch. According to our strategy, two kinds of asymmetric precursors were synthesized: [2, 2-BuO] (4',5"-dibromo-4-butoxy-1,1':2',1":2",1'''-quaterphenyl) and [3, 2-BuO] (4',5"-dibromo-4-butoxy-1,1':2',1":2",1'''':4''',1''''-quinquephenyl) (Figure 3-1c).

3.3.2 Stereoregular on-surface polymerization

The on-surface polymerization of [2, 2-BuO] and [3, 2-BuO] precursors was attempted using our two-zone CVD technique.^[13] Two-zone CVD is based on the independent control of temperatures at precursor sublimation (T_{pre}), tube hot wall (T_{wall}) in zone 1 and Au(111) substrate (T_{sub}) in zone 2 to optimize the yield of products (Figure 3-2). To identify the produced species, ex-situ low-temperature scanning tunneling microscopy (LT-STM) measurements at 77 K under UHV conditions were conducted on samples transferred from the two-zone CVD apparatus. LT-STM images of two-zone chemical vapor deposited [2, 2-BuO] precursors on Au(111) at a T_{sub} of 250 °C reveal the formation of linear strands with dots at their edges (Figure 3-3a). The spacing of the dots along each strand's side is measured to be 0.74 nm (Figure 3-3b) and its width is found to be 1.72 nm (Figure 3-3c). These values are in good agreement with those based on the [2, 2-BuO] polymer structure shown in Figure 3-3d. By analyzing the magnified LT-STM images as shown in Figure 3-3e, two kinds of dot patterns - single dots depicted in green and unequally sized pairs of dots, referred to as 'binary', marked red - are seen at the edges along the strands. Moreover, the positions of the dots appearing at one side of the strands and those on opposite sides are found to be roughly

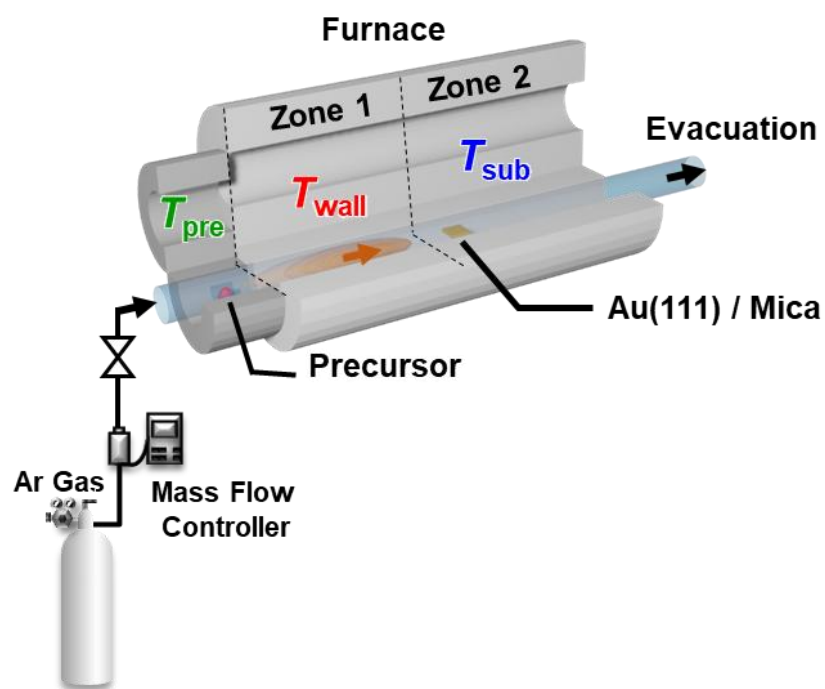


Figure 3-2. Experimental setup of two-zone CVD.

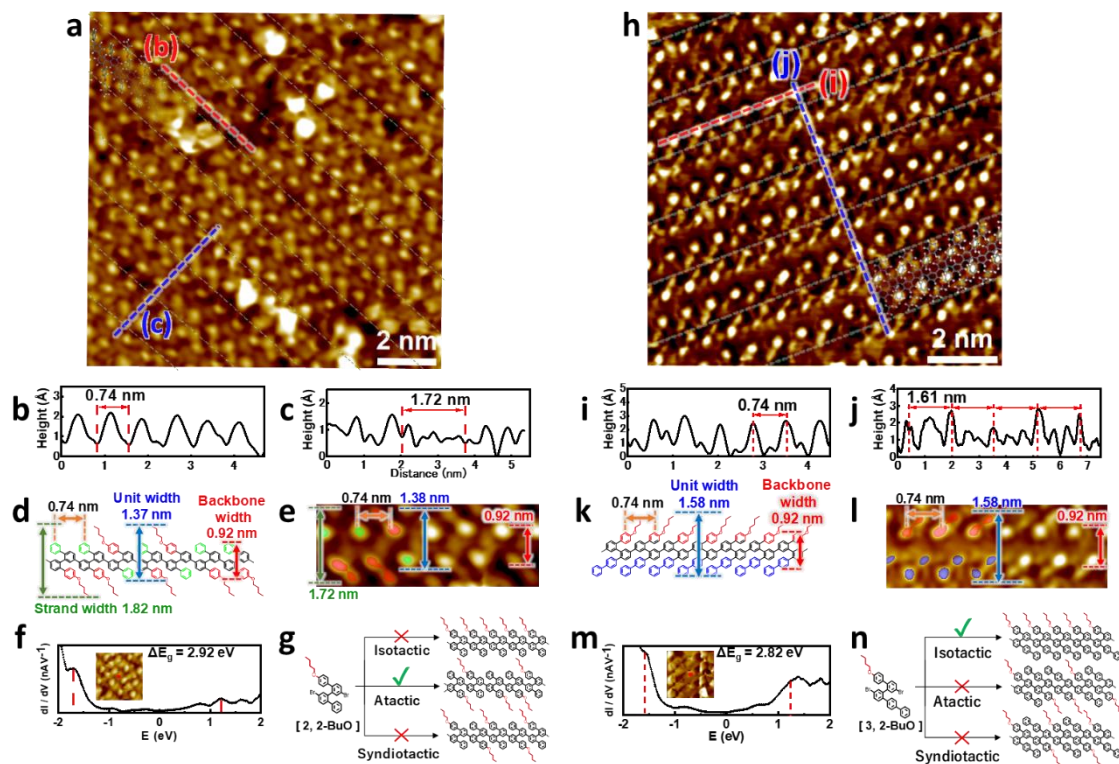


Figure 3-3. Stereoregular on-surface polymerization. (a, h) LT-STM images and superimposed structures of [2, 2-BuO] (Bias voltage = -0.51 V, feedback current = 580 pA) and [3, 2-BuO] (-0.11 V, 580 pA) polymer strands. The white lines indicate strand boundaries and the red and blue dotted lines mark the locations of the lateral and perpendicular topographic analysis paths, respectively. (b, i) Topographic profiles of the red lines in (a) and (h). (c, j) Topographic profiles of the blue lines in (a) and (h). (d, k) Chemical structures of [2, 2-BuO] and [3, 2-BuO] polymers. (e, l) Magnified LT-STM images of single [2, 2-BuO] (-0.75 V, 300 pA) and [3, 2-BuO] (-0.11 V, 580 pA) polymer strands. Green dots indicate edge phenyl groups, red binary dots indicate the butoxyphenyl groups and the twinned blue dots represent the biphenyl groups. (f, m) 5 times averaged STS profiles of [2, 2-BuO] and [3, 2-BuO] polymers. The insets indicate the STS measurement locations (red dots). The band gap is estimated from the difference in potentials of the peaks indicated by red dotted lines. (g, n) [2, 2-BuO] and [3, 2-BuO] polymer tacticity. [2, 2-BuO] precursors undergo atactic polymerization while [3, 2-BuO] precursors undergo isotactic polymerization.

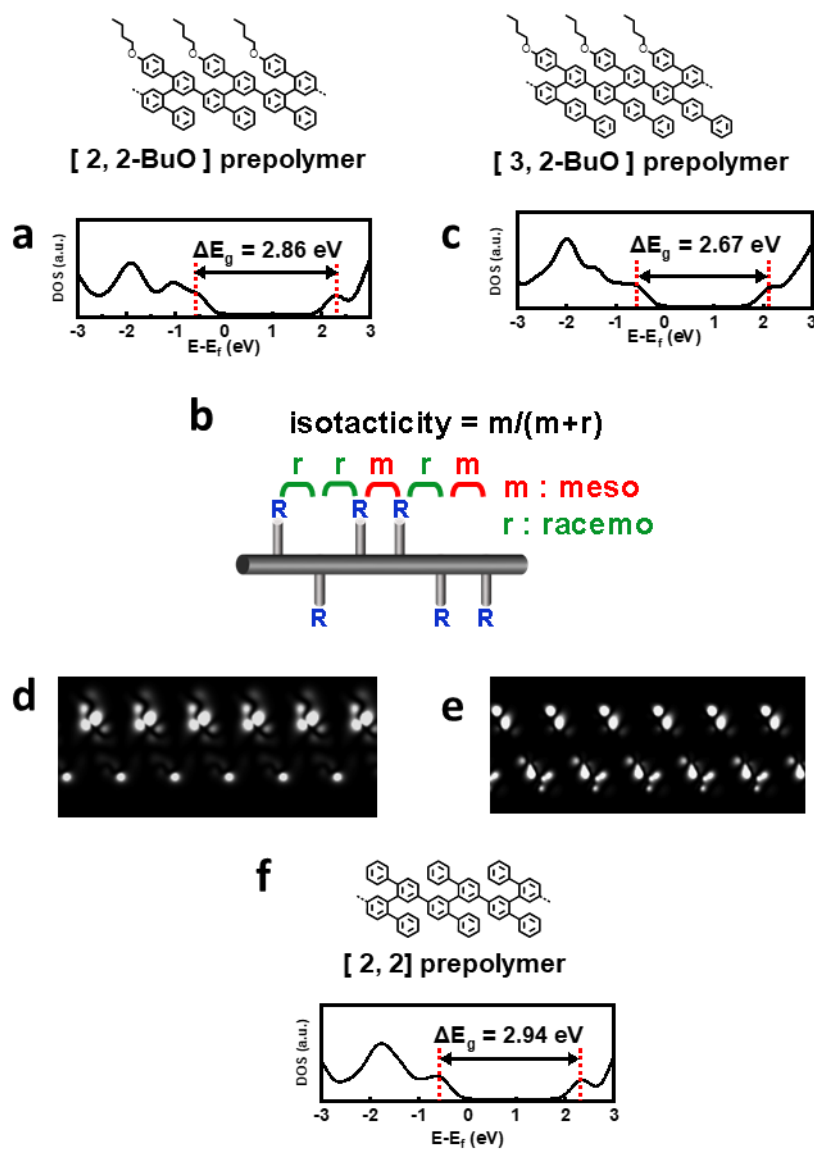


Figure 3-4. Polymer DOS and STM simulations and tacticity. (a, c and f) Simulated density of states (DOS) of [2, 2-BuO], [3, 2-BuO] and [2, 2] polymers indicating the band gap values. b, Illustration of the method used to calculate isotacticity. (d, e) Simulated STM images of isotactic [2, 2-BuO] and [3, 2-BuO] polymers.

180° out of phase relative to each other. These results suggest that the binary dots correspond to the butoxyphenyl group, whereas the single dots are attributed to the edge phenyl groups (Figure 3-3d, e) supported by the STM simulation (Figure 3-4d). According to the results of scanning tunneling spectroscopy (STS), the bandgap of [2, 2-BuO] is found to be 2.92 eV, as depicted in Figure 3-3f. This closely resembles the bandgap of poly-p-phenylene on Au(111), which is 3.23 eV.^[14] The density functional theory (DFT) predicted the bandgap value of [2, 2-OBu] to be 2.86 eV, as seen in Figure 3-4a. The simulated HOMO and LUMO energy levels are located at -0.58 and +2.28 eV, respectively, which are akin to those of [2, 2] without the butoxy group (Figure 3-4f), which are -0.60 and +2.34 eV, correspondingly. Furthermore, the simulation of [2, 2-BuO] revealed the appearance of the HOMO+1 peak at -1.04 eV, indicating the contribution of the butoxy group. Next, we focus on the stereoregularity of the [2, 2-BuO] polymer. In general, polymer stereoregularity is categorized into three types: atactic, in which the asymmetric substituents are randomly arranged along the polymer backbone, alternately arranged in syndiotactic and unidirectionally arranged in the isotactic conformation (Figure 3-3g).^[15] The LT-STM image shown in Figure 3-3e provides evidence that the polymer strands are atactic because the strand substituents appear to be joined in random orientations. Using a definition of $m / (m + r)$, where m and r denote meso and racemo consecutive substituent ordering, respectively, as shown in Figure 3-4b,^[15] the overall isotacticity of [2, 2-BuO] polymers is assigned a value of 0.76 (Figure 3-3a).

LT-STM images of samples produced by two-zone CVD using [3, 2-BuO]

precursors (Figure 3-3h) reveals that the dots' spacing is 0.74 nm along the strand (Figure 3-3i) similar to that of [2, 2-BuO], however, a larger unit width of 1.61 nm (Figure 3-3j) is observed (compared with [2, 2-BuO]'s value of 1.38 nm as shown in Figure 3-3e). These values are in good agreement with those based on the [3, 2-BuO] polymer chemical structure depicted in Figure 3-3k. Different from [2, 2-BuO] polymers, high-resolution LT-STM images of [3, 2-BuO] polymers clearly show that two kinds of dots exist exclusively at the opposite sides of the strands; binary dots represented in red appearing at one side of the strand, while similarly sized 'twinned' dots depicted in blue are seen at the opposite side (Figure 3-3l) supported by the STM simulation (Figure 3-4e). The dots are also roughly 180° out of phase. These results suggest that the binary dots correspond to the butoxyphenyl group, whereas the twinned dots are attributed to the biphenyl group at the edge of the other side (Figure 3-3k, l). Based on STS analysis, the products indicate a bandgap of 2.82 eV (Figure 3-3m) which is in good agreement with the DFT predicted value of 2.67 eV using the [3, 2-BuO] polymer model (Figure 3-4c). These results imply that [3, 2-BuO] polymers were successfully formed. In stark contrast to [2, 2-BuO], analysis of the substrate's LT-STM images (Figure 3-3h, l) demonstrates that the isotacticity of [3, 2-BuO] polymers is unity, as the asymmetric substituents are arranged in a unidirectional manner each along only one side of the polymer backbone (Figure 3-3n). This perfect isotacticity implies that the [3, 2-BuO] precursors spontaneously organize themselves unidirectionally -analogous to compass behavior- and then undergo radical coupling reactions to form covalent bonds.

3.3.3 Mechanism of stereoselective on-surface polymerization

We conducted a theoretical study with practical accuracy using quantum mechanics/molecular mechanics (QM/MM) simulations on the conformation of the precursor diradical on Au(111) as the polymer intermediate. Our aim is to understand the reason behind the isotactic polymerization in [3, 2-BuO] precursors compared to [2, 2-BuO] based on our previous report.^[12] The conformation simulation on the [3, 2-BuO] and [2, 2-BuO] precursor diradicals generates eight chiral isomers in both precursor cases categorized by two important factors: axis chirality (horizontal-axis chirality and vertical-axis chirality)^[16] and enantiomerism (right-handed (R) and left-handed (S)) as shown in Figure 3-5a and Figure 3-6. Consequently, the eight isomers are named as a combination of the relative heights of the two hinge benzenes with regard to the Au(111) plane; if the height of one of the benzenes at the hinge is distant from the aforementioned plane, it is denoted as ‘u’ (up), whereas if it is located closer to character belongs the benzene of the aryl branch, which is denoted in blue, while the second letter belongs to the butoxy-group branch benzene which is denoted in red. Horizontal-axis chirality covers the [uu] and [dd] conformers which possess a chiral axis parallel to the Au(111) plane. On the other hand, the vertical-axis chirality group contains the [ud] and [du] conformers whose chiral axis is normal to the Au(111) plane. Additionally, the energy of all conformers was calculated by QM/MM to assess their thermodynamic stability. As a result, the [2, 2-BuO] precursor diradical favors the [dd] conformer on the Au(111) surface (Figure 3-5b) while the [3, 2-BuO] precursor diradical favors the [ud] conformer form (Figure 3-5c). Due to the

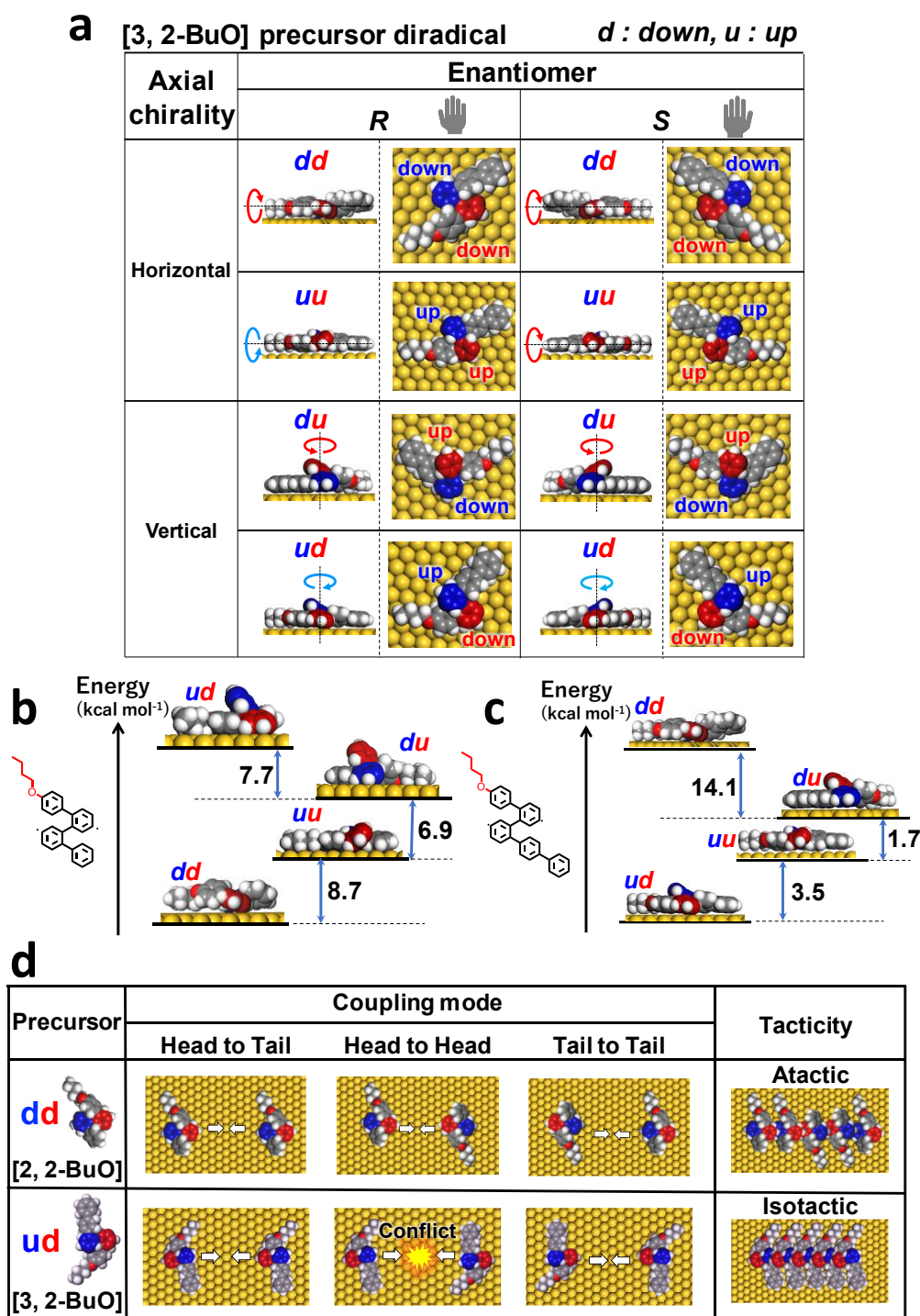
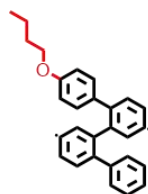


Figure 3-5. Mechanism of stereoregular on-surface polymerization. (a) DFT predicted conformers of [3, 2-BuO] precursor diradicals on Au(111). (b, c) Energy diagrams of the optimized [2, 2-BuO] and [3, 2-BuO] precursor diradical conformers on Au(111) highlighting the energy difference between them. (d) [2, 2-BuO] and [3, 2-BuO] precursor diradicals' coupling modes.



[2, 2-BuO] precursor diradical

d : down, u : up

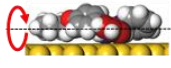
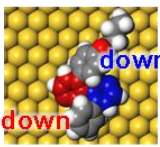
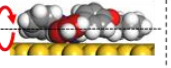
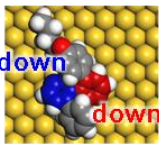
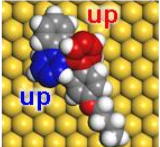
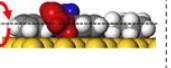
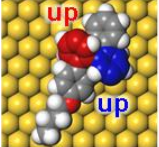
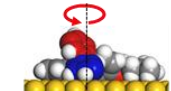
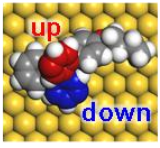
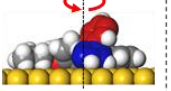
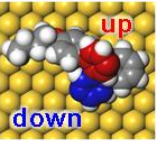
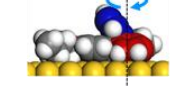
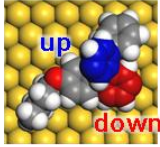
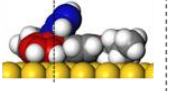
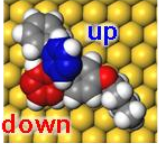
Axial chirality	Enantiomer			
	<i>R</i>		<i>S</i>	
Horizontal				
				
Vertical				
				

Figure 3-6. DFT predicted conformers of [2, 2-BuO] precursor diradicals on Au(111).

difference in the metal-molecule interaction strength between the polar butoxy group and the nonpolar phenyl groups, the butoxy group branch is expected to adhere to the metal surface in contrast to the aryl branch benzenes which may levitate above the Au(111), resulting in the driving force behind the conformation change of the precursor diradicals.

The coupling reactions' modes were investigated using the previously generated chiral conformers to elucidate the stereoregular polymerization. Coupling reactions cover three modes: head-to-head, head-to-tail and tail-to-tail.^[17] Homo-coupling of the horizontally axial ($[dd]+[dd]$) [2, 2-BuO] precursor diradicals can adopt all three coupling modes due to the lack of steric hindrance between the coupling radicals, suggesting that atactic polymerization based on randomly oriented monomers should take place (Figure 3-5d). In sharp contrast, homo-coupling of the vertically axial ($[ud]+[ud]$) [3, 2-BuO] precursor diradicals exhibits no steric hindrance in the head-to-tail and tail-to-tail modes, while the head-to-head mode is disturbed (Figure 3-5d). Polymer growth can only proceed in head-to-tail mode since the tail-to-tail mode causes strand termination, resulting in isotactic polymerization. These considerations support the experimental results, where the [2, 2-BuO] polymers are atactic (Figure 3-3g), while the [3, 2-BuO] polymers are isotactic (Figure 3-3n). According to previous in-solution studies, isotactic polymerization of asymmetric monomers (i.e. propylene) requires chiral catalysts such as Zeigler-Natta or metallocene which can coordinate and direct monomers for polymerization.^[18,19] Our on-surface isotactic polymerization does not require chiral catalysts because the z-bar-linkage

precursors spontaneously alter their shapes into chiral forms to unidirectionally align themselves.

3.3.4 UHV on-surface synthesis of [3, 2-BuO] polymers

In sharp contrast to the purely isotactic polymers obtained using two-zone CVD, LT-STM images of [3, 2-BuO] polymers prepared by the traditional UHV on-surface technique at 250 °C present mixtures of two kinds of polymers; those possessing chain-dot spacing of 0.75 nm (isotactic) and 1.48 nm in the other (syndiotactic; alternating sequential orientation) (Figure 3-7 a-c).

It is well known that cleaved bromine atoms adhere to Au(111) under UHV on-surface synthetic techniques' conditions^[20,21] which might alter the conformation of [3, 2-BuO] precursor diradicals on Au(111),^[22] resulting in a change of coupling modes. Contrary to the UHV on-surface technique, two-zone CVD can provide large bromine-free Au(111) surfaces indicated by weak bromine XPS signals in the sample (Figure 3-8). The reason behind the low bromine-Au(111) contamination might be the result of the separation of the molecular cleavage and polymer growth zones and the exhaust of the bromine atoms in the argon gas flow^[12] in contrast to the UHV techniques where the halogens are trapped. This feature of two-zone CVD makes it a prerequisite for on-surface isotactic polymerization. (Figure 3-9)

After thermal annealing at 400 °C, carbon monoxide-functionalized tip constant-height LT-STM images of in-situ synthesized polymers using the UHV apparatus reveal the formation of GNRs of two kinds reflecting the

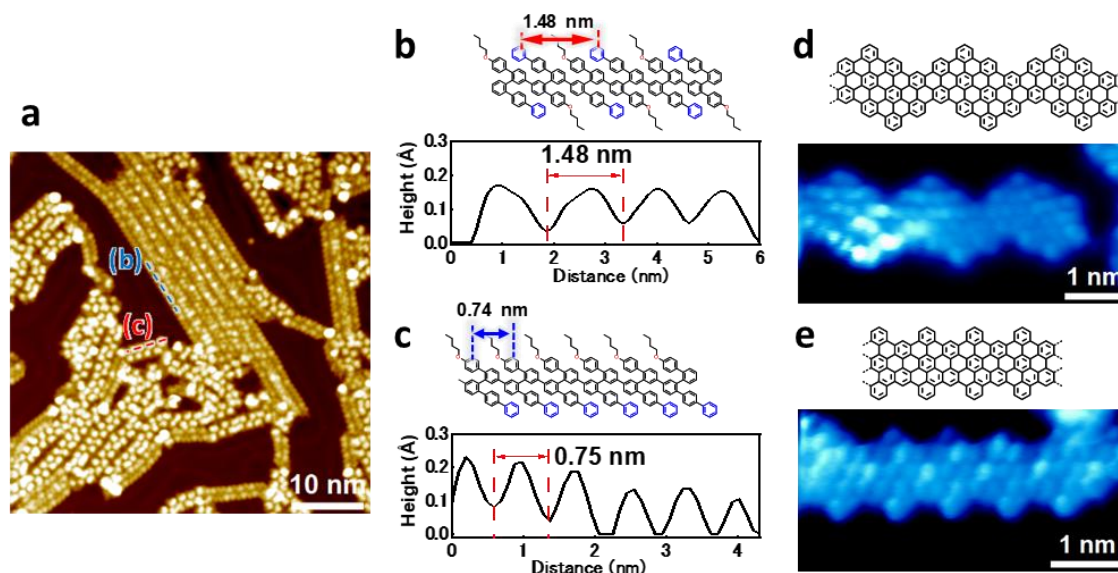


Figure 3-7. UHV on-surface synthesis of [3, 2-BuO] polymers. (a) LT-STM (4K) image of [3, 2-BuO] polymer (-0.20 V, 10 pA) produced via the UHV deposition method at a substrate temperature of 250 °C. (b, c) Topographic profiles of the lines in (a) demonstrating the different dot spacing between syndiotactic (1.48 nm) and isotactic (0.75 nm) polymer aggregates. The expected chemical structures are illustrated. (d, e) Constant-height dI/dV images (1 mV, 10 pA) using a CO-functionalized tip of selected strands of UHV deposited [3, 2-BuO] polymers annealed at 400 °C and their expected chemical structures.

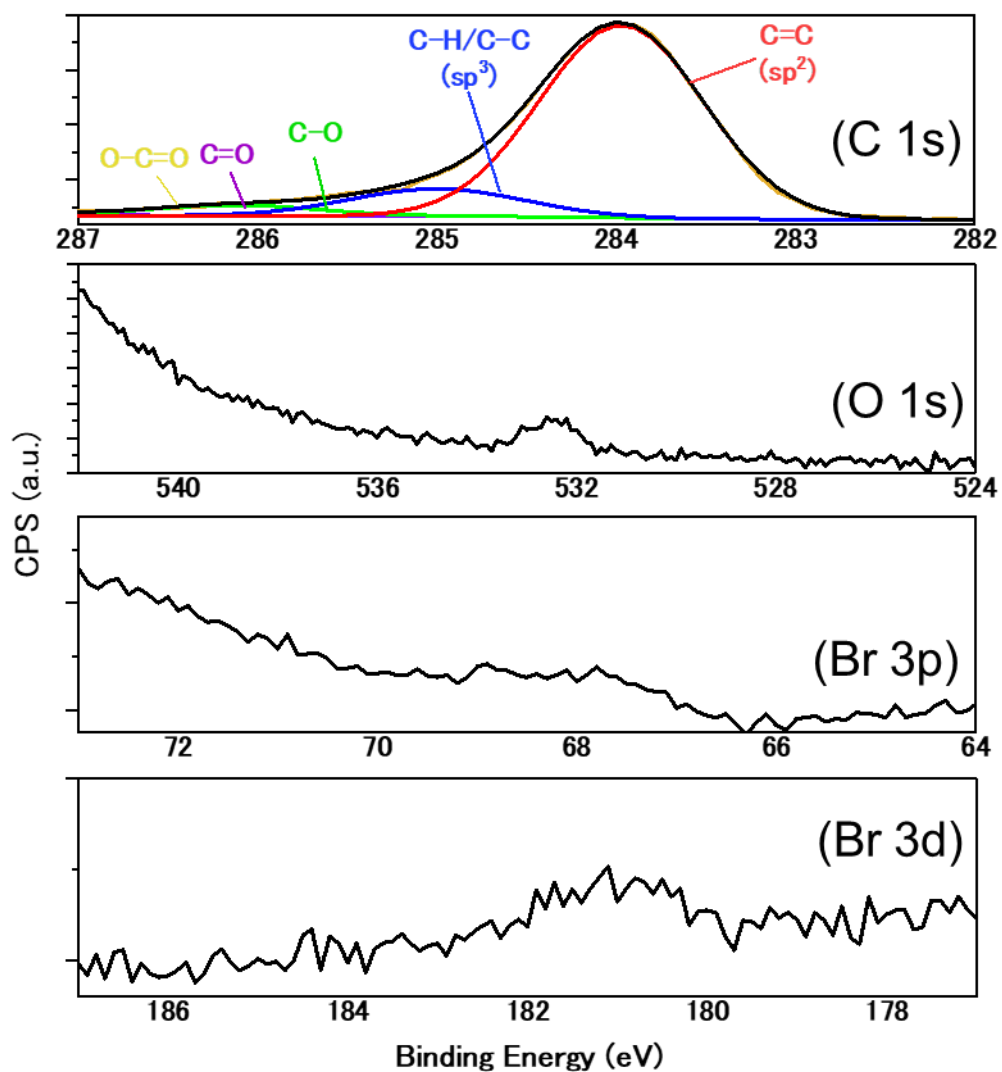


Figure 3-8. C1s, O1s, Br3d and Br3p XPS spectra of [3, 2-BuO] polymer. The spectrum in the top is deconvoluted into 5 carbon bonding modes.

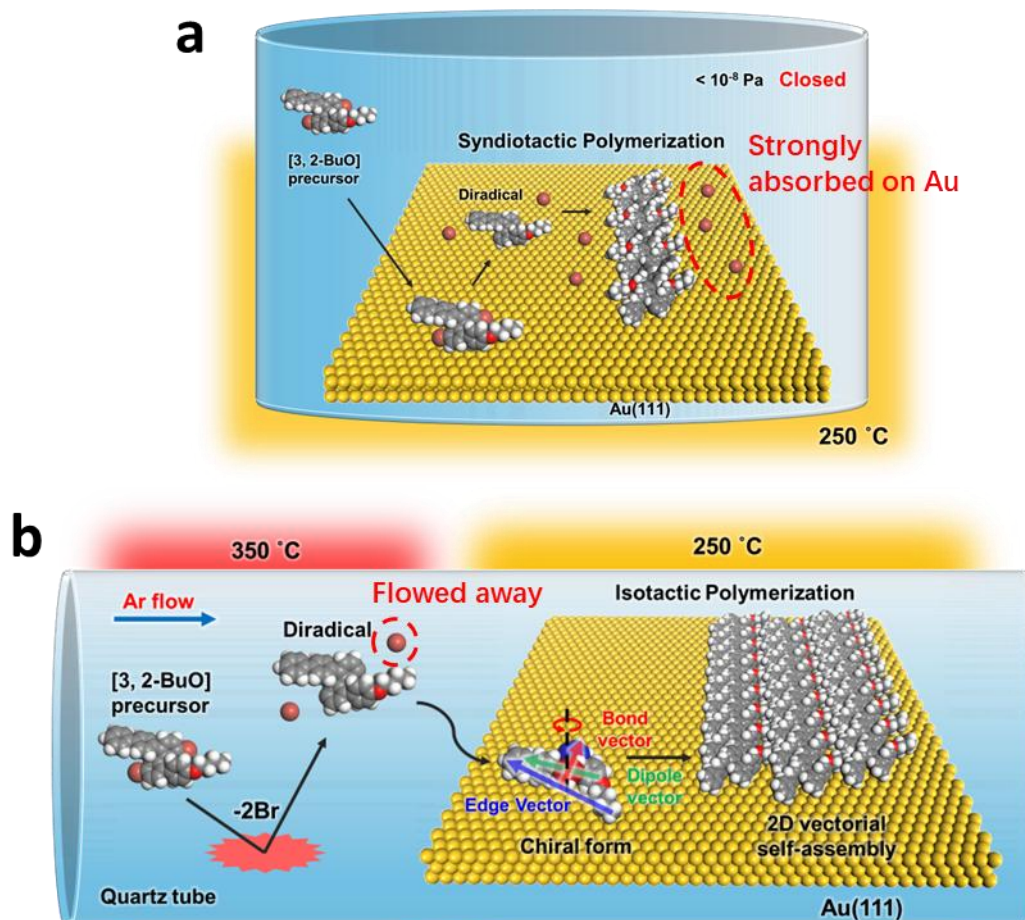


Figure 3-9. Comparison between (a) UHV method and (b) 2Z-CVD method to explain why 2Z-CVD can achieve isotactic polymerization but UHV cannot.

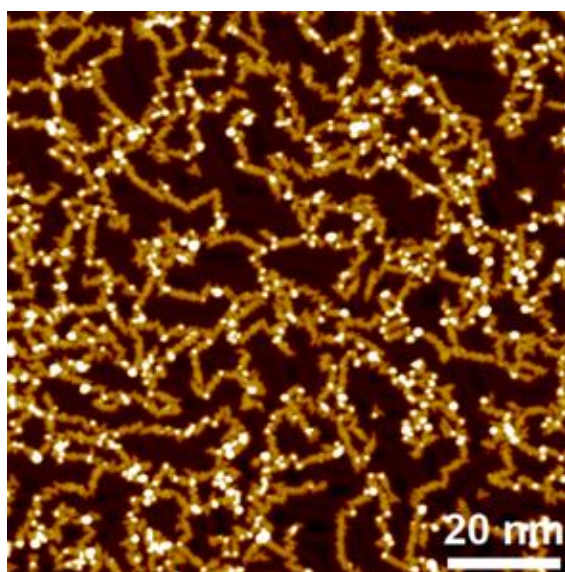


Figure 3-10. LT-STM (-0.20 V, 10 pA) image of UHV deposited [3, 2-BuO] polymer annealed at 400 °C.

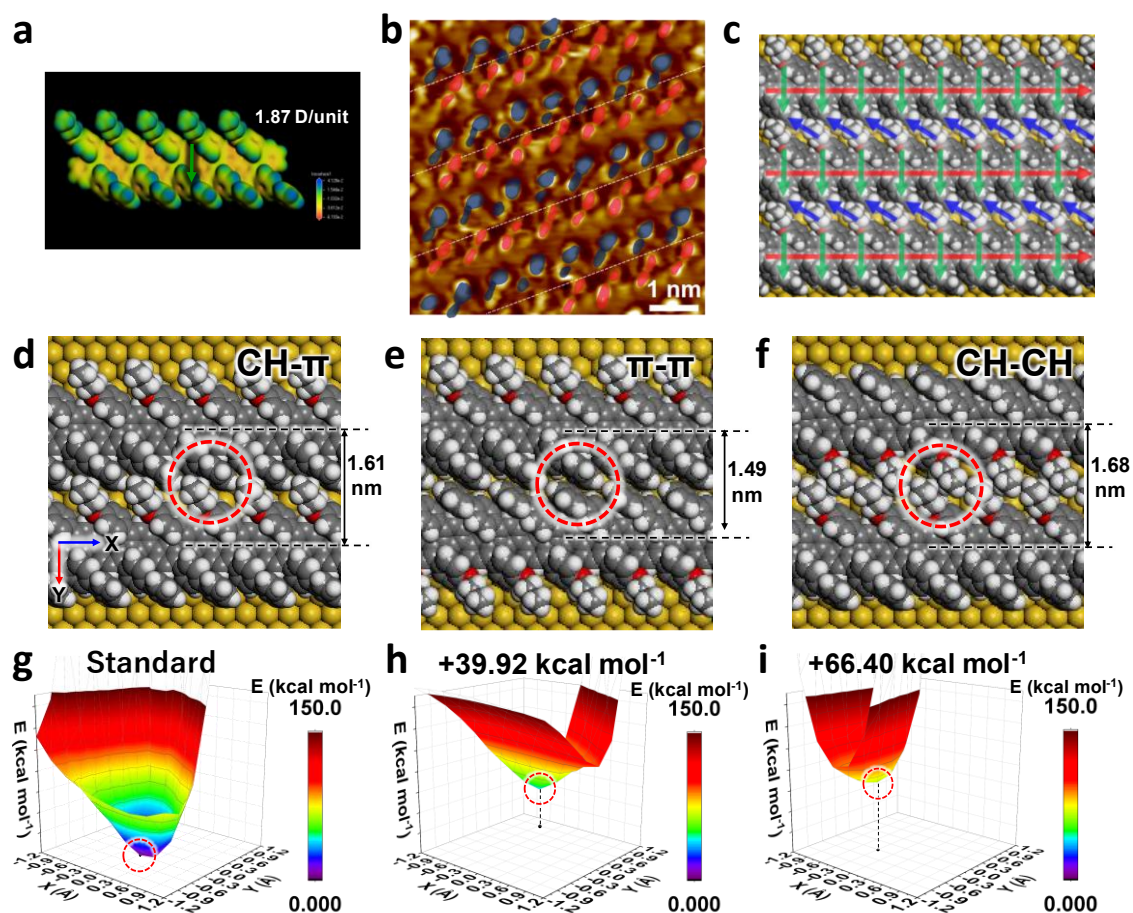


Figure 3-11. Polar 2D polymer crystals. (a) Simulated electrostatic potential map of a [3, 2-BuO] 5mers. The green arrow indicates the per-monomer electric dipole of 1.87 Debye. (b) STM image of [3,2-BuO] polymer shows non-centrosymmetric crystal (c) Illustration of a polar 2D polymer crystal domain. The red, blue and green arrows represent the bonding, edge and dipole vectors, respectively. (d-f) Illustrated interaction models of the optimized [3, 2-BuO] polymers indicating the optimum strand spacing for each interaction mode. The secondary polymer displacement axes are illustrated in (d). The red dotted circles indicate the typical interacted position. (g-i) Contour maps of edge-group interaction energy as a function of X and Y displacement. The red dotted circles indicate the minimum energy at the optimum inter-strand distances.

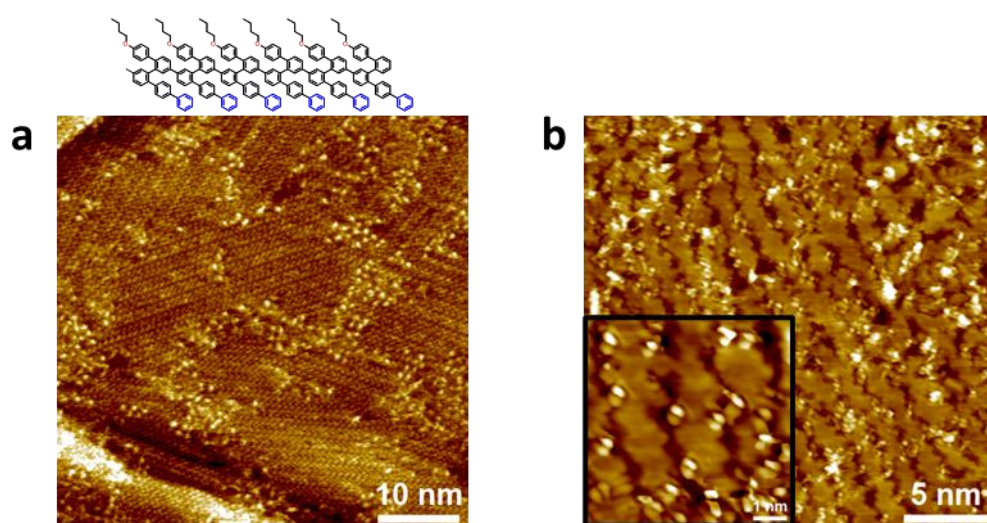


Figure 3-12. (a) Large area LT-STM image of [3, 2-OBu] polymer strands (-0.30 V, 580 pA). (b) LT-STM image of [3, 2-OBu] (-0.028 V, 580 pA) polymers traditionally annealed at $T_{\text{sub}} = 400\text{ }^{\circ}\text{C}$.

tacticity of their parent polymers; isotactic and syndiotactic (Figure 3-7d, e, 3-9). The lack of functional groups in these GNRs provides evidence for their decomposition, proving that UHV synthesis is not suitable for creating asymmetric isotactic polymers.^[23-25]

3.3.5 Polar 2D polymer crystals

The simulated electrostatic potential mapping of [3, 2-BuO] polymers suggests that the per-monomer unit electric dipole is 1.87 Debye virtually perpendicular to the strand axis (Figure 3-11a). As the maximum observed length of strands measured in the LT-STM images of [3, 2-BuO] Polymers (Figure 3-12a) is 35.3 nm (corresponding to 47 monomer units), strands are estimated to possess dipole moments of 88 Debye. To achieve thermodynamic stability, strands of polar polymers such as polyvinylidene difluoride (PVDF) tend to orient in an antiparallel manner to reduce the overall polarization.^[26] On the contrary, the STM image of [3, 2-BuO] polymers (Figure 3-11b) showed the unusual non-centrosymmetric 2D crystalline symmetry group in which every domain's strands' electric dipoles align unidirectionally virtually perpendicular to the strands' (Figure 3-11c). In addition, the observed inter-strands' uniform 1.61 nm spacing (Figure 3-3j) also supports the proposed polar 2D-crystal domains model. Consequently, the 2D polar polymer agglomerates can be categorized into the P1 space group. It is well known that dielectric materials can be categorized according to the point groups of their crystals.^[27] Among the 32 crystal symmetry point groups, 21 are non-centrosymmetric and can further belong to the special property classes of

piezoelectric, pyroelectric and ferroelectric materials.^[27] Thus, the 2D crystals of [3, 2-BuO] polymers are believed to be pyroelectric since their structure is non-centrosymmetric and polar. A theoretical study based on the inter-chain interaction energies of two molecular groups (aryl and alkyl) was conducted on [3, 2-BuO] polymers to identify the reason for the overall polar inter-chain arrangement of the [3, 2-BuO] polymers. Three modes of inter-chain interactions can be considered, CH- π interactions (Figure 3-11d), π - π (Figure 3-11e) and CH-CH interactions (Figure 3-11f).^[28-30] The energy for the three interaction modes was calculated by DFT using the generalized gradient approximation of the Perdew-Burke-Ernzerhof (GGA- PBE) functional which accounts for the noncovalent molecular interactions without solid surfaces.^[31] In this calculation one strand's coordinates were fixed and the second's was placed in close proximity to the fixed one and its location adjusted in small increments in the X and Y directions (Figure 3-11d). DFT energy calculations were performed at all secondary strand coordinates. Assigning the energy minimum value (CH- π , Figure 3-11g) to zero, the relative energy landscapes based on this model reveal the energy difference for the other two interaction modes' minimum values to be 39.92 kcal mol⁻¹ for π - π (Figure 3-11h), and 66.40 kcal mol⁻¹ for CH-CH (Figure 3-11i). The optimized strands' geometry at the minimum energy for the three modes is represented in Figure 3-11 d-f. Among the three modes of interaction, the CH- π mode possesses the least energy, suggesting that the structure resulting from it -the polar crystalline structure- is the most energetically favorable. The theoretical study also estimates that the inter-strand distance in the optimized CH- π configuration is

1.61 nm (Figure 3-11d). In principle, π - π interactions are known to be stronger than CH- π interactions and CH-CH interactions in solutions.^[28] However, the results we obtained deviate from the norm. The reason behind this phenomenon presumably originates from steric hindrance; narrow spaces resulting from the massive edge-phenyl groups hinder π - π inter-chain interaction by forbidding the approach of neighboring strands' phenyl groups (Figure 3-11e). As a result, [3, 2-BuO] polymers express the unusual CH- π chemical interaction rather than that of π - π or CH-CH.

3.4 Conclusion

To summarize, the alignment of polymer strands in their crystal domains is a result of two of the precursors' three vectors. The bond vector aligns the diradicals along the polymerization 'latitude' based on the energetic stability of the precursors' chiral conformities. The asymmetry vector of the edge butoxy and phenyl groups provides 'longitudinal' inter-chain forces due to inter-strand edge group interaction, which we call '2D vectorial self-assembly.' This process is capable of producing polar crystals (as shown in Figure 3-11b,c). These findings open up the possibility of creating polar 2D assemblies of 3-vectorial building blocks, which could lead to a new approach in polar crystal engineering.^[32]

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Chapter 4

Molecular-Vapor-Assisted Low-Temperature Growth of Graphene Nanoribbons

4.1 Introduction

Graphene nanoribbons (GNRs), one-dimensional carbon-based materials, have attracted much attention because theoretical studies predict various functions controlled by their widths and edge structures.^[1–6] Conventional on-surface synthesis, using ultra-high vacuum (UHV) deposition, has created various types of GNRs, including armchair,^[7–10] zigzag,^[11] and chiral edge structures,^[12,13] as well as junctions of different widths, and heteroatom-doped GNRs.^[14–17]

On-surface synthesis of GNRs involves two steps, including polymerization of precursor and dehydrogenation reactions.^[18,19] Dehydrogenation requires high temperature because its mechanism is apparently catalytic, in which a metal substrate extracts hydrogens from prepolymers contacting the surface.^[20,21] Dehydrogenation reactions at high temperatures suffer from side reactions that yield undesired products and decompose functional substituents,^[22–24] which are theoretically predicted to introduce ferroelectricity and ferromagnetism^[3–6] into GNR backbones. Traditional thermal annealing at high temperatures reportedly decomposes functional groups such as cyano^[22] and fluorine^[23,24] during dehydrogenation of prepolymers into GNRs. Therefore, a new dehydrogenation reaction at lower temperature, independent of metal surface catalysis is desired.

Dehydrogenation reactions known as “Scholl reactions” in solution synthesis use a strong oxidant such as 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) or ferric chloride to extract hydrogens from precursor molecules, creating C-C bonds between adjacent benzene rings toward fused aromatic hydrocarbons.^[25] Thus, we developed a new process called molecular-vapor-assisted, low-temperature growth (MVLTG) in a gas-solid interface system, inspired by the Scholl reaction in solution, to convert polar polymer to polar GNRs under low temperature (Figure 4-1a,b). MVLTG is based on a massive excess of gaseous hydrogen-accepting molecules (DDQ or oxygen) relative to the prepolymer on the metal surface at lower temperature to greatly enhance dehydrogenation of GNRs with high efficiency due to direct collisions between the molecular vapor and prepolymers.(Figure 4-1c,d) In contrast, it has been reported that oxygen adsorbed on Cu(111) promotes dehydrogenation of polyparaphenylene,^[26] and that atomic hydrogen adsorbed on Au(111) enhances C-C covalent bond formation of polycyclic aromatic hydrocarbons.^[27] These reactions are believed to involve collision of reactants on the solid surface,^[28] which may limit reaction efficiency. So far as we know, there are no reports regarding GNR on-surface synthesis by exposure of reactive molecules at the gas-solid interface. Additionally, MVLTG successfully promoted dehydrogenation reactions of prepolymers

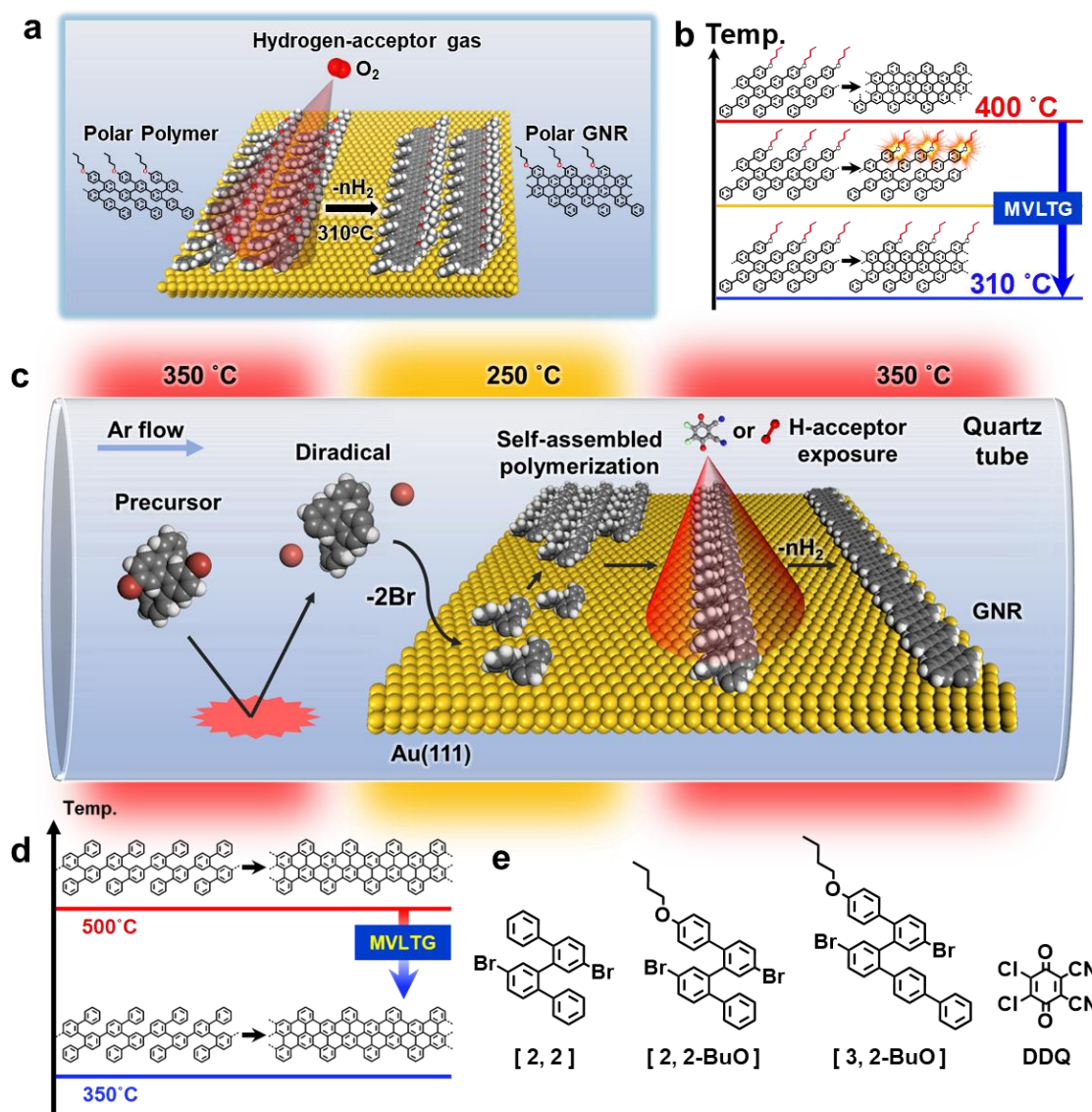


Figure 4-1. (a) Concept illustration of molecular-vapor-assisted low-temperature growth (MVLTG) of polar graphene nanoribbons. (b) Dehydrogenation temperatures for [3,2-BuO] prepolymer under traditional annealing (red lines) and MVLTG (blue lines). (c) Schematic representation of the MVLTG synthesis process from symmetric Z-bar-linkage precursor, indicating the precursor diradical formation and consequent polymerization via two-zone CVD. Subsequent steps indicate the MVLTG process (dehydrogenation) and conversion to GNRs. (d) [2, 2] Prepolymer dehydrogenation temperatures for traditional annealing (red lines) and MVLTG (blue lines). (e) Illustrations of chemical compounds utilized in this study.

made from functionalized precursors of [3,2-BuO] or [2,2-BuO], producing asymmetric GNRs with controlled stereoregularity by suppressing decomposition of substituents. MVLTG not only realizes a new class of GNRs but also enables unprecedented on-surface synthesis.

4.2 Experimental

4.2.1 General information

The experimental details of this chapter have been described in Chapter 2. The kinetic studies were conducted using MATLAB[®].

4.2.2 Kinetic studies

We use the *dsolve* function found in MATLAB[®] to provide an analytical solution to the system of partial differential equations. The grid search protocol starts with an initial grid of values and proceeds to guess the closest set of parameters by minimizing the size of the grid with every iteration until it zeroes in on the optimum set of parameters. To estimate the goodness-of-fit for the resulting set of parameters, we use the correlation coefficient R^2 for evaluation.

We began modelling kinetics of the MVLTG reaction by identifying participating compounds. Based on transient-state STM images (see Figure 4-3 in Chapter 4), we identified four distinct phases:

- (i) Precursor polymer or prepolymer (*PP*),
- (ii) Partially-fused GNR (*pGNR*),

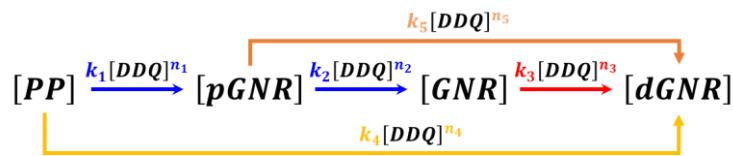
(iii) Full GNR (*GNR*), and

(iv) Degraded GNR (*dGNR*)

Using Raman spectra obtained experimentally, we are able to estimate the rates at which each of the phases proceed to the next and terminate. Thus, by trial-and-error, we propose the following empirical model to best represent the kinetics of the DDQ MVLTG reaction. In a similar manner, we model the reaction kinetics of the oxygen MVLTG reaction with the same phases of transition (*PP*, *pGNR*, *GNR*, *dGNR*). Note that oxygen has a reduced oxidation potential compared to DDQ. Thus, we do not observe side reactions leading to degradation of the GNR chains. The reaction time is also significantly longer. With these considerations in mind, we propose the following empirical model. We use the *dsolve* function found in MATLAB[®] to provide an analytical solution to the system of partial differential equations.

(1) Reaction modeling

(i) DDQ MVLTG



Where, for $i = 1, 2, 3, 4, 5$; k_i : Reaction rate constant

n_i : order

The system of differential equations is as follows.

$$\frac{\partial}{\partial t} [PP] = -k_1[DDQ]^{n_1}[PP] - k_4[DDQ]^{n_4}[PP] \quad (\text{Eq. 1})$$

$$\frac{\partial}{\partial t}[pGNR] = k_1[DDQ]^{n_1}[PP] - k_2[DDQ]^{n_2}[pGNR] - k_5[DDQ]^{n_5}[pGNR] \quad (\text{Eq. 2})$$

$$\frac{\partial}{\partial t}[GNR] = k_2[DDQ]^{n_2}[pGNR] - k_3[DDQ]^{n_3}[GNR] \quad (\text{Eq. 3})$$

$$\frac{\partial}{\partial t}[dGNR] = k_3[DDQ]^{n_3}[GNR] + k_4[DDQ]^{n_4}[PP] + k_5[DDQ]^{n_5}[pGNR] \quad (\text{Eq. 4})$$

Where,

$i: 1,2,3,4,5$

k_i : Reaction rate constant

n_i : order

The DDQ MVLTG analytical solution is as follows.

$$[GNR](t) = \frac{[DDQ]k_1k_2e^{-t([DDQ]k_2+[DDQ]k_5)}}{\sigma_1(k_2 - k_4 + k_5 - [DDQ]k_1)} - \frac{[DDQ]k_1k_2e^{-t(k_1[DDQ]^2+k_4[DDQ])}}{\sigma_2 + \sigma_3} + \frac{[DDQ]k_1k_2e^{-[DDQ]^2k_3t}}{\sigma_1(k_4 + [DDQ]k_1 - [DDQ]k_3)} \quad (\text{Eq. 5})$$

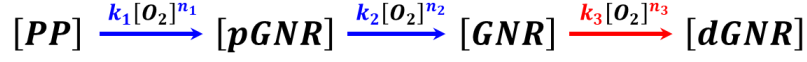
Where,

$$\sigma_1 = k_2 + k_5 - [DDQ]k_3$$

$$\sigma_2 = k_2k_4 + k_4k_5 - k_4^2 - [DDQ]^2k_1^2 + [DDQ]k_1k_2 - 2[DDQ]k_1k_4 - [DDQ]k_2k_3$$

$$\sigma_3 = [DDQ]k_1k_5 + [DDQ]k_3k_4 - [DDQ]k_3k_5 + [DDQ]^2k_1k_3$$

(ii) O₂ MVLTG



Where, for $i = 1, 2, 3$; k_i : Reaction rate constant

n_i : order

The system of differential equations is as follows.

$$\frac{\partial}{\partial t} [PP] = -k_1[O_2]^{n_1}[PP] \quad (\text{Eq. 6})$$

$$\frac{\partial}{\partial t} [pGNR] = k_1[O_2]^{n_1}[PP] - k_2[O_2]^{n_2}[pGNR] \quad (\text{Eq. 7})$$

$$\frac{\partial}{\partial t} [GNR] = k_2[O_2]^{n_2}[pGNR] - k_3[O_2]^{n_3}[GNR] \quad (\text{Eq. 8})$$

$$\frac{\partial}{\partial t} [dGNR] = k_3[O_2]^{n_3}[GNR] \quad (\text{Eq. 9})$$

Where,

$i: 1, 2, 3$

k_i : Reaction rate constant

n_i : order

O₂ MVLTG analytical solution is as follows.

$$[GNR](t) = \frac{k_1 k_2 e^{-[O_2]k_3 t}}{(k_2 - \sqrt{[O_2]}k_3)(k_1 - k_3)} - \frac{k_1 k_2 e^{-[O_2]k_1 t}}{(k_2 - \sqrt{[O_2]}k_1)(k_1 - k_3)} + \frac{\sqrt{[O_2]}k_1 k_2 e^{-\sqrt{[O_2]}k_2 t}}{(k_2 - \sqrt{[O_2]}k_1)(k_2 - \sqrt{[O_2]}k_3)} \quad (\text{Eq. 10})$$

(2) Grid search protocol

The grid search protocol starts with an initial grid of values and proceeds to guess the closest set of parameters by minimizing the size of the grid with every iteration until it zeroes in on the optimum set of parameters. For our problem, we run the grid optimization on the set of rate constants $[k_1, k_2, k_3, k_4, k_5]$ while choosing an order set $[n_1, n_2, n_3, n_4, n_5]$ by trial-and-error (Figure 4-12).

(3) Goodness-of-fit

To estimate the goodness-of-fit for the resulting set of parameters, we use the correlation coefficient R^2 for evaluation. We calculate R^2 according to the following equation.

$$R^2 = 1 - \frac{\sum_i (z_i - f_i(x_i, y_i))^2}{\sum_i (\bar{z}_i - f_i(x_i, y_i))^2} \quad (\text{Eq. 11})$$

Where,

z_i : *Experiment data point*

$\bar{z}_i$: *Mean of experimental data*

$f_i(x_i, y_i)$: *Corresponding curve data point*

This parameter has been used in a number of publications related to kinetic parameter estimation to calculate the goodness-of-fit.

4.3 Results and discussion

4.3.1 Demonstration of molecular-vapor-assisted low-temperature growth of GNRs

We previously designed a Z-type precursor containing two rigid polyphenylene branches and a flexible hinge like the letter “z”.^[29] Using our developed two-zone CVD^[30] (Figure 4-2a), we found that 4'',5'''-dibromo-1,1':4',1'':2'',1'':2''',1''':4''',1''''-sexiphenyl, symmetric Z-type precursors with C_{2h} symmetry adopting chiral conformations on Au(111) were polymerized into homochiral polymers, followed by conversion to cove-type GNRs by annealing at 500 °C.^[29]

In this study, we apply MVLTG (Figure 4-3a) using multiple exposure times of a controlled amount of vaporized DDQ as a hydrogen acceptor to prepolymers made from symmetric Z-type precursors of 4',5''-dibromo-1,1':2''chemi',1'':2''-quaterphenyl (abbreviated as [2, 2], Figure 4-1d, the numbers in the $[n, m]$ notation refer to the number of benzene units in the two branches of the Z-shaped precursor). The concentration of vaporized DDQ was monitored by a temporal profile of light transmission of deposited DDQ solid using a laser and photodiode placed at the outlet of the quartz tube (Figure 4-3a and 4-4).

An LT-STM image of [2, 2] prepolymers (Figure 4-3b) alters the periodic dot structures corresponding to polyphenylenes to those consisting of flat strands with dots at either edge after four 0.5-mg DDQ doses at 350 °C (Figure 4-3c). Observed dots in the flat strands after DDQ addition are assigned to

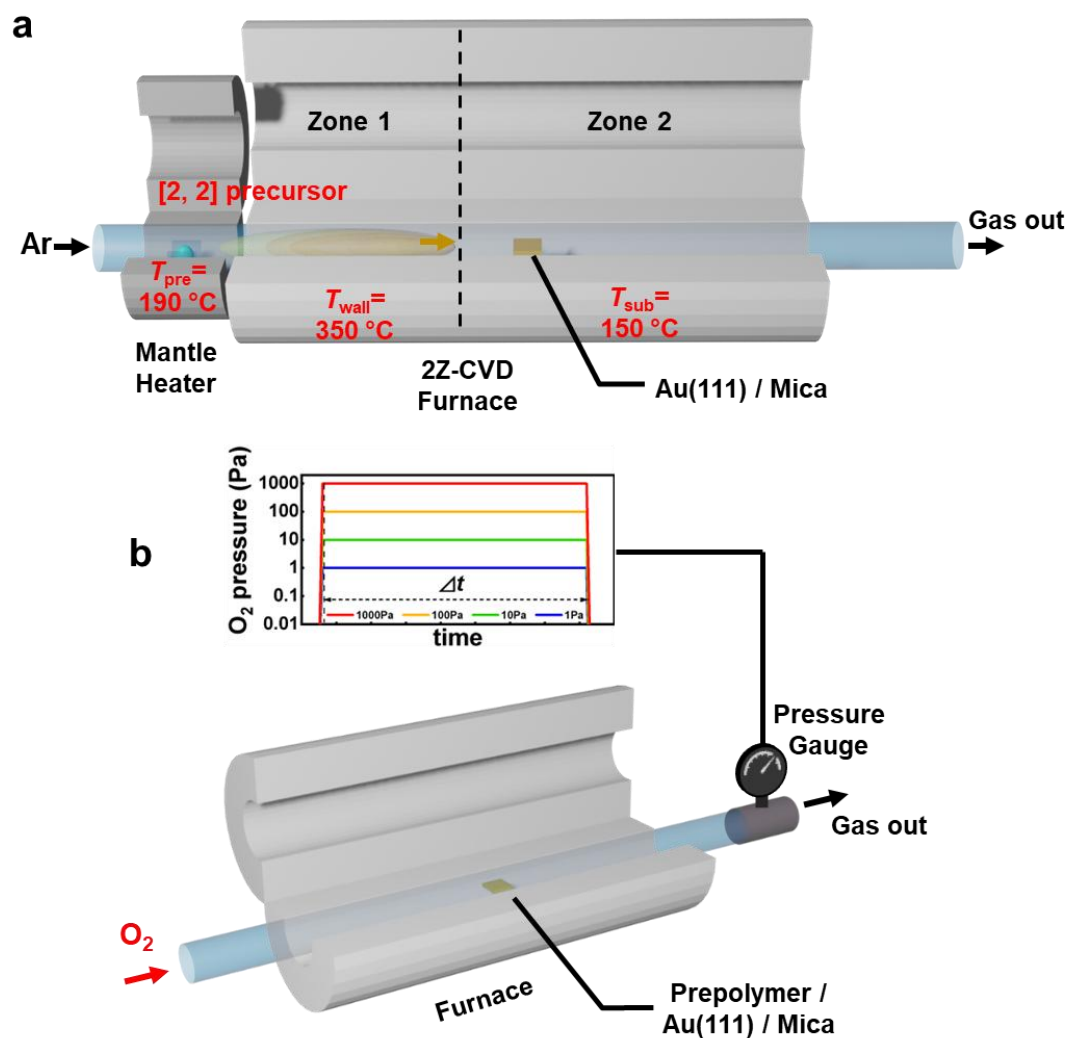


Figure 4-2. Experimental setup of (a) two-zone CVD to produce the prepolymer. (b) The oxygen dose MVLTG system with inset showing the temporal profile of oxygen exposure.

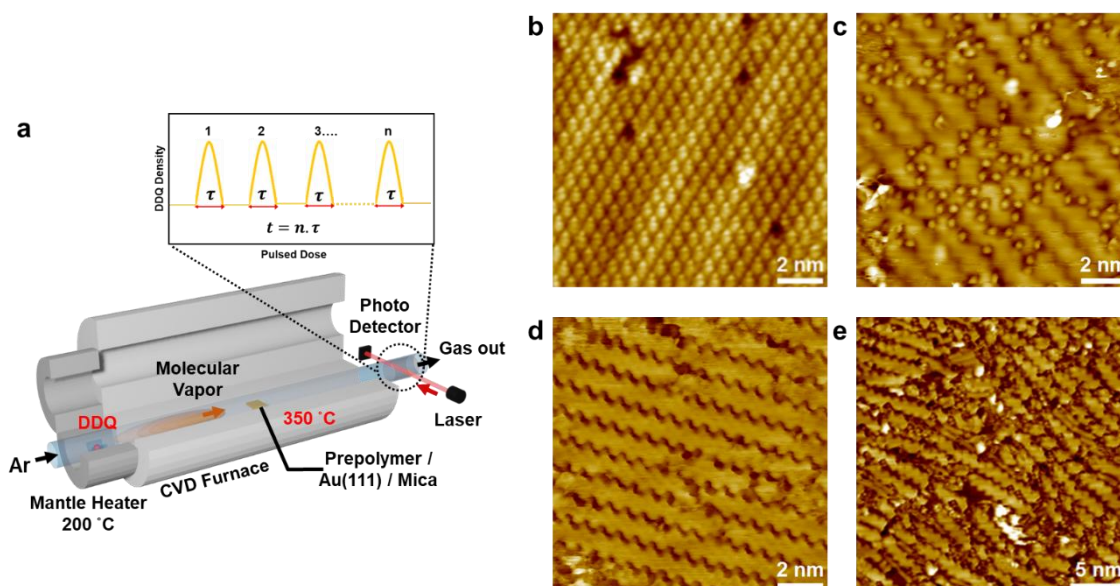


Figure 4-3. (a) Experimental setup of MVLGTG using DDQ as a hydrogen acceptor. The concentration of vaporized DDQ was monitored by a temporal profile of light transmission at end of the quartz tube using a laser and photodiode. LT-STM images of (b) [2, 2] prepolymers annealing at 350 °C, (c) 4 cycles of 0.5-mg DDQ treatment of (a) at 350 °C, (d) 8 cycles of 0.5-mg DDQ treatment of (a) at 350 °C, and (e) 12 cycles of 0.5-mg DDQ treatment of (a) at 350 °C.

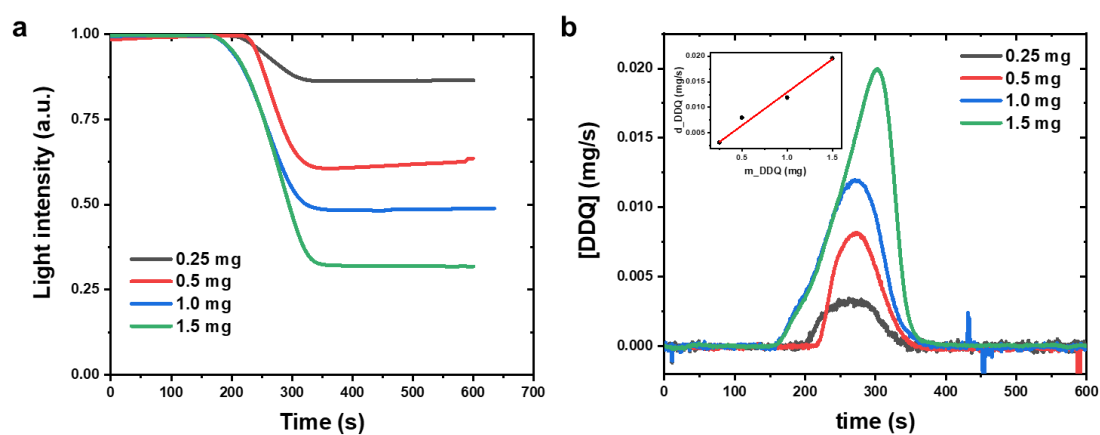


Figure 4-4. (a) Monitoring of deposited DDQ at the end of the quartz tube using an optical transmission technique. (b) Temporal profile of calculated DDQ mass flux. Inset shows the flux versus the input DDQ amount.

unfused phenyl groups in which three types of partially fused structures appear (Figure 4-5). Eight additions of 0.5 mg of gaseous DDQ alter the LT-STM image to that of stranded structures with regularly cove-shaped edges (Figure 4-3d), identical to cove-type GNRs produced by conventional thermal annealing at 500 °C.^[31] As a reference, LT-STM images of prepolymers without DDQ show no change before or after annealing at 350 °C (Figure 4-6). The disordered array of GNRs with shorter lengths appears after twelve additions of gaseous DDQ, suggesting decomposition of GNRs (Figure 4-3e).

Three characteristic peaks in Raman spectra^[32,33] of [2, 2] prepolymers grow with additional additions of DDQ (Figure 4-7a-c). DFT Raman simulation reproduces three peaks consisting of the G band, corresponding to an in-plane vibrational mode of sp^2 carbon, D_1 and D_2 bands corresponding to in-plane vibrational modes of edge carbons along the short and long axes of GNR, respectively (Figure 4-7e,f). Excess DDQ alters the Raman spectra with decreased intensities and broader peaks, suggesting decomposition of GNRs (Figure 4-7d). These Raman spectra are consistent with those of LT-STM. MVLTG demonstrates that gaseous DDQ exposure promotes dehydrogenation of prepolymers, converting them to GNRs at low temperatures.

Oxygen was studied as another gaseous hydrogen acceptor for MVLTG (Figure 4-2b). The LT-STM image of [2, 2] prepolymers at 350 °C with oxygen at 50 Pa for 60 min (Figure 4-8a) shows the flat strands with dots along the edges, suggesting partially fused GNRs. Continuous flat strands with cove edges corresponding to fully-fused GNRs appear at 50 Pa for 100 min (Figure 4-5b).

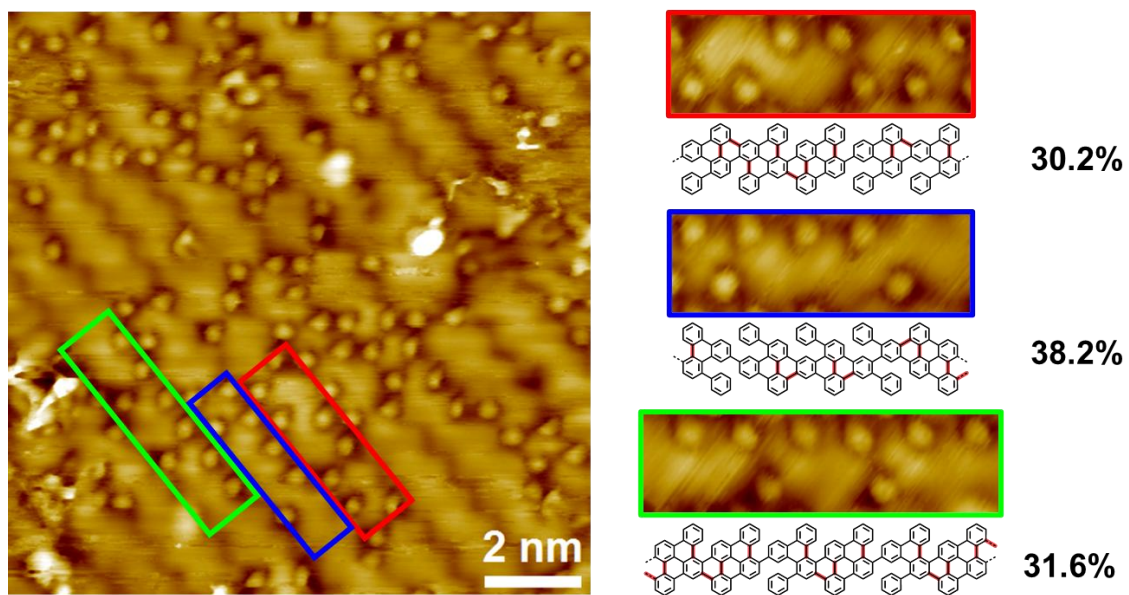


Figure 4-5. LT-STM image of partially fused [2,2] GNR strands with three chemical structures.

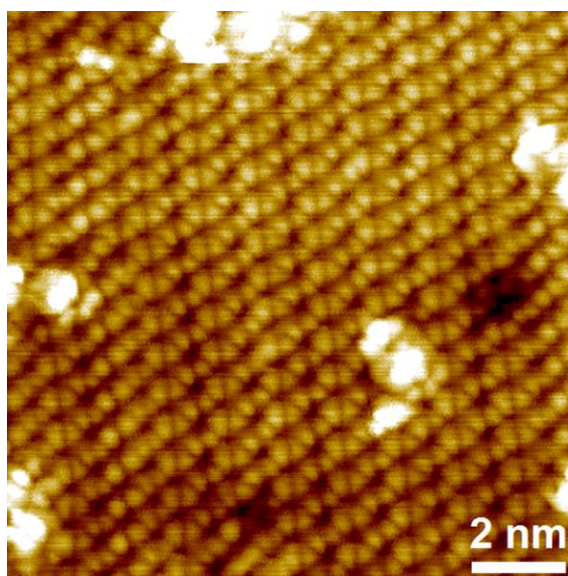


Figure 4-6. LT-STM image of [2, 2] prepolymer annealed at 350 °C (-0.35 V, 50 pA).

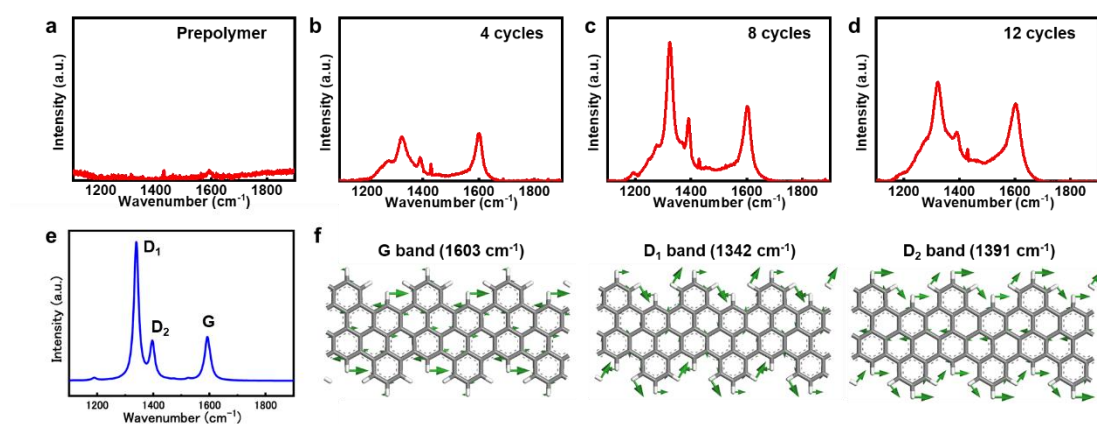


Figure 4-7. Experimental Raman spectra of (a) [2, 2] prepolymers, and (b-d) MVLTG treatment of (a) at 350 °C by exposure to 4, 8, and 12 additions of 0.5 mg DDQ, respectively. (e) DFT simulated Raman spectrum. (f) Illustration of the main vibration modes of the G band (1603 cm⁻¹), D₁ band (1342 cm⁻¹), and D₂ band (1391 cm⁻¹).

Disordered strands with short lengths attributed to decomposed GNRs appear under at 50 Pa for 180 min (Figure 4-5c). LT-STM images of these oxygen effects are consistent with those of DDQ, suggesting that oxygen acts as a hydrogen acceptor of MVLTG. The oxygen dose effect on Raman spectra also shows similar behavior of DDQ (Figure 4-9).

4.3.2 Mechanism of molecular-vapor-assisted dehydrogenation

Kinetic studies of MVLTG were performed by analyzing Raman spectra to clarify the mechanism. A gas-2D solid-state reaction system is considered a suitable model because the prepolymer on the metal surface is exposed to a gaseous hydrogen acceptor. This model is based on assumptions that (1) gaseous hydrogen acceptors immediately react with prepolymers on the solid surface, and (2) the Langmuir adsorption / desorption equilibrium^[28] is neglected due to the short diffusion length of hydrogen acceptors on the solid surface.

Four possible chemical species, prepolymer (PP), partially fused GNRs (pGNR), fully-fused GNRs (GNR) and decomposed GNRs (dGNR), are considered in a gas-2D solid-state reaction model, according to LT-STM and Raman spectra (Figure 4-10a). Reaction pathways of these models are defined to account for experimental data trends of the hydrogen-acceptor addition effect on Raman spectra. Reaction pathways for the DDQ-exposure model contain GNR growth and decomposition (Figure 4-10b). GNR growth is assumed to be sequential conversion from PP to pGNR followed by GNR. Decomposition into dGNR by excess DDQ exposure is assumed to occur from PP, pGNR, and GNR.

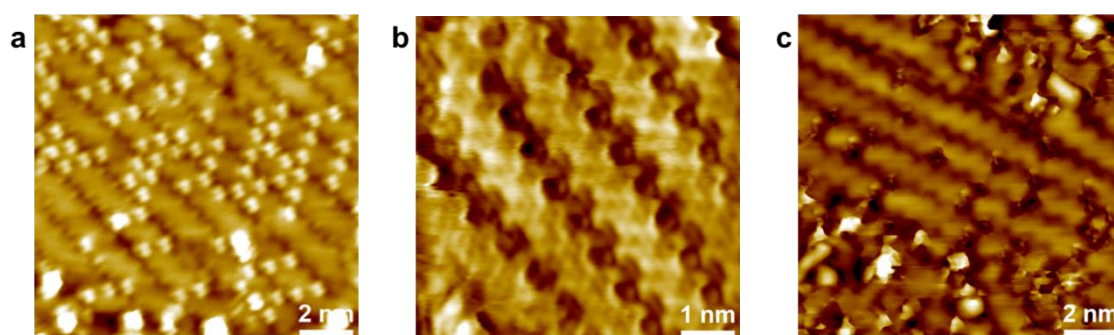


Figure 4-8. LT-STM images of 50 Pa oxygen dosed [2, 2] prepolymers of (a) 60 min (b) 100 min (c) 180 min at 350 °C.

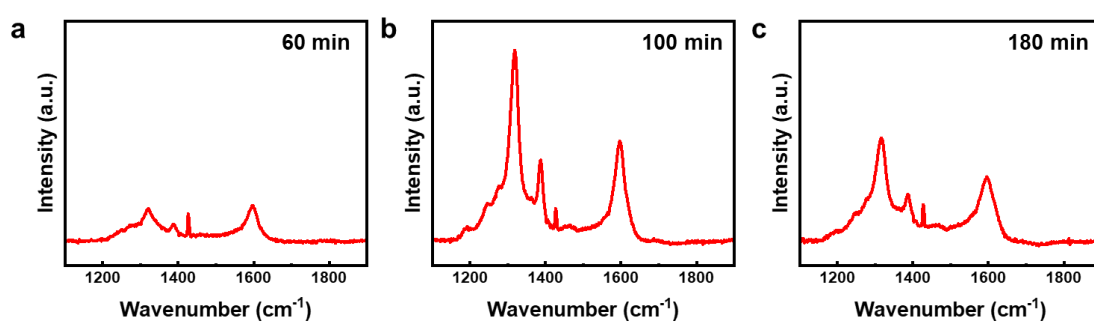


Figure 4-9. Raman spectra of 50 Pa oxygen dosed [2, 2] prepolymers of (a) 60 min (b) 100 min (c) 180 min at 350 °C.

Similarly, a model of oxygen MVLTG is proposed, such that decomposition to dGNR occurs only from GNR because Raman measurements did not show decomposition from PP and pGNR (Figure 4-10h).

Rate constants for each process and the reaction order of the hydrogen acceptor are defined as k and n , respectively. Rate equations are formularized according to reaction pathways in Section 4.2.2. The matrix of time-dependent GNR yield as a function of the hydrogen acceptor concentration, extracted from Raman spectra in MVLTG, is required to solve the rate equations (Figure 4-10c,i). After deconvolution of Raman spectra, GNR yield ($[GNR]$) can be estimated from the intensity of the D_2 peak, which is sensitive to GNR structure (Figure 4-11). The grid search algorithm (Figure 4-12) is applied to solve these differential equations. Grid search^[34,35] is essentially an optimization to guess the closest set of parameters by minimizing the grid size with every iteration until it zeroes in on the optimum set of parameters through trial-and-error. To solve our rate equations, the protocol of the grid search algorithm is conducted by inputting a range of rate constants. Then the error sum of squares (SSE) is calculated.^[36–38] Optimization continues until the deviation distribution between the experimental data and simulation reaches an acceptable goodness of fit. To determine the reaction orders (n_i) best fitting the experimental data, differential equations corresponding to a plausible combination of reaction order (n_i) should be solved using the grid search method. As a result, the optimal combination of reaction orders is $[2,1,2,1,1]$ ($R_2 = 0.92$) for the DDQ system, and $[1,0.5,1]$ ($R_2 = 0.91$) for the oxygen system (Figure 4-13).

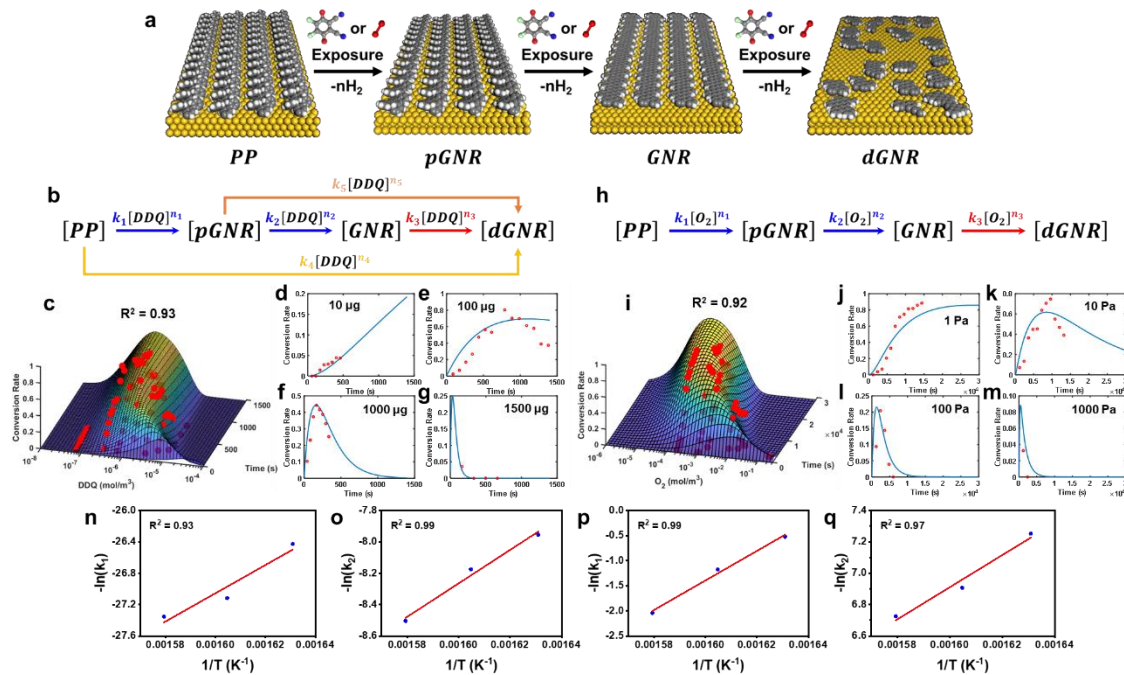


Figure 4-10. (a) Gas-2D solid reaction model illustration from prepolymer (PP) to degraded GNR (dGNR). Reaction pathways for MVLTG using (b) DDQ and (h) oxygen as hydrogen acceptors. Simulated 3D contour maps with experimental plot (red dots) of GNR yield (obtained from Raman spectra) as a function of hydrogen acceptor concentration and time under (c) DDQ and (i) oxygen MVLTG at 350 °C. (d-g, j-m) Temporal profiles of GNR yields (red dots) and simulation (blue curves) with different concentration of hydrogen acceptors (d-g) 10 μg , 100 μg , 1000 μg , 1500 μg of DDQ, and (j-m) 1 Pa, 10 Pa, 100 Pa, 1000 Pa of Oxygen. (n-q) Arrhenius plots of k_1 and k_2 for DDQ MVLTG (n,o), and oxygen MVLTG (p, q) at temperature from 340 °C to 360 °C.

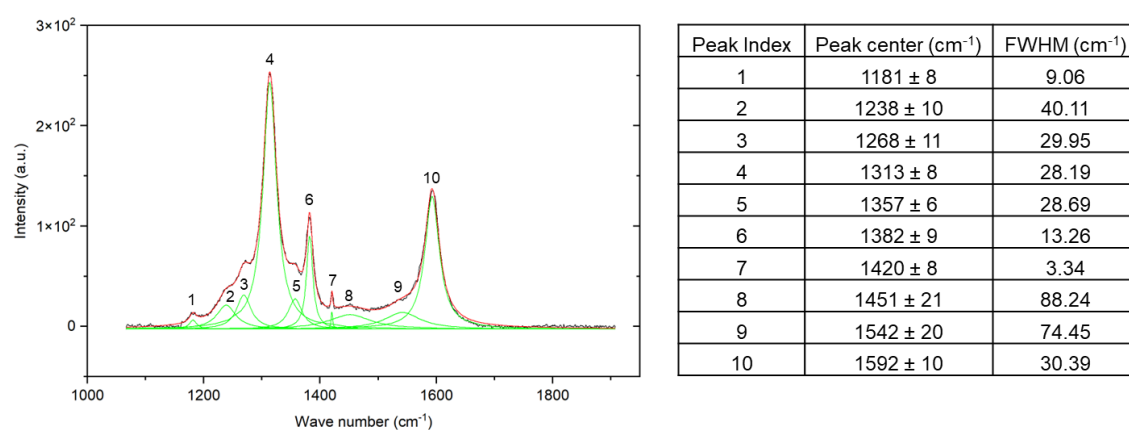


Figure 4-11. Deconvolution analysis of Raman spectrum of [2, 2] prepolymers after DDQ dose (0.5 mg, 8 cycles, 350 °C). Green lines show deconvoluted peaks and red line shows the fitted curve.

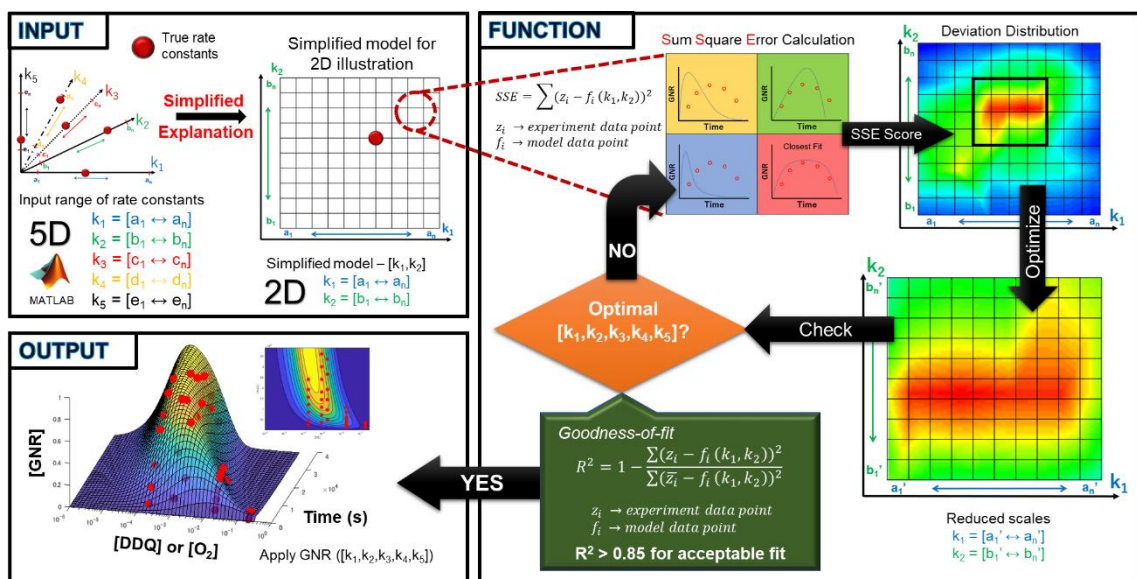


Figure 4-12. Schematic representation of Grid Search Protocol.

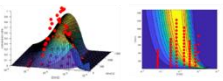
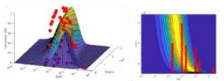
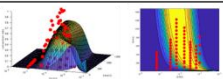
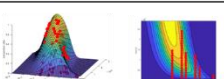
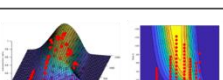
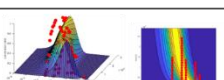
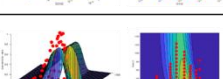
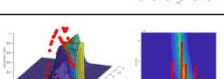
a			b		
DDQ MVLTG			O₂ MVLTG		
$[n_1, n_2, n_3, n_4, n_5]$	Model Fitting	Goodness-of-fit R^2	$[n_1, n_2, n_3]$	Model Fitting	Goodness-of-fit R^2
[1,2,2,1,1]		0.7109	[1,1,1]		0.5483
[1,2,2,1,1]		0.5975	[1,0.5,1]		0.9155
[2,1,2,1,1]		0.9278	[1,2,1]		0.5500
[2,2,2,1,1]		0.6073	[2,2,1]		0.1052

Figure 4-13. Optimization of reaction orders sets in (a) DDQ and (b) oxygen MVLTG. The red font shows optimized sets.

Experimental and simulated 3D contour maps of GNR yield ([GNR]) under MVLTG at 350 °C as a function of hydrogen acceptor concentration and time are shown in Figure 4-10c-g and i-m. Correlation coefficients (R^2) for the DDQ and oxygen systems are 0.93 and 0.92, respectively. Good agreement between experiment and simulation supports the validity of our proposed gas-2D solid-state reaction model of the dehydrogenation reaction of pre-polymers in MVLTG.

Temperature dependence (340 - 360 °C) of the reaction rate constants (k_1 , k_2) of the GNR growth process is measured to determine the activation energy of the dehydrogenation reaction. 3D contour maps of the experimental and simulated GNR yields for the DDQ system and those for the oxygen system are shown in Figure 4-14 a,b and c,d, respectively. Arrhenius plots of rate constants for the DDQ and oxygen systems are shown in Figure 4-10 n,o and p,q, respectively. Correlation coefficients of all Arrhenius plots exceed 0.93 (Figure 4-10n-q), suggesting the high accuracy of experiments. Activation energies of E_{a1} and E_{a2} for the DDQ system are estimated to be 1.55 eV and 0.91 eV, respectively (Figure 4-15a). Those for the oxygen system are 2.27 eV and 0.88 eV, respectively (Figure 4-15b). The temperature dependence of all reaction rate constants, including the decomposition process is shown in Table 4-1. Activation energies of E_{a1} for the dehydrogenation reaction from PP to pGNR are greater than those of E_{a2} from pGNR to GNR in the DDQ and oxygen systems.

The activation energy of the dehydrogenation reaction is thought to depend

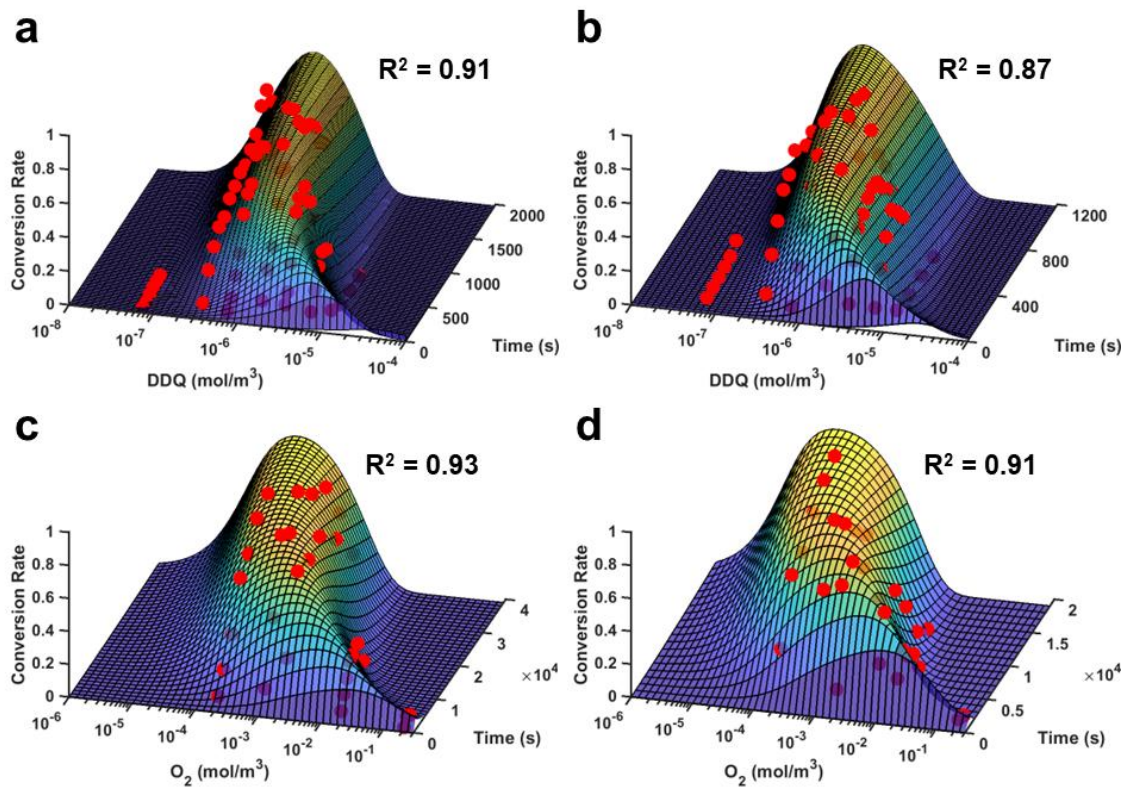


Figure 4-14. 3D curve fitting for (a, b) DDQ-dosed MVLTG at 340 °C and 360 °C and (c, d) Oxygen-dosed MVLTG at 340 °C and 360 °C.

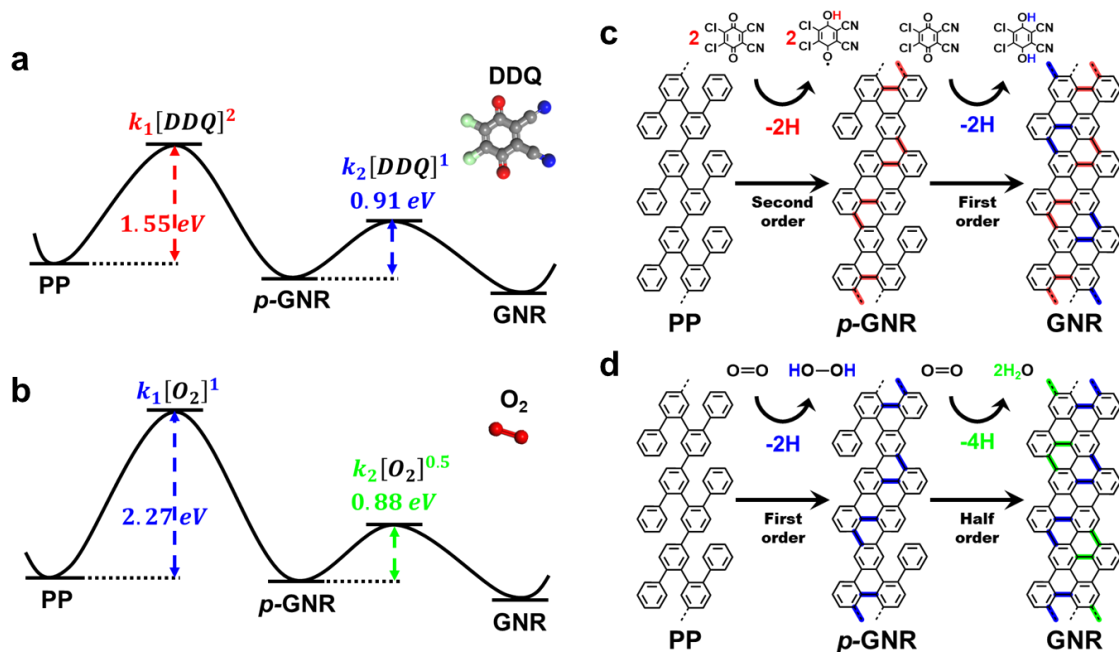


Figure 4-15. (a, b) Activation energy of GNR-growth rate constants of k_1 and k_2 for (a) DDQ and (b) oxygen MVLTG. (c, d) Proposed mechanism of reaction pathways of (c) DDQ and (d) oxygen MVLTG.

Table 4-1. Kinetic summary of MVLTG

(reaction orders, rate constants and activation energies).

Reaction Order						
H-acceptor		n_1	n_2	n_3	n_4	n_5
DDQ		2	1	2	1	1
O ₂		1	0.5	1	-	-
Rate constant						
H-acceptor	Temperature	k_1	k_2	k_3	k_4	k_5
	°C	/ mol ⁻¹ m ³ s ⁻¹	/ s ⁻¹	/ mol ⁻¹ m ³ s ⁻¹	/ mol ⁻¹ m ³ s ⁻¹	/ mol ⁻¹ m ³ s ⁻¹
DDQ	340	3.00E+11	2.85E+03	1.60E+07	1.00E+01	4.11E+02
	350	5.98E+11	3.55E+03	2.54E+07	1.26E+01	5.98E+02
	360	7.57E+11	4.94E+03	4.02E+07	1.00E+01	1.51E+03
H-acceptor	Temperature	k_1	k_2	k_3	-	-
	°C	/ s ⁻¹	/ mol ^{0.5} m ^{-1.5} s ⁻¹	/ s ⁻¹		
O ₂	340	1.69E+00	7.09E-04	1.56E-02	-	-
	350	3.24E+00	1.00E-03	3.01E-02	-	-
	360	7.70E+00	1.20E-03	4.20E-02	-	-
H-acceptor	Activation energy / eV					
DDQ		1.55 ± 0.42	0.91 ± 0.11	-	-	-
O ₂		2.27 ± 0.23	0.88 ± 0.15	-	-	-

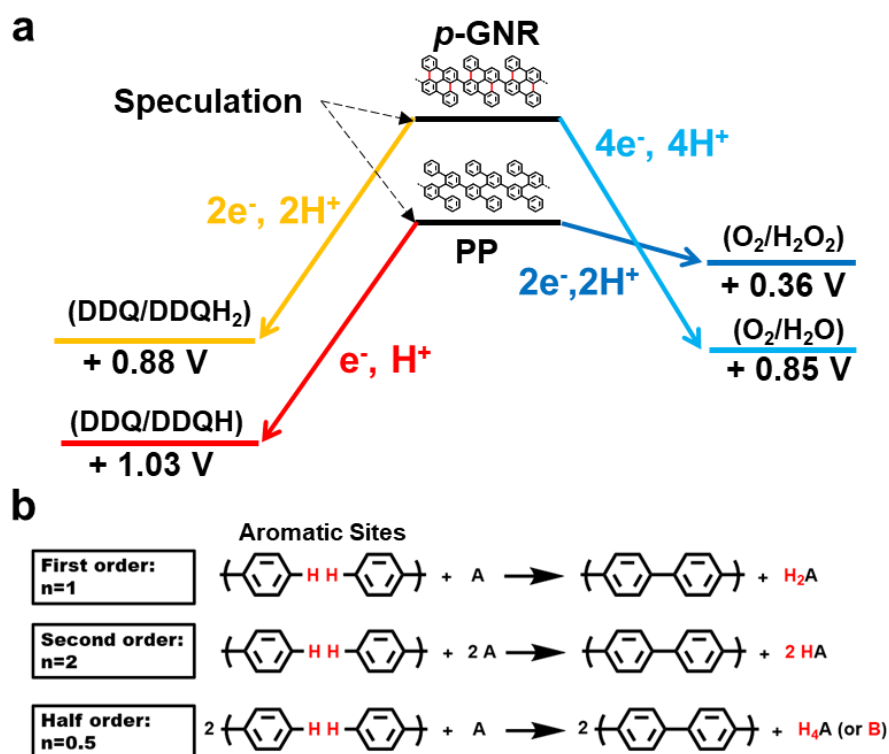


Figure 4-16. (a) The thermodynamic spontaneity of MVLGT process. The downhill path shows the speculated energy landscape of H-transfer (redox) reactions. (b) General description of chemical reactions according to different reaction orders.

on the planarity of the molecule. The dehydrogenation reaction from PP to pGNR requires high activation energy because the bulky conformation of PP presumably disturbs access to hydrogens in aromatic rings. On the other hand, the low activation energy for conversion from pGNR to GNR may originate from a more planar structure of pGNR, which offers easy access to aromatic hydrogens. The higher E_a in the oxygen system probably reflects the lower oxidation potential of DDQ compared to that of oxygen (Figure 4-16a).^[39]

A possible reaction mechanism based on the reaction order of the dehydrogenation reaction is shown in Figure 4-15c,d and Figure 4-16b. To form one C-C bond requires two DDQ molecules in the first step reaction and one in the second. In the first step, two DDQ molecules extract two hydrogens from adjacent benzene rings of PP, resulting in formation of pGNR with conversion of DDQ to DDQH $\cdot$. In the second step, a DDQ molecule extracts two hydrogens from the adjacent benzene ring of pGNR, resulting in formation of GNR, with conversion of DDQH $\cdot$ to DDQH $_2$. In sharp contrast, in the oxygen system, the dehydrogenation reaction in the first step requires a single molecule, and half a molecule in the second step. In the first step, oxygen is hypothesized to extract two hydrogen atoms from adjacent benzene rings of PP, resulting in formation of pGNR with conversion of oxygen to hydrogen peroxide. In the second step, oxygen is thought to extract four hydrogen atoms from the adjacent benzene ring of pGNR, resulting in formation of GNR with conversion of oxygen to water. One of the most promising reaction mechanisms for hydrogen extraction is electron transfer associated with proton transfer.^[25] Therefore, thermodynamic validity of the

mechanism of the dehydrogenation reaction can be verified from the redox potential comparison. The dehydrogenation reaction of pGNR to GNR is more likely to occur than that of PP to pGNR because the HOMO energy level of pGNR may be higher than that of PP, resulting in a strong driving force. The one- and two-electron oxidation potentials (vs. NHE)^[39] of DDQ in solution are reported to be +0.88 V and +1.03 V, respectively, while the two- and four-electron oxidation potentials of oxygen are +0.36 V and +0.85 V, respectively. These oxidation potentials of hydrogen acceptors are higher than the HOMO energy levels of PP and pGNR and likely drive spontaneous dehydrogenation (Figure 4-16a). From these discussions, the dehydrogenation reaction mechanism of MVLTG is concluded to be a Scholl reaction in the gas phase.

4.3.3 Edge functionalization at low temperature

MVLTG was performed on [2, 2-BuO] (4',5''-dibromo-4-butoxy-1,1':2',1'':2'',1'''-quaterphenyl) and [3, 2-BuO] (4',5''-dibromo-4-butoxy-1,1':2',1'':2'',1'''-quinquephenyl) prepolymers having electron-donating functional butoxy groups (abbreviated as -BuO) to investigate the validity of polymer dehydrogenation without decomposition of substituents. LT-STM images of on-surface polymerized [2, 2-BuO] and [3, 2-BuO] precursors (Figure 4-1c) using a 2Z-CVD technique show linear strands with dots at the edges, suggesting formation of prepolymers (Figure 4-17a,c). LT-STM images (Figure 4-17b,e) of MVLTG-treated (exposed to oxygen at a pressure of 0.8 kPa for 5 min at 310 °C, Figure 4-18) [2, 2-BuO] prepolymers show the 0.92-nm backbones much brighter than those before oxygen, which maintain dot

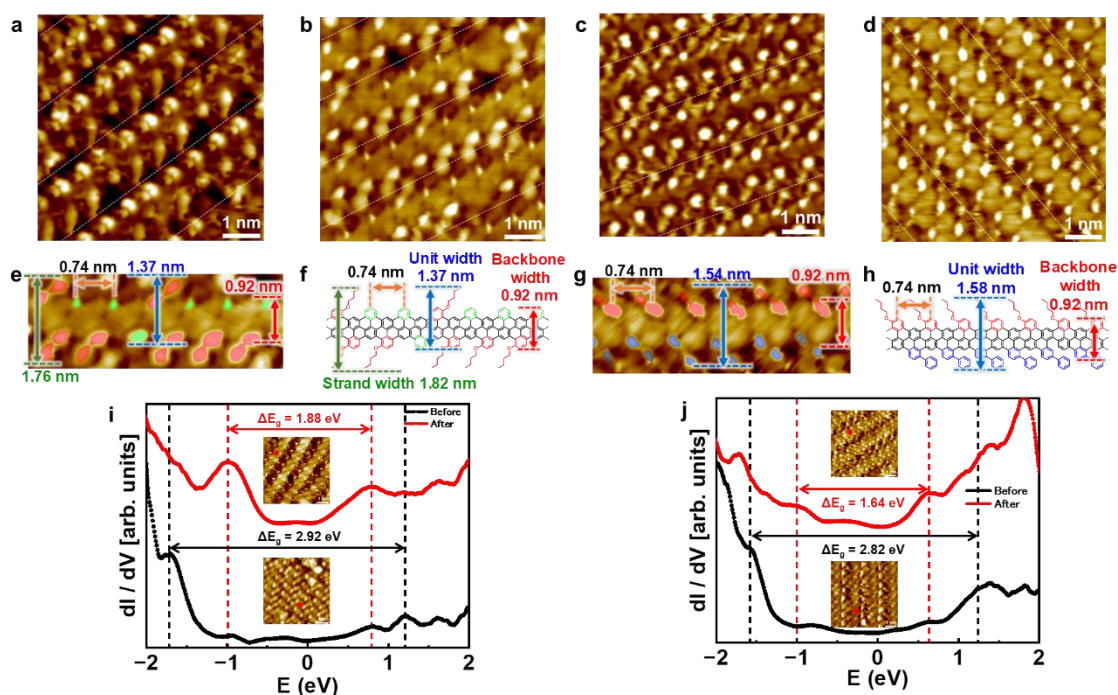


Figure 4-17. (a,c) LT-STIM images of [2, 2-BuO] (Bias voltage = -0.51 V, feedback current = 580 pA) and [3, 2-BuO] (-0.11 V, 580 pA) prepolymer strands before MVLTG treatment. (b,d) LT-STIM images of MVLTG-treated [2, 2-BuO] (-0.78 V, 580 pA) and [3, 2-BuO] (-0.10 V, 580 pA) polymer strands. The white lines indicate strand boundaries. (e,f) Magnified LT-STIM images of MVLTG-treated (e) [2, 2-BuO] and (f) [3, 2-BuO] polymer strands. Green dots indicate edge phenyl groups, red binary dots indicate the butoxyphenyl groups and the twinned blue dots represent the biphenyl groups. (g,h) Five-times averaged STS profiles of [2, 2-BuO] and [3, 2-BuO] polymer strands before (black line) and after (red line) oxygen. Insets indicate STS measurement locations (red dots). Band gaps of prepolymers before (black dotted line) and after (red dotted line) oxygen, estimated from the difference in potentials of the peaks. The spectra are shifted for clarity.

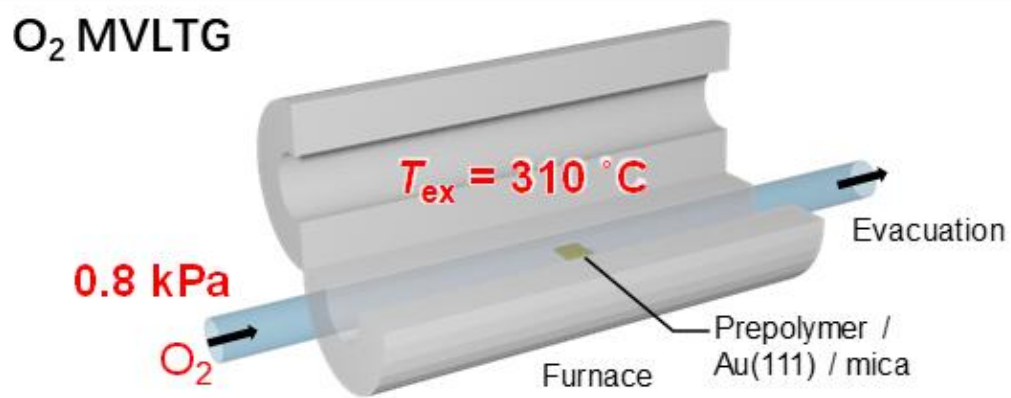


Figure 4-18. Experimental setup of O₂ dosed MVLTG.

spacing of 0.74 nm, and strand width of 1.76 nm. By analyzing magnified LT-STM images (Figure 4-17e), two kinds of dot patterns, single dots depicted in green and unequally sized pairs of dots, referred to as ‘binary’, marked red, are seen at the edges of the strands. Moreover, the positions of the dots appearing at one side of the strands and those on opposite sides are roughly 180° out of phase. These results suggest that the binary dots correspond to butoxyphenyl groups, whereas single dots are attributed to edge phenyl groups. Introduction of electron-donating butoxy groups is believed to alter the electronic structure of the backbone, resulting in brighter, discontinuous segments in the STM image (Figure 4-17b,e). The appearance of backbone-edge benzene groups as bright dots in [2, 2-BuO] in STM images (Figure 4-17b,e) is probably an electronic contribution rather than a topographic contribution (Figure 4-19c). The measured band gap of [2, 2-BuO] the sample after oxygen addition is 1.88 eV, which is in good agreement with the simulated band gap of 1.76 eV, while the band gap of the prepolymer is 2.92 eV (Figure 4-17g and 4-19b). After oxygen addition, the Raman spectrum greatly increased in intensity (Figure 4-20). These results suggest that MVLTG promotes dehydrogenation without decomposition of butoxy groups.

The LT-STM image of MVLTG-treated (exposed to oxygen at a pressure of 0.8 kPa for 5 min and temperature of 310 °C) [3, 2-BuO] prepolymers reveals 1.54-nm-wide strands possessing two kinds of dots, binary and twinned (Figure 4-17d,f), exclusively positioned on opposite sides of the significantly brighter 0.92-nm backbones and out of phase, where binary dots (represented in red) correspond to butoxyphenyl groups and twinned dots

(depicted in blue) can be attributed to remaining biphenyl groups (Figure 4-19f). In contrast to results of MVLGTG-treated [2, 2-BuO] prepolymers, these observations regarding the MVLGTG-treated [3, 2-BuO] case suggest that prepolymers may undergo two-band fusion (Figure 4-19d) (where ‘band’ is used to denote a row of collinear benzene rings), which is presumed to result in unrestrained edge phenyl groups, explained by localization of twinned dots that appear at strand edges in the STM image. STS measurement of [3, 2-BuO] prepolymers treated via MVLGTG reveals a band gap of 1.64 eV, which is in good agreement with the simulated band gap of 1.66 eV, and the prepolymer value is 2.82 eV (Figure 4-17h and 4-19e). Additionally, the remarkably increased Raman intensity of samples also supports fusion of [3, 2-BuO] prepolymers (Figure 4-20). Moreover, X-ray photoelectron spectroscopy (XPS) was conducted to confirm the elemental composition of the produced compounds. C_{1s} peaks of oxygen-bonded carbons, as well as O_{1s} oxygen peaks^[40] appear for [3, 2-BuO] prepolymers and those treated by MVLGTG, whereas the intensity of these peaks is remarkably reduced in samples annealed traditionally at 500 °C (Figure 4-21). As a reference, LT-STM images of conventionally annealed [2, 2-BuO] and [3, 2-BuO] prepolymers at 400 °C exhibit erratic fusion and decomposition of butoxy substituents^[41], which is further supported by Raman spectra (Figure 4-22). Accordingly, our MVLGTG procedure enhances fusion of prepolymers. Although constant-height LT-STM imaging using a carbon monoxide (CO)-functionalized tip to obtain atomically resolved STM images of products failed, due to the surface full coverage, comparison of experimental Raman spectra and simulations suggests the most

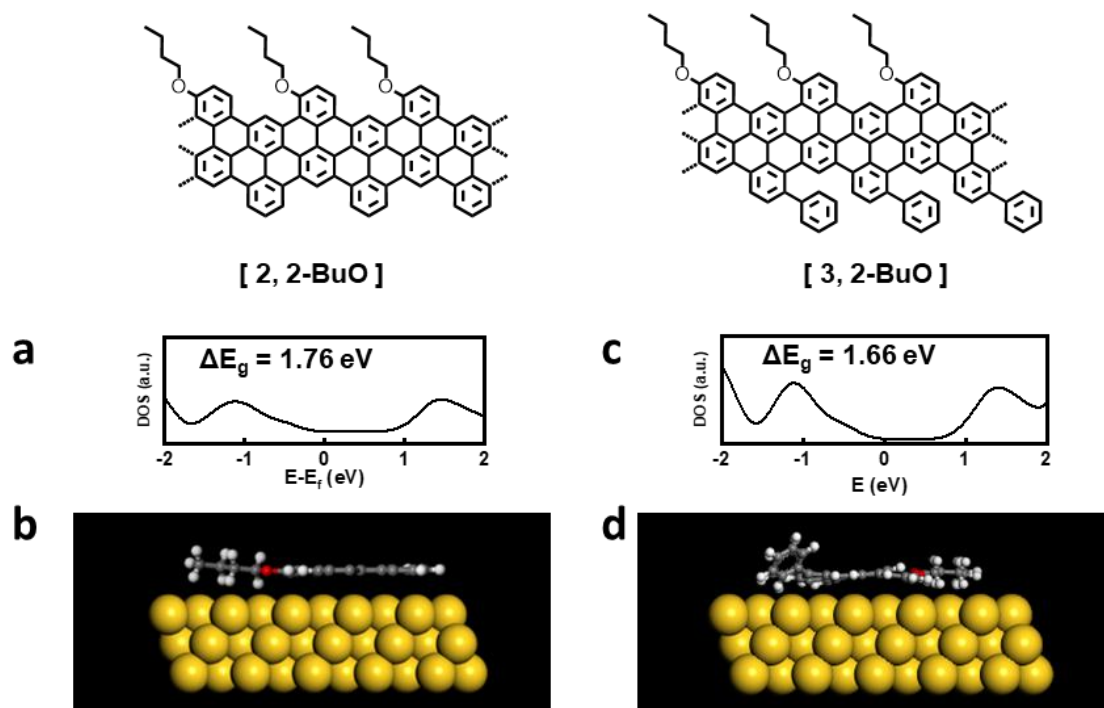


Figure 4-19. MVLTG treated [2, 2-BuO] and [3, 2-BuO] polymers' (a, d) plausible chemical structures, (b, e) simulated DOS with the band gap values and (c, f) side views of the molecular models on Au(111), respectively.

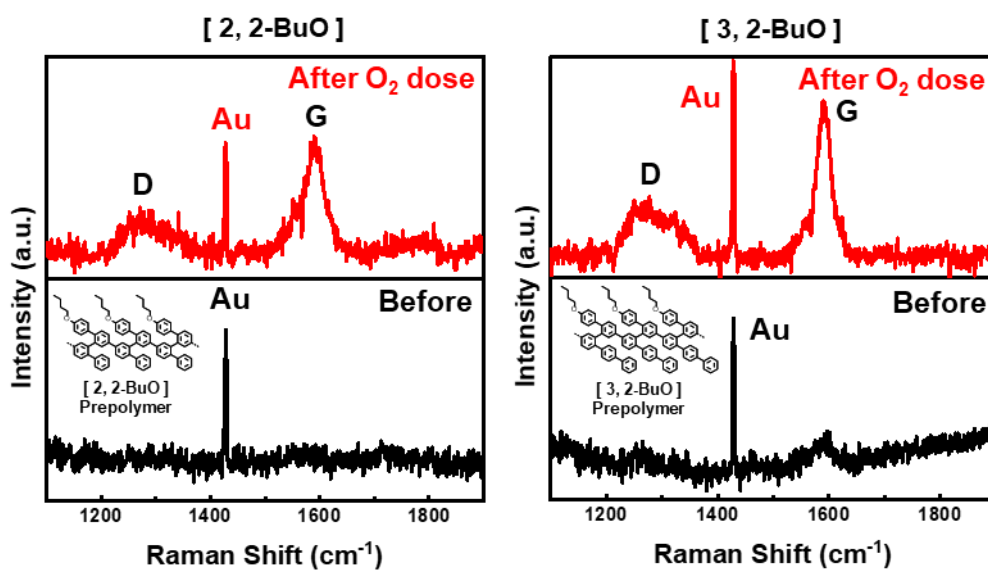


Figure 4-20. Raman spectra of [2, 2-BuO] and [3, 2-BuO] prepolymers before and after oxygen dose.

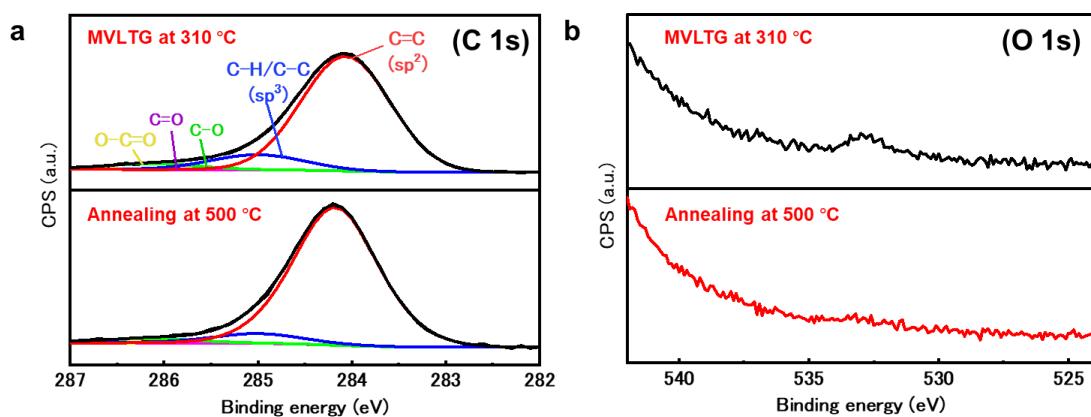


Figure 4-21. XPS spectra. (a, b) C_{1s}, O_{1s} peaks of [3, 2-BuO] prepolymers after MVLTG dose, and traditionally annealed (500 °C) prepolymers (top to bottom). The spectrum in (a) is deconvoluted into 5 types of carbon bonds.

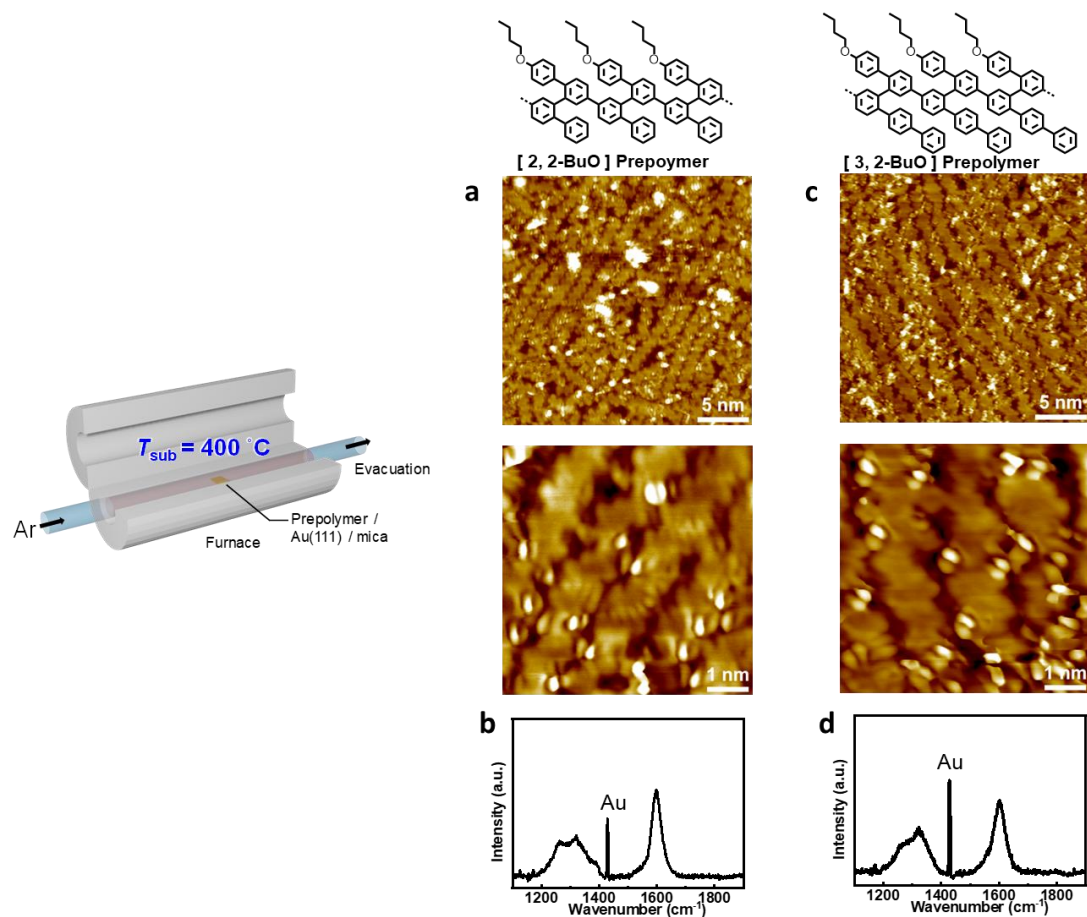


Figure 4-22. Thermal decomposition of GNRs. (a, c) LT-STM images of [2, 2-OBu] (-0.10 V, 580 pA) and [3, 2-OBu] (-0.028 V, 580 pA) prepolymers traditionally annealed at $T_{\text{sub}} = 400\text{ }^{\circ}\text{C}$. (b, d) Raman spectra of the samples in (a) and (c).

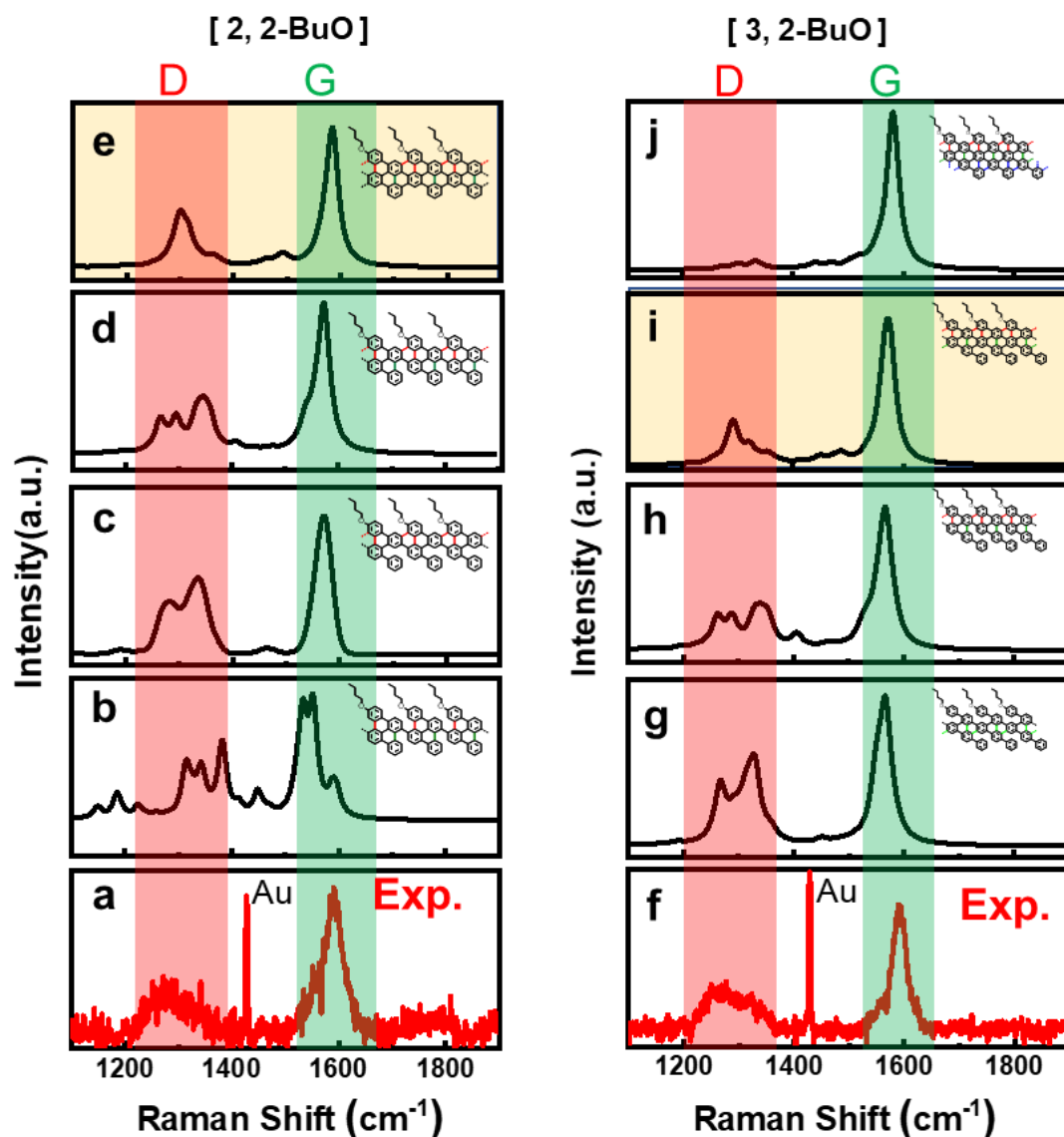


Figure 4-23. Experimental and simulated Raman Spectra of MVLTG-treated prepolymers. (a, f) Experimental MVLTG-treated [2, 2-BuO] and [3, 2-BuO] prepolymer Raman spectra. The 1428 cm^{-1} peak originates from the Au substrate. (b-e, g-j) Simulated Raman spectra of four [2, 2-BuO] and [3, 2-BuO] GNR structures (insets) expressing various degrees of band fusion. Locations of the D and G peaks are marked and highlighted spectra are believed to be the most probable structures.

probable chemical structures (Figure 4-19a,d and 4-23).

4.4 Conclusions

In conclusion, we demonstrate a newly developed MVLTG method, based on a massive excess of gaseous hydrogen-accepting molecules (DDQ or oxygen) relative to the prepolymer on the metal surface at low temperature. MVLTG demonstrated that symmetric Z-type [2, 2] prepolymers were converted into GNR via a dehydrogenation reaction at 350 °C, rather than the conventional thermal annealing method at 500 °C. The mechanism of MVLTG was revealed by kinetic study of GNR yields using Raman spectroscopy as a function of hydrogen-acceptor concentration and time. This was in good agreement with simulation based on a gas-2D solid-state reaction model, which formularized the rate equations according to reaction pathways classified into a growth and decomposition process. These results suggest that a dehydrogenation reaction in the growth process of MVLTG comprises two steps converting PP to pGNR, and pGNR to GNR. The possible dehydrogenation reaction mechanism by DDQ, based on the reaction order supposes one electron oxidation of PP by DDQ in the first step, and two electron oxidations of pGNR in second step, converting it into GNR. In sharp contrast, two electron oxidations of PP by oxygen in the first step, and four electron oxidations of pGNR, convert it into GNR in the second step. Finally, MVLTG demonstrates dehydrogenation reactions of polymers with functional substituents such as [2,2-BuO] and [3,2-BuO] without decomposition of substituent butoxy groups. Our newly developed MVLTG technique is able to produce functionalized GNRs with specific physical properties.

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Chapter 5

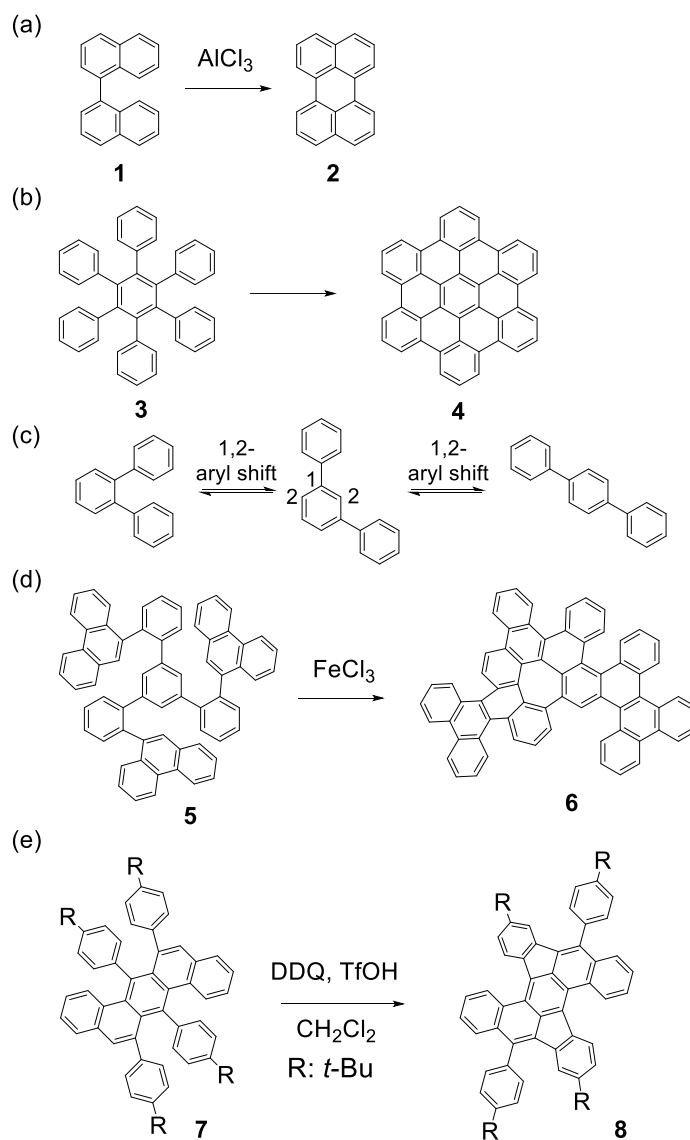
Aryl Shift Rearrangement in Scholl-type Reaction toward Nanographene

5.1 Introduction

In this chapter, we attempt to scale up GNR production via in-solution synthesis based on Z-bar-linkage precursor capable for asymmetric structures. Generally, the potential application of GNRs, such electronic, photonic, and magnetic, requires large-amount fabrication of GNRs. The conventional GNR on-surface synthesis is always limited to less-amount production, which limits its energy application. On the other hand, in-solution synthesis, such as Scholl reaction, is an effective method to increase the production scale of GNRs. To achieve large-scale production of GNRs, we conducted in-solution synthesis using our originally designed Z-bar-linkage precursors **12**. Even we didn't obtain the expected structure, we established the 1,4-aryl shift arrangement mechanism in the Scholl-type reaction.

The Scholl reaction is a highly efficient method for producing fused polycyclic aromatic compounds through oxidative cyclodehydrogenation. This method was first reported by Scholl over a century ago, using 1,1'-binaphthalene (**1**) to obtain perylene (**2**) (Scheme 5-1a).^[1] Since then, various oxidizing reagents or combinations of reagents have been used to achieve this reaction, including FeCl_3 , MoCl_5 , $\text{Cu}(\text{OTf})_2 + \text{AlCl}_3$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) + Brønsted or Lewis acid, and [bis(trifluoroacetoxy)iodo]benzene (PIFA) + $\text{BF}_3 \cdot \text{Et}_2\text{O}$.^[2] The Scholl reaction

is a versatile chemical reaction that can be used to synthesize a wide range of polycyclic aromatic frameworks with different geometries and sizes. For example, hexaphenylbenzene (**3**) can be transformed into hexabenzocoronene (**4**) (Scheme 5-1b).^[3] However, due to aryl migration (i.e., an o-terphenyl framework to m- and p-isomers) (Scheme 5-1c), unexpected reaction products may be produced. This can lead to undesired cyclization or incomplete cyclization, as illustrated by representative examples.^[4-9] For instance, Durola and colleagues reported a reaction in which an aryl group migrated and cyclodehydrogenation of **5** occurred, leading to the formation of **6**, a seven-membered ring-containing polycyclic aromatic hydrocarbon (Scheme 5-1d).^[4b] Feng, Müllen and co-workers reported that the reaction of 6,7,13,14-tetraarylbenzo[k]-tetraphene **7** with DDQ and trifluoromethanesulfonic acid (TfOH) afforded **8** with five-membered rings via 1,2-aryl migrations (Scheme 5-1e).^[4c] Despite numerous attempts to fully understand the mechanism of the Scholl reaction, control of reaction selectivity remains elusive.^[10-17] More understanding and control of this reaction are pivotal for further developing the chemistry of synthesizing polycyclic aromatic hydrocarbons and nanographene.^[18-23]



Scheme 5-1. (a) An example of cyclodehydrogenation reaction reported by Scholl. (b) A typical example of cyclodehydrogenation of hexaphenylbenzene to give hexabenzocoronene. (c) 1,2-aryl shift of terphenyl framework. (d) Aryl shift and cyclodehydrogenation of C₃-symmetric precursor to give twisted polycyclic arene. (e) Aryl shift and cyclodehydrogenation of 6,7,13,14-tetraarylbenzo[*k*]tetraphene to give five-membered rings in polycyclic aromatic hydrocarbon.

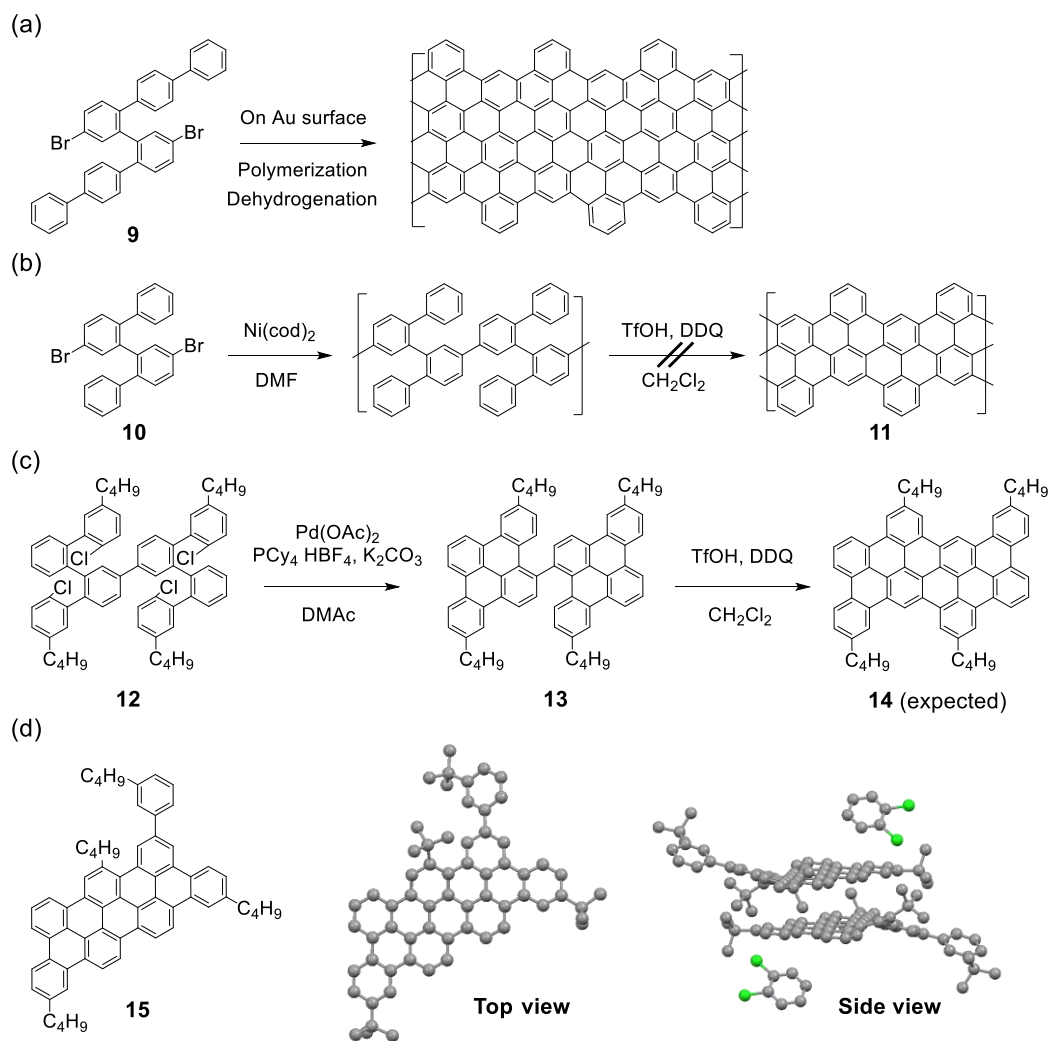
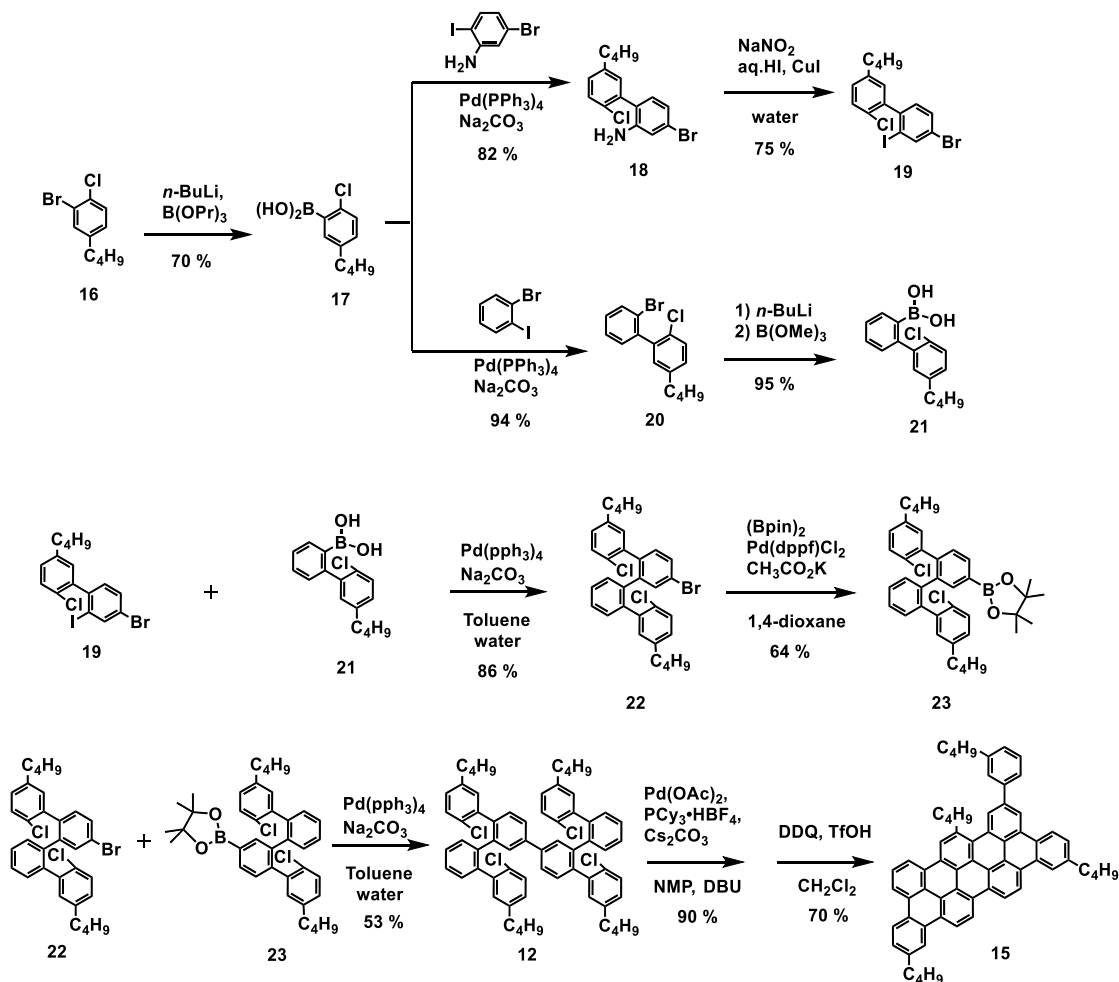


Figure 5-1. (a) On-surface synthesis and (b) organic synthesis of graphene nanoribbon based on Z-shaped molecules. (c) Modified synthetic route to expected nanographene **14** by Pd-catalyzed cyclization followed by dehydrogenation. (d) Top view and side view of single-crystal X-ray crystallographic analysis of obtained product **15**.

We discovered the rearranged product **15** (Figure 5-1d) through both 1,4-aryl- and 1,2-aryl shifts. We previously reported the successful on-surface synthesis of graphene nanoribbons using a precursor **9** (Figure 5-1a).^[24] The polymerization reaction was initiated by radical species produced by dissociating bromine atoms through heating, followed by dehydrogenation reactions catalyzed by the Au surface. Inspired by this work, we prepared prepolymer using a Z-shaped precursor **10** to synthesize graphene nanoribbon **11** and examined various reaction conditions for general oxidative dehydrogenations. However, the expected product **11** was not obtained, and we ended up with an insoluble solid that was difficult to analyze (Figure 5-1b). It is well-known that partially fused structures, like a triphenylene moiety, ensure the successful occurrence of subsequent dehydrogenation reactions.^[25] We modified the method for producing nanographene using the dimer precursor **12** with Cl atoms, synthesized through Scheme 5-2, by conducting Pd-catalyzed partial ring closure reactions, followed by dehydrogenation reactions (Figure 5-1c). However, the expected product **14** could not be observed; instead, we obtained product **15**, which was generated via 1,4-aryl- and 1,2-aryl shifts. To the best of our knowledge, the mechanism investigation of the 1,4-aryl shift toward nanographene has been rarely reported. To understand the mechanism behind this unexpected rearrangement, we conducted theoretical studies based on density functional theory (DFT).

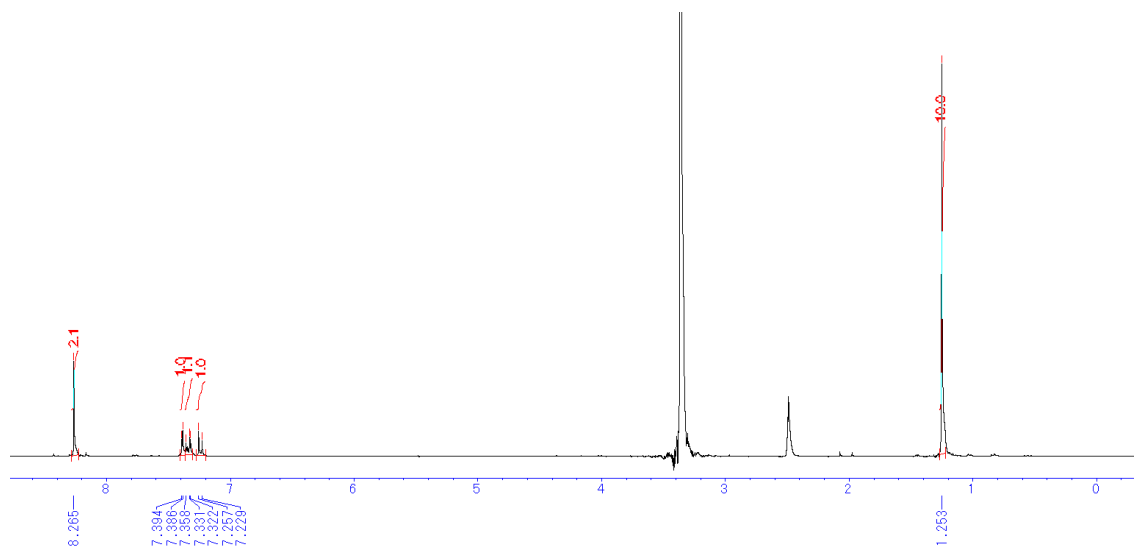
5.2 Experimental

5.2.1 Organic synthesis procedure

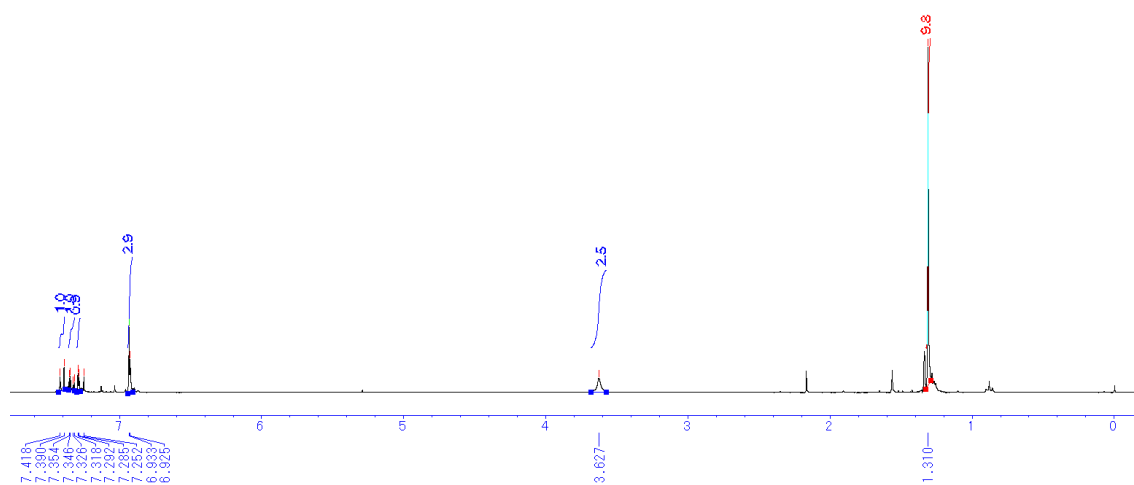


2-bromo-4-*tert*-butyl-1-chlorobenzene (**16**) was prepared according to the previously reported method.

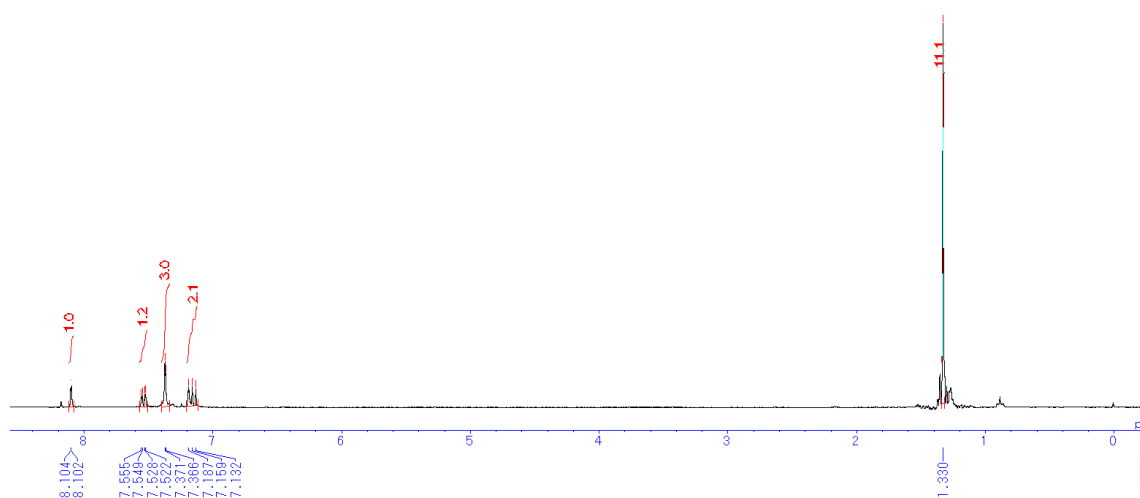
(2-chloro-5-*tert*-butylphenyl)boronic acid **17**. *n*-BuLi (1.6 M, 11.6 mL, 18.6 mmol) was added dropwise to a solution of **16** (4.40 g, 16.0 mmol) and triisopropyl borate (4.40 mL, 19.2 mmol) in THF (7.5 mL) and toluene (30 mL) at $-80\text{ }^{\circ}\text{C}$ under a nitrogen atmosphere. After stirring at the same temperature, the solution was warmed to $-20\text{ }^{\circ}\text{C}$. HCl solution (1 M, 30 mL) was added, and then the reaction mixture gradually warmed to room temperature. The reaction mixture was extracted with AcOEt, and the extract was washed with brine and dried over anhydrous MgSO_4 . Removal of the solvent afforded **17** (3.60 g, 70% yield) as a white solid. The product was used for the next step without further purification. **17**: 300 MHz ^1H NMR (CDCl_3): $\delta = 8.27$ (s, 2H), 7.39 (d, $J = 2.4$ Hz, 1H), 7.34 (dd, $J = 8.4, 2.4$ Hz, 1H), 7.24 (d, $J = 8.4$ Hz, 1H), 1.25 (s, 9H).



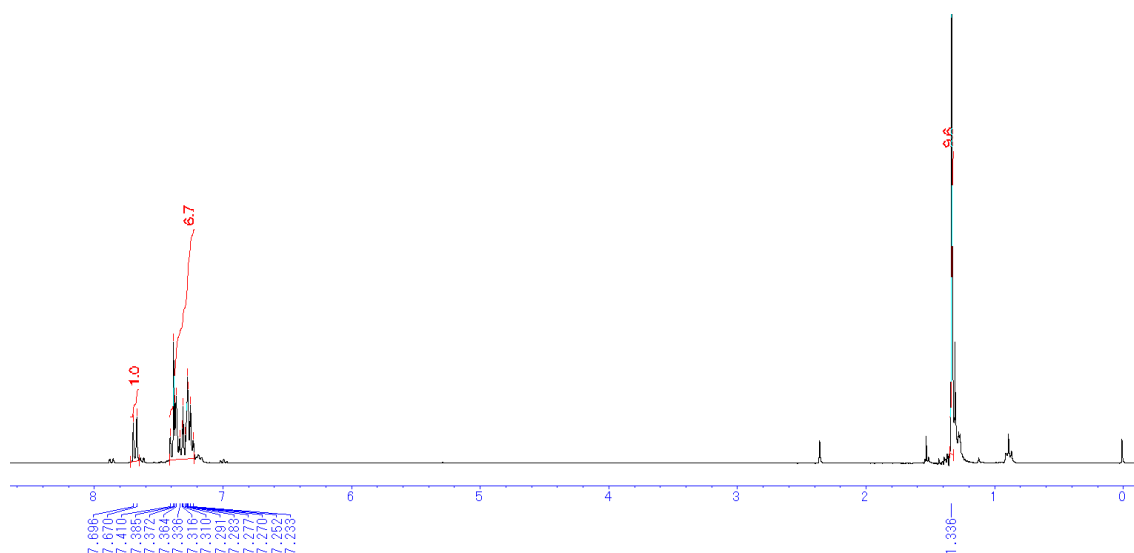
Compound 18. A solution of **17** (3.80 g, 16.0 mmol), 5-bromo-2-iodoaniline (4.30 g, 14.3 mmol), Na₂CO₃ (9.20 g, 86.0 mmol), Pd(PPh₃)₄ (350 mg, 0.300 mmol) in toluene (30 mL) and water (15 mL) was heated at 80 °C under a nitrogen atmosphere overnight. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂. The extract was washed with brine. After the removal of the solvent, the residue was purified by chromatography (silica gel, hexane : CH₂Cl₂ = 2 : 1) to afford **18** (4.10 g, 82% yield) as a yellow solid. **18**: 300 MHz ¹H NMR (CDCl₃): δ = 7.40 (d, *J* = 7.8 Hz, 1H), 7.33 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.29 (d, *J* = 2.4 Hz, 1H), 6.93-6.92 (m, 3H), 3.63 (s, 2H) 1.31 (s, 9H).



Compound 19. 18 (4.10 g, 11.2 mmol) and CuI (1.06 g, 5.60 mmol) were suspended in HI (12 g), water (60 mL) and CH₃CN (60 mL). After cooling to 0 °C, a solution of NaNO₂ (0.77g, 11.2 mmol) in water (10 mL) was added dropwise at 0 °C, and the reaction was gradually warmed to room temperature. After stirring at room temperature overnight, aq.Na₂SO₃ was added and extracted with CH₂Cl₂. After the removal of the solvent, the residue was purified by chromatography (silica gel, hexane : CH₂Cl₂ = 1 : 1) to afford **19** (3.50 g, 75% yield) as a yellow solid. **19**: 300 MHz ¹H NMR (CDCl₃): δ = 8.10 (s, 1H), 7.53 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.37-7.36 (m 3H), 7.19-7.13 (m 2H), 1.32 (s, 9H).



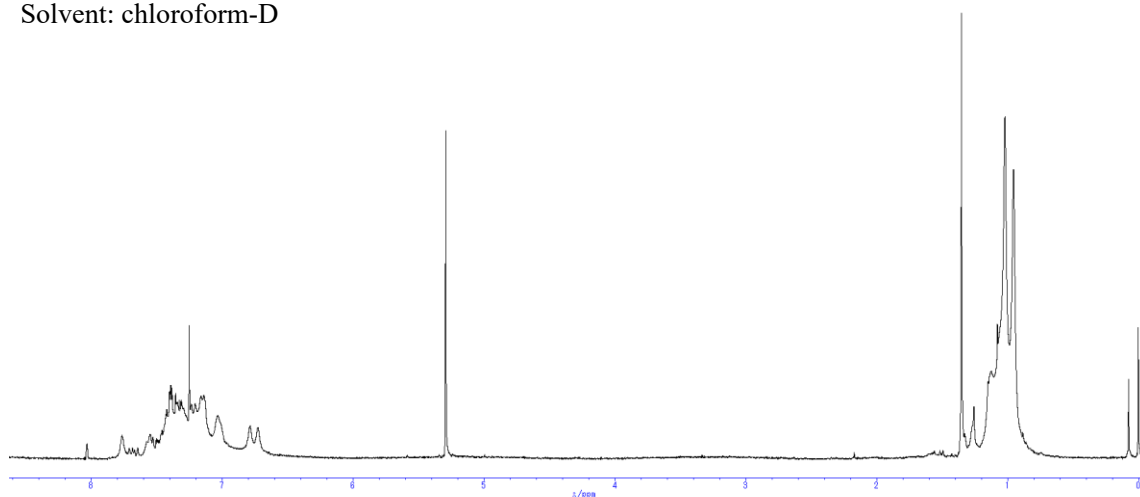
Compound 20. A solution of **17** (1.40 g, 5.80 mmol), 1-bromo-2-iodobenzene (1.50 g, 5.30 mmol), Na₂CO₃ (3.40 g, 32.0 mmol), Pd(PPh₃)₄ (115 mg, 0.100 mmol) in toluene (10 mL) and water (10 mL) was heated at 80 °C under a nitrogen atmosphere overnight. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂. The extract was washed with brine. After the removal of the solvent, the residue was purified by chromatography (silica gel, hexane : CH₂Cl₂ = 1 : 1) to afford **20** (1.70 g, 94% yield) as a white solid. **20**: 300 MHz ¹H NMR (CDCl₃): δ = 7.68 (d, *J* = 7.8 Hz, 1H), 7.41-7.23 (m, 5H), 1.34 (s, 9H).



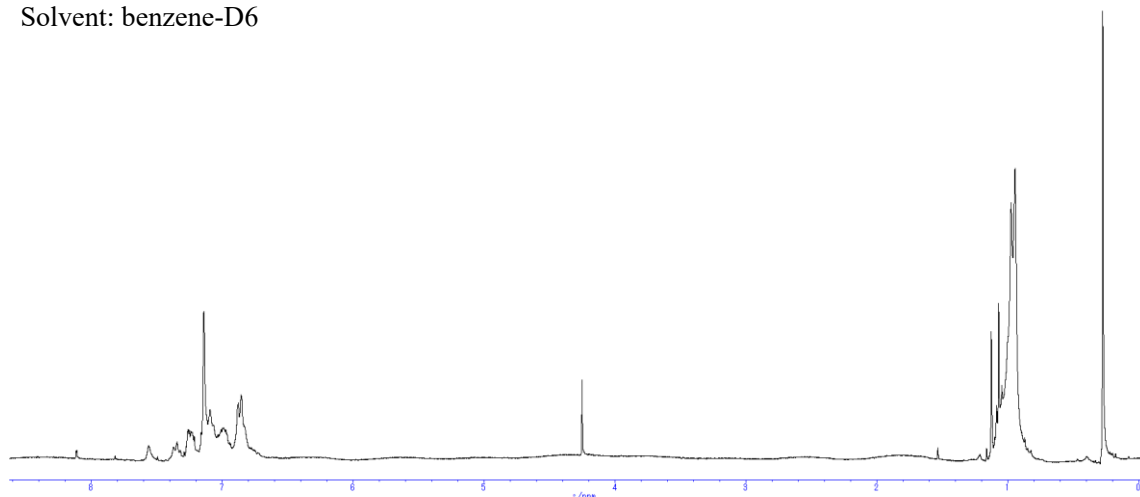
Compound 21. *n*-BuLi (1.6 M, 3.30 mL, 5.30 mmol) was added dropwise to a solution of **20** (1.70 g, 4.80 mmol) in THF (30 mL) at $-80\text{ }^{\circ}\text{C}$. After stirring at the same temperature for 1 h under a nitrogen atmosphere, trimethyl borate (0.81 mL, 6.40 mmol) was added. The solution was gradually warmed to room temperature and stirred overnight. Then, HCl solution (1 M, 30 mL) was added, and the reaction mixture was stirred for 1 h. The reaction mixture was diluted with water and extracted with AcOEt. The extract was washed with brine and dried over anhydrous MgSO_4 . Removal of the solvent afforded **21** (1.50 g, 95% yield) as a white solid. The product was used for the next step without further purification.

Compound 22. A solution of **19** (2.30 g, 4.8 mmol), **21** (1.7 g, 5.30 mmol), Na₂CO₃ (4.00 g, 40.0 mmol), Pd(PPh₃)₄ (115 mg, 0.100 mmol) in toluene (30 mL) and water (15 mL) was heated at 80 °C under a nitrogen atmosphere overnight. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂. The extract was washed with brine. After the removal of the solvent, the residue was purified by chromatography (silica gel, hexane 100%) to afford **22** (2.50 g, 86% yield) as a white solid. **22**: 300 MHz ¹H NMR (CDCl₃ or C₆D₆): The spectrum showed very broad signals. The signal pattern is very difficult to analyze.

Solvent: chloroform-D

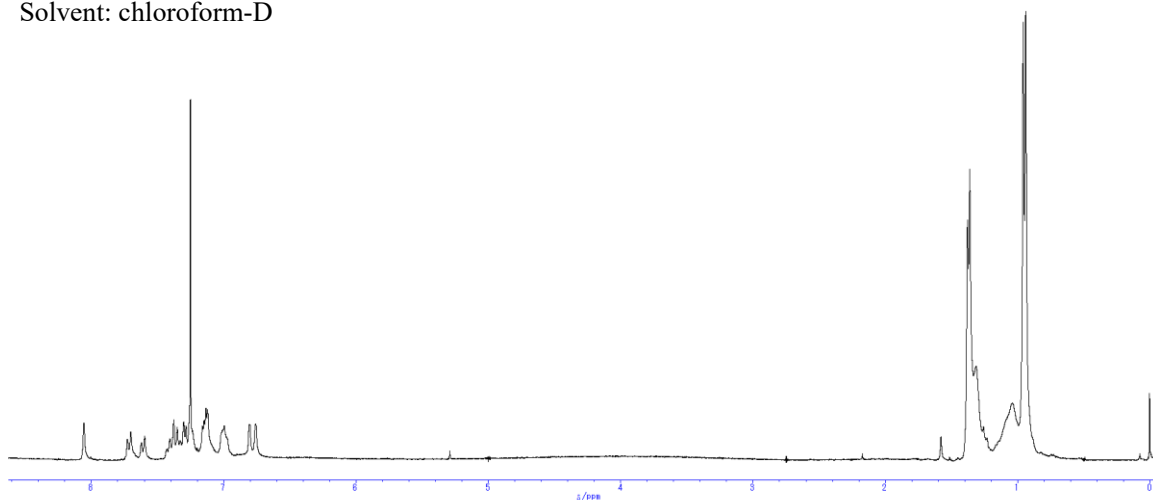


Solvent: benzene-D6

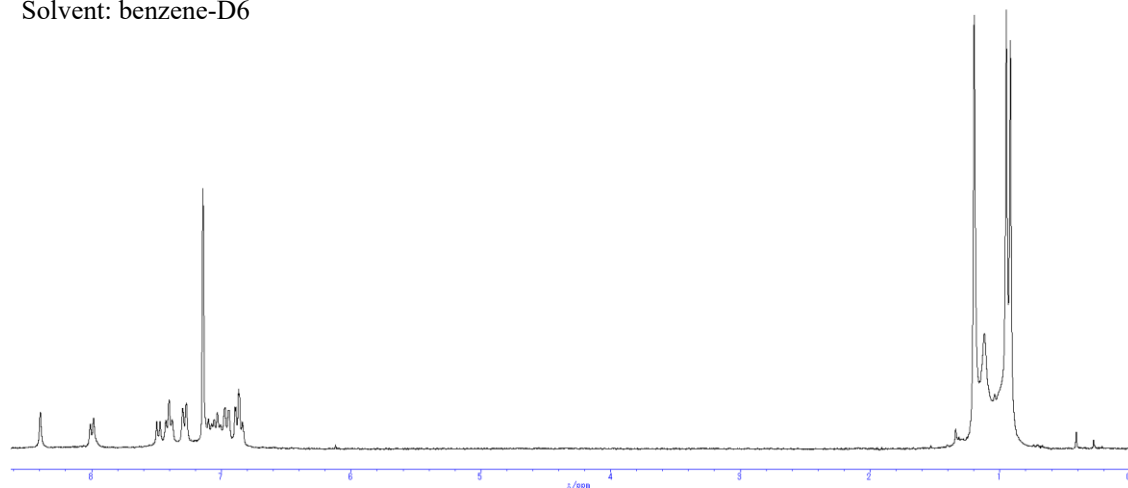


Compound 23. A solution of **22** (1.50 g, 2.40 mmol), bis(pinacolato)diboron(0.95 g, 3.60 mmol), CH₃COOK (2.40 g, 24.0 mmol) and Pd(dppf)Cl₂ (98.0 mg, 0.120 mmol) in 1,4-dioxane (10 mL) was heated at 85 °C under a nitrogen atmosphere for overnight. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂. The extract was washed with brine. After the removal of the solvent, the residue was purified by chromatography (silica gel, CH₂Cl₂ 100%) to afford **23** (0.90 g, 64% yield) as a white solid. **23**: 300 MHz ¹H NMR (CDCl₃ or C₆D₆): The spectrum showed very broad signals. The signal pattern is very difficult to analyze.

Solvent: chloroform-D

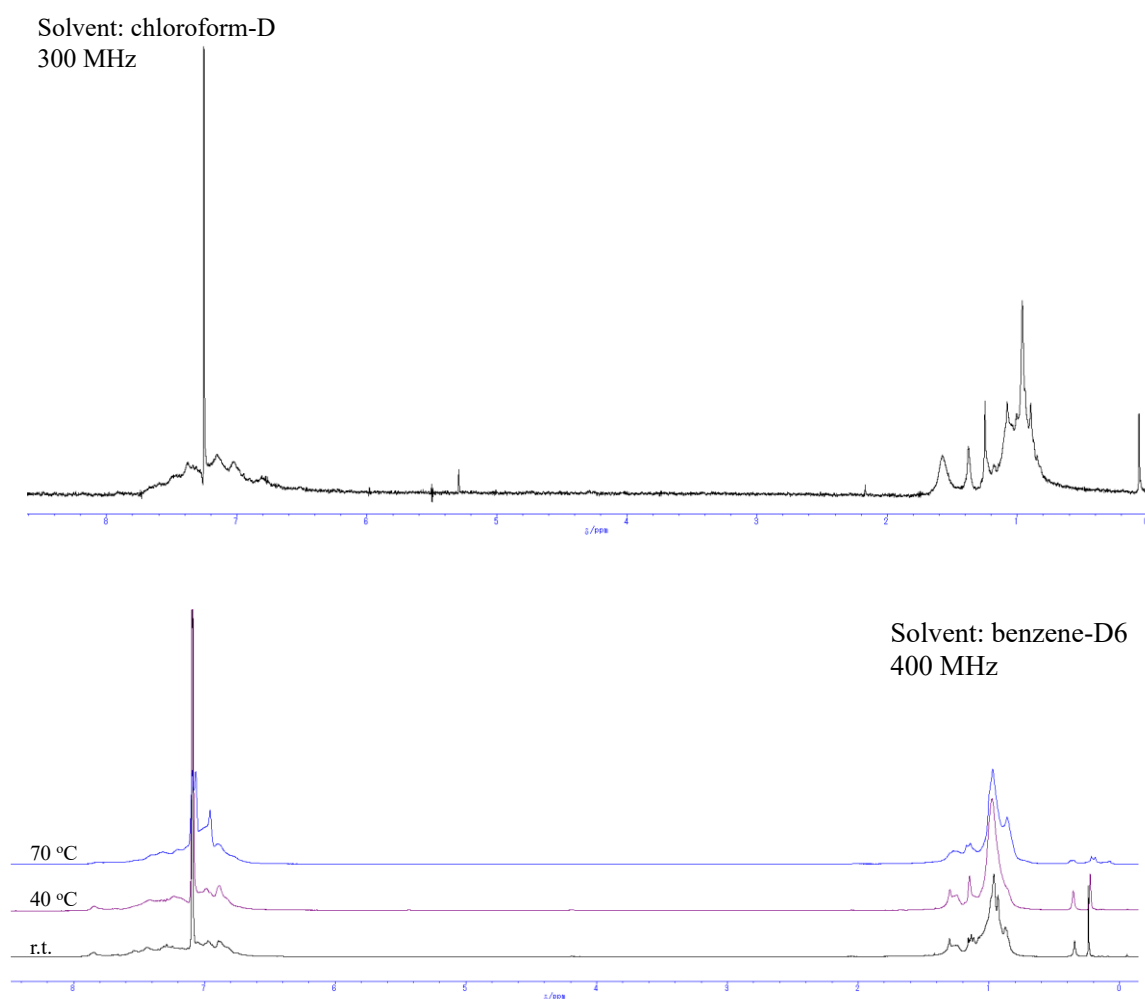


Solvent: benzene-D6

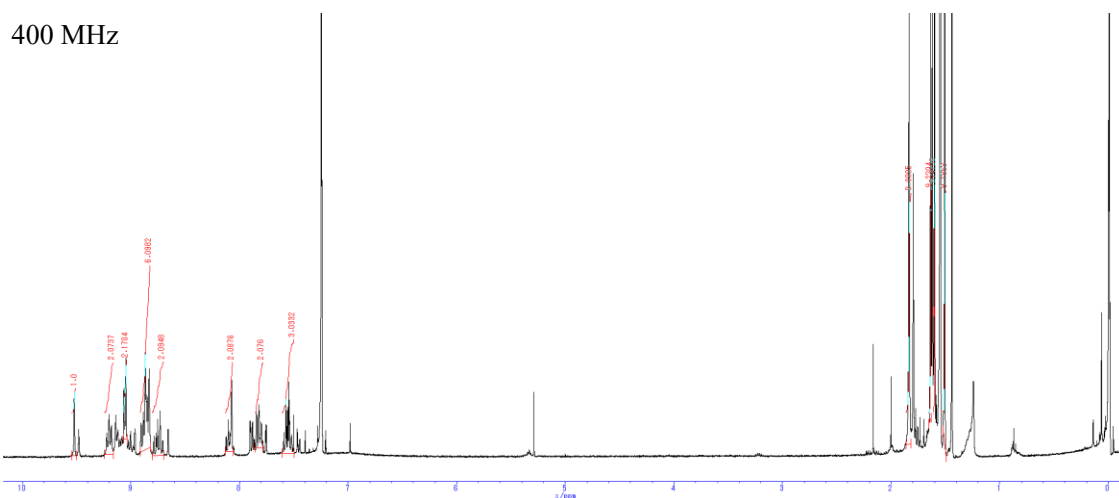


Compound 12. A solution of **22** (85.0 mg, 0.140 mmol), **23** (100 mg, 0.150 mmol), Na₂CO₃ (90.0 g, 0.810 mmol), Pd(PPh₃)₄ (4.0 mg, 0.030 mmol) in toluene (10 mL) and water (5 mL) was heated at 80 °C under a nitrogen atmosphere overnight. After cooling to room temperature, the reaction mixture was extracted with CH₂Cl₂. The extract was washed with brine. After the removal of the solvent, the residue was purified by chromatography (silica gel, hexane : CH₂Cl₂ = 2 : 1) to afford **12** (80.1 mg, 53% yield) as a white solid.

12: ¹H NMR (CDCl₃ or C₆D₆): The spectrum showed very broad signals. The signal pattern is very difficult to analyze.



Compound 15. A solution of **12** (40.0 mg, 0.037 mmol), $\text{PCy}_3\cdot\text{HBF}_4$ (11.0 mg, 0.03 mmol), Cs_2CO_3 (24.5 mg, 0.075 mmol), $\text{Pd}(\text{OAc})_2$ (3.4 mg, 0.015 mmol) in *N*-Methyl-2-pyrrolidone (5 mL) and DBU (11.4 mg, 0.075 mmol) was heated at 150 °C under a nitrogen atmosphere for 3 days. After cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2 . The extract was washed with brine. After the removal of the solvent, the residue was purified by chromatography (silica gel, hexanes : CH_2Cl_2 = 4:1) to afford product mixture (30.5 mg) as a white solid. The solid and DDQ (18 mg, 0.08 mmol) were dissolved in CH_2Cl_2 (10 mL). After cooling to -80 °C, trifluoromethanesulfonic acid (0.25 mL) was added dropwise, and the reaction mixture was stirred at the same temperature for one hour under a nitrogen atmosphere. Then, Et_3N (3 mL) was added, and the reaction mixture was extracted with CH_2Cl_2 . After the removal of the solvent, the residue was purified by chromatography (silica gel, hexane : CH_2Cl_2 = 4:1) followed by GPC (CHCl_3) to afford **15** (20.3 mg, 70% yield) as a yellow solid. 400MHz ^1H NMR (CDCl_3): δ = 9.52 (s, 1H), 9.20 (t, 2H), 9.07-9.04 (m, 2H), 8.92-8.82 (m, 6H), 8.81-8.70 (m, 2H), 8.13-8.06 (m, 2H), 7.85-7.78 (m, 2H), 7.60-7.49 (m, 3H), 1.84 (s, 9H), 1.64 (s, 9H), 1.60 (s, 9H), 1.51 (s, 9H).



5.2.2 X-ray crystallographic analysis

The single crystal X-ray analysis for product **15** was performed with Rigaku XtaLAB P200D. The X-ray diffraction data were collected with an imaging plate diffractometer with graphite monochromated CuK α radiation. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on F_o^2 by the full-matrix least-squares method using SHELXL-2013. Hydrogen atoms were placed at calculated positions and refined “riding” on their corresponding carbon atoms. In the subsequent refinement, the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R_1 = \Sigma (||F_o| - |F_c||) / \Sigma |F_o|$ and $wR_2 = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma (w F_o^2)^2]^{1/2}$.

Crystal data for **15**: Formula C₆₄H₅₆·C₆H₄Cl₂, $M_r = 972.08$, $0.10 \times 0.05 \times 0.30$ mm³, $T = 93(2)$ K, triclinic, space group $P-1$, $a = 11.863$ Å, $b = 15.798$

$\text{\AA}$, $c = 16.151 \text{ \AA}$, $\alpha = 114.61^\circ$, $\beta = 111.19^\circ$, $\gamma = 91.45^\circ$, $V = 2510.0 \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.286 \text{ gcm}^{-3}$, $\mu = 0.068 \text{ mm}^{-1}$, $F(000) = 1028$, $2\theta_{\text{max}} = 73.8^\circ$, $R_1 (I > 2\theta(I)) = 0.0527$, $wR_2 (\text{all data}) = 0.148$ and GOF = 1.010 for 9573 reflections and 649 parameters.

5.2.3 Mass spectrum analysis

Atmospheric pressure chemical ionization (APCI) mass spectra were recorded on a spectrometer in positive mode.

Matrix-assisted laser desorption ionization-Fourier transform ion cyclotron resonance (MALDI-FT-ICR) mass spectrometry was conducted. The sample was analyzed using high-resolution mass spectrometry (HRMS) in positive ion mode. *trans*-2-[3-(4*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as a matrix.

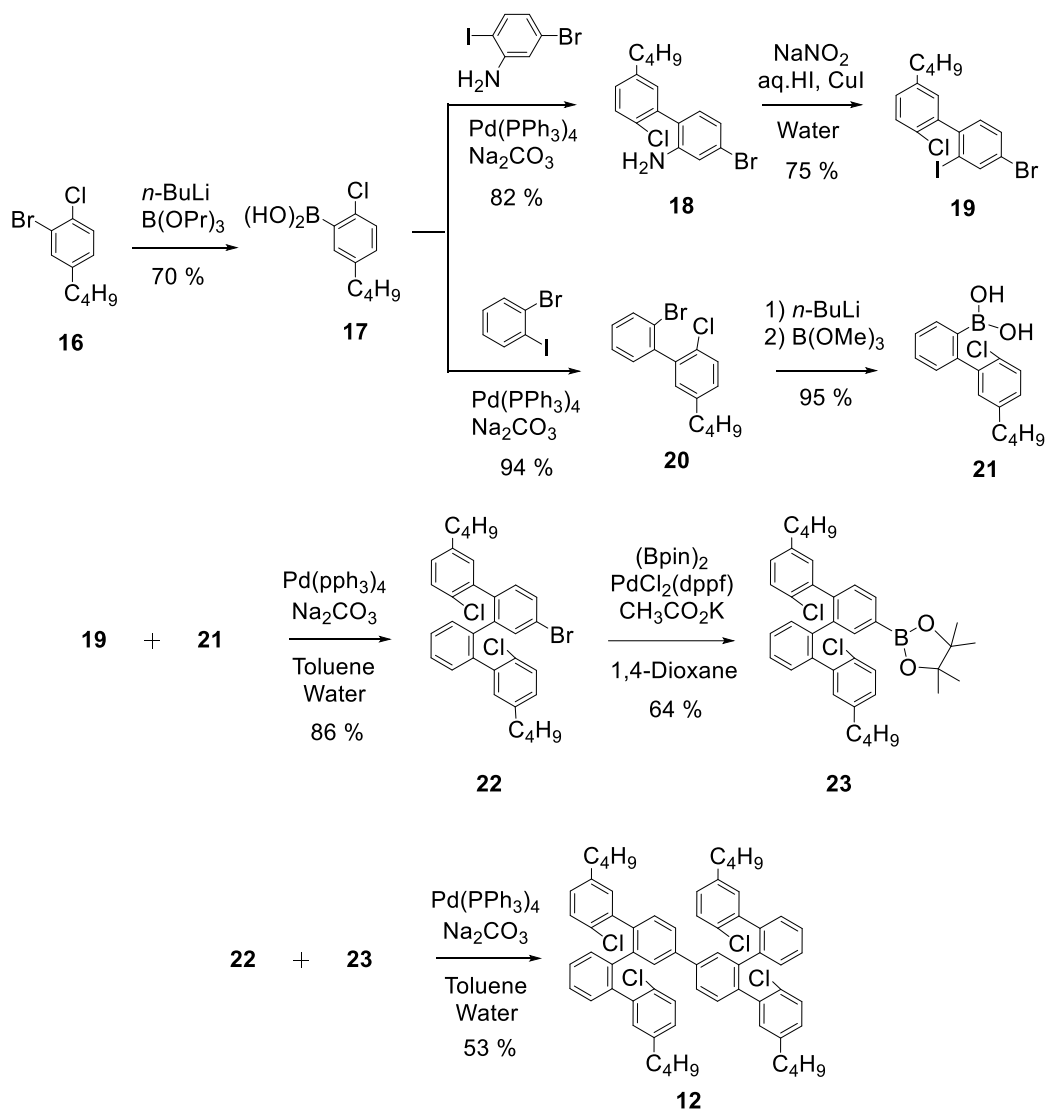
5.2.4 Rearrangement calculations

DFT calculations were performed with the Gaussian 16 program. All geometry optimizations were carried out at the (R)B3LYP level of density functional theory with the 6-311G(d,p) basis set. The nature of the stationary points was assessed by means of vibrational frequency analysis. In the implicit solvent model, by using B3LYP/6-311G(d,p) method, the CPCM polarizable conductor calculation model was used to the polarizable continuum model (PCM) in the self-consistent reaction field (SCRF) procedure.

5.3 Results and discussion

5.3.1 Organic synthesis of precursor

The compound 5,5''''-dibutyl-4''',6''-bis(5-butyl-2-chlorophenyl)-2,2''''-dichloro-1,1':2',1'':3'',1''':3''',1''':2''',1''''-sexiphenyl (**12**) was synthesized as described in Scheme 5-2. First, 2-bromo-4-butyl-1-chlorobenzene (**16**) and triisopropyl borate reacted to produce (5-butyl-2-chlorophenyl)boronic acid (**17**) with a yield of 70%. 4-bromo-5'-butyl-2'-chloro-[1,1'-biphenyl]-2-amine (**18**) and 2'-bromo-5-butyl-2-chloro-1,1'-biphenyl (**20**) were prepared through a Suzuki coupling reaction of **17** with 5-bromo-2-iodoaniline and 1-bromo-2-iodobenzene, respectively, with yields of 82% and 94%. 4-bromo-5'-butyl-2'-chloro-2-iodo-1,1'-biphenyl (**19**) was prepared via a Sandmeyer reaction of **18** with a yield of 75%. (5'-butyl-2'-chloro-[1,1'-biphenyl]-2-yl)boronic acid (**21**) was prepared via a Miyaura boronation reaction of **20** with a yield of 95%. Then, **19** and **21** were used to produce 4'-bromo-5,5''''-dibutyl-2,2''''-dichloro-1,1':2',1'':2'',1''''-quaterphenyl (**22**) through a Suzuki coupling reaction with a yield of 86%. 2-(5,5''''-dibutyl-2,2''''-dichloro-[1,1':2',1'':2'',1''''-quaterphenyl]-4'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**23**) was prepared from **22** with a yield of 64%. Finally, precursor **12** was synthesized via a Suzuki coupling reaction of **22** and **23** with a yield of 53%. The precursor **12** was confirmed by the atmospheric-pressure chemical ionization (APCI) mass spectrum, which displayed a molecular ion peak at 971.37 m/z ([**12**+H]⁺). (Figure 5-4)



Scheme 5-2. Synthetic route of precursor **12**.

5.3.2 Scholl reaction toward rearranged product

We studied the typical Pd-catalyzed cyclization reaction and oxidative dehydrogenation reaction conditions of the dimer precursor **12**, using DDQ and TfOH in dichloromethane.^[23] The ¹H NMR spectrum of the resulting product (refer to the spectrum of **15**) displayed complex signal patterns, making it difficult to assign the exact chemical structure. This implies that a structural rearrangement might have occurred during the reaction. Unfortunately, the mass signal of the product could not be detected in the matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectral analysis. Therefore, it was difficult to determine the structure of the product based on these spectral data.

We successfully determined the structure of the product through X-ray crystallographic analysis (Figure 5-1d).^[26] We obtained a crystal of the product suitable for X-ray crystallographic analysis by vapor diffusion of acetonitrile into an *o*-dichlorobenzene solution. The X-ray analysis reveals that the chemical structure of the product is **15**. Two molecules stack on top of each other to maximize the overlap of their π surface. Regarding the chemical structure of **15**, it is found that one monomer unit in the dimer precursor forms an unexpectedly fused framework, while another monomeric unit is fused to maintain the original Z-shaped framework. These results indicate that skeletal rearrangements may occur due to incomplete dehydro-chlorination reactions.

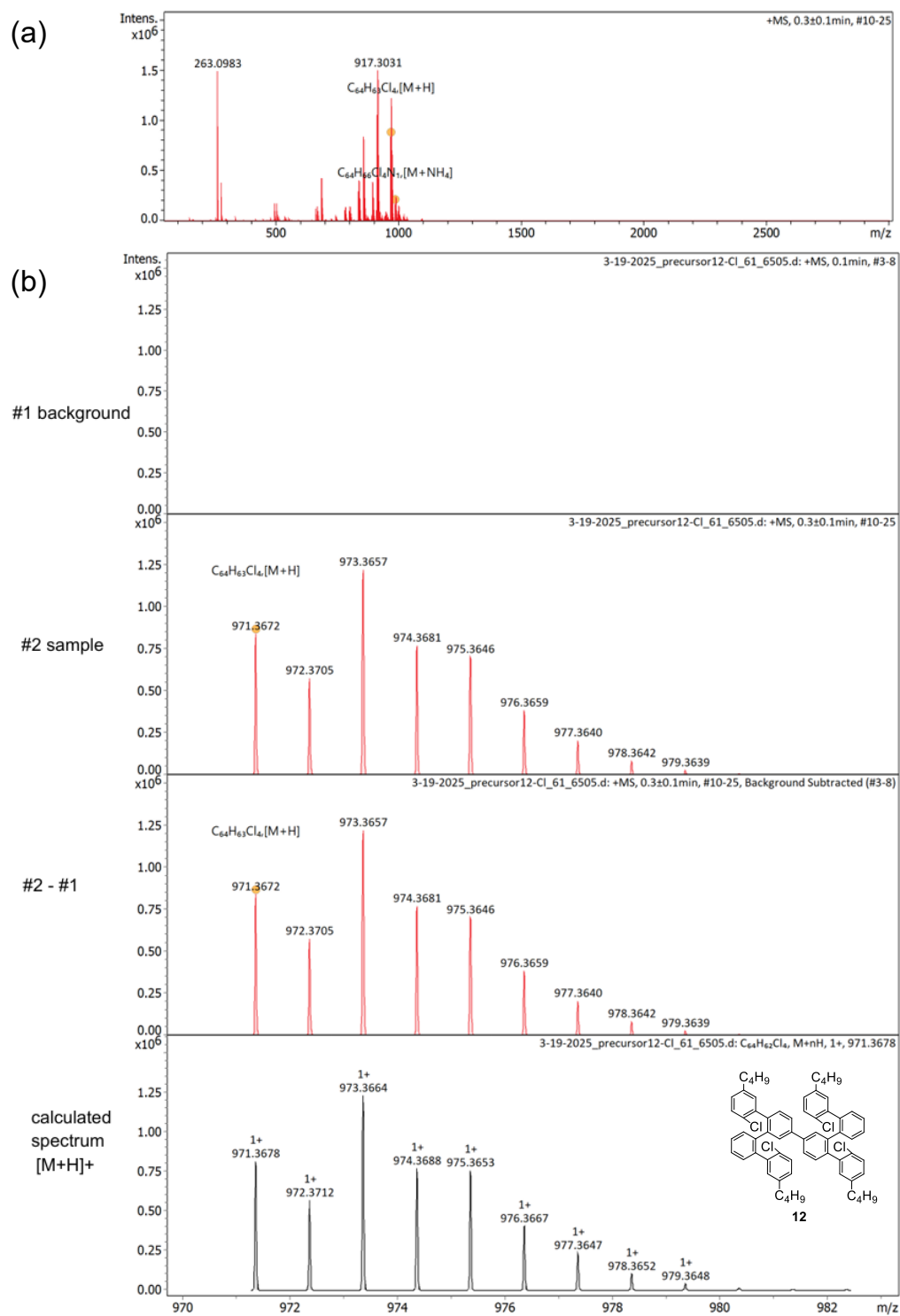


Figure 5-4. APCI mass spectra of (a) full-range and (b) analysis for compound **12**.

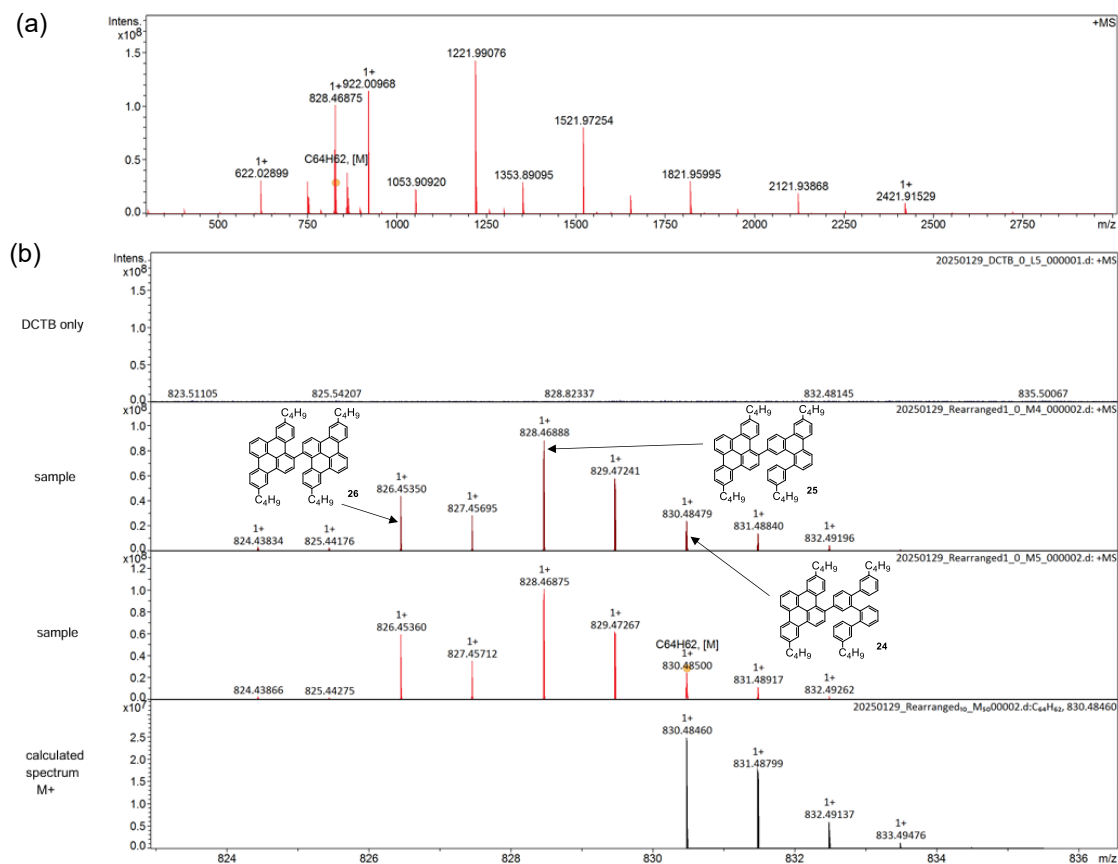


Figure 5-5. MALDI-FT-ICR mass spectra of (a) full-range and (b) analysis for the product after Pd-catalyzed cyclization reaction of compound **12**. DCTB was used as a matrix. The insets show the chemical structures corresponding to the molecular ion peaks.

To clarify the reaction pathway from **12** to **15**, the matrix-assisted laser desorption ionization-Fourier transform ion cyclotron resonance (MALDI-FT-ICR) mass spectrometry was conducted on the intermediate products after the Pd-catalyzed cyclization reaction of compound **12**. Three molecular ion peaks at 830.48, 828.47, and 826.45 m/z were detected (Figure 5-5). We assigned these peaks as chemical structures **24**, **25**, and **26**, respectively (Figure 5-6a). These results show different degrees of cyclization, in which one monomer unit is fully fused via cyclodechlorination, while another monomer unit undergoes partial cyclodechlorination. Compound **24** can undergo skeletal rearrangements to produce the final product **15** via 1,4-aryl shifts and 1,2-aryl shifts. Compound **26** cannot form **15** because of the complete fusion of dimer units. Compound **25** has the potential to form product **15** via double 1,2-aryl shifts of the *m*-butylphenyl and bond rotation of the dimer axis C-C bond. However, energetically, it is unfavorable to occur because of a higher activation energy involved in 1,2-aryl shift than cyclization. The details are explained in the later chapter of DFT calculation.

5.3.3 Mechanism of aryl shifts in Scholl reaction

The proposed rearrangement mechanism is depicted in Figure 5-6 – 5-9. There are three aryl shifts from **12** to **15**. The rearrangement from **24** to **27** and from **29** to **30** occurs through 1,4-aryl shift, while the process **27** to **28** involves the 1,2-aryl shift. The example of 1,4-aryl shift rearrangement in the Scholl reaction was reported in the cyclization reaction of aniline-linked perylene bisimide.^[27] In general, it is well established that the Scholl reaction involves

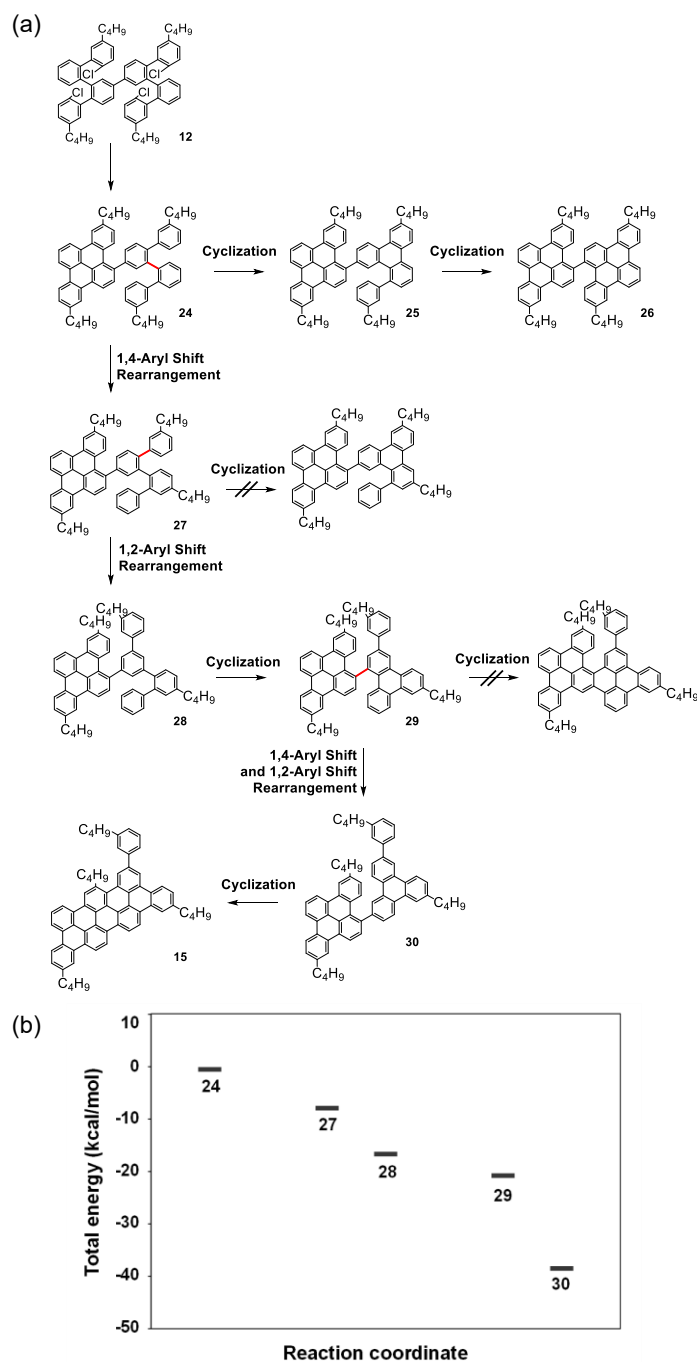


Figure 5-6. (a) Proposed reaction mechanism of rearrangement and cyclodehydrogenation reactions to give the product **15**. The highlighted red bonds indicate the C-C bonds broken during the rearrangement. (b) Calculated energies of possible intermediates for rearrangements and cyclodehydrogenation reaction pathways for product **15**.

two mechanisms: the arenium cation (proton transfer) and the radical cation (electron transfer).^[15] We propose a reaction mechanism to understand why compound **15** is formed instead of the expected product **14**. To confirm the reaction pathways, we carried out theoretical studies by comparing the total energies of possible intermediates. All structures were optimized using the DFT level of theory with the B3LYP functional and 6-31G(d) basis set in Gaussian 16 program package.^[28] Because the presence of the solvent significantly influenced the energy, we conducted the geometric optimization in an environment with the same dielectric constant as DCM (dichloromethane) (more details in the SI).

Initially, our research focuses on investigating the 1,4-shift mechanism of the aryl group in the rearrangements from **24** to **27** (Figure 5-7). Four potential reaction pathways from **24** are proposed, including 1,2-aryl shift of monophenyl (**R2'**/**A2'**), 1,4-aryl shift of biphenyl (**R2**/**A2**), cyclization pathways 1 (**R3**/**A3**) and 2 (**R3'**/**A3'**) (Figure 5-10). The calculation results show that 1,4-aryl shift has a lower activation energy than 1,2-aryl shift, suggesting more likely to occur. Meanwhile, cyclization 1 has a lower activation energy than cyclization 2, suggesting more likely to occur. Then, we focused on the comparison between 1,4-aryl shift and cyclization 1 (which is referred as “cyclization” in Figure 5-7 and hereinafter). The aryl groups have been reported to undergo rearrangement following either the radical cation or the arenium cation mechanism.^[3a,15,29,30] In our case, the arenium cation **A1** can be generated through the protonation of **24**, while the radical cation **R1** can be created by the oxidation of **24** (Figure 5-7a). The **A2** and **R2**

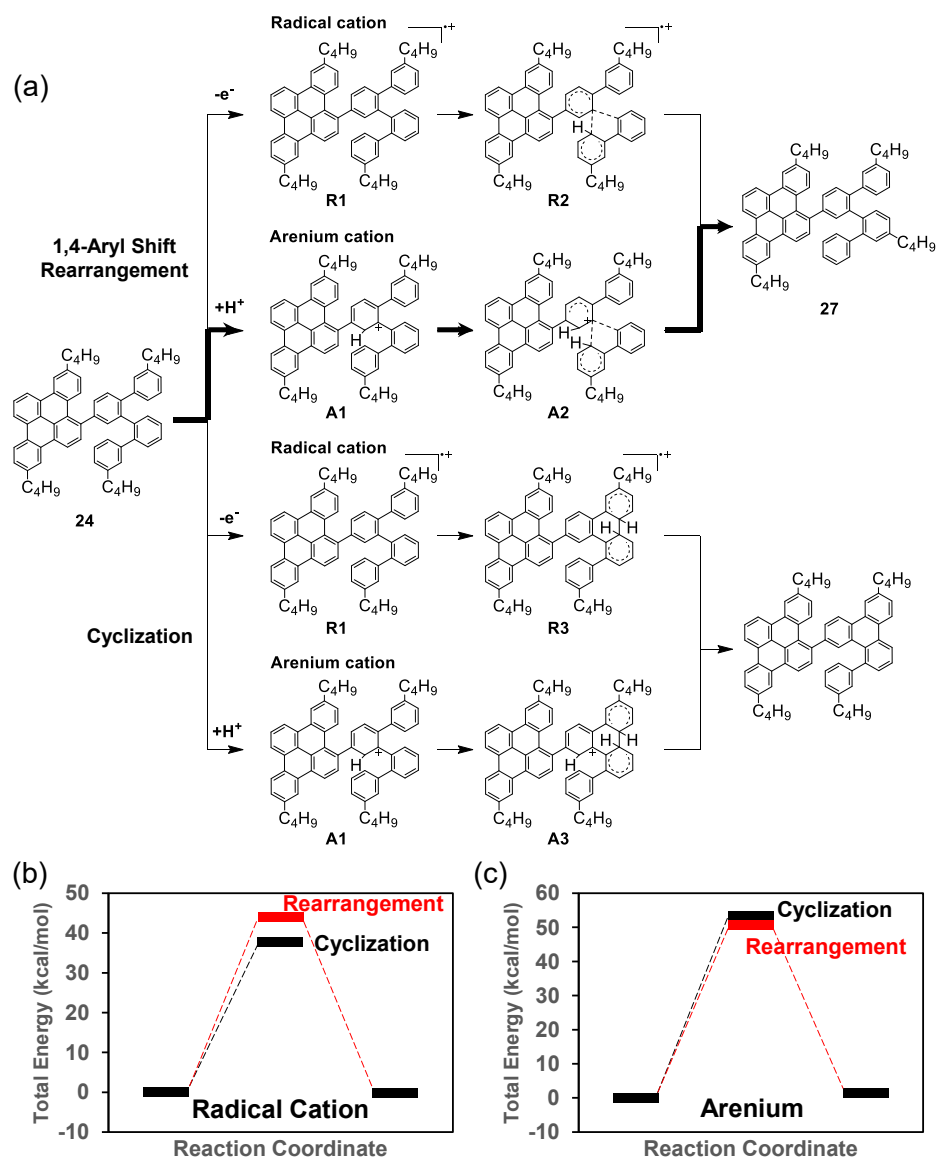


Figure 5-7. (a) Comparison between radical cation and arenium cation mechanisms for the aryl shift from **24** to **27**. (b-c) Calculated energies of rearrangements and cyclodehydrogenation reaction pathways from **24** to **27** through (b) radical cation mechanism and (c) arenium cation mechanism.

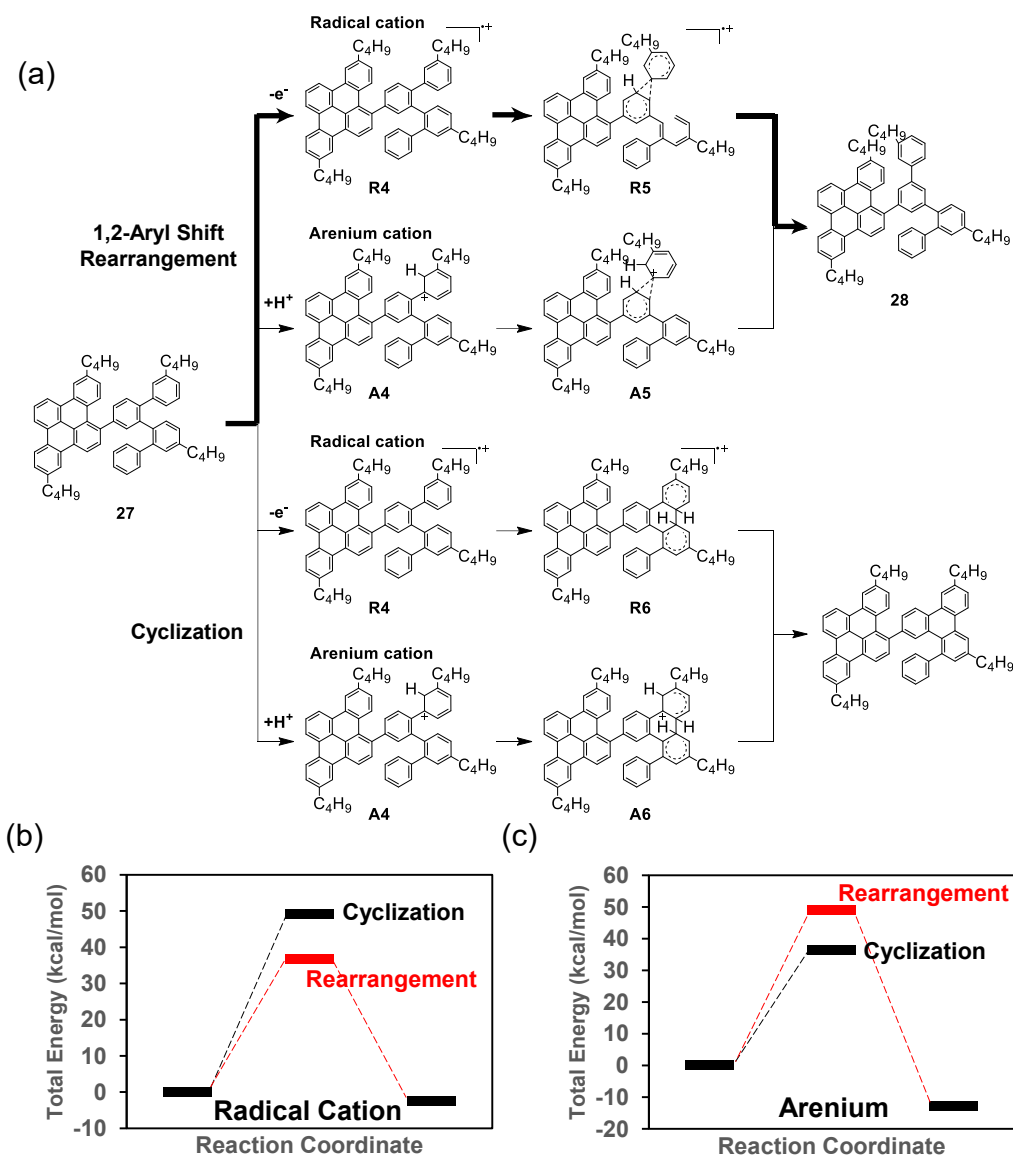


Figure 5-8. (a) Comparison between radical cation and arenium cation mechanisms for the aryl shift from **27** to **28**. (b-c) Calculated energies of rearrangements and cyclodehydrogenation reaction pathways from **27** to **28** through (b) radical cation mechanism and (c) arenium cation mechanism.

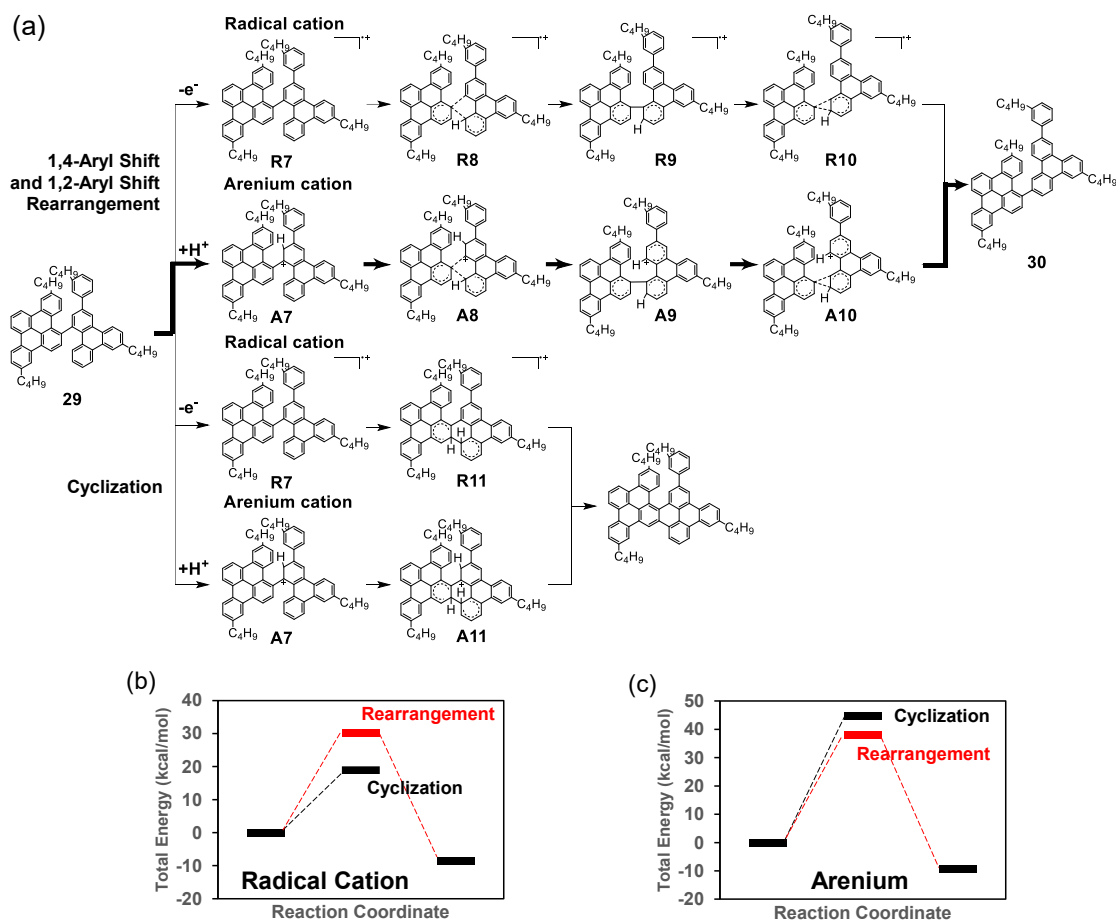


Figure 5-9. (a) Comparison between radical cation and arenium cation mechanisms for the aryl shift from **29** to **30**. (b-c) Calculated energies of rearrangements and cyclodehydrogenation reaction pathways from **29** to **30** through (b) radical cation mechanism and (c) arenium cation mechanism.

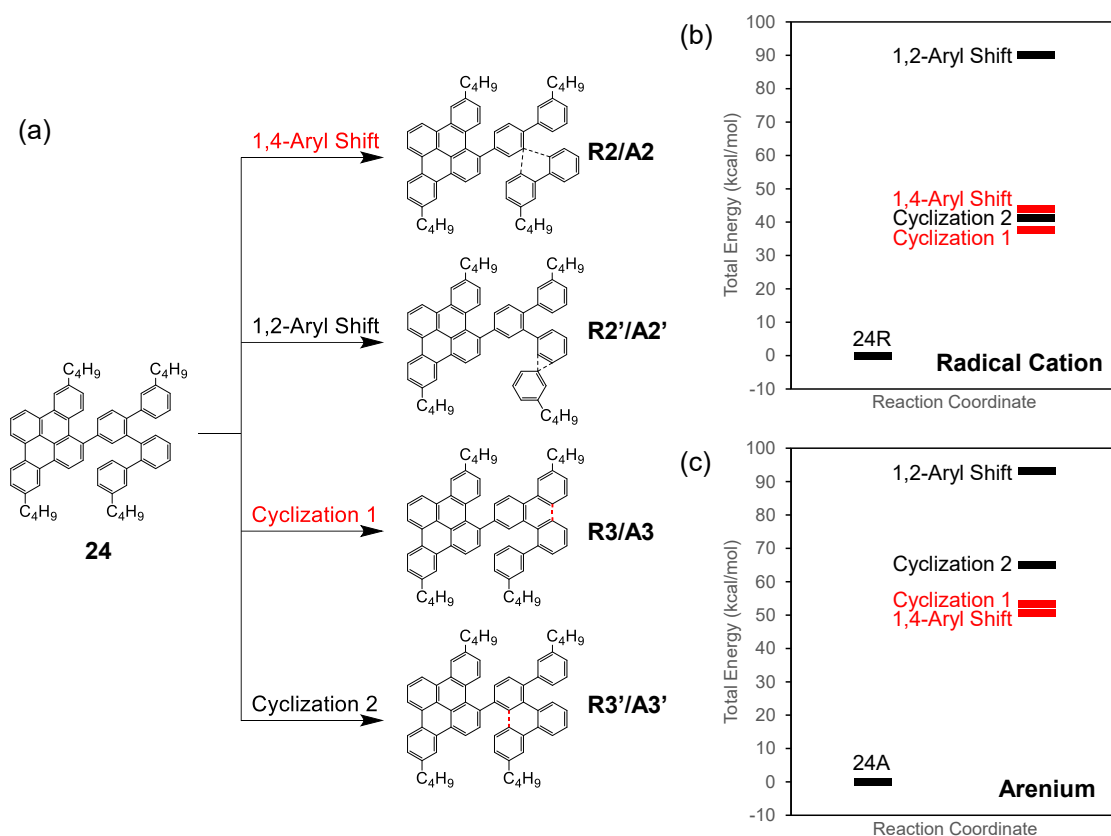


Figure 5-10. (a) Comparison of potential pathways from **24**. (b-c) Calculated energies of rearrangements and cyclodehydrogenation reaction pathways from **24** through (b) radical cation mechanism and (c) arenium cation mechanism.

are expected to be formed from **A1** and **R1** through 1,4-shift rearrangement, respectively. The energy calculation of intermediates based on the radical cation mechanism indicates a preference for cyclization over rearrangement by an energy difference of 0.27 eV (Figure 5-7b). In contrast, the energy of the intermediate produced by rearrangement, based on the arenium cation mechanism, is 0.12 eV smaller than that produced by cyclization (Figure 5-7c). This suggests that the rearrangement is due to the arenium cation mechanism rather than the radical cation mechanism, leading to the formation of **27**. This result is consistent with the phenomena described in the literature, where the rearrangement of aryl groups typically occurs through arenium cation intermediates.^[15] To clarify the driving force behind the rearrangement, we investigate the relative stability of **24** and **27** (Figure 5-6b). The energy of **27** is 0.27 eV more stable than **24**, suggesting that the aryl shift induced by a proton transfer is exergonic. Significant energy stabilization may stem from steric hindrance.

The mechanism of the 1,2-aryl shift that converts from **27** to **28** is investigated through energy calculations of intermediates (Figure 5-8a). It's noteworthy that in comparison to **24-27**, the energy calculation for intermediates using the radical cation mechanism shows a preference for rearrangement over cyclization with an energy difference of 0.54 eV (Figure 5-8b). On the other hand, the energy of the intermediate formed by cyclization, based on the arenium cation mechanism, is 0.40 eV lower than that produced by rearrangement (Figure 5-8c). This indicates that the rearrangement occurs through the radical cation mechanism rather than the arenium cation

mechanism, leading to the formation of **28**.

Next, we investigate the 1,4-shift mechanism of the aryl group in the reaction from **29** to **30**. The arenium cation **A7** can be formed by protonating **29**, while the radical cation **R7** can be created by oxidizing **29** (Figure 5-9a). **A8** and **R8**, which have a five-membered ring, are expected to be created from **A7** and **R7**, respectively, through 1,4-shift rearrangement. The energy calculation of intermediates, based on the radical cation mechanism, shows a preference for cyclization over rearrangement by an energy difference of 0.49 eV (Figure 5-9b). On the other hand, the energy of the intermediate produced by rearrangement, based on the arenium cation mechanism, is 0.30 eV smaller than that produced by cyclization (Figure 5-9c). This suggests that the rearrangement is due to the arenium cation mechanism rather than the radical cation mechanism, leading to the formation of **30**. Once the arenium cation **A10** forms, it can undergo a cyclization reaction to produce product **15**.

It is essential to understand the origin of the mechanism selection, whether it follows an arenium cation- or radical cation mechanism in rearrangements. Our calculations (Figure 3-5) show that routes **24-27** and **27-28** follow the arenium cation mechanism, while route **29-30** follows the radical cation mechanism. These mixed mechanisms are due to differences in the sizes and positions of the aryl groups that shift during the rearrangement. For example, in a study on the intramolecular Scholl reaction between large reaction sites in adjacent phenylbenzenes,^[3a] the Wheland intermediate during the cyclization from o-terphenyl to triphenylene has a much lower energy (~15 kcal/mol)

than the radical cation. This lower energy is also observed in the subsequent deprotonation and dehydrogenation steps. The arenium cation mechanism seems to be favored because these intermediates play a key role in the rate-determining process in proton transfer and oxidation barriers.^[3a] Furthermore, another example suggests the trend that it is less likely that the radical cation mechanism is feasible for larger reaction sites in intramolecular Scholl reactions, such as the cyclization of 1,2,3-triphenylbenzene and 1,2,3,4-tetraphenylbenzene. Based on their DFT calculations, the comparison of these two mechanisms revealed that the arenium cation mechanism involves lower energy transition states than the radical cation mechanism. This reference suggested that the radical cation mechanism was significantly disfavored in larger molecules.^[3a] It is reasonable to infer that the rearrangement routes **24-27** and **29-30** in our work follow the arenium cation mechanism due to the presence of large molecular groups such as biphenyl or triphenylenyl. In contrast, rearrangements at small reaction sites such as monophenyl groups favor a radical cation mechanism rather than an arenium cation mechanism. In an article discussing the unexpected Scholl reaction of five-membered rings in polycyclic aromatic hydrocarbons,^[6] the energy barrier for the 1,2-shift of the 4-tert-butylphenyl group in 6,7,13,14-tetraarylbenzo[k]tetraphene based on the radical cation mechanism was much lower than that of the arenium mechanism. This study concluded that the radical cation mechanism prevailed over the arenium route when the monophenyl migration step was concerned. Similarly, rearrangement route **27-28** in our work follows the radical cation mechanism for the 1,2-aryl shift due to a small reaction site of 2-tert-

butylphenyl. We consider the reasons for the 1,4-aryl shift in reaction route **29-30**. Previous references have shown that during the conversion of precursor molecules into nanographene, increased steric hindrance or electronic energy changes due to substitution at the edges of precursor molecules could inhibit the oxidative cyclodehydrogenation reaction.^[2b] In our study on the 1,4-aryl shift rather than the cyclization of route **29-30**, we observe that intermediate **A8** of the five-membered ring releases significant steric hindrance, as supported by the increased stability after the 1,4-aryl shift (Figure 5-9c).

The absorption spectrum of product **15** (Figure 5-11) shows a weak absorption band in the long wavelength region, extending to approximately 670 nm. To understand the origin of this absorption band, we conducted DFT calculations to study the electronic properties of the armchair nanographene. This band is attributed, through TD-DFT calculations (using the B3LYP/6-31G* method with the implicit solvent model in CH₂Cl₂), to the HOMO–LUMO transition. (Table 5-1 and Figure 5-12)

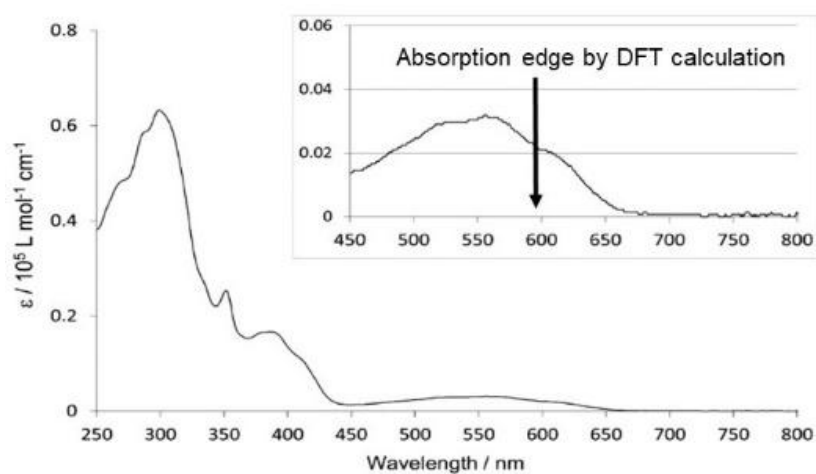


Figure 5-11. UV-vis absorption spectrum of **15**. Inset: Enlarged view at longer wavelength region. The absorption edge is estimated at 595 nm by DFT calculation.

Table 5-1. Selected dominant excitations and involved molecular orbitals of compound **15**.

Excitation	E / eV	λ / nm	orbital	oscillator strength f
1	2.44	509	HOMO $\rightarrow$ LUMO (96%)	0.1287
2	2.87	432	HOMO-1 $\rightarrow$ LUMO (52%)	0.0131
3	3.11	399	HOMO-2 $\rightarrow$ LUMO (71%)	0.0023

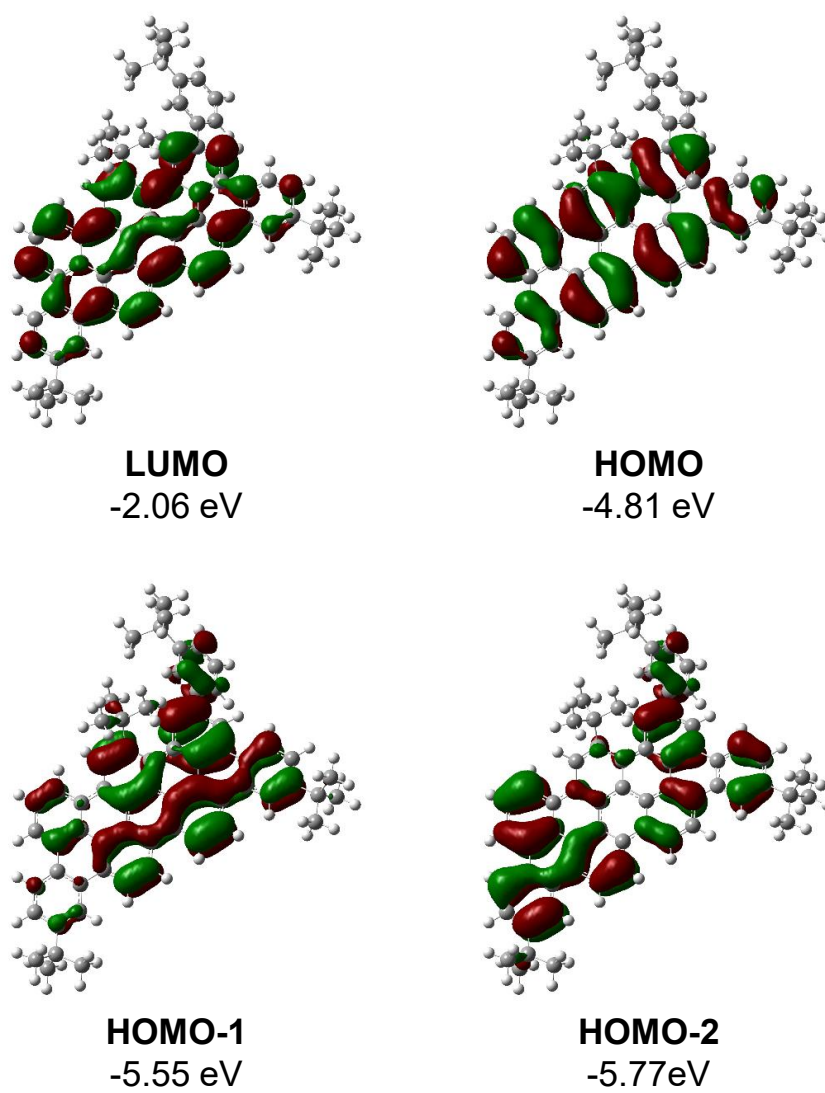
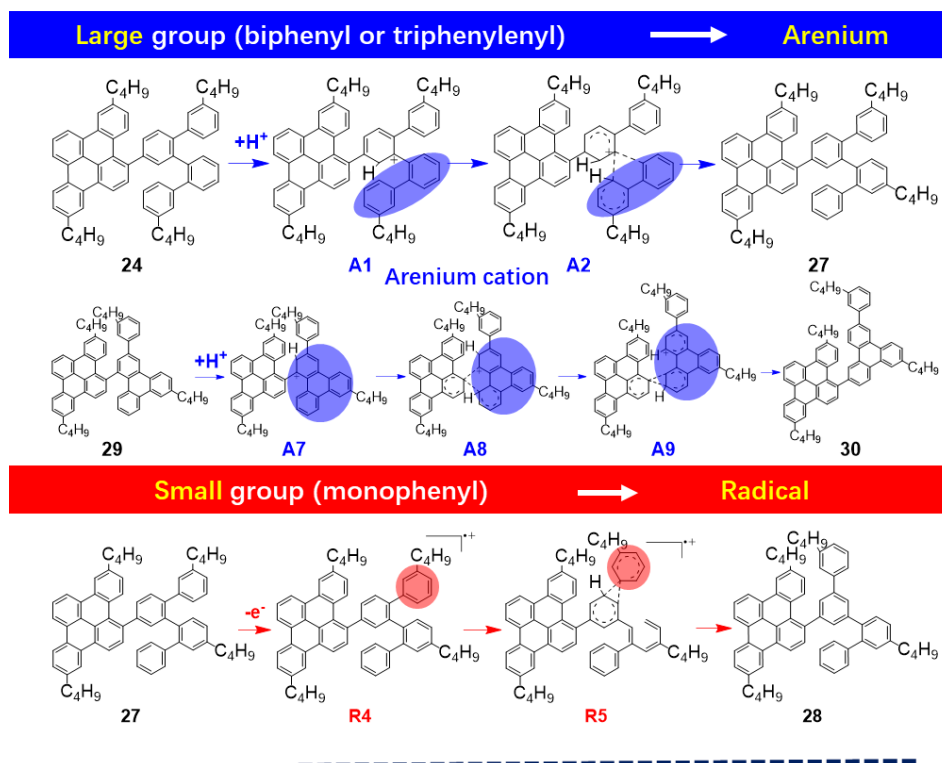


Figure 5-12. Involved frontier molecular orbitals of compound **15**.

5.4 Conclusions

In summary, we have synthesized an armchair nanographene **15** through Pd-catalyzed cyclization followed by oxidative dehydrogenation reactions, which involved 1,4-aryl- and 1,2-aryl shift rearrangements. The unexpected product **15** was characterized by single-crystal X-ray crystallographic analysis. The rearrangement mechanism was investigated by thermodynamic and kinetic studies using DFT calculations. DFT calculations indicate that the steps of **24-27** and **29-30** follow arenium cation mechanism, while the step of **27-28** follows the radical cation mechanism. It is suggested that the selection of arenium cation- or radical cation mechanisms depends on the sizes and positions of the shifting aryl groups. (Figure 5-13) The biphenyl site in **24-27** and triphenylenyl group in **29-30** result in arenium cation mechanism, while monophenyl group in **27-28** favors the radical cation mechanism. Our discoveries have potential in practical applications for synthesizing innovative nanographenes through rearrangement methods.

This work (in one molecule)



Other works (separated cases)

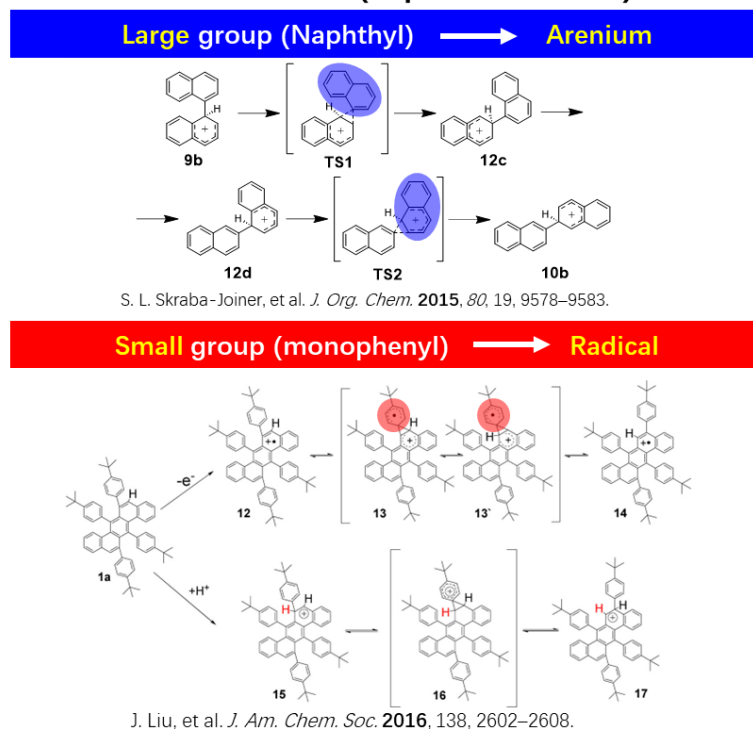


Figure 5-13. Mechanism selection rule.

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Chapter 6

General Conclusions

This thesis addresses three major issues and challenges in the on-surface synthesis of polar GNRs - stereoselective polymerization, the decomposition of introduced functional groups, and the polar crystal formation.

In Chapter 3, we introduced a fundamentally new approach, "vectorial on-surface synthesis," enabling the isotactic polymerization of designed "compass" precursors on low-halogen-contaminated surfaces. This method achieves unprecedented stereoregular control without chiral catalysts, overcoming the inherent limitations of traditional on-surface synthesis (stereoregularity challenges, polarity cancellation). The resulting polar 2D crystalline polymers arise from unique inter-edge CH- π interactions, a novel technique in crystal engineering.

In Chapter 4, we developed the molecular vapor-assisted low-temperature growth (MVLTG) method, a breakthrough strategy overcoming the critical limitation of functional group decomposition during high-temperature dehydrogenation. By utilizing a massive excess of gaseous hydrogen acceptors (DDQ or O₂), MVLTG drastically lowers the GNR growth temperature (e.g., from 500°C to 350°C) while efficiently promoting dehydrogenation (the gas-phase "Scholl reaction") via a gas-2D solid-state reaction mechanism. This enables the successful synthesis of polar GNR 2D crystals.

In Chapter 5, we discovered and mechanistically elucidated an unusual

Scholl-type reaction pathway involving 1,4-aryl and 1,2-aryl shifts to synthesize asymmetric nanographene. This rearrangement is governed by both arenium cation and radical cation mechanisms, depending on the size and/or position of the migrating group. It offers a powerful and unexpected route to synthesize specific armchair nanographenes that are usually difficult to access by design. This represents a novel synthetic methodology that leverages controllable rearrangements.

In summary, this thesis establishes unique synthetic methodologies (vectorial on-surface polymerization, MVLTG, aryl shift rearrangement) that overcome long-standing challenges in GNR science, enabling the targeted creation of novel asymmetric and functionalized nanostructures and revealing fundamental new reaction mechanisms. The methodologies and insights developed in this thesis open diverse avenues for future research and applications:

The development of vectorial on-surface synthesis opens up the possibility of creating polar GNRs, which could lead to a new approach in polar crystal engineering. The developed MVLTG technique is able to produce functionalized GNRs. The discovery of aryl shifts in Scholl reaction have potential in synthesizing innovative nanographenes.

Appendix

Crystal data for compound 15

Formula $\text{C}_{64}\text{H}_{56}\cdot\text{C}_6\text{H}_4\text{Cl}_2$

$M_r = 972.08$

$0.10 \times 0.05 \times 0.30 \text{ mm}^3$

$T = 93(2) \text{ K}$

Triclinic

Space group $P-1$

$a = 11.863 \text{ \AA}$, $b = 15.798 \text{ \AA}$, $c = 16.151 \text{ \AA}$

$\alpha = 114.61^\circ$, $\beta = 111.19^\circ$, $\gamma = 91.45^\circ$

$V = 2510.0 \text{ \AA}^3$

$Z = 2$

$\rho_{\text{calcd}} = 1.286 \text{ gcm}^{-3}$

$\mu = 0.068 \text{ mm}^{-1}$

$F(000) = 1028$

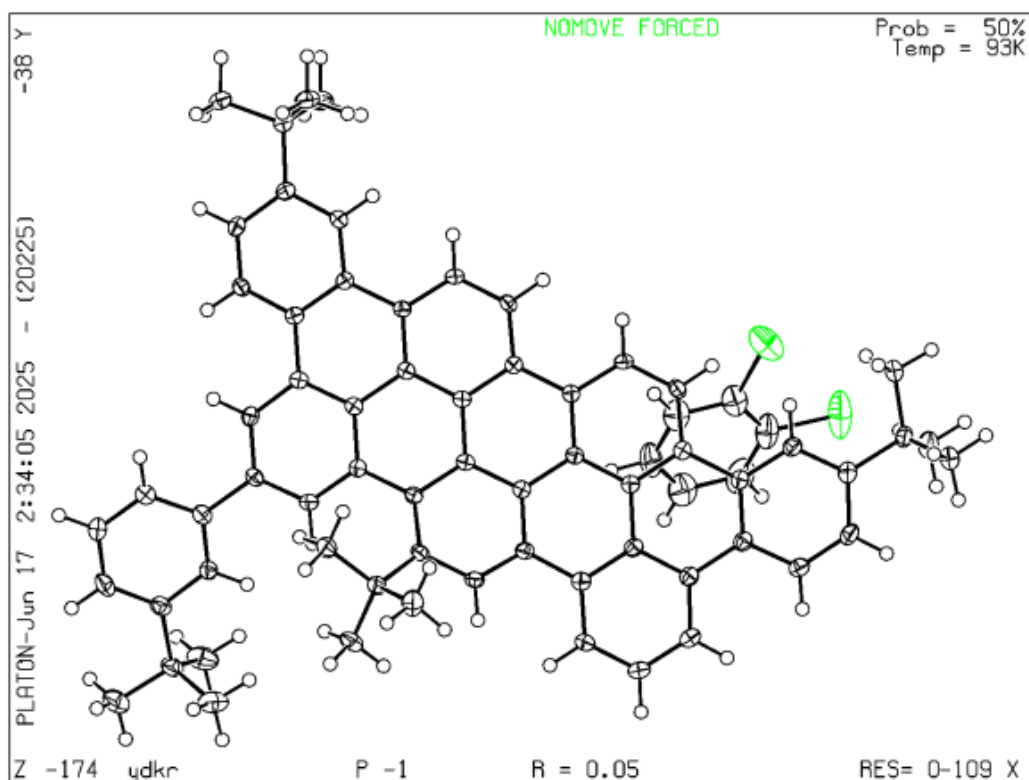
$2\theta_{\text{max}} = 73.8^\circ$

$R_1 (I > 2\sigma(I)) = 0.0527$

$wR_2 (\text{all data}) = 0.148$

GOF = 1.010 for 9573 reflections and 649 parameters.

CCDC No. 2334223



Atomic coordinations of crystal 15

Number	Atom	X	Y	Z
1	C	4.18347	-1.86687	-0.02389
2	C	3.021158	-2.69901	0.125191
3	C	3.166777	-4.10794	-0.00079
4	C	4.40797	-4.6733	-0.23162
5	C	5.543226	-3.87019	-0.33752
6	C	5.45916	-2.46286	-0.23637
7	H	2.291679	-4.74548	0.049437
8	H	4.50187	-5.75101	-0.33519
9	H	6.498963	-4.34883	-0.51155
10	C	6.63862	-1.61676	-0.33809
11	C	7.935709	-2.15039	-0.52186
12	C	6.513171	-0.19995	-0.24466
13	C	9.05177	-1.34671	-0.6093
14	H	8.074656	-3.22284	-0.59408

15	C	7.687973	0.59536	-0.33739
16	C	8.952968	0.063456	-0.51688
17	H	10.02151	-1.81533	-0.74965
18	H	7.588249	1.668378	-0.26117
19	C	5.206252	0.392701	-0.06441
20	C	4.053958	-0.43572	0.048277
21	C	5.01958	1.808271	0.002074
22	C	2.758239	0.153026	0.211696
23	C	3.784836	2.373293	0.138784
24	H	5.874985	2.468512	-0.07028
25	C	2.601188	1.576889	0.229851
26	C	1.611106	-0.67817	0.36667
27	H	3.713096	3.454007	0.166269
28	C	0.309514	-0.11809	0.454543
29	C	1.754959	-2.10257	0.396939
30	C	-0.8449	-0.97623	0.598791
31	C	0.63361	-2.86761	0.862488
32	C	-0.61038	-2.34306	1.095939
33	H	0.838357	-3.8818	1.183559
34	C	1.296719	2.145802	0.299092
35	C	0.144303	1.295587	0.341876
36	C	1.073315	3.559807	0.295139
37	C	-1.16677	1.856968	0.257699
38	C	-0.18495	4.09039	0.278222
39	H	1.917915	4.238373	0.296833
40	C	-1.35107	3.267059	0.228136
41	H	-0.28578	5.169007	0.256652
42	C	-2.10429	-0.44729	0.176755
43	C	-3.17053	-1.28375	-0.25363
44	C	-2.2847	0.97626	0.089286

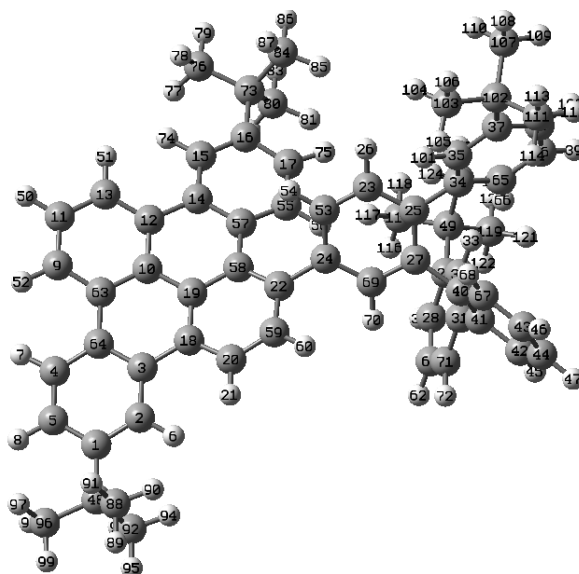
45	C	-4.39845	-0.76899	-0.65973
46	H	-2.9866	-2.34677	-0.3433
47	C	-3.57114	1.505315	-0.20693
48	C	-4.5995	0.620675	-0.58523
49	H	-5.57641	1.007567	-0.84733
50	C	-2.68398	3.816496	0.118028
51	C	-3.78596	2.943019	-0.11493
52	C	-2.92896	5.211794	0.223942
53	C	-5.07053	3.521359	-0.22876
54	C	-4.19083	5.770024	0.107187
55	H	-2.09045	5.864123	0.423793
56	C	-5.26971	4.882075	-0.12556
57	H	-5.93663	2.88668	-0.37939
58	H	-6.28084	5.26848	-0.21505
59	C	-5.48136	-1.64942	-1.17346
60	C	-5.74953	-2.89389	-0.58571
61	C	-6.27031	-1.243	-2.2632
62	C	-6.77335	-3.74025	-1.0417
63	H	-5.15493	-3.19378	0.27214
64	C	-7.28629	-2.06691	-2.7337
65	H	-6.06565	-0.29526	-2.75295
66	C	-7.5381	-3.30171	-2.13076
67	H	-7.8871	-1.75242	-3.58337
68	H	-8.33987	-3.91782	-2.52176
69	C	-1.55455	-3.15106	2.044592
70	C	-2.70975	-2.32113	2.648618
71	C	-2.1128	-4.41143	1.34361
72	C	-0.72287	-3.62667	3.271099
73	H	-2.33706	-1.39669	3.103253
74	H	-3.47921	-2.04792	1.927218

75	H	-3.19255	-2.90861	3.438207
76	H	-1.3026	-5.05284	0.9792
77	H	-2.7147	-5.00039	2.047059
78	H	-2.74765	-4.1671	0.486529
79	H	-1.38028	-4.13977	3.983023
80	H	0.072661	-4.32709	3.003301
81	H	-0.26279	-2.77642	3.786066
82	C	-7.024	-5.08795	-0.33783
83	C	-5.75572	-5.96781	-0.44077
84	C	-7.35635	-4.83978	1.152812
85	C	-8.19675	-5.8664	-0.96441
86	H	-5.49837	-6.16345	-1.48802
87	H	-4.89045	-5.49313	0.033097
88	H	-5.91925	-6.93258	0.055127
89	H	-8.25749	-4.22457	1.256072
90	H	-7.53404	-5.79228	1.667115
91	H	-6.54124	-4.32734	1.674096
92	H	-8.33737	-6.81295	-0.43045
93	H	-9.13792	-5.30851	-0.90045
94	H	-8.01163	-6.10665	-2.01755
95	C	-4.45833	7.279782	0.228143
96	C	-5.4287	7.537266	1.405962
97	C	-3.17252	8.08897	0.481116
98	C	-5.09901	7.792233	-1.08416
99	H	-6.38501	7.021916	1.268316
100	H	-4.99636	7.192123	2.352018
101	H	-5.63901	8.609818	1.498749
102	H	-2.44949	7.971076	-0.33411
103	H	-3.41622	9.154827	0.554167
104	H	-2.68453	7.797787	1.418291

105	H	-5.30834	8.866516	-1.01156
106	H	-4.4279	7.633049	-1.93585
107	H	-6.04365	7.283833	-1.30399
108	C	10.223	0.925178	-0.61529
109	C	10.90559	0.677552	-1.98206
110	C	9.926089	2.431554	-0.49414
111	C	11.19737	0.533795	0.521693
112	H	11.18285	-0.37323	-2.11659
113	H	10.24105	0.956056	-2.80783
114	H	11.82093	1.276303	-2.06463
115	H	9.467526	2.680849	0.46961
116	H	10.8606	2.998634	-0.57074
117	H	9.261653	2.782042	-1.29222
118	H	12.11518	1.131203	0.459203
119	H	10.7436	0.708789	1.503808
120	H	11.48394	-0.52179	0.469682

Rearrangement computational results

1. Cartesian coordinates for optimized geometry of **24**



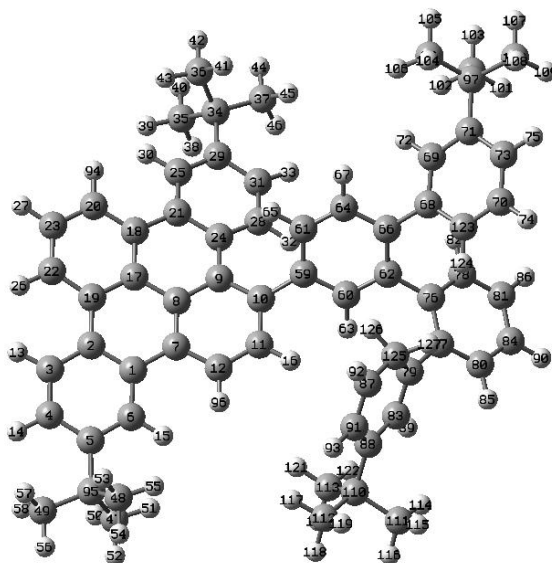
Total Energy = -2476.283 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	7.466614	-2.5482	-0.25398	64	6.268687	-0.07581	-1.01965
2	6.091376	-2.35324	-0.19598	65	-5.51649	-0.75076	-0.21954
3	5.466197	-1.14964	-0.5722	66	-5.19688	-0.58434	0.800984
4	7.660154	-0.27104	-1.07071	67	-3.82671	-3.66502	0.260059
5	8.245113	-1.46929	-0.70583	68	-3.83445	-3.65123	-0.82292
6	5.474844	-3.15908	0.177449	69	-1.09581	-1.43621	0.296737
7	8.307735	0.538506	-1.38046	70	-0.62678	-1.96829	1.115268
8	9.322044	-1.55478	-0.7614	71	-1.55384	-1.96243	4.147056
9	6.373327	2.21476	-2.00887	72	-1.20236	-2.98736	4.187196
10	4.262617	1.405517	-1.10882	73	0.017638	5.998758	-0.2572
11	5.778723	3.424772	-2.33274	74	2.438633	5.058199	-1.20841
12	3.682653	2.678553	-1.36653	75	-1.11373	3.690367	0.72221
13	4.45289	3.660601	-2.00177	76	0.962214	7.023574	-0.91081
14	2.319374	2.939104	-0.90546	77	1.926749	7.073953	-0.39825
15	1.813201	4.256119	-0.84877	78	1.143683	6.794106	-1.96445

16	0.575395	4.567022	-0.31062	79	0.512676	8.018996	-0.86249
17	-0.16419	3.499952	0.236538	80	-0.19918	6.414713	1.21643
18	4.013369	-0.98272	-0.49783	81	-0.902	5.752439	1.726413
19	3.431529	0.303799	-0.66701	82	0.743326	6.392118	1.770104
20	3.161752	-2.07025	-0.28223	83	-0.60075	7.431538	1.268244
21	3.562015	-3.07041	-0.18955	84	-1.33477	6.045259	-1.00639
22	1.187083	-0.65116	-0.40031	85	-2.06745	5.366262	-0.56466
23	-2.29785	-0.11487	-1.79334	86	-1.7527	7.056151	-0.97232
24	-0.29828	-0.65816	-0.54809	87	-1.20892	5.764217	-2.05555
25	-3.10358	-0.89827	-0.95008	88	7.494363	-5.03051	-0.69053
26	-2.76894	0.426473	-2.60576	89	7.920886	-5.99354	-0.39322
27	-2.47675	-1.59156	0.110716	90	6.408792	-5.10285	-0.59306
28	-1.49262	0.301785	4.978957	91	7.724249	-4.86792	-1.74699
29	-2.46887	0.701329	4.05352	92	7.732267	-4.15977	1.666172
30	-1.08551	1.018607	5.682115	93	8.133811	-3.37009	2.306879
31	-2.52633	-1.59999	3.210262	94	6.653561	-4.20665	1.83172
32	-2.95791	-0.2662	3.170732	95	8.161558	-5.11291	1.990299
33	-3.71415	0.001626	2.446167	96	9.608169	-3.9148	0.034265
34	-4.56816	-0.94938	-1.22669	97	9.919318	-3.75562	-1.00178
35	-5.02232	-1.16039	-2.53967	98	10.08796	-3.15528	0.657411
36	-6.87301	-0.76191	-0.52678	99	9.992768	-4.88887	0.348061
37	-6.37999	-1.18014	-2.86999	100	-8.3646	-0.98049	-2.04012
38	-7.30082	-0.97426	-1.83228	101	-4.28003	-1.32945	-3.30827
39	-7.60318	-0.60133	0.258983	102	-6.88365	-1.42141	-4.30528
40	-3.18742	-2.61638	0.94062	103	-5.73276	-1.61793	-5.30879
41	-3.15447	-2.65025	2.352462	104	-5.08201	-0.74081	-5.35923
42	-3.76305	-3.72872	3.01555	105	-5.11783	-2.48683	-5.05941
43	-4.42551	-4.72132	0.932855	106	-6.14323	-1.7814	-6.30885
44	-4.39416	-4.75446	2.324071	107	-7.71985	-0.20511	-4.767
45	-3.75173	-3.73996	4.099533	108	-8.08764	-0.36186	-5.78579

46	-4.90742	-5.51495	0.373104	109	-8.58562	-0.03857	-4.12222
47	-4.85967	-5.56908	2.867464	110	-7.11741	0.707323	-4.75945
48	8.075496	-3.89367	0.181982	111	-7.76741	-2.69012	-4.33317
49	-2.99887	2.147197	4.076743	112	-8.63296	-2.59623	-3.67357
50	6.353749	4.190859	-2.84062	113	-8.13762	-2.87347	-5.34665
51	4.013748	4.615043	-2.25768	114	-7.19865	-3.56802	-4.01479
52	7.410293	2.056609	-2.27179	115	-1.8208	3.146086	4.023772
53	-0.92868	-0.00478	-1.61551	116	-1.15863	3.046298	4.886206
54	-0.34358	0.593496	-2.3032	117	-1.21804	2.998097	3.124723
55	0.299562	2.202573	0.186582	118	-2.19875	4.173087	4.018265
56	-0.29122	1.426563	0.648881	119	-3.79015	2.366185	5.388118
57	1.525784	1.871843	-0.42873	120	-4.17592	3.389561	5.434853
58	2.022647	0.491609	-0.50323	121	-4.63833	1.679093	5.451363
59	1.790553	-1.90845	-0.27721	122	-3.16179	2.202882	6.26696
60	1.157211	-2.78549	-0.22145	123	-3.93506	2.448211	2.891755
61	-1.03529	-1.00932	5.019005	124	-3.4401	2.286705	1.930294
62	-0.27426	-1.29273	5.737941	125	-4.83804	1.832756	2.916576
63	5.643661	1.194334	-1.38603	126	-4.25355	3.493376	2.932611

2. Cartesian coordinates for optimized geometry of A1



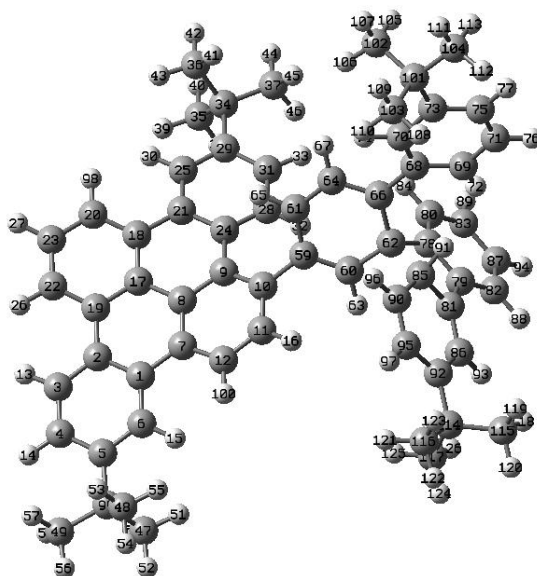
Total Energy = -2476.645 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	4.965721	0.696892	-0.50917	65	-1.02715	1.718606	-1.45305
2	5.510627	1.987944	-0.78253	66	-3.43517	-0.5734	-0.63404
3	6.892217	2.072394	-1.0419	67	-3.3581	1.146746	-1.93011
4	7.705786	0.954104	-1.03242	68	-4.82742	-0.87002	-1.0343
5	7.193062	-0.33274	-0.75339	69	-5.74826	0.183579	-1.18834
6	5.831287	-0.422	-0.49723	70	-6.5494	-2.40317	-1.77053
7	3.543348	0.565718	-0.25601	71	-7.06858	-0.02238	-1.60886
8	2.725258	1.723883	-0.12544	72	-5.42411	1.18928	-0.93855
9	1.335745	1.592606	0.1736	73	-7.44913	-1.34098	-1.90406
10	0.725513	0.290912	0.088832	74	-6.87028	-3.41147	-2.01588
11	1.566469	-0.83958	0.011836	75	-8.45612	-1.5543	-2.24323
12	2.92754	-0.70675	-0.13404	76	-3.26901	-2.50497	1.05326
13	7.353097	3.03351	-1.23563	77	-2.66849	-3.78884	1.123032
14	8.762083	1.085585	-1.23506	78	-4.41075	-2.24093	1.831424
15	5.422913	-1.39589	-0.2601	79	-1.46383	-4.18244	0.333181
16	1.122628	-1.82833	-0.03881	80	-3.24594	-4.74973	1.969668
17	3.291301	3.034254	-0.34497	81	-4.96075	-3.20606	2.668338

18	2.476577	4.194637	-0.21942	82	-4.85724	-1.25227	1.789314
19	4.647194	3.161155	-0.76169	83	-0.37948	-4.78915	0.98339
20	2.996302	5.438226	-0.62314	84	-4.37462	-4.47025	2.736532
21	1.155264	4.070237	0.383128	85	-2.80651	-5.7423	2.003044
22	5.12038	4.431059	-1.14116	86	-5.83792	-2.97127	3.264023
23	4.298352	5.550239	-1.09237	87	-0.26297	-4.41369	-1.75517
24	0.609619	2.767493	0.614726	88	0.773232	-5.2133	0.300217
25	0.424624	5.194783	0.806594	89	-0.44096	-4.92235	2.05982
26	6.134504	4.549264	-1.50236	90	-4.7971	-5.23867	3.377532
27	4.678084	6.515112	-1.41359	91	0.810092	-5.0107	-1.08615
28	-0.59121	2.684107	1.365051	92	-0.21686	-4.28379	-2.83321
29	-0.7888	5.107332	1.487639	93	1.671325	-5.32692	-1.66375
30	0.844256	6.178532	0.638822	94	2.37684	6.326255	-0.58726
31	-1.26785	3.811282	1.782347	95	8.076663	-1.59278	-0.71684
32	-0.97008	1.714856	1.659966	96	3.516747	-1.60792	-0.24477
33	-2.17032	3.684342	2.368142	97	-8.03298	1.17276	-1.72709
34	-1.52012	6.38516	1.929718	98	-8.19221	1.841713	-0.34074
35	-0.61538	7.186367	2.898051	99	-7.4586	2.200509	-2.73141
36	-1.83303	7.249036	0.683253	100	-9.42944	0.748382	-2.22019
37	-2.84736	6.079195	2.64998	101	-8.60498	1.138084	0.390943
38	-0.37512	6.599081	3.791187	102	-7.23697	2.209986	0.049185
39	0.327413	7.485944	2.428652	103	-8.87424	2.697007	-0.40985
40	-1.12948	8.098826	3.220464	104	-7.33703	1.754998	-3.72511
41	-2.47854	6.710453	-0.01968	105	-8.13646	3.056756	-2.8248
42	-2.35173	8.16591	0.984871	106	-6.48319	2.584868	-2.41351
43	-0.92466	7.543759	0.147578	107	-10.0762	1.62922	-2.29136
44	-3.33873	7.018378	2.924021	108	-9.39101	0.288749	-3.21424
45	-3.54096	5.519912	2.011616	109	-9.91048	0.043539	-1.53271
46	-2.69266	5.510926	3.574053	110	1.923768	-5.87659	1.08089
47	8.013872	-2.22075	0.696481	111	1.40283	-7.16048	1.770475

48	7.5582	-2.61338	-1.75853	112	3.100713	-6.26747	0.167086
49	9.550297	-1.28045	-1.04113	113	2.452341	-4.89822	2.156806
50	8.378698	-1.52079	1.456371	114	0.591895	-6.94619	2.47442
51	6.994811	-2.5135	0.971531	115	1.025845	-7.87679	1.032143
52	8.639064	-3.11996	0.736219	116	2.210417	-7.64485	2.331776
53	7.592689	-2.19678	-2.77136	117	3.535983	-5.3961	-0.33672
54	8.179765	-3.51576	-1.74203	118	3.892539	-6.73173	0.764733
55	6.526015	-2.91924	-1.55608	119	2.801164	-6.99061	-0.59944
56	10.13535	-2.20532	-1.0082	120	3.269801	-5.36018	2.722612
57	9.668909	-0.85401	-2.04372	121	2.836745	-3.97843	1.69871
58	9.993069	-0.58826	-0.31603	122	1.673804	-4.61458	2.872594
59	-0.71069	0.060199	-0.08761	123	-5.25242	-2.18183	-1.32977
60	-1.33861	-1.05391	0.500588	124	-4.58778	-3.01302	-1.21903
61	-1.48671	0.874846	-0.95008	125	-1.39261	-3.9995	-1.05768
62	-2.67534	-1.38165	0.269854	126	-1.31538	-3.12433	-1.66843
63	-0.77808	-1.6595	1.203747	127	-2.40448	-4.34736	-1.05923
64	-2.80293	0.552504	-1.212				

3. Cartesian coordinates for optimized geometry of A2



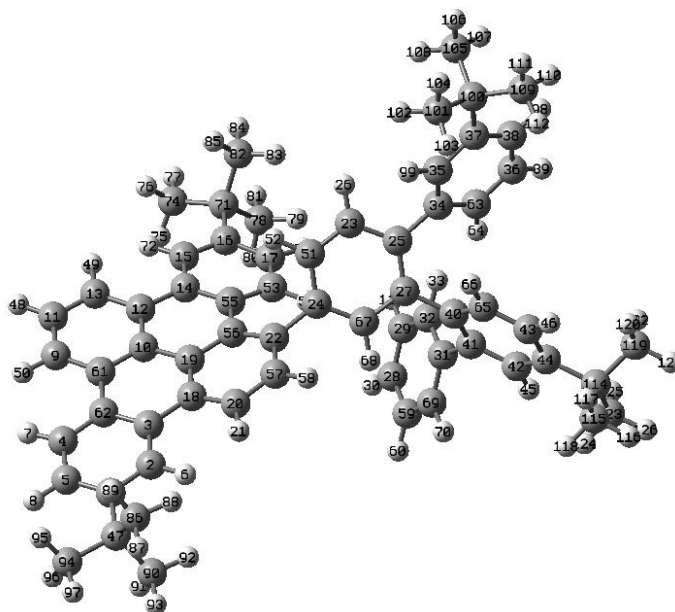
Total Energy = -2476.565 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	5.227819	-0.81983	-0.64432	65	-0.3629	1.821603	-1.45761
2	6.112212	0.255377	-0.90616	66	-3.30179	0.452883	-0.36275
3	7.467365	-0.04997	-1.13443	67	-2.76979	2.016394	-1.72797
4	7.938335	-1.35222	-1.11239	68	-4.73133	0.5163	-0.70354
5	7.07917	-2.43474	-0.84687	69	-5.76281	0.189889	0.208099
6	5.739157	-2.13245	-0.61501	70	-5.11323	0.87154	-2.01882
7	3.809821	-0.54209	-0.40242	71	-7.09293	0.237867	-0.19432
8	3.364855	0.800377	-0.22285	72	-5.53418	-0.04104	1.240514
9	1.998963	1.073405	0.101905	73	-6.44552	0.926653	-2.44057
10	1.054398	0.016206	0.022717	74	-4.33397	1.070313	-2.74587
11	1.512702	-1.29026	-0.19341	75	-7.43433	0.603663	-1.49674
12	2.857521	-1.57035	-0.35963	76	-7.8767	0.002643	0.520047
13	8.181317	0.746618	-1.30971	77	-8.48212	0.634425	-1.77139
14	8.994015	-1.52124	-1.29026	78	-3.30168	-0.42347	2.076794
15	5.066843	-2.9478	-0.37568	79	-3.57288	-1.68739	2.645504
16	0.786765	-2.09403	-0.28152	80	-3.41912	0.736478	2.83421

17	4.280509	1.897296	-0.46841	81	-3.34056	-2.71207	1.648624
18	3.827139	3.244434	-0.37082	82	-3.96889	-1.7912	3.986948
19	5.609995	1.629983	-0.90838	83	-3.81733	0.624665	4.170611
20	4.660703	4.277759	-0.81998	84	-3.20073	1.708767	2.402566
21	2.529741	3.511247	0.254984	85	-3.31993	-2.06598	0.316177
22	6.408729	2.701838	-1.33425	86	-3.01933	-4.04563	1.812141
23	5.932291	4.006326	-1.31034	87	-4.09276	-0.62711	4.740523
24	1.651691	2.431616	0.534754	88	-4.19778	-2.75846	4.424972
25	2.168171	4.807324	0.668955	89	-3.90505	1.520278	4.778485
26	7.405513	2.518972	-1.71737	90	-2.75176	-2.8847	-0.7624
27	6.558633	4.817695	-1.66961	91	-4.36055	-1.80929	0.034217
28	0.505515	2.711174	1.308235	92	-2.56629	-4.82564	0.727318
29	0.999375	5.091643	1.374714	93	-3.05707	-4.48064	2.805967
30	2.853603	5.621598	0.468291	94	-4.4069	-0.687	5.777964
31	0.181896	3.998453	1.709403	95	-2.41832	-4.19278	-0.54974
32	-0.12114	1.897265	1.648617	96	-2.6643	-2.45169	-1.75532
33	-0.7062	4.143839	2.314238	97	-2.0462	-4.7758	-1.38327
34	0.680503	6.538225	1.793466	98	4.314719	5.30468	-0.80692
35	1.801458	7.068444	2.7194	99	7.56531	-3.89492	-0.79013
36	0.591975	7.429711	0.531727	100	3.15318	-2.59727	-0.53662
37	-0.65761	6.64377	2.549921	101	-6.77414	1.31476	-3.89515
38	1.886923	6.456255	3.624202	102	-6.20365	2.722156	-4.1927
39	2.777255	7.068748	2.222853	103	-6.13506	0.285069	-4.85761
40	1.58438	8.098662	3.025182	104	-8.29158	1.345093	-4.15986
41	-0.20282	7.084974	-0.13981	105	-6.64036	3.474207	-3.52618
42	0.371505	8.465736	0.814288	106	-5.11522	2.759144	-4.07452
43	1.529541	7.432635	-0.03378	107	-6.43269	3.010689	-5.2247
44	-0.85232	7.690084	2.808463	108	-6.52542	-0.72235	-4.67366
45	-1.49964	6.292715	1.941818	109	-6.36089	0.550279	-5.89659
46	-0.6457	6.07269	3.485392	110	-5.04484	0.248332	-4.75637

47	7.304068	-4.47092	0.622112	111	-8.47532	1.633236	-5.20004
48	6.796921	-4.73531	-1.83787	112	-8.75572	0.364343	-4.00579
49	9.071821	-4.01973	-1.08819	113	-8.80472	2.074267	-3.52274
50	7.84101	-3.89741	1.385937	114	-2.20469	-6.29636	0.952308
51	6.239557	-4.45589	0.880045	115	-3.44517	-7.03862	1.513863
52	7.645207	-5.51162	0.676635	116	-1.75854	-7.00635	-0.34045
53	6.968303	-4.35363	-2.85068	117	-1.0455	-6.38033	1.980519
54	7.131849	-5.77894	-1.80714	118	-3.78542	-6.61784	2.465307
55	5.716679	-4.72761	-1.65606	119	-4.28188	-7.0029	0.807796
56	9.369231	-5.07308	-1.04477	120	-3.19429	-8.09048	1.687957
57	9.323169	-3.64793	-2.08796	121	-0.8498	-6.56354	-0.76321
58	9.680386	-3.47669	-0.35642	122	-1.5349	-8.05427	-0.11795
59	-0.42345	0.203832	-0.00228	123	-2.54087	-6.99548	-1.10757
60	-1.26927	-0.58659	0.719583	124	-0.78119	-7.43007	2.147803
61	-1.01271	1.168098	-0.8861	125	-0.15277	-5.86091	1.615248
62	-2.76529	-0.5409	0.632094	126	-1.31766	-5.94847	2.948757
63	-0.862	-1.30537	1.425546	127	-6.36089	0.550279	-5.89659
64	-2.38895	1.263779	-1.04605				-

4. Cartesian coordinates for optimized geometry of **27**



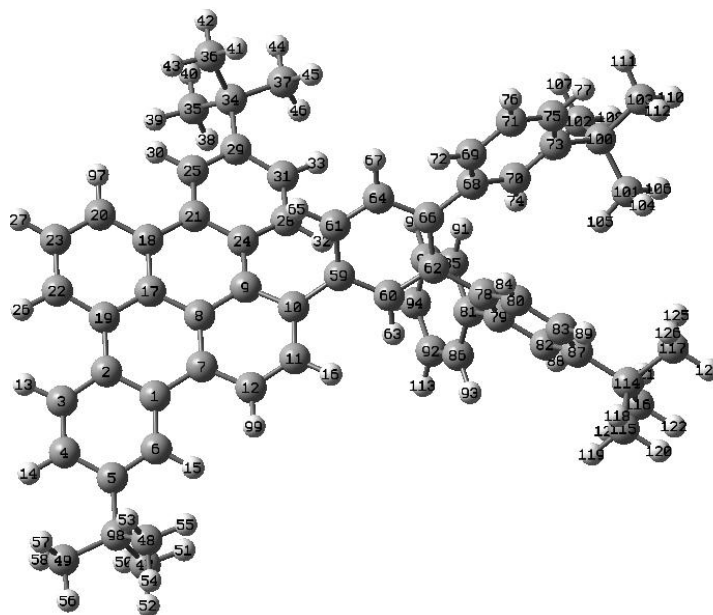
Total Energy = -2476.283 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	-7.18923	-3.23268	1.05465	64	4.924863	0.897413	-0.67816
2	-5.86878	-2.82835	0.899477	65	4.265519	-2.25214	0.365808
3	-5.48808	-1.48159	0.748769	66	4.217612	-2.11243	1.439184
4	-7.82684	-0.89778	0.906484	67	1.079082	-0.77426	-0.03052
5	-8.17078	-2.22807	1.055791	68	0.780327	-1.5642	-0.70732
6	-5.10122	-3.59097	0.884632	69	1.807774	-1.65449	-3.70161
7	-8.62561	-0.16708	0.898439	70	1.78753	-2.73449	-3.65178
8	-9.21796	-2.48211	1.166874	71	-1.22672	6.018727	-1.90479
9	-7.0706	1.945953	0.708119	72	-3.5372	5.026936	-0.79388
10	-4.7707	1.271323	0.288807	73	0.305544	3.717852	-2.11204
11	-6.71802	3.277159	0.545608	74	-2.48091	6.905904	-2.01668
12	-4.42854	2.635393	0.068878	75	-3.21334	6.479244	-2.70591
13	-5.41396	3.617696	0.220869	76	-2.96553	7.054955	-1.04966
14	-3.07941	2.972179	-0.38536	77	-2.1999	7.89242	-2.39174
15	-2.77537	4.265682	-0.85785	78	-0.5341	6.003758	-3.28462
16	-1.5635	4.590614	-1.4471	79	0.437519	5.508692	-3.25068

17	-0.63254	3.546297	-1.60033	80	-1.14964	5.494616	-4.02966
18	-4.08345	-1.09614	0.588592	81	-0.36443	7.027776	-3.626
19	-3.73738	0.251541	0.295722	82	-0.26694	6.647312	-0.86793
20	-3.05192	-2.02754	0.742161	83	0.648558	6.059646	-0.77315
21	-3.27096	-3.06325	0.967896	84	0.009753	7.662558	-1.16688
22	-1.35889	-0.32068	0.398904	85	-0.73694	6.696941	0.116568
23	1.844708	1.240596	1.683475	86	-6.80846	-5.29061	2.453904
24	0.08965	-0.00091	0.580781	87	-7.0728	-6.34137	2.60122
25	2.842889	0.473103	1.063241	88	-5.72292	-5.2316	2.354527
26	2.144902	2.042439	2.35015	89	-7.09426	-4.73745	3.350966
27	2.446605	-0.55756	0.186133	90	-7.05356	-5.49303	-0.04562
28	1.081106	0.395351	-4.73203	91	-7.53239	-5.09918	-0.94458
29	1.895595	1.117381	-3.86262	92	-5.973	-5.41758	-0.18058
30	0.455348	0.912536	-5.45477	93	-7.30616	-6.5536	0.03963
31	2.633778	-0.95052	-2.82545	94	-9.03797	-4.96484	1.376096
32	2.669367	0.447061	-2.91829	95	-9.43029	-4.46962	2.267424
33	3.324876	1.0044	-2.25956	96	-9.60291	-4.61076	0.510729
34	4.271282	0.790409	1.368729	97	-9.23017	-6.03464	1.480704
35	4.675812	0.936258	2.703371	98	7.93868	1.707085	2.241617
36	6.527259	1.31925	0.68759	99	3.934627	0.770477	3.473792
37	5.990806	1.257826	3.057217	100	6.415159	1.450942	4.523893
38	6.911043	1.449188	2.018794	101	5.39994	0.837447	5.507217
39	7.258009	1.477766	-0.09931	102	4.428039	1.331825	5.458924
40	3.42806	-1.48402	-0.45653	103	5.251879	-0.22795	5.316337
41	3.492605	-1.69513	-1.84525	104	5.767807	0.948088	6.529744
42	4.389457	-2.64732	-2.35438	105	6.523583	2.967068	4.807305
43	5.144466	-3.18759	-0.15773	106	6.838857	3.143125	5.839766
44	5.230733	-3.4061	-1.53984	107	7.250925	3.440172	4.144402
45	4.420148	-2.77068	-3.43035	108	5.561485	3.461426	4.655729
46	5.767561	-3.75497	0.525719	109	7.785044	0.789861	4.78926

47	-7.52677	-4.72562	1.208453	110	8.587333	1.254848	4.214443
48	-7.46554	4.052567	0.663553	111	8.045226	0.886169	5.846137
49	-5.16874	4.661888	0.087034	112	7.763252	-0.27346	4.540286
50	-8.09575	1.709718	0.953602	113	1.938175	2.197469	-3.93303
51	0.495592	1.01897	1.450103	114	6.204605	-4.45594	-2.09797
52	-0.24765	1.635618	1.940652	115	5.799044	-5.84987	-1.56836
53	-0.89189	2.278737	-1.12023	116	6.469693	-6.61792	-1.96366
54	-0.15908	1.509814	-1.30007	117	5.8453	-5.89263	-0.47843
55	-2.09079	1.96393	-0.44545	118	4.779506	-6.0982	-1.87103
56	-2.37181	0.620147	0.091382	119	7.641403	-4.13364	-1.63268
57	-1.72936	-1.63571	0.690432	120	7.729546	-4.14474	-0.54505
58	-0.94965	-2.35263	0.911579	121	8.341692	-4.87319	-2.03023
59	1.047637	-0.99036	-4.65274	122	7.951327	-3.1472	-1.98439
60	0.389317	-1.54736	-5.31213	123	6.198804	-4.50064	-3.63634
61	-6.12091	0.923878	0.581966	124	5.221382	-4.78634	-4.03164
62	-6.49071	-0.48499	0.751022	125	6.47438	-3.53648	-4.06944
63	5.217137	0.989233	0.358757	126	6.922903	-5.24058	-3.98419

5. Cartesian coordinates for optimized geometry of **R4**



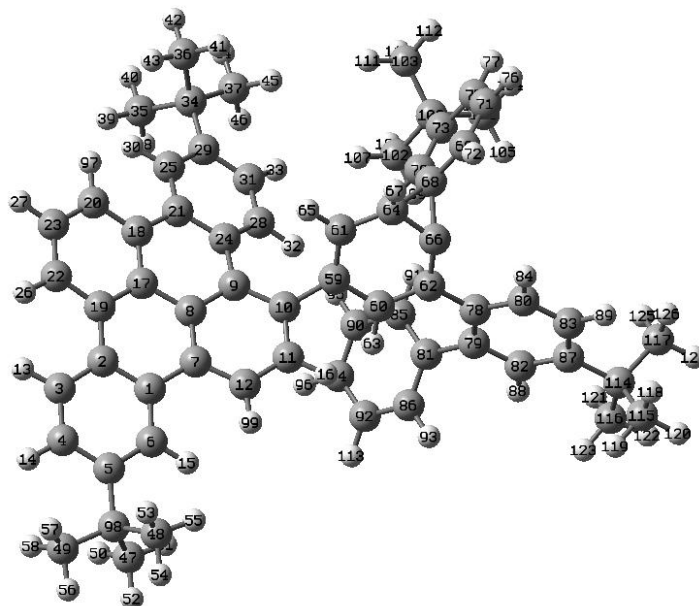
Total Energy = -2476.057 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	5.61115	-1.52017	-0.39158	64	-1.44894	1.236155	-2.20897
2	6.625407	-0.52441	-0.52788	65	0.651053	1.634146	-2.13575
3	7.963907	-0.95872	-0.58357	66	-2.54844	0.479731	-1.74068
4	8.299822	-2.29808	-0.50844	67	-1.63318	2.03131	-2.92408
5	7.315746	-3.30185	-0.36391	68	-3.89259	0.834118	-2.24568
6	5.994188	-2.87933	-0.30766	69	-4.06214	1.157962	-3.60833
7	4.219209	-1.11355	-0.34789	70	-5.00794	0.921777	-1.39195
8	3.873361	0.266183	-0.28773	71	-5.31036	1.538879	-4.07925
9	2.504934	0.661129	-0.19629	72	-3.22469	1.073875	-4.29444
10	1.478103	-0.32301	-0.42357	73	-6.26965	1.331482	-1.84291
11	1.848588	-1.68367	-0.42258	74	-4.87631	0.683008	-0.34336
12	3.168284	-2.06661	-0.36477	75	-6.40054	1.631816	-3.20729
13	8.768257	-0.23777	-0.66674	76	-5.44483	1.766658	-5.13283
14	9.348288	-2.56801	-0.5526	77	-7.35841	1.943415	-3.60723
15	5.227092	-3.63161	-0.17663	78	-3.35159	-1.49244	-0.29856
16	1.083897	-2.43825	-0.57135	79	-3.57466	-1.74297	1.075133

17	4.905706	1.272682	-0.36888	80	-4.07877	-2.24228	-1.23989
18	4.563261	2.653301	-0.31403	81	-2.89017	-0.99371	2.170293
19	6.259538	0.884724	-0.58046	82	-4.50584	-2.73272	1.439498
20	5.556583	3.611686	-0.58615	83	-4.98462	-3.21842	-0.85046
21	3.214114	3.033225	0.086944	84	-3.90621	-2.06933	-2.29799
22	7.216172	1.885488	-0.83412	85	-2.86241	0.410925	2.204376
23	6.863771	3.229192	-0.8573	86	-2.2923	-1.6933	3.232191
24	2.202853	2.025467	0.188941	87	-5.22237	-3.49125	0.507906
25	2.889418	4.354615	0.441458	88	-4.677	-2.88405	2.498788
26	8.244744	1.616613	-1.04053	89	-5.50831	-3.77807	-1.61953
27	7.613981	3.981672	-1.07942	90	-2.25777	1.09013	3.261822
28	0.959342	2.397764	0.761238	91	-3.33553	0.977689	1.407756
29	1.64117	4.728868	0.937741	92	-1.68118	-1.01488	4.287198
30	3.657311	5.114341	0.369829	93	-2.29877	-2.77997	3.222336
31	0.687508	3.70226	1.117725	94	-1.6613	0.38017	4.306599
32	0.216329	1.639965	0.972322	95	-2.26939	2.177037	3.279507
33	-0.27362	3.924215	1.565667	96	-1.19319	0.909795	5.131495
34	1.366784	6.194577	1.311216	97	5.308105	4.666016	-0.60223
35	2.350519	6.635519	2.422906	98	7.660054	-4.79874	-0.26159
36	1.570816	7.084109	0.060155	99	3.394964	-3.12342	-0.42097
37	-0.07022	6.407567	1.824645	100	-7.44079	1.437294	-0.84781
38	2.230916	6.021755	3.322577	101	-7.70538	0.049155	-0.21711
39	3.394887	6.562264	2.102217	102	-7.07868	2.447923	0.266843
40	2.160766	7.679432	2.696906	103	-8.73935	1.914949	-1.52517
41	0.882223	6.800408	-0.74366	104	-7.97523	-0.6855	-0.98396
42	1.38208	8.133459	0.313028	105	-6.83089	-0.33387	0.319087
43	2.591161	7.016376	-0.33129	106	-8.53404	0.113367	0.49791
44	-0.22261	7.467243	2.053725	107	-6.8848	3.442589	-0.15043
45	-0.81925	6.122184	1.077154	108	-7.90641	2.535307	0.979993
46	-0.26617	5.844315	2.744068	109	-6.19077	2.138942	0.828997

47	7.157625	-5.34824	1.095376	110	-9.5397	1.976557	-0.78027
48	6.968739	-5.56367	-1.41599	111	-8.62807	2.910296	-1.97017
49	9.176626	-5.05515	-0.35422	112	-9.07277	1.223063	-2.30691
50	7.632989	-4.82646	1.933411	113	-1.2221	-1.57828	5.094912
51	6.072983	-5.24272	1.20584	114	-6.2322	-4.57828	0.913512
52	7.3967	-6.41433	1.180585	115	-5.7696	-5.93918	0.338633
53	7.307207	-5.19726	-2.39158	116	-6.36315	-4.71943	2.441713
54	7.206229	-6.63169	-1.35425	117	-7.62527	-4.2265	0.338291
55	5.878425	-5.46504	-1.37989	118	-5.69886	-5.9201	-0.75393
56	9.370145	-6.1303	-0.2811	119	-4.78703	-6.22045	0.734323
57	9.593894	-4.71202	-1.30776	120	-6.48258	-6.7257	0.611575
58	9.726433	-4.56845	0.459314	121	-6.7174	-3.79423	2.910295
59	0.10251	0.001072	-0.81259	122	-7.08946	-5.50479	2.676259
60	-0.98135	-0.78253	-0.37625	123	-5.41327	-5.00103	2.910391
61	-0.16309	1.029167	-1.75237	124	-8.35263	-4.99925	0.612735
62	-2.29497	-0.56142	-0.79313	125	-7.98355	-3.26864	0.732196
63	-0.80107	-1.57876	0.337925	126	-7.61233	-4.15714	-0.75447

6. Cartesian coordinates for optimized geometry of **R5**



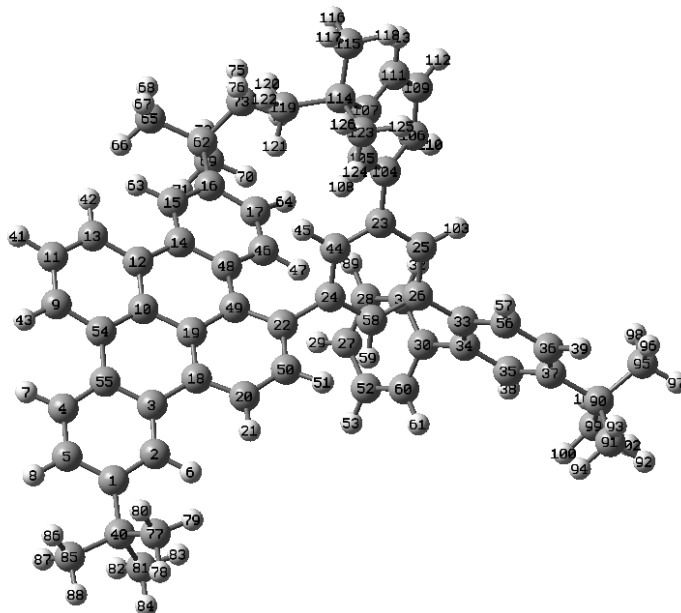
Total Energy = -2475.978 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	5.227819	-0.81983	-0.64432	64	-2.38895	1.263779	-1.04605
2	6.112212	0.255377	-0.90616	65	-0.3629	1.821603	-1.45761
3	7.467365	-0.04997	-1.13443	66	-3.30179	0.452883	-0.36275
4	7.938335	-1.35222	-1.11239	67	-2.76979	2.016394	-1.72797
5	7.07917	-2.43474	-0.84687	68	-4.73133	0.5163	-0.70354
6	5.739157	-2.13245	-0.61501	69	-5.76281	0.189889	0.208099
7	3.809821	-0.54209	-0.40242	70	-5.11323	0.87154	-2.01882
8	3.364855	0.800377	-0.22285	71	-7.09293	0.237867	-0.19432
9	1.998963	1.073405	0.101905	72	-5.53418	-0.04104	1.240514
10	1.054398	0.016206	0.022717	73	-6.44552	0.926653	-2.44057
11	1.512702	-1.29026	-0.19341	74	-4.33397	1.070313	-2.74587
12	2.857521	-1.57035	-0.35963	75	-7.43433	0.603663	-1.49674
13	8.181317	0.746618	-1.30971	76	-7.8767	0.002643	0.520047
14	8.994015	-1.52124	-1.29026	77	-8.48212	0.634425	-1.77139
15	5.066843	-2.9478	-0.37568	78	-3.30168	-0.42347	2.076794
16	0.786765	-2.09403	-0.28152	79	-3.57288	-1.68739	2.645504

17	4.280509	1.897296	-0.46841	80	-3.41912	0.736478	2.83421
18	3.827139	3.244434	-0.37082	81	-3.34056	-2.71207	1.648624
19	5.609995	1.629983	-0.90838	82	-3.96889	-1.7912	3.986948
20	4.660703	4.277759	-0.81998	83	-3.81733	0.624665	4.170611
21	2.529741	3.511247	0.254984	84	-3.20073	1.708767	2.402566
22	6.408729	2.701838	-1.33425	85	-3.31993	-2.06598	0.316177
23	5.932291	4.006326	-1.31034	86	-3.01933	-4.04563	1.812141
24	1.651691	2.431616	0.534754	87	-4.09276	-0.62711	4.740523
25	2.168171	4.807324	0.668955	88	-4.19778	-2.75846	4.424972
26	7.405513	2.518972	-1.71737	89	-3.90505	1.520278	4.778485
27	6.558633	4.817695	-1.66961	90	-2.75176	-2.8847	-0.7624
28	0.505515	2.711174	1.308235	91	-4.36055	-1.80929	0.034217
29	0.999375	5.091643	1.374714	92	-2.56629	-4.82564	0.727318
30	2.853603	5.621598	0.468291	93	-3.05707	-4.48064	2.805967
31	0.181896	3.998453	1.709403	94	-4.4069	-0.687	5.777964
32	-0.12114	1.897265	1.648617	95	-2.41832	-4.19278	-0.54974
33	-0.7062	4.143839	2.314238	96	-2.6643	-2.45169	-1.75532
34	0.680503	6.538225	1.793466	97	-2.0462	-4.7758	-1.38327
35	1.801458	7.068444	2.7194	98	4.314719	5.30468	-0.80692
36	0.591975	7.429711	0.531727	99	7.56531	-3.89492	-0.79013
37	-0.65761	6.64377	2.549921	100	3.15318	-2.59727	-0.53662
38	1.886923	6.456255	3.624202	101	-6.77414	1.31476	-3.89515
39	2.777255	7.068748	2.222853	102	-6.20365	2.722156	-4.1927
40	1.58438	8.098662	3.025182	103	-6.13506	0.285069	-4.85761
41	-0.20282	7.084974	-0.13981	104	-8.29158	1.345093	-4.15986
42	0.371505	8.465736	0.814288	105	-6.64036	3.474207	-3.52618
43	1.529541	7.432635	-0.03378	106	-5.11522	2.759144	-4.07452
44	-0.85232	7.690084	2.808463	107	-6.43269	3.010689	-5.2247
45	-1.49964	6.292715	1.941818	108	-6.52542	-0.72235	-4.67366
46	-0.6457	6.07269	3.485392	109	-6.36089	0.550279	-5.89659

47	7.304068	-4.47092	0.622112	110	-5.04484	0.248332	-4.75637
48	6.796921	-4.73531	-1.83787	111	-8.47532	1.633236	-5.20004
49	9.071821	-4.01973	-1.08819	112	-8.75572	0.364343	-4.00579
50	7.84101	-3.89741	1.385937	113	-8.80472	2.074267	-3.52274
51	6.239557	-4.45589	0.880045	114	-2.20469	-6.29636	0.952308
52	7.645207	-5.51162	0.676635	115	-3.44517	-7.03862	1.513863
53	6.968303	-4.35363	-2.85068	116	-1.75854	-7.00635	-0.34045
54	7.131849	-5.77894	-1.80714	117	-1.0455	-6.38033	1.980519
55	5.716679	-4.72761	-1.65606	118	-3.78542	-6.61784	2.465307
56	9.369231	-5.07308	-1.04477	119	-4.28188	-7.0029	0.807796
57	9.323169	-3.64793	-2.08796	120	-3.19429	-8.09048	1.687957
58	9.680386	-3.47669	-0.35642	121	-0.8498	-6.56354	-0.76321
59	-0.42345	0.203832	-0.00228	122	-1.5349	-8.05427	-0.11795
60	-1.26927	-0.58659	0.719583	123	-2.54087	-6.99548	-1.10757
61	-1.01271	1.168098	-0.8861	124	-0.78119	-7.43007	2.147803
62	-2.76529	-0.5409	0.632094	125	-0.15277	-5.86091	1.615248
63	-0.862	-1.30537	1.425546	126	-1.31766	-5.94847	2.948757

7. Cartesian coordinates for optimized geometry of **28**



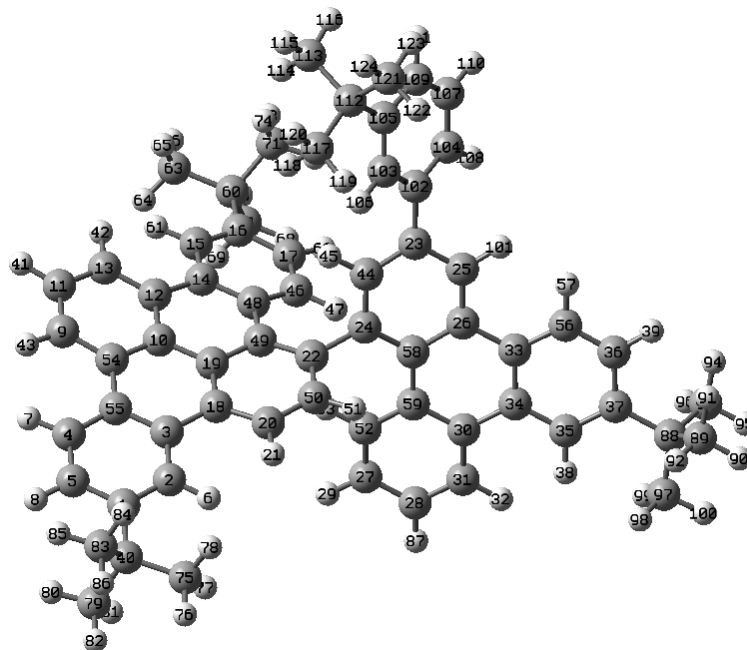
Total Energy = -2476.290 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	6.485629	-3.60568	-1.18834	64	-1.14908	2.310895	3.311407
2	5.16968	-3.1699	-1.08365	65	1.685344	5.207986	4.600531
3	4.812181	-1.91137	-0.56457	66	2.511255	4.655322	5.056696
4	7.16436	-1.49016	-0.21221	67	2.058797	5.704832	3.700903
5	7.48575	-2.72764	-0.73786	68	1.382191	5.986568	5.305705
6	4.38178	-3.84048	-1.39738	69	0.010948	3.657989	5.619119
7	7.970418	-0.86595	0.150048	70	-0.8738	3.033473	5.476535
8	8.528041	-3.01381	-0.78169	71	0.795678	3.032296	6.052846
9	6.466213	1.209716	0.755034	72	-0.24432	4.436782	6.344463
10	4.121587	0.560677	0.732102	73	-0.64936	5.171827	3.711127
11	6.129426	2.429309	1.322265	74	-1.54952	4.587985	3.506684
12	3.793701	1.77821	1.391096	75	-0.91713	5.963418	4.417922
13	4.810712	2.705006	1.651287	76	-0.33799	5.641963	2.77452
14	2.414463	1.997509	1.826467	77	6.247417	-5.1	-3.20434
15	2.100005	3.014812	2.753699	78	6.462106	-6.08712	-3.62536
16	0.831931	3.186467	3.284961	79	5.165882	-4.95094	-3.2397

17	-0.15289	2.261307	2.887726	80	6.709066	-4.34717	-3.84896
18	3.413268	-1.48705	-0.47285	81	6.121443	-6.08128	-0.88273
19	3.069844	-0.31132	0.24996	82	6.492491	-6.03495	0.144648
20	2.38828	-2.20319	-1.09884	83	5.036242	-5.96079	-0.85065
21	2.612854	-3.08313	-1.68561	84	6.335061	-7.07943	-1.2776
22	0.709314	-0.61982	-0.3325	85	8.306035	-5.29248	-1.80311
23	-2.26548	1.535031	-1.31396	86	8.841428	-4.57512	-2.43104
24	-0.69929	-0.16021	-0.52657	87	8.752007	-5.27492	-0.80502
25	-3.31797	0.635389	-1.09243	88	8.475559	-6.28805	-2.2218
26	-3.08647	-0.65136	-0.59798	89	-2.91117	0.212368	4.275935
27	-2.37822	-1.86581	4.43571	90	-7.50432	-4.52787	-0.39579
28	-2.9645	-0.76594	3.811287	91	-7.25926	-5.58442	-1.49832
29	-1.8577	-1.7447	5.378796	92	-8.075	-6.31382	-1.51302
30	-3.72111	-2.17372	1.983282	93	-7.2002	-5.13047	-2.49009
31	-3.62543	-0.9169	2.595888	94	-6.3244	-6.12309	-1.32113
32	-4.08342	-0.05776	2.120156	95	-8.83547	-3.79311	-0.67799
33	-4.21761	-1.6141	-0.45752	96	-8.82228	-3.2867	-1.64577
34	-4.47931	-2.35668	0.711228	97	-9.66774	-4.50375	-0.68422
35	-5.5306	-3.28834	0.708957	98	-9.03582	-3.04126	0.090135
36	-6.08276	-2.75033	-1.54475	99	-7.63782	-5.26235	0.950527
37	-6.34915	-3.51145	-0.39866	100	-6.73427	-5.82608	1.197972
38	-5.71369	-3.82562	1.629874	101	-7.84679	-4.57222	1.772277
39	-6.68321	-2.87891	-2.43806	102	-8.46641	-5.97372	0.898782
40	6.794462	-5.00119	-1.76129	103	-4.33253	0.936375	-1.32706
41	6.900242	3.167105	1.514698	104	-2.53388	2.895993	-1.84956
42	4.573655	3.660253	2.099278	105	-1.69438	3.464059	-2.81407
43	7.502305	1.015703	0.513613	106	-3.63503	3.640518	-1.4026
44	-0.96165	1.120487	-1.02801	107	-1.91286	4.742455	-3.34539
45	-0.13685	1.806044	-1.17958	108	-0.8588	2.874573	-3.17275
46	0.121003	1.265608	1.974991	109	-3.86926	4.908875	-1.91458

47	-0.66119	0.562339	1.735511	110	-4.28787	3.233689	-0.63905
48	1.394193	1.12706	1.382516	111	-3.01972	5.456657	-2.8757
49	1.699734	0.064695	0.41562	112	-4.7167	5.48516	-1.55912
50	1.081931	-1.75538	-1.05902	113	-3.23299	6.448021	-3.25243
51	0.325985	-2.27101	-1.63962	114	-0.95244	5.298388	-4.41334
52	-2.46563	-3.12014	3.837773	115	-1.34228	6.71677	-4.86824
53	-2.00944	-3.9819	4.312279	116	-1.3238	7.4293	-4.03909
54	5.485767	0.253273	0.462073	117	-0.63132	7.068032	-5.62087
55	5.834035	-1.04585	-0.11223	118	-2.33804	6.74069	-5.31921
56	-5.04495	-1.83093	-1.56943	119	0.481792	5.356305	-3.83819
57	-4.84374	-1.28221	-2.48275	120	0.523363	6.005218	-2.95917
58	-1.76898	-1.03606	-0.31834	121	0.841507	4.368826	-3.54116
59	-1.57427	-2.03055	0.0642	122	1.175143	5.752006	-4.58678
60	-3.13537	-3.27264	2.625804	123	-0.97054	4.374328	-5.65325
61	-3.19324	-4.25115	2.161632	124	-0.65513	3.358052	-5.40706
62	0.484831	4.29522	4.291969	125	-1.97461	4.317984	-6.08254
63	2.895761	3.660503	3.091134	126	-0.29229	4.757451	-6.42201

8. Cartesian coordinates for optimized geometry of **29**



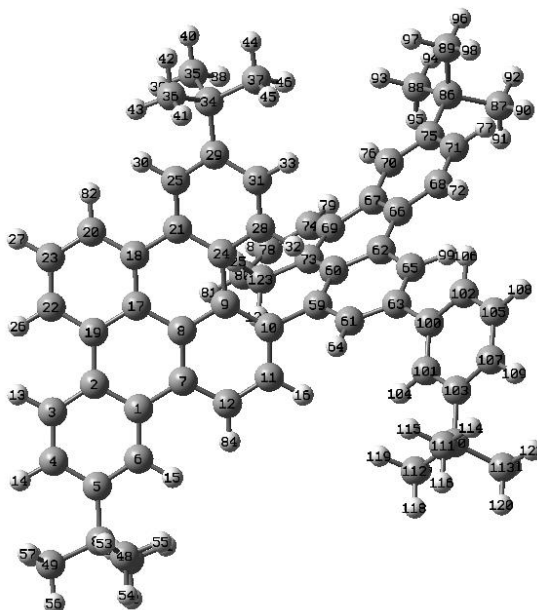
Total Energy = -2475.099 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	6.087484	-3.67141	-1.37014	63	1.964766	5.102745	4.991295
2	4.800745	-3.19777	-1.17147	64	2.763884	4.479416	5.401832
3	4.523772	-1.94876	-0.57137	65	2.346203	5.609521	4.100533
4	6.907632	-1.63238	-0.33535	66	1.733252	5.870962	5.733932
5	7.14709	-2.84959	-0.93406	67	0.215984	3.629901	6.000642
6	3.970004	-3.81873	-1.46803	68	-0.71032	3.068483	5.860163
7	7.755739	-1.05535	0.008275	69	0.968885	2.940204	6.391667
8	8.173409	-3.17688	-1.053	70	0.029593	4.396741	6.758917
9	6.368509	1.035861	0.799291	71	-0.38914	5.253941	4.16619
10	3.997888	0.486424	0.861904	72	-1.33198	4.739178	3.968711
11	6.112728	2.2402	1.435789	73	-0.58379	6.035739	4.9069
12	3.755444	1.685994	1.587601	74	-0.07132	5.735615	3.237567
13	4.823785	2.555779	1.838567	75	5.115197	-5.78416	-2.43715
14	2.407212	1.953341	2.088384	76	5.38638	-6.73847	-2.89645
15	2.182464	2.957946	3.054818	77	4.471165	-6.00284	-1.58106
16	0.944352	3.191642	3.630832	78	4.53324	-5.21935	-3.17062

17	-0.10963	2.349178	3.229458	79	7.164003	-5.91851	-1.01271
18	3.150027	-1.48148	-0.38069	80	8.107704	-5.46017	-0.70846
19	2.888821	-0.32507	0.40557	81	6.57081	-6.09223	-0.11088
20	2.066834	-2.13905	-0.97544	82	7.394302	-6.88967	-1.46156
21	2.228833	-2.99655	-1.61351	83	7.257976	-4.81528	-3.28064
22	0.48756	-0.5603	-0.02203	84	6.732209	-4.19559	-4.01206
23	-2.2888	1.690629	-1.17322	85	8.204446	-4.32342	-3.04519
24	-0.92117	-0.05087	-0.13618	86	7.489715	-5.77562	-3.75141
25	-3.41459	0.924267	-0.90624	87	-2.10149	-5.04074	3.534415
26	-3.34438	-0.31564	-0.24918	88	-8.05523	-3.79142	-0.01941
27	-0.95284	-3.38079	2.764389	89	-8.4547	-4.12524	-1.4759
28	-2.08914	-4.18661	2.866775	90	-9.33922	-4.76955	-1.48878
29	-0.07206	-3.59204	3.359884	91	-8.68966	-3.22567	-2.04926
30	-3.24694	-2.75895	1.259598	92	-7.64487	-4.6482	-1.9917
31	-3.2139	-3.86556	2.133517	93	-9.22587	-3.05938	0.677728
32	-4.10052	-4.46975	2.266122	94	-9.48422	-2.128	0.168849
33	-4.54206	-1.15305	-0.11918	95	-10.1181	-3.69299	0.686181
34	-4.47701	-2.39043	0.556509	96	-8.97168	-2.81534	1.712743
35	-5.61512	-3.22775	0.56667	97	-7.80749	-5.11576	0.725044
36	-6.87284	-1.62417	-0.66461	98	-7.0085	-5.70052	0.261086
37	-6.81729	-2.87947	-0.02681	99	-7.5484	-4.95004	1.774379
38	-5.53867	-4.18894	1.049771	100	-8.71563	-5.724	0.702445
39	-7.78756	-1.29745	-1.14537	101	-4.36945	1.293276	-1.25098
40	6.391466	-5.03259	-2.01799	102	-2.39687	3.005184	-1.85546
41	6.92329	2.935216	1.624053	103	-1.46704	3.382229	-2.83831
42	4.651083	3.499547	2.336997	104	-3.42757	3.89395	-1.53322
43	7.382884	0.809945	0.500732	105	-1.53923	4.60847	-3.50286
44	-1.0448	1.156644	-0.81338	106	-0.68752	2.678111	-3.0955
45	-0.14056	1.699511	-1.05967	107	-3.51664	5.121236	-2.18287
46	0.077977	1.36525	2.282904	108	-4.13992	3.637056	-0.75769

47	-0.76235	0.736658	2.036563	109	-2.58704	5.474353	-3.15383
48	1.325808	1.151179	1.658464	110	-4.31195	5.811595	-1.92328
49	1.541857	0.089867	0.664201	111	-2.68112	6.437206	-3.64247
50	0.779443	-1.66697	-0.82562	112	-0.53024	5.026356	-4.58858
51	-0.03235	-2.15017	-1.35632	113	0.183371	6.326772	-4.15095
52	-0.95639	-2.29442	1.911303	114	0.725396	6.177022	-3.21333
53	-0.07313	-1.67888	1.874286	115	0.902867	6.639689	-4.91391
54	5.333974	0.136252	0.510849	116	-0.52211	7.14728	-4.00169
55	5.598773	-1.14529	-0.13897	117	0.544278	3.952638	-4.83903
56	-5.77192	-0.79762	-0.71325	118	1.13376	3.748391	-3.94128
57	-5.86821	0.13856	-1.24518	119	0.10771	3.011608	-5.18428
58	-2.08879	-0.78624	0.232745	120	1.233732	4.299203	-5.6135
59	-2.07636	-1.96353	1.115964	121	-1.27967	5.275613	-5.91815
60	0.698157	4.283587	4.684472	122	-1.79131	4.369085	-6.25273
61	3.025381	3.544619	3.384835	123	-2.02837	6.065063	-5.82094
62	-1.09207	2.4538	3.674748	124	-0.5757	5.577386	-6.69986

9. Cartesian coordinates for optimized geometry of A7



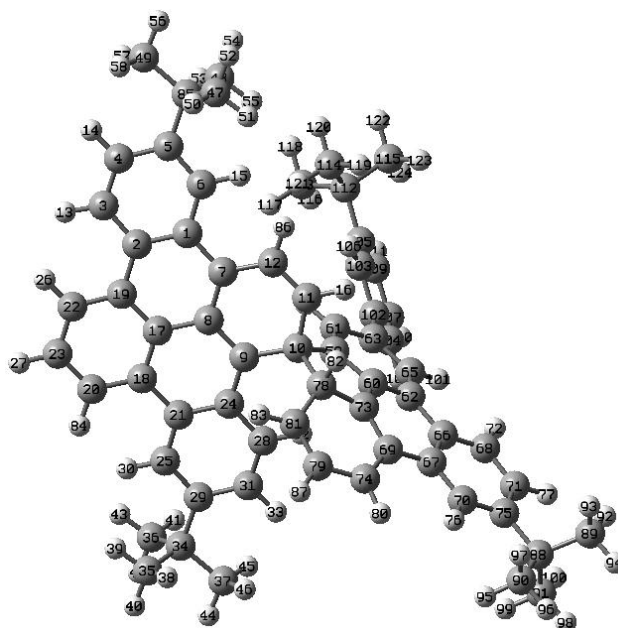
Total Energy = -2475.469 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	5.031421	-0.82338	-0.60124	64	0.276847	2.696487	0.684973
2	5.405965	-2.11925	-0.16954	65	-2.97619	2.247441	-0.10672
3	6.759244	-2.48683	-0.29093	66	-4.16313	0.31677	-1.08609
4	7.705873	-1.62505	-0.81946	67	-4.11406	-0.82897	-1.9074
5	7.357557	-0.33117	-1.25116	68	-5.43437	0.782628	-0.68352
6	6.019642	0.035084	-1.12435	69	-2.80198	-1.33626	-2.30709
7	3.634967	-0.40171	-0.48059	70	-5.31409	-1.46343	-2.29342
8	2.701936	-1.19615	0.253734	71	-6.59396	0.151744	-1.08648
9	1.364437	-0.73237	0.472966	72	-5.51886	1.632641	-0.01712
10	0.918323	0.417018	-0.23684	73	-1.60629	-0.84477	-1.6828
11	1.850716	1.15911	-0.9834	74	-2.68584	-2.27454	-3.33454
12	3.175685	0.777587	-1.08374	75	-6.5659	-0.9958	-1.90983
13	7.092683	-3.45753	0.057552	76	-5.26305	-2.36899	-2.88267
14	8.733451	-1.96391	-0.8806	77	-7.5446	0.545338	-0.74111
15	5.737498	1.039071	-1.41738	78	-1.46873	-2.86681	-3.75899
16	1.508088	2.0386	-1.52051	79	-3.58479	-2.56537	-3.86665

17	3.093737	-2.52183	0.693038	80	-0.32797	-2.55051	-3.09795
18	2.146597	-3.37503	1.329574	81	0.621769	-3.01757	-3.3432
19	4.399098	-3.01625	0.396813	82	1.75965	-5.39794	1.99119
20	2.482195	-4.71842	1.555628	83	8.38313	0.664822	-1.8234
21	0.871911	-2.81217	1.778236	84	3.842104	1.383443	-1.68486
22	4.687171	-4.36412	0.655735	85	-1.47741	-3.57484	-4.58111
23	3.734408	-5.20933	1.210603	86	-7.8801	-1.67829	-2.32077
24	0.510604	-1.48867	1.3969	87	-8.75128	-0.66566	-3.10352
25	0.024986	-3.52628	2.647898	88	-7.64941	-2.9104	-3.21559
26	5.65698	-4.77182	0.397387	89	-8.6373	-2.13559	-1.05015
27	3.972106	-6.25528	1.380898	90	-8.99078	0.219876	-2.50583
28	-0.64086	-0.93626	2.000854	91	-8.24431	-0.32941	-4.01493
29	-1.14427	-2.99715	3.190296	92	-9.69825	-1.13344	-3.39524
30	0.318173	-4.52415	2.948536	93	-7.06917	-3.68737	-2.70415
31	-1.44661	-1.66361	2.860136	94	-8.61414	-3.35118	-3.48665
32	-0.88681	0.103003	1.837619	95	-7.13657	-2.64956	-4.14883
33	-2.30671	-1.17131	3.298969	96	-9.58116	-2.61706	-1.32946
34	-2.00997	-3.84304	4.140785	97	-8.04563	-2.8574	-0.47589
35	-2.47269	-5.1247	3.40706	98	-8.87786	-1.2962	-0.38957
36	-1.17827	-4.23532	5.385727	99	-3.9231	2.768795	-0.07035
37	-3.26284	-3.0837	4.617848	100	-1.91452	4.284858	0.893191
38	-3.07457	-4.87853	2.524532	101	-0.8434	5.185699	0.723374
39	-1.62647	-5.73601	3.076351	102	-3.05212	4.710747	1.598144
40	-3.08627	-5.74124	4.073988	103	-0.87943	6.489613	1.224577
41	-0.83655	-3.34607	5.926917	104	0.018146	4.858279	0.153826
42	-1.78602	-4.83728	6.071193	105	-3.10198	6.001498	2.115794
43	-0.29503	-4.82565	5.120421	106	-3.87577	4.026064	1.776062
44	-3.85686	-3.73041	5.272225	107	-2.03408	6.877143	1.92913
45	-3.00512	-2.18659	5.191973	108	-3.97475	6.326659	2.674722
46	-3.90381	-2.7846	3.780289	109	-2.10308	7.879077	2.341657

47	7.961167	1.072326	-3.25539	110	0.273678	7.491032	1.030961
48	8.43506	1.923567	-0.92472	111	0.804512	7.930903	2.416666
49	9.800668	0.065191	-1.89368	112	1.447059	6.889084	0.23514
50	7.920998	0.20002	-3.91754	113	-0.24733	8.729076	0.262306
51	6.976245	1.551502	-3.27188	114	0.02768	8.411106	3.020533
52	8.68253	1.783298	-3.67472	115	1.187666	7.074265	2.982685
53	8.736301	1.665694	0.096735	116	1.621882	8.651107	2.296023
54	9.161694	2.64209	-1.32165	117	1.145178	6.585749	-0.77419
55	7.464815	2.428998	-0.87004	118	2.238931	7.637804	0.128119
56	10.49135	0.804508	-2.313	119	1.884035	6.020927	0.742459
57	10.17864	-0.21105	-0.90291	120	0.561911	9.455116	0.123179
58	9.838927	-0.82159	-2.53654	121	-0.62549	8.448678	-0.72734
59	-0.47678	0.958251	-0.26982	122	-1.05644	9.234859	0.799287
60	-1.64599	0.309056	-0.84704	123	-0.33494	-1.57932	-1.98573
61	-0.60532	2.235583	0.255131	124	0.509159	-0.88482	-2.09628
62	-2.92445	0.968198	-0.66733	125	-0.05033	-2.13948	-1.07289
63	-1.83625	2.921502	0.335759				

10. Cartesian coordinates for optimized geometry of **A8**



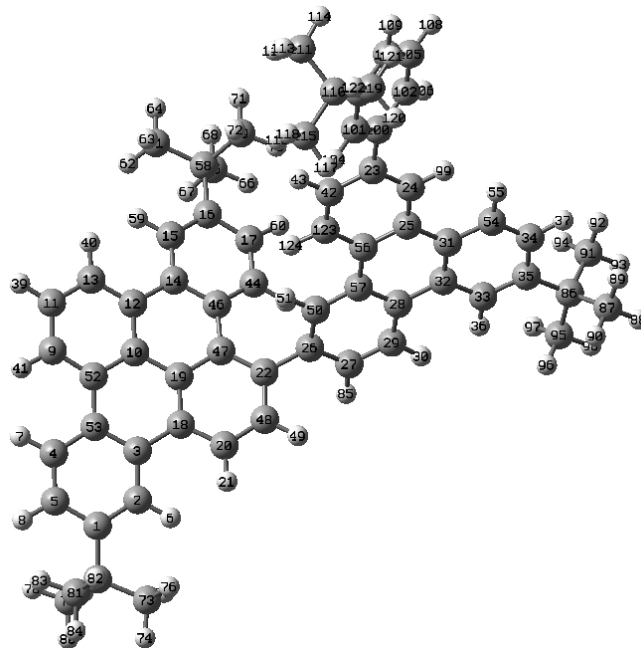
Total Energy = -2475.409 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	4.467441	-0.97402	-1.31239	63	-1.07088	2.648647	0.822871
2	5.09862	-2.01665	-0.57363	64	0.84654	1.625468	0.741954
3	6.500633	-2.10274	-0.63297	65	-2.41398	2.653199	0.396877
4	7.257956	-1.21327	-1.37682	66	-4.28325	1.491069	-0.95256
5	6.662038	-0.16391	-2.10777	67	-4.64147	0.300665	-1.6661
6	5.277907	-0.07367	-2.05244	68	-5.30617	2.414678	-0.66328
7	3.0313	-0.85329	-1.28808	69	-3.61353	-0.69708	-2.00295
8	2.231773	-1.66942	-0.42083	70	-5.98628	0.105108	-2.03796
9	0.826369	-1.47316	-0.31467	71	-6.61452	2.191515	-1.04946
10	0.108553	-0.49001	-1.23241	72	-5.0633	3.331034	-0.13396
11	1.037454	0.218917	-2.16378	73	-2.2901	-0.32579	-1.77524
12	2.374624	0.08063	-2.1563	74	-3.8111	-2.0405	-2.39152
13	7.025349	-2.86886	-0.07538	75	-6.9915	1.024354	-1.75031
14	8.334951	-1.33338	-1.37784	76	-6.23532	-0.79135	-2.59258
15	4.806055	0.74213	-2.58324	77	-7.36208	2.94061	-0.80796
16	0.568654	0.905189	-2.86468	78	-1.08045	-1.12755	-2.125

17	2.883536	-2.71559	0.344426	79	-2.71757	-2.95481	-2.43108
18	2.119135	-3.56413	1.192117	80	-4.81102	-2.43003	-2.55121
19	4.288085	-2.93351	0.218438	81	-1.41202	-2.58422	-2.22577
20	2.751267	-4.65145	1.822765	82	-0.79348	-0.85881	-3.15637
21	0.705532	-3.28243	1.395288	83	-0.61244	-3.31473	-2.30096
22	4.869422	-4.02786	0.875955	84	2.180293	-5.33676	2.436031
23	4.107107	-4.88629	1.658185	85	7.477743	0.853491	-2.92699
24	0.076036	-2.23981	0.637331	86	2.95403	0.656997	-2.8646
25	-0.05775	-3.99856	2.33217	87	-2.94115	-4.00081	-2.62204
26	5.927722	-4.22981	0.768592	88	-8.45761	0.821828	-2.16743
27	4.574395	-5.73766	2.143317	89	-8.88843	1.98135	-3.0981
28	-1.30419	-2.00893	0.888892	90	-8.67847	-0.50553	-2.91677
29	-1.41252	-3.7635	2.567177	91	-9.35052	0.818465	-0.90282
30	0.429684	-4.76258	2.922983	92	-8.80054	2.956326	-2.60767
31	-2.02075	-2.74057	1.814066	93	-8.27627	2.005889	-4.00664
32	-1.82126	-1.21437	0.379633	94	-9.93508	1.854502	-3.39759
33	-3.06702	-2.50032	1.959945	95	-8.41686	-1.37308	-2.2997
34	-2.16908	-4.59074	3.618476	96	-9.73546	-0.60277	-3.18564
35	-2.10052	-6.0896	3.235879	97	-8.09925	-0.55339	-3.84612
36	-1.51053	-4.38174	5.004284	98	-10.4012	0.684639	-1.18458
37	-3.65215	-4.18644	3.722065	99	-9.07405	0.001326	-0.22685
38	-2.56311	-6.27003	2.259038	100	-9.27527	1.756848	-0.34367
39	-1.07009	-6.45756	3.193206	101	-3.07159	3.418643	0.794365
40	-2.6357	-6.69005	3.980039	102	-0.5999	3.659177	1.800771
41	-1.54625	-3.32843	5.303797	103	0.691781	4.20868	1.688254
42	-2.04182	-4.96803	5.76247	104	-1.42592	4.08823	2.850014
43	-0.46255	-4.69895	5.015011	105	1.174824	5.170662	2.581089
44	-4.1478	-4.8064	4.476172	106	1.311432	3.891452	0.857338
45	-3.77243	-3.14099	4.02768	107	-0.96119	5.040874	3.753791
46	-4.18454	-4.33358	2.775435	108	-2.41358	3.65541	2.979388

47	7.034711	0.792098	-4.40856	109	0.318398	5.574703	3.620705
48	7.228703	2.276664	-2.37251	110	-1.59788	5.364017	4.572719
49	8.990888	0.569478	-2.86468	111	0.652638	6.317293	4.339022
50	7.201903	-0.20534	-4.83015	112	2.578286	5.792485	2.458639
51	5.973466	1.034793	-4.53075	113	3.381038	5.50093	3.749171
52	7.608593	1.511732	-5.00327	114	3.369792	5.228274	1.263637
53	7.536952	2.351434	-1.32367	115	2.446804	7.322793	2.27013
54	7.804232	3.010623	-2.94788	116	2.893829	5.916261	4.637207
55	6.173164	2.563279	-2.43386	117	3.497784	4.422328	3.905357
56	9.527011	1.312408	-3.46415	118	4.381146	5.945035	3.681813
57	9.3794	0.633095	-1.8419	119	2.870935	5.432294	0.309096
58	9.240407	-0.41826	-3.26869	120	4.358387	5.698224	1.22399
59	-0.62116	0.708231	-0.54234	121	3.523547	4.146	1.349239
60	-1.95603	0.774414	-0.98894	122	3.439155	7.781689	2.188737
61	-0.16476	1.654079	0.34935	123	1.886741	7.560443	1.358627
62	-2.90534	1.694916	-0.50383	124	1.931191	7.795727	3.112165

11. Cartesian coordinates for optimized geometry of **30**



Total Energy = -2475.114 Hartree

Number	X	Y	Z	Number	X	Y	Z
1	-8.36145	0.021712	-2.24469	63	-0.62877	-3.42551	5.406334
2	-7.10512	0.519671	-1.93902	64	-0.29303	-2.9076	7.058969
3	-6.21699	-0.12446	-1.04881	65	-0.61201	-0.22315	6.752041
4	-7.90394	-1.82563	-0.73485	66	-0.24029	0.767906	6.482499
5	-8.74403	-1.18094	-1.61594	67	-1.686	-0.13828	6.938549
6	-6.79673	1.452986	-2.38357	68	-0.12585	-0.51858	7.686972
7	-8.25898	-2.7287	-0.25651	69	1.200965	-1.35916	5.413407
8	-9.72071	-1.60888	-1.80972	70	1.623579	-0.40213	5.099813
9	-6.02337	-3.26473	1.026212	71	1.70726	-1.66232	6.335078
10	-4.5413	-1.33662	0.947845	72	1.433243	-2.09535	4.639201
11	-5.18507	-3.8793	1.94347	73	-8.74417	2.01833	-3.79839
12	-3.73128	-1.93747	1.951681	74	-9.46942	2.473712	-4.47795
13	-4.05995	-3.21782	2.413088	75	-8.51554	2.752912	-3.02141
14	-2.61461	-1.17486	2.50992	76	-7.83222	1.826694	-4.3705
15	-1.99015	-1.57775	3.710688	77	-10.633	1.08633	-2.45388
16	-1.00893	-0.82915	4.340296	78	-11.128	0.200984	-2.04852

17	-0.67104	0.40233	3.745888	79	-10.4244	1.763337	-1.62111
18	-4.89499	0.430617	-0.75434	80	-11.3374	1.582606	-3.12852
19	-4.10717	-0.11926	0.295115	81	-9.66818	-0.22912	-4.37954
20	-4.36398	1.491699	-1.49584	82	-8.76528	-0.49759	-4.93459
21	-4.91889	1.916685	-2.32062	83	-10.1331	-1.15403	-4.03089
22	-2.29877	1.453587	-0.21365	84	-10.3641	0.252747	-5.07319
23	4.724729	-1.40876	-0.70807	85	-1.38387	4.025925	-0.04841
24	4.974034	-0.04375	-0.64321	86	5.171398	6.639216	-0.24747
25	3.949603	0.915767	-0.52164	87	5.931186	7.049158	-1.53087
26	-0.88488	1.928899	-0.18183	88	6.193614	8.110944	-1.49364
27	-0.58195	3.301559	-0.13735	89	6.856446	6.481933	-1.65456
28	1.809267	2.831785	-0.28725	90	5.315347	6.881487	-2.41857
29	0.72845	3.731431	-0.18382	91	6.07052	6.897262	0.984349
30	0.912793	4.795818	-0.1381	92	7.000032	6.325579	0.936104
31	4.247786	2.348464	-0.45539	93	6.334118	7.957595	1.046391
32	3.199482	3.290986	-0.33838	94	5.555138	6.619851	1.90785
33	3.523068	4.665334	-0.27282	95	3.922954	7.531193	-0.12465
34	5.850827	4.186908	-0.43518	96	3.256189	7.418222	-0.98392
35	4.822341	5.143272	-0.31846	97	3.354658	7.313258	0.78377
36	2.718274	5.377264	-0.18203	98	4.225752	8.58066	-0.07912
37	6.886698	4.503078	-0.47513	99	6.00197	0.281935	-0.71683
38	-9.33238	0.723944	-3.20851	100	5.834913	-2.38675	-0.83389
39	-5.41312	-4.87758	2.299737	101	5.707471	-3.50347	-1.67659
40	-3.4257	-3.71513	3.134056	102	7.026492	-2.22016	-0.12067
41	-6.89808	-3.79859	0.681096	103	6.727309	-4.44564	-1.82792
42	3.383523	-1.83294	-0.64904	104	4.790369	-3.60965	-2.24011
43	3.152101	-2.89147	-0.66942	105	8.054639	-3.14788	-0.25663
44	-1.25457	0.8155	2.567832	106	7.137058	-1.38325	0.559138
45	-0.98057	1.781568	2.173893	107	7.908756	-4.2447	-1.09778
46	-2.20943	0.027835	1.889448	108	8.973459	-3.01971	0.305355

47	-2.84806	0.465375	0.640796	109	8.726309	-4.95115	-1.18285
48	-3.08747	1.959585	-1.25216	110	6.600407	-5.66663	-2.75779
49	-2.66264	2.710259	-1.90861	111	6.758231	-6.96164	-1.9272
50	0.169451	1.033427	-0.29524	112	5.983095	-7.02877	-1.15897
51	-0.07312	-0.01831	-0.34627	113	6.673387	-7.8402	-2.57422
52	-5.73298	-1.99027	0.521732	114	7.728332	-7.00842	-1.42735
53	-6.62265	-1.32356	-0.42697	115	5.239366	-5.72188	-3.4752
54	5.569078	2.84024	-0.50046	116	4.408708	-5.79298	-2.76781
55	6.399137	2.152662	-0.58757	117	5.076455	-4.84594	-4.10878
56	2.604354	0.472098	-0.46749	118	5.200499	-6.60522	-4.11822
57	1.515363	1.444075	-0.34735	119	7.708995	-5.61015	-3.8345
58	-0.3253	-1.26577	5.646195	120	7.618627	-4.7038	-4.4393
59	-2.32402	-2.49174	4.176696	121	8.707014	-5.61717	-3.39059
60	0.05102	1.05643	4.220445	122	7.634335	-6.47401	-4.50225
61	-0.81976	-2.63732	6.139853	123	2.36153	-0.91595	-0.53104
62	-1.88973	-2.62835	6.365242	124	1.348937	-1.2905	-0.47599

List of publications

1. Kojima, T.; Patel, K.; Nobusue, S.; Mahmoud, A.; **Xie, C.**; Nakae, T.; Kawai, S.; Fukami, K.; Sakaguchi, H. Vectorial On-Surface Synthesis of Polar 2D Polymer Crystals. *Advanced Materials Interfaces* **2023**, 10 (23), 2300214. (Editors' Choice, selected as cover art)
(Chapter 3)
2. Kojima, T.; **Xie, C.**; Patel, K.; Nobusue, S.; Fukami, K.; Sakaguchi, H. Molecular-Vapor-Assisted Low-Temperature Growth of Graphene Nanoribbons. *The Journal of Physical Chemistry C* **2023**, 127 (22), 10541–10549. (Selected as cover art)
(Chapter 4)
3. Kojima, T.; **Xie, C.**; Sakaguchi, H. On-Surface Fabrication toward Polar 2D Macromolecular Crystals. *ChemPlusChem* **2024**, 89 (7), e202300775. (Invited review, selected as cover art)
(Chapter 3&4)
4. Nobusue, S.; **Xie, C.**; Patel, K.; Kojima, T.; Sakaguchi, H. Aryl Shift Rearrangement in Scholl-Type Reaction Toward Nanographene. *Chemistry – A European Journal* **2025**, 31(36), e202501221.
(Chapter 5)

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XIE CONG

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