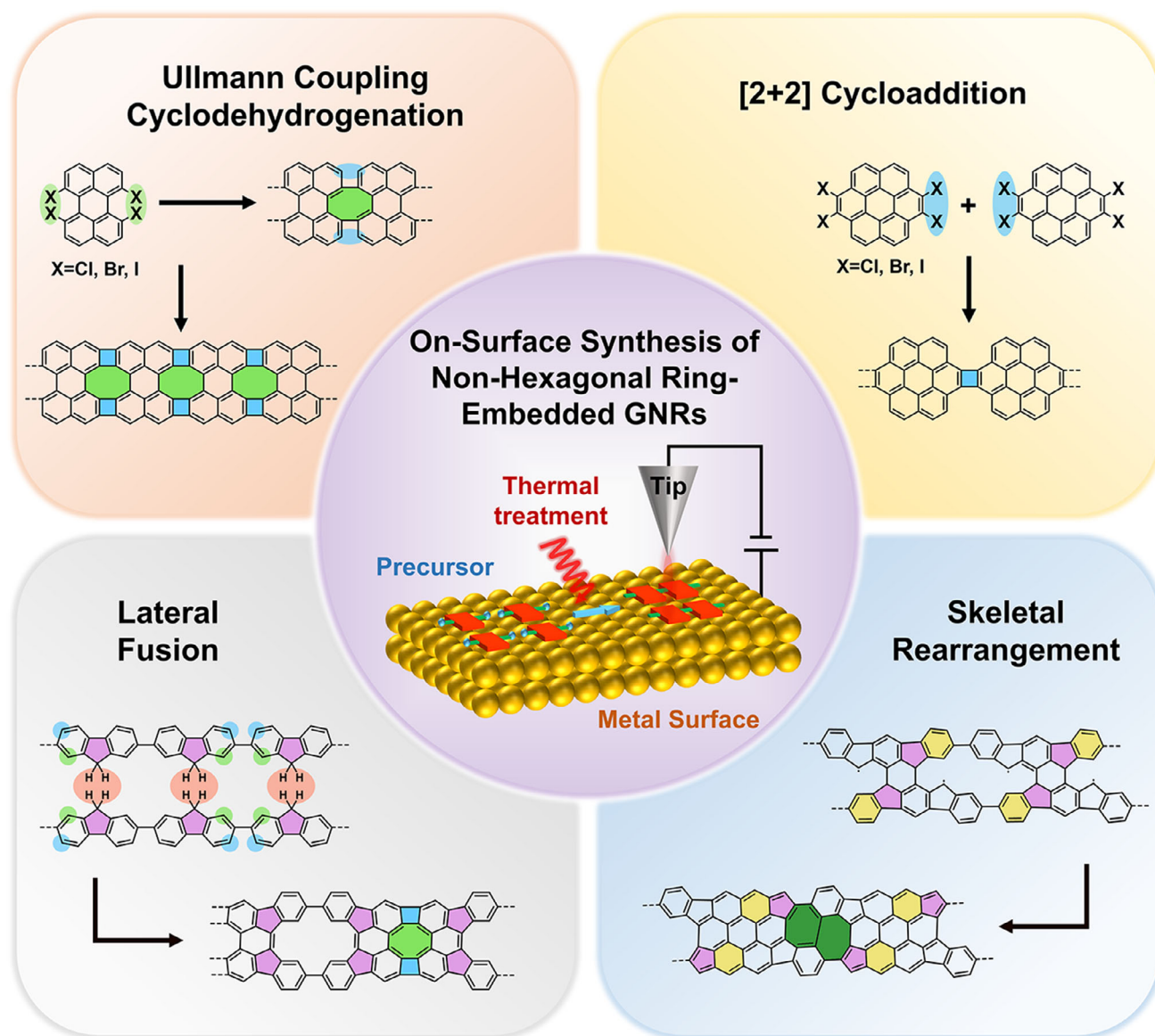


On-Surface Precise Synthesis of Non-Hexagonal Ring-Embedded Graphene Nanoribbons

Hao Qu,^[a] Mali Zhao,^{*[a]} and Wei Xu^{*[a]}



Graphene nanoribbons (GNRs), as quasi-one-dimensional carbon nanostructures, combine the exceptional properties of graphene with tunable bandgaps. The incorporation of periodic non-hexagonal ring motifs into GNR frameworks offers an effective approach to significantly tailor their electronic and magnetic properties. However, synthesis of GNRs incorporating non-hexagonal rings remains challenging, due to the thermodynamic instability compared to their hexagonal counterparts. Advancements in on-surface synthesis and in-situ characteriza-

tion techniques have emerged as powerful methods for the atomically precise fabrication of novel carbon nanostructures. In this review, we comprehensively summarize the recent progress in on-surface synthesis of non-hexagonal ring-embedded GNRs via sophisticated design of precursors and optimized reaction pathways. This review aims to provide insights into strategies for constructing carbon polygons into nanostructures via surface-mediated chemical reactions, thereby enabling their multifunctional applications in electronics and spintronics.

1. Introduction

Graphene nanoribbons (GNRs), quasi-1D strips with widths ranging from a few to several tens of nanometers, have emerged as promising candidates for next-generation electronics and quantum computing due to their tunable electrical and magnetic properties.^[1] The bandgaps of GNRs are highly sensitive to their width and edge configuration.^[2–4] For example, armchair graphene nanoribbons (AGNRs) possess a width-dependent bandgap, while zigzag and chiral configurations host spin-polarized edge states.^[5–9] To fulfill the performance of GNRs with multiple design functions, various strategies for bandgap modulation have been explored, such as edge structure engineering for generating spin-polarized states, including chevron GNRs (CGNRs), GNR heterojunctions, and GNR superlattices.^[10–12] Heteroatom substitution for chemical functionality, such as oxygen (O), nitrogen (N), boron (B), and sulfur (S) atoms,^[13,14] Structural engineering through nanopores and vacancies also enables tailored electronic and magnetic properties.^[15,16]

Alternatively, incorporating structural imperfection of non-hexagonal rings into sp²-hybridized carbon lattice is also a promising strategy to tailor the band structures of GNRs, owing to the introduction of local sublattice imbalance. Theoretical predictions indicate that non-hexagonal ring structures, such as Stone–Wales defects^[17,18] or 5–6–8-membered ring configurations,^[19] can induce localized electronic states as well as pronounced metallic or magnetic features. AGNRs with periodic tetragons and octagons (T-AGNRs) are most likely to exhibit a bandgap with diamagnetic feature. In contrast, zigzag-like T-GNRs (T-ZGNRs) display metallic and ferromagnetic characteristics.^[20] Additionally, the zigzag-edged phagraphene nanoribbons with 5–6–7-membered rings are predicted to have significantly localized edge magnetism.^[21,22]

However, synthesis of GNRs with non-hexagonal rings remains challenging due to the thermodynamic instability compared to their hexagonal counterparts. Traditional top-down methods, such as lithographic cutting^[23,24] and solution sonication,^[25,26] have limitations in achieving the atomic precision necessary for embedding non-hexagonal rings. In stark

contrast, on-surface synthesis has emerged as a powerful strategy for constructing atomically precise carbon nanostructures through surface-assisted chemical reactions.^[27] By depositing precursor molecules onto suitable substrates (especially metal surfaces), chemical reactions can be induced through thermal activation, photo-irradiation, tip manipulation, or other excitation methods.^[28–30] Additionally, by rigorously controlling the thermodynamic or kinetic processes of the reaction, the reaction pathway can be precisely regulated to achieve the target products. Moreover, advanced on-surface characterization techniques, primarily based on scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM), enable the structural and property analysis of the final products, while theoretical calculations provide insights into the reaction mechanisms.^[31–36] Typical on-surface chemical reactions include Ullmann coupling, Glaser coupling, Sonogashira coupling, cyclodehydrogenation, Bergman cyclization, alkane polymerization, etc.^[37–44] In recent years, with the rapid development of on-surface synthesis techniques, GNRs with various edge configurations have been successfully achieved. Notably, the sophisticated design of precursor molecules, optimization of reaction pathways, and the rational selection of template substrates are critical to realizing the atomically precise synthesis of GNRs with structural imperfections.

In this review, we summarize the recent advances in the bottom-up synthesis of GNRs containing non-hexagonal rings, focusing on the strategies to construct the carbon polygons, such as Ullmann coupling followed by cyclodehydrogenation, [2 + 2] cycloaddition, lateral fusion, and thermally induced skeletal rearrangement. We highlight the design principles for precursor molecules and reaction pathways that enable precise incorporation of non-hexagonal rings into GNRs. By bridging theoretical predictions and experimental achievements, this review aims to provide insights into the atomically precise synthesis of GNRs incorporating non-hexagonal rings and to guide future research in developing functional carbon nanostructures with tailored electronic and magnetic properties for next-generation device applications.

2. Ullmann Coupling Followed by Cyclodehydrogenation

In 1904, Fritz Ullmann reported the cleavage of carbon–halogen bond in aryl groups in the presence of copper powder, leading

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to the formation of biaryls via C–C homocoupling.^[45] Nearly a century later, Rieder and his colleagues demonstrated the first surface-assisted Ullmann coupling on Cu(111) via injecting electrons into iodobenzene.^[46] Further studies revealed that Ullmann coupling could also be efficiently achieved through thermal activation.^[47,48]

Surface-assisted C–H activation reaction has also emerged as a pivotal method for achieving C–C coupling. In 2008, Otero et al. reported the formation of fullerene with 100% yield through Pt(111) surface-catalyzed cyclodehydrogenation of aromatic precursors (with sp^2 hybridization).^[40] Subsequently, selective C(sp^2)–H activation and C–C coupling were reported on Au, Ag, and Cu surfaces.^[49,50] In 2011, Zhong et al. demonstrated C(sp^3)–H activation in alkyl groups and subsequent dehydrogenative C–C coupling on the anisotropic Au(110) surface, leading to the formation of linear alkanes.^[43]

The combination of surface-assisted Ullmann coupling and subsequent cyclodehydrogenation enables atomically precise synthesis of various low-dimensional carbon nanostructures, particularly GNRs. In the pioneering work in 2010, Cai et al. synthesized 7-AGNRs on Au(111) surface using 10,10'-dibromo-9,9'-bianthryl (DBBA) as the precursor. The surface-assisted reaction process involved two distinct thermally activated steps. Initially, the linear polyphenylene chains were formed via C(sp^2)–Br bond cleavage and C–C homocoupling of bianthryl units. Subsequently, the elevated-annealing temperature induced C(sp^2)–H bond activation within aryl groups and intramolecular aryl–aryl coupling, yielding 7-AGNRs.^[51] Since then, a series of GNRs featuring a pristine hexagonal lattice have been synthesized via Ullmann coupling and cyclodehydrogenation of aromatic

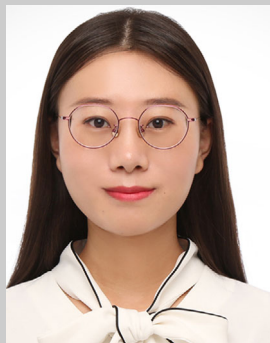
precursors with diverse activation sites on various crystalline surfaces.^[51–53] Notable examples include the synthesis of ZGNRs on Au(111) via a U-shaped molecular precursor^[53] and CGNRs on Cu(111) using DBBA molecules.^[52] Ullmann coupling followed by cyclodehydrogenation has also emerged as a powerful approach to construct non-hexagonal rings in GNRs. By carefully designing aromatic precursors with specific substitution sites and functional groups, and by strategically selecting metal substrates, carbon polygons can be effectively introduced into GNRs. Here, we summarize the strategies for embedding tetragons, pentagons, and octagons in GNRs through Ullmann coupling followed by cyclodehydrogenation of benzylic rings, methyl groups, and tri-angulene units, highlighting the precise control of structural heterogeneities in GNRs.

2.1. Ullmann Coupling Followed by Cyclodehydrogenation of Benzylic Rings

The classical Ullmann coupling followed by cyclodehydrogenation between benzylic rings (sp^2 hybridization) has been extensively studied and utilized for synthesizing GNRs containing carbon tetragons, pentagons, and octagons on noble metal (111) substrates. Liu et al. reported the synthesis of GNRs periodically embedded with 4–6–8-membered rings through Ullmann coupling and cyclodehydrogenation of 1,6,7,12-tetrabromo-3,4,9,10-perylene-tetracarboxylic-dianhydride (Br_4 -PTCDA) molecules on Au(111). After depositing Br_4 -PTCDA molecules on Au(111) and subsequent annealing to 493 K, the aryl C(sp^2)–Br bonds were fully activated, yielding PTCDA–Au polymers. Further annealing



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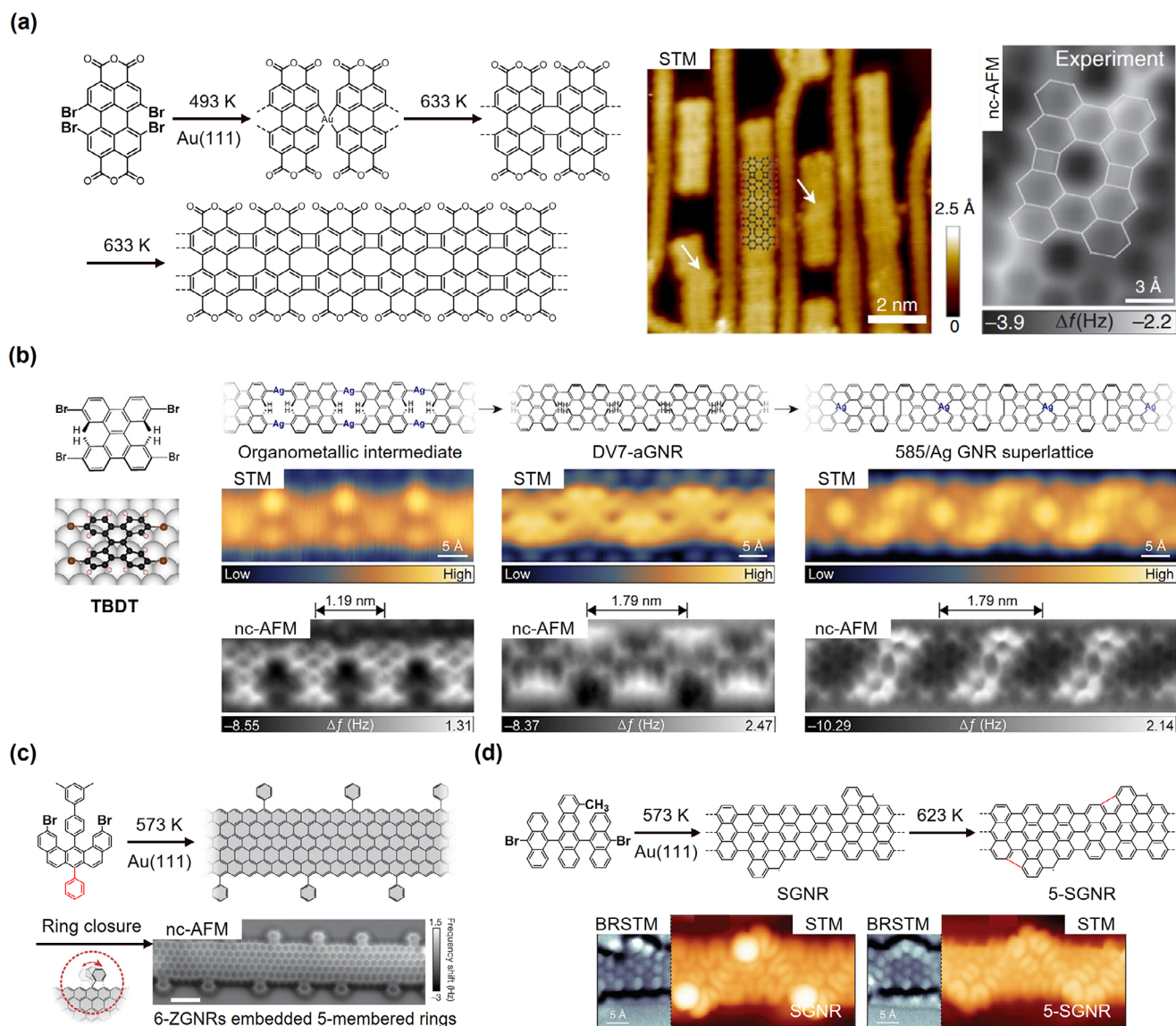


Figure 1. On-surface synthesis of GNRs incorporating non-hexagonal rings via Ullmann coupling and cyclodehydrogenation of benzylic rings. a) Synthetic route to the GNRs composed of 4–6–8-membered rings. STM and nc-AFM images confirm the formation of four- and eight-membered rings in the ribbon. b) Reaction scheme for the synthesis of 585/Ag GNRs. The corresponding STM and nc-AFM images show the structures of organometallic intermediate, DV7-aGNR, and 585/Ag GNR superlattice. c) The atomic-precise synthesis of 6-ZGNRs containing five-membered rings. d) Reaction scheme and characterization of the formation of 5-SGNR by edge cyclodehydrogenation. Reproduced with permission from Ruffieux et al.^[53–56] Copyright 2017 CC-BY 4.0; Copyright 2023 American Chemical Society; Copyright 2016 Springer Nature; Copyright 2020 American Association for the Advancement of Science.

to 633 K cleaved the C–Au bonds, forming octagons via C–C homocoupling at the bay regions. Simultaneously, cyclodehydrogenation at the ortho positions resulted in tetragons, ultimately yielding flat nanoribbons composed of 4–6–8-membered rings, as illustrated in Figure 1a.^[54] Similarly, Wang et al. achieved 7-AGNRs incorporating alternating 585-ringed divacancies and Ag atoms (585/Ag GNRs) on Ag(111). In their work, the 2,7,10,15-tetrabromodibenzo[*a,c*]triphenylene (TBDT) was used as the precursor, where Br substituents are symmetrically disposed at the termini of the extended π -conjugated system. Upon depositing TBDT molecules on Ag(111) and annealing to 430 K, Ullmann coupling occurred with the assistance of Ag atoms. Further annealing triggered the dissociation of Ag atoms from the organometallic intermediates. Subse-

quent annealing at 840 K induced cyclodehydrogenation at the hydrogenated divacancies, forming 585/Ag GNRs, as shown in Figure 1b.^[55]

Introducing phenyl groups in aryl precursor molecules can facilitate the formation of pentagons in GNRs through additional cyclodehydrogenation between phenyl groups and the neighboring aryl polymer skeleton. In 2016, Ruffieux et al. introduced a phenyl group (marked in red) through a single bond into the U-shaped precursor to synthesize the edge-modified 6-ZGNRs on the Au(111) surface. Upon annealing to 573 K, the external phenyl group underwent a ring closure by dehydrogenation of either of the neighboring zigzag-edge carbon atoms, forming a fluoranthene-type subunit that incorporated a five-membered ring, as depicted in Figure 1c.^[53] Crommie and coworkers

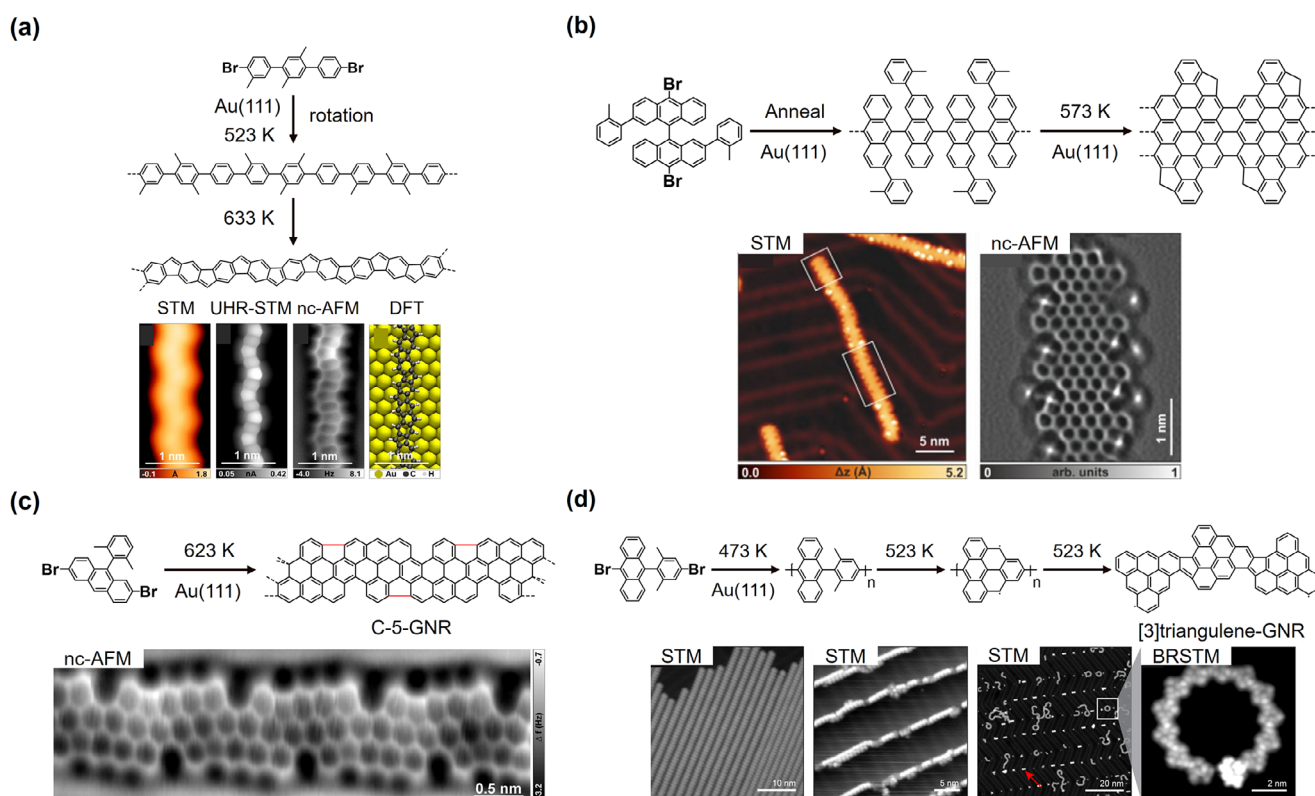


Figure 2. On-surface synthesis of GNRs containing five-membered rings via Ullmann coupling and cyclodehydrogenation of benzylic methyl groups rings. a) Synthesis strategy of GNRs with 5–6-membered rings. b) Pentagon-fused GNRs obtained through methyl cyclodehydrogenation. c) On-surface synthesis of C-5-GNR through cyclodehydrogenation between triangulene units. The nc-AFM image confirmed the formation of carbon pentagons in GNRs. d) Fabrication steps for [3]triangulene-GNRs via cyclodehydrogenation between head-to-tail triangulene units. Reproduced with permission from Di Giovannantonio et al.^[57–60] Copyright 2020 American Chemical Society; Copyright 2021 CC-BY 4.0; Copyright 2024 American Chemical Society; Copyright 2024 CC-BY 4.0.

further advanced this approach, achieving the synthesis of 5-sawtooth GNRs (5-SGNRs) on Au(111). They extended the central anthracene unit to methyl-tetracene in the 10,10'-dibromo-9,9':10',9''-teranthracene precursor. This structural modification facilitated a secondary cyclodehydrogenation along the cove regions at 623 K, leading to the formation of pentagons along the edges of SGNRs, as shown in Figure 1d.^[56]

2.2. Ullmann Coupling Followed by Cyclodehydrogenation of Benzylic Methyl Groups

In addition to aryl C(sp²)–H activation, the sp³-hybridized C–H activation (e.g., methyl groups) has also been employed for creating non-hexagonal rings, particularly pentagons embedded in GNRs. In 2020, Di Giovannantonio et al. synthesized GNRs composed of 5–6-membered rings by cyclodehydrogenation between methyl groups and benzylic rings.^[57] Specifically, after deposition of dibromo-trimethyl-*p*-terphenyl molecules on Au(111), Ullmann coupling was induced at 433 K, yielding methyl-substituted *poly-p*-phenylene (PPP) structures. Further annealing at 633 K triggered cyclodehydrogenation between methyl groups and benzylic rings, resulting in the alternating 5–6-membered rings, as confirmed by STM, nc-AFM, and

DFT calculations, see Figure 2a. Soon after Fasel's work, Xu et al. produced pentagon-fused AGNRs through cyclodehydrogenation of benzylic methyl groups on Au(111), employing ortho-tolyl-substituted dibromobianthryl as a precursor, see Figure 2b.^[58]

The formation of pentagons in GNRs has also been demonstrated through cyclodehydrogenation between triangulene units. Ping Yu et al. employed 2,6-dibromo-9-(2,6-dimethylphenyl) anthracene as a precursor. After thermally induced polymerization, the cyclodehydrogenation of methyl groups was triggered with the adjacent benzylic rings, resulting in the formation of *cis-trans* alternating *poly*-triangulene chains on Au(111). Further cyclodehydrogenation between neighboring triangulene units generated pentagons implemented in the zigzag edges. Further annealing at 623 K, triangulenes fused completely, ultimately yielding the GNRs with five-membered rings at the cove edges (C-5-GNRs),^[59] see Figure 2c. Additionally, Daugherty et al. employed a precursor with the same molecular backbone but different bromine substitution sites to construct pentagon rings in GNRs, see Figure 2d. Specifically, thermal treatment induced the bending of the [3]triangulene-GNR backbone and the formation of conjugated five-membered rings via cyclodehydrogenation between head-to-tail *poly*-triangulene units.^[60]

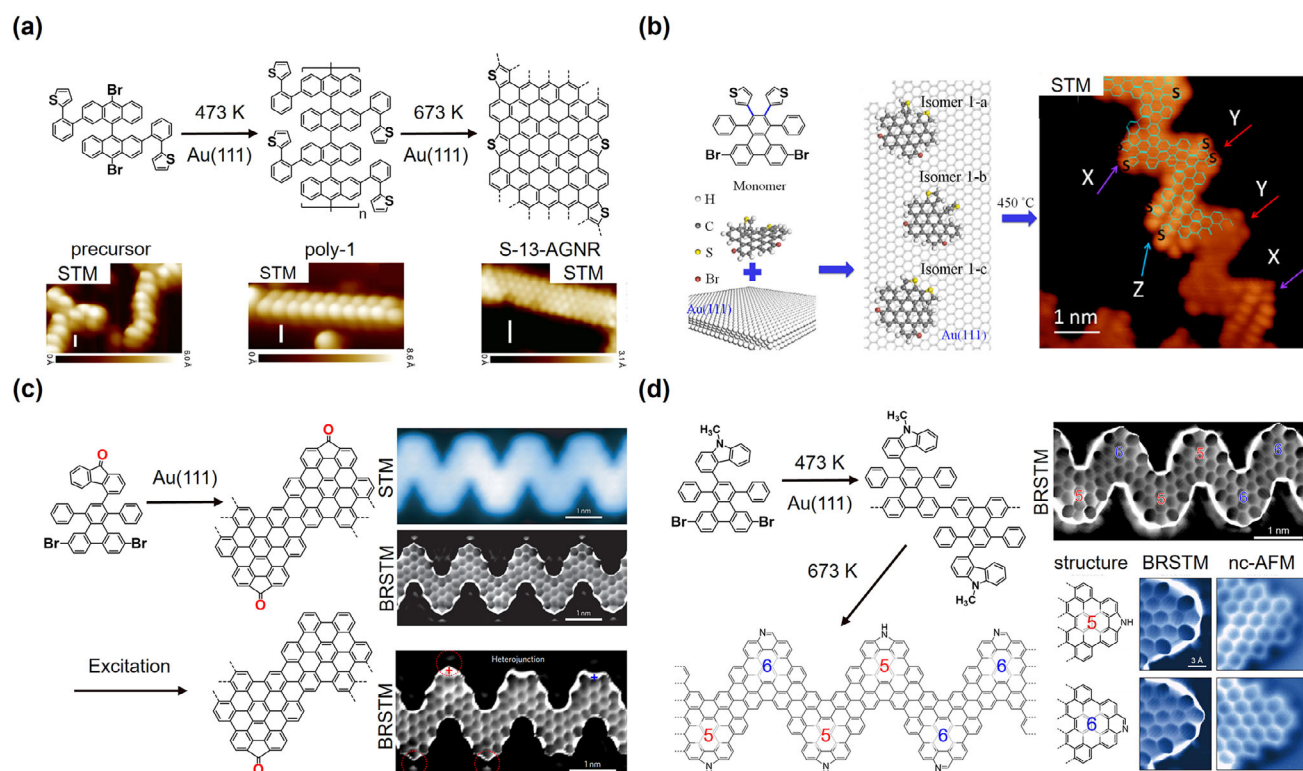


Figure 3. Synthesis of carbon polygons in GNRs by introduction of non-hexagonal groups in precursor molecules. a) Reaction pathway and structure characterization of S-13-AGNRs. b) On-surface synthesis of sulfur-GNR heterojunctions via Ullmann coupling and cyclodehydrogenation. c) Synthetic strategy to GNR heterojunctions functionalized with fluorenone substituents. d) Reaction route of another nitrogen-doped GNR heterojunctions. BRSTM and nc-AFM images confirm two different edge structures. Reproduced with permission from Nguyen et al.^[61–64] Copyright 2016 American Chemical Society; Copyright 2017 Springer Nature; Copyright 2017 Springer Nature; Copyright 2019 American Chemical Society.

3. Introduction of Non-Hexagonal Groups Into Precursor Molecules

Compared to constructing non-hexagonal rings via on-surface chemical reactions, embedding non-hexagonal rings, such as thiazole, pyrrole, and imidazole, directly into the carbon backbones of the precursor molecules offers a more straightforward route to synthesize GNRs composed of non-hexagonal rings. This strategy also allows the introduction of heteroatoms (e.g., N, O, and S), thereby modulating the band structure of GNRs. Nguyen et al. reported the formation of sulfur-containing 13-AGNRs (S-13-AGNRs) via classical Ullmann coupling and cyclodehydrogenation on Au(111) (see Figure 3a).^[61] They employed a precursor featuring a DBBA molecular backbone functionalized with bis(2-(thiophen-2-yl)phenyl) groups.

The atomic-precision synthesis of GNR heterostructures is a promising strategy for developing nanoscale electronic devices. In 2016, Zhang et al. produced sulfur-GNR heterostructures on Au(111) using 6,11-dibromo-1,4-diphenyl-2,3-di-(thien-3-yl)-triphenylene (Figure 3b).^[62] To expand the family of GNR heterostructures, Nguyen et al. designed a chevron-type GNR functionalized with fluorenone substituents. Notably, carbonyl groups could partially dissociate from the GNR framework upon further annealing to 623 K, leading to the formation of GNR heterojunctions, as shown in Figure 3c.^[63] The same group also reported the synthesis of nitrogen-doped GNR hetero-

junctions by depositing precursor molecules equipped with methyl-carbazole groups on Au(111), followed by annealing to 473 and 673 K (see Figure 3d). Besides conventional Ullmann coupling and cyclodehydrogenation, the methyl-carbazole groups underwent spontaneous edge reconstruction during cyclodehydrogenation, yielding carbazole and phenanthridine at the edges of GNRs.^[64]

Furthermore, Durr et al. also synthesized a series of sulfur-, oxygen-, and nitrogen-doped CGNRs composed of five-membered rings on Au(111) through Ullmann coupling and subsequent cyclodehydrogenation of precursors functionalized with thiophene, furan, and pyrrole groups.^[65] The precise control over the edge structure and dopant positions highlights the potential for designing functional GNR-based nanomaterials with tailored electronic and structural characteristics.

4. [2 + 2] Cycloaddition for the Tetragon-Embedded GNRs

The formation of cyclic structures through cycloaddition reactions is crucial for synthesizing complex low-dimensional carbon nanostructures.^[66–68] The [2 + 2] cycloaddition reaction is particularly notable for its ability to form cyclobutadiene structures, which are valuable for modulating the electronic properties of GNRs due to their pronounced antiaromatic character.^[69]

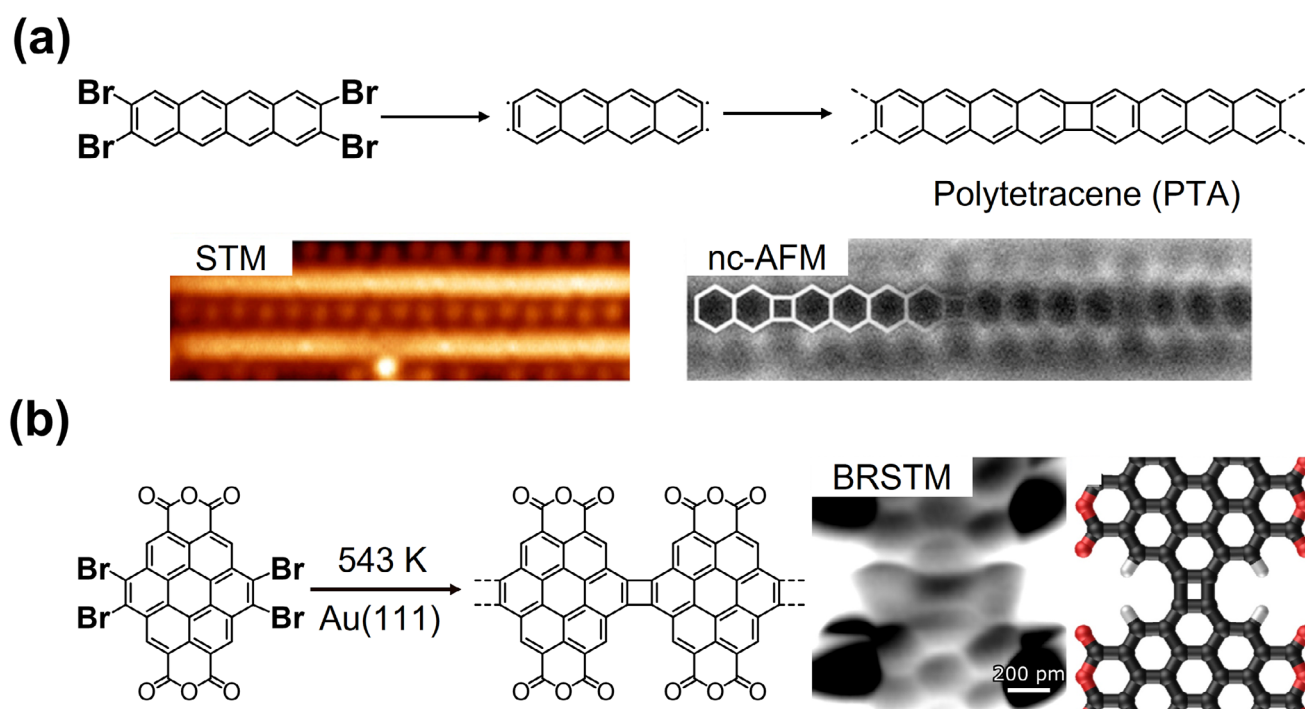


Figure 4. Fabrication of tetragon-embedded GNRs via [2 + 2] cycloaddition. a) Reaction scheme for the synthesis of tetracene-based nanoribbons on Ag(111). STM and nc-AFM images identify the tetragons in the nanoribbons. b) On-surface synthesis of coronene-cyclobutadienoid GNRs (cor₄GNR) on Au(111). BRSTM image and corresponding model confirm the formation of cor₄GNR. Reproduced with permission from Jacobse et al.^[69,70] Copyright 2019 Wiley-VCH; Copyright 2021 CC-BY 4.0.

Therefore, it is a promising strategy to synthesize GNRs with four-membered rings. The presence of two halogen substituents at the ortho positions of an aryl group has been demonstrated to realize the formation of four-membered rings via [2 + 2] cycloaddition reaction.

Sánchez-Sánchez et al. successfully triggered [2 + 2] cycloaddition by depositing 2,3,8,9-tetrabromotetracene molecules on Ag(111) held at 475 K, yielding linear nanoribbon structures with four-membered rings, as depicted in Figure 4a.^[70] The nc-AFM image confirmed the formation of tetragons. Similarly, Jacobse et al. deposited tetrabromocoronene dianhydride molecules onto Au(111) and subsequently annealed to 543 K, obtaining a novel ribbon-like structure composed of 4–6-membered rings through [2 + 2] cycloaddition.^[69] The backbone of 4–6-membered rings was confirmed by bond-resolved STM (BRSTM), see Figure 4b.

5. Lateral Fusion for the Diverse Polygons in GNRs

In 2015, Mauro Sami et al. developed a surface-assisted polymerization reaction to form 6-AGNRs through lateral dehydrogenative coupling of PPP nanowires derived from 4,4'-dibromo-*p*-terphenyl (DBTP).^[71] Subsequent studies demonstrated that AGNRs with various widths can be synthesized by the fusion of narrower AGNRs and PPP nanowires.^[72–74] Lateral fusion reactions significantly expand the scope of precursor molecules for the on-surface synthesis of GNRs and have been widely applied in fabricating GNRs containing non-hexagonal rings in recent years.

Combining dehalogenative coupling and lateral fusion through sp² aryl C–H activation, Fan et al. successfully prepared nanoribbons with diverse non-hexagonal rings on Au(111). Specifically, annealing Au(111) pre-deposited with 2,6-dibromoazulene (2,6-DBAz) at 690 K induced dehalogenative coupling, forming polyazulene chains. Further annealing to 730 K triggered lateral fusion between adjacent polyazulene chains, yielding two distinct nanoribbons: the phagraphene nanoribbon and tetrapenta-hepta (TPH) GNR, as seen in Figure 5a. The 5–6–7-membered rings embedded in phagraphene nanoribbons were formed through lateral fusion between the two oppositely oriented polyazulene chains. In contrast, 4–5–7-membered rings in TPH GNRs emerged when two oppositely oriented polyazulene chains fused with a relative shift.^[75]

Besides, diverse polygons of carbon nanoribbons can also be achieved via lateral fusion through dehydrogenative coupling of C(sp³)–H in cyclopentadiene units. Kang et al. synthesized nanoribbons composed of 4–5–6–8-membered rings via lateral fusion of polyfluorene chains on Au(111). In their work, 2,7-diiodo-9*H*-fluorene (DIF) was selected as the precursor and deposited onto Au(111) held at ~100 K. After annealing to 490 K, polyfluorene chains formed through Ullmann coupling. To trigger the interchain fusion, the sample was further annealed at 650 K, yielding GNRs with 4–5–6–8-membered rings, confirmed by nc-AFM image (see Figure 5b).^[76] They proposed that face-to-face dehydrogenative coupling of –CH₂– groups is essential for the final product formation. Similarly, Fasel et al. reported on-surface synthesis of porous GNRs through lateral fusion of zigzag poly(10,12-dihydroindeno[1,2-*b*]fluorene)

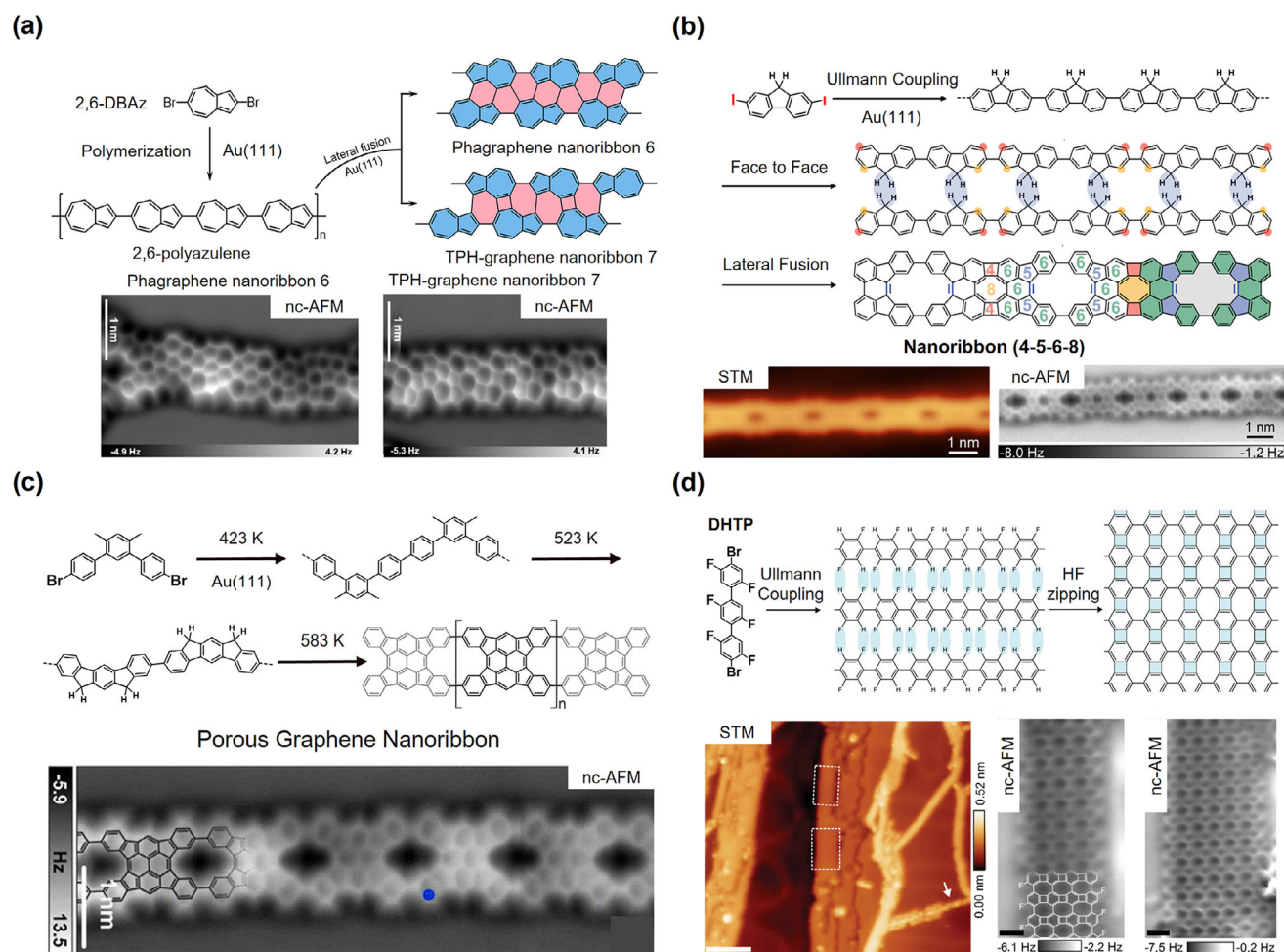


Figure 5. Preparation of diverse polygons in GNRs via lateral fusion. a) Reaction scheme for the preparation of phagraphene nanoribbon 6 and TPH-graphene nanoribbon 7. b) Carbon nanoribbons composed of 4–5–6–8-membered rings formed through Ullmann Coupling and lateral fusion of DIF molecules. c) Synthetic route to obtain porous GNRs containing 5–6-membered rings, the following nc-AFM image and corresponding model reveal the chemical bonds of pentagons. d) On-surface synthesis of BPRs from DHTP on Au(111) through HF-zipping. Zoom-in nc-AFM images of the BPRs are outlined by the white rectangles in the STM image. Reproduced with permission from Fan et al.^[75–78] Copyright 2019 American Chemical Society; Copyright 2023 American Chemical Society; Copyright 2019 American Chemical Society; Copyright 2021 American Association for the Advancement of Science.

(*poly*-2H-IF) chains on Au(111). Using 4,4'-dibromo-4',6'-dimethyl-1,1':3',1''-terphenyl (DBDMTP) as the precursor, they achieved surface-assisted Ullmann coupling and cyclodehydrogenation between methyl groups and adjacent aromatic rings, forming zigzag *poly*-2H-IF chains. Further annealing to 583 K led to the formation of porous nanoribbons composed of five-membered rings through lateral fusion of the *poly*-2H-IF chains, as shown in the nc-AFM image in Figure 5c.^[77]

In 2021, Fan et al. introduced an on-surface lateral dehydrofluorination (HF-zipping) fusion strategy to achieve the formation of biphenylene nanoribbons (BPRs) with periodic 4–6–8-membered rings. This method provided a novel approach for synthesizing non-benzenoid 2D carbon allotropes. By depositing 4,4'-dibromo-2,2',5,5',5''-hexafluoro-1,1':4',1''-terphenyl (DHTP) on Au(111) and annealing to 500 K, the *poly*(2,5-difluoro-*para*-phenylene) (PFPP) chains were formed via Ullmann coupling. Further annealing to 680 K induced inter-polymer HF-zipping of PFPP chains with the same chirality to form BPRs, shown in Figure 5d.^[78]

6. Skeletal Rearrangement

In recent decades, Ullmann coupling and cyclodehydrogenation have been extensively studied and applied in on-surface synthesis, enabling the successful fabrication of various carbon nanostructures. Beyond these, rearrangement reactions, such as Bergman and Fritsch–Buttenberg–Wiechell (FBW) cyclization, have emerged as crucial tools for synthesizing novel carbon nanostructures, such as polyphenylene and polyyne compounds.^[41,79,80] Compared to the strategies of regioselective cyclodehydrogenation, [2 + 2] cycloaddition, and lateral fusion, rearrangement reactions offer new insights and opportunities for the precise synthesis of a broader range of GNRs containing non-hexagonal rings.^[81,82] Herein, we summarize the recent works of bottom-up synthesis of GNRs incorporated with non-hexagonal rings via rearrangement reactions.

Chen et al. elucidated the mechanism of ring rearrangement of indeno[2,1-*b*]fluorene (IF) units on Au(111) and achieved the atomically precise synthesis of GNRs composed of pentagons

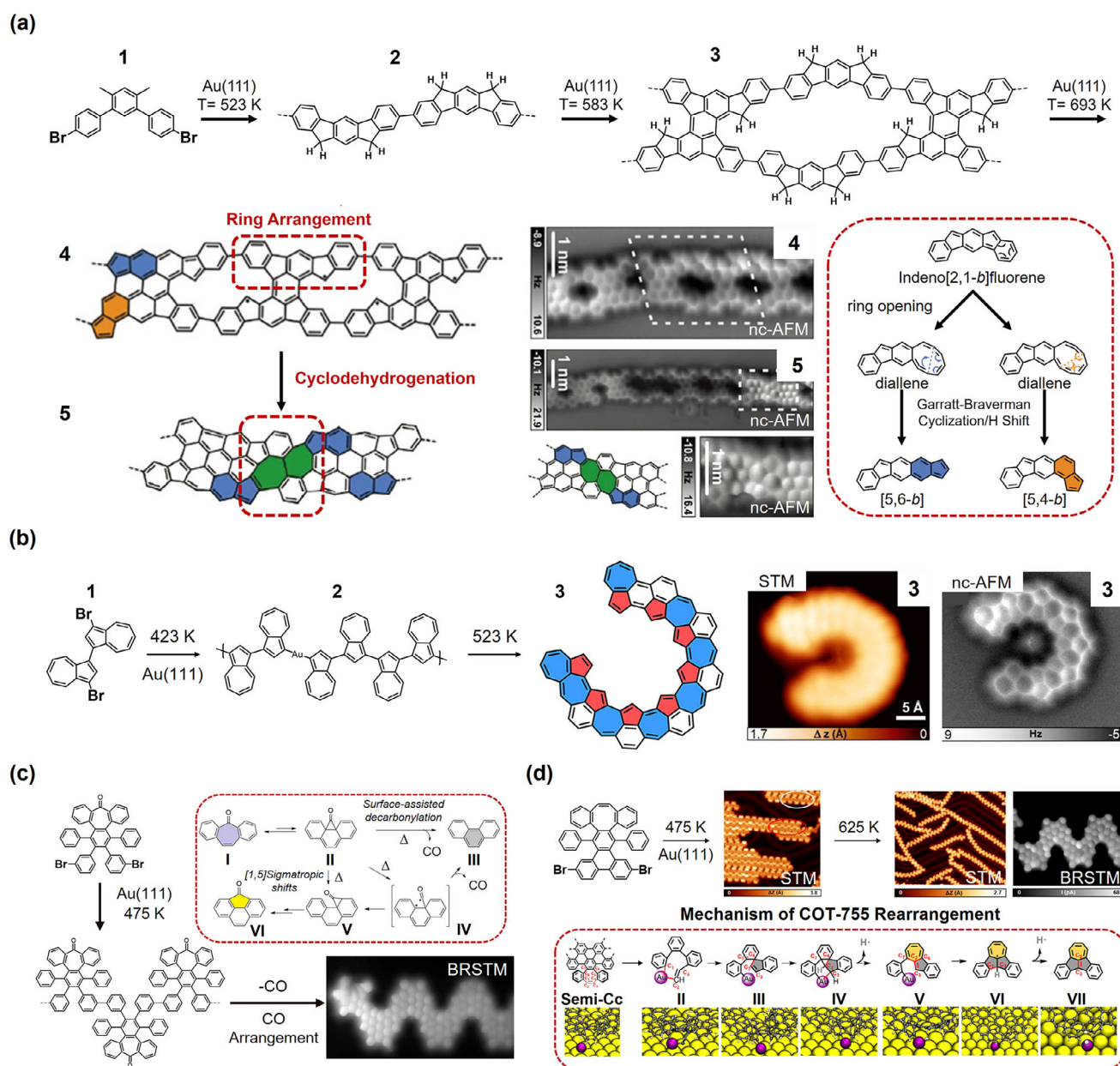


Figure 6. Synthesis of carbon polygons in GNRs via skeleton rearrangement. a) Reaction pathway of nanoribbon 5 through lateral fusion and skeletal rearrangement. Red dashed lines highlight the proposed rearrangement mechanism of the IF unit. The following nc-AFM images show the structures of nanoribbons 4 and 5. b) Synthetic route of nanoribbons composed of 5–6–7-membered rings. STM and nc-AFM images show the formation of the curved nanoribbon 3. c) Schematic representation of the possible reaction pathway of the formation of heterojunctions of chevron-type and fluorenone GNRs. d) Synthetic strategy and characterization of the poly (475 K) and 755-GNRs (625 K). QM/MM simulations give a possible mechanism of the COT-755 rearrangement. Reproduced with permission from Chen et al.^[83–86] Copyright 2023 CC-BY 4.0; Copyright 2020 CC-BY 4.0; Copyright 2022 CC-BY 4.0; Copyright 2025 CC - BY - NC - ND 4.0.

and heptagons, using DBDMTP molecules. Thermal treatment at 583 K induced alternating lateral fusion of 2H-IF polymer chains, forming porous nanoribbon 3. Further annealing to 693 K led to the complete dehydrogenation of 2H-IF units. Nc-AFM image indicated the ring rearrangement occurred in localized regions, where the 6–5–6–5–6 ring of the IF unit was transformed into the 6–5–6–6–5 ring system. Notably, they also observed fully fused nanoribbon 5 composed of heptagons (Figure 6a) owing to cyclodehydrogenation of the pores.^[83] The mechanism involved two sequential steps: initial ring-opening of IF

units generated metastable diallene intermediates, which subsequently underwent the Garratt–Braverman cyclization to form hexagon–pentagon pairs in GNRs.

The following work provided novel mechanistic insights into the rearrangement pathways of higher-order non-hexagonal ring systems. Hou et al. deposited 1,1'-dibromo-3,3'-biazulenyl onto Au(111) held at RT and annealed to 423 K, dehalogenative coupling was triggered and led to linear polymer chains partially connected by C–Au–C bonds. Further annealing to 523 K induced ring rearrangement and cyclodehydrogenation,

yielding curved GNR 3 composed of 5–6–7-membered rings, as clearly revealed by the nc-AFM image in Figure 6b. They proposed that the rearrangement reaction was initially triggered by the thermally activated dissociation of Au atoms from the structure, followed by subsequent C–H bond cleavage at azulenyl end-groups. Subsequently, the resulting radical species attacked the neighboring azulenediyl moieties, thereby triggering a chain reaction through a sequence of repetitive steps, including homoallyl-cyclopropylcarbinyl-radical-rearrangement, 1,2-hydrogen-shift, and interazulenediyl-radical-attack, which eventually gave rise to curved GNR 3.^[84]

Márquez et al. introduced cycloheptatrienone moieties into the polyphenylene precursor. Annealing the precursor-covered Au(111) substrate to 675 K induced either CO elimination or rearrangement of tropone units (I), ultimately leading to the transformation of partial units into 4H-Cyclopenta[def]phenanthren-4-one (VI). This process resulted in the formation of chevron-type fluorenone GNR heterojunctions (Figure 6c).^[85] In 2025, the same group synthesized cyclopenta[c,d]azulene-based GNRs (755-GNRs) by sequential annealing dibrominated tribenzoannulated cyclooctatetraene (COT) monomers at 475 K and 625 K on Au(111). BRSTM image revealed the 5–7-membered rings in GNRs (see Figure 6d), indicating skeletal rearrangement occurred during the cyclodehydrogenation process. Theoretical calculations were performed to investigate the reaction pathway. Initially, adsorbed Au atoms inserted into the C₁–C₂ bond of the cyclodehydrogenation intermediate with a concave configuration. Subsequently, the C₂–Au bond underwent cleavage, followed by Au-atom-catalyzed C₂–C₆ radical aromatic addition. The intermediate III then underwent several skeletal rearrangements to form intermediate V, resulting in free energy reduction of the system. Finally, further demetallation and cyclodehydrogenation led to the formation of 755-GNRs.^[86]

Skeletal rearrangement reaction is a promising strategy for constructing carbon polygons in nanostructures. However, due to the complexity of the mechanism and challenges in process control, this method is currently employed as an auxiliary approach in on-surface chemistry strategies.

7. Summary and Perspectives

The incorporation of non-hexagonal rings into the graphene lattice can dramatically alter its electronic and magnetic properties. Therefore, the precise fabrication and structural control of GNRs containing non-hexagonal rings are crucial for exploring their intrinsic physical properties and potential applications. Recent advances in on-surface synthesis and in situ characterization have enabled the fabrication of diverse polygon-embedded GNRs through sophisticated precursor design, reaction pathway optimization, and substrate selection. This review highlights the key surface-assisted reaction strategies for synthesizing non-hexagonal ring-containing GNRs. Ullmann coupling followed by cyclodehydrogenation represents the most basic and important approach for constructing carbon polygons (e.g., tetragons, pentagons, and octagons) in GNRs. [2 + 2] cycloaddition offers a direct route to introduce tetragons into GNRs. Addition-

ally, lateral fusion enables the simultaneous creation of diverse polygons within GNRs. Skeleton rearrangement provides a supplementary approach for synthesizing GNRs that are inaccessible through conventional methods. These strategies not only expand the structural diversity of GNRs, but also deepen our understanding of their structure–property relationships, paving the way for innovative applications in next-generation electronic and quantum devices.

Although on-surface synthesis of GNRs with diverse structural imperfections has advanced rapidly, significant challenges remain. Current strategies rely on dehydrogenation reactions, which demand high annealing temperatures and exhibit poor selectivity, leading to a decrease in yield.^[87,88] Therefore, exploration of novel on-surface synthesis strategies with low activation energy barriers is essential. Additionally, further structural innovation is required to expand the types and quantum states of GNRs for applications in electronics and quantum computing. The combination and optimization of diverse structural disorders, including non-hexagonal rings, heterostructures, heteroatoms,^[12,89,90] and asymmetric edge configurations,^[91] hold great promise for tailoring the band structures. Furthermore, on-surface synthesis of GNRs is currently restricted to coinage metal surfaces. Although progress has been made in transferring GNRs to insulating substrates, issues like edge oxidation and contamination persist. Developing synthesis methods on nonmetallic substrates is crucial to avoid the transfer-related problems. Recent attempts to synthesize carbon nanostructures on semiconducting surfaces have been hindered by low reactivity, typically resulting in low yields.^[92,93] Thus, developing new reaction strategies on nonmetallic surfaces is essential for meeting the requirements of electronic and spintronic devices. Addressing these challenges will significantly strengthen the fundamental research and practical applications of GNRs in electronic devices, bridging nanomaterials science with real-world applications.^[94]

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Conflict of Interests

The authors declare no conflicts of interest.

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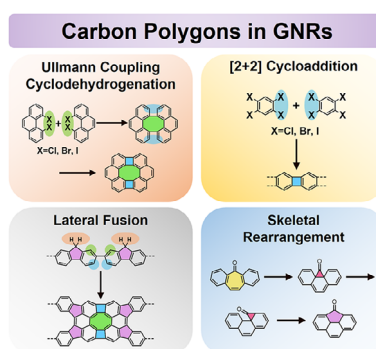
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REVIEW

Advanced on-surface synthesis enables fabrication of non-hexagonal ring-embedded graphene nanoribbons via four principal strategies: Ullmann coupling followed by cyclodehydrogenation, [2 + 2] cycloaddition, lateral fusion reactions, and skeletal rearrangement.



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On-Surface Precise Synthesis of Non-Hexagonal Ring-Embedded Graphene Nanoribbons