

Programmable Fabrication of Monodisperse Graphene Nanoribbons via Deterministic Iterative Synthesis

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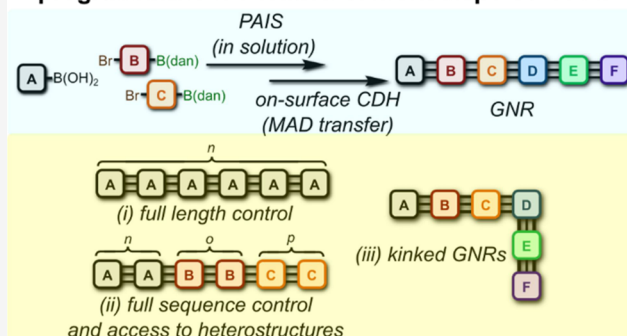
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ABSTRACT: While enormous progress has been achieved in synthesizing atomically precise graphene nanoribbons (GNRs), the preparation of GNRs with a fully predetermined length and monomer sequence remains an unmet challenge. Here, we report a fabrication method that provides access to structurally diverse and monodisperse “designer” GNRs through utilization of an iterative synthesis strategy, in which a single monomer is incorporated into an oligomer chain during each chemical cycle. Surface-assisted cyclodehydrogenation is subsequently employed to generate the final nanoribbons, and bond-resolved scanning tunneling microscopy is utilized to characterize them.

programmable fabrication of monodisperse GNRs



INTRODUCTION

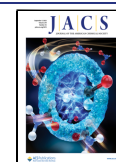
Graphene nanoribbons (GNRs), defined as nanometer-wide strips of graphene, have recently attracted much attention because of their versatile electronic,^{1–4} optical,⁵ and magnetic^{6,7} properties. This gives them potential for impactful future nanoelectronic, spintronic, photonic, sensing, quantum information processing, and energy conversion applications. The physical behavior of GNRs is dictated by their precise structure and can thus be tuned by altering parameters such as length, width, heteroatom doping, edge structure, defect incorporation, and so forth.^{8–13} These parameters cannot be effectively controlled using top-down methods (such as e-beam lithography), but the development of chemistry-based bottom-up synthesis techniques has enabled fabrication of numerous atomically precise GNR structures with engineered properties.^{14–21} For example, the electronic band gap and work function of GNRs have been shown to be readily tunable through chemical modifications of molecular precursors.^{22–24} GNR heterostructures have also been produced by covalently bonding GNR segments having different electronic characters, showing promise for use in electronic devices such as field-effect transistors (FETs).^{25–31} Topological engineering,^{24,32–35} metallicity,³⁶ and magnetism^{37,38} have all been successfully implemented in GNRs, further consolidating them as attractive nanomaterials for use in spintronic, qubit, and memory devices.^{39–46}

Despite this progress, however, it is still not possible to synthesize monodisperse GNRs having well-defined length or well-defined heterogeneous monomer sequence, important milestones that would enable new GNR functionality through flexible electronic interface engineering.^{27,29,32,33} The state-of-

the-art for bottom-up synthesis of GNRs, either in liquid phase or on surfaces, mainly relies on conventional polymerization strategies (Figure 1a), and the resulting GNRs are invariably polydisperse and do not exhibit controlled monomer sequences beyond the simplest repeating subunits.^{14–17} As such, bottom-up synthesized GNRs, while highly controlled in many aspects, still feature a range of different characteristics even for a single targeted structure. Elegant new strategies, including hierarchical^{29,47} and chain-growth polymerization,⁴⁸ have been explored to partially alleviate this problem, but the selective, monodisperse preparation of GNRs having a well-defined monomer sequence remains an unmet challenge.²¹ In addition, GNRs made from the controlled assembly of more than two different types of building blocks are elusive because current bottom-up strategies typically can only handle one or two different types of monomers during the polymerization process. Hence, while GNRs exhibiting irregular, nonperiodic structural motifs have been predicted to have highly desirable properties in proposed nanoelectronic architectures,^{31,49} there has so far been a lack of selective methods for their preparation. Herein, we describe our development of a general fabrication method for preparing diverse GNR structures assembled from multiple types of monomers and for yielding precisely controlled GNR sequence, length, and shape, enabled

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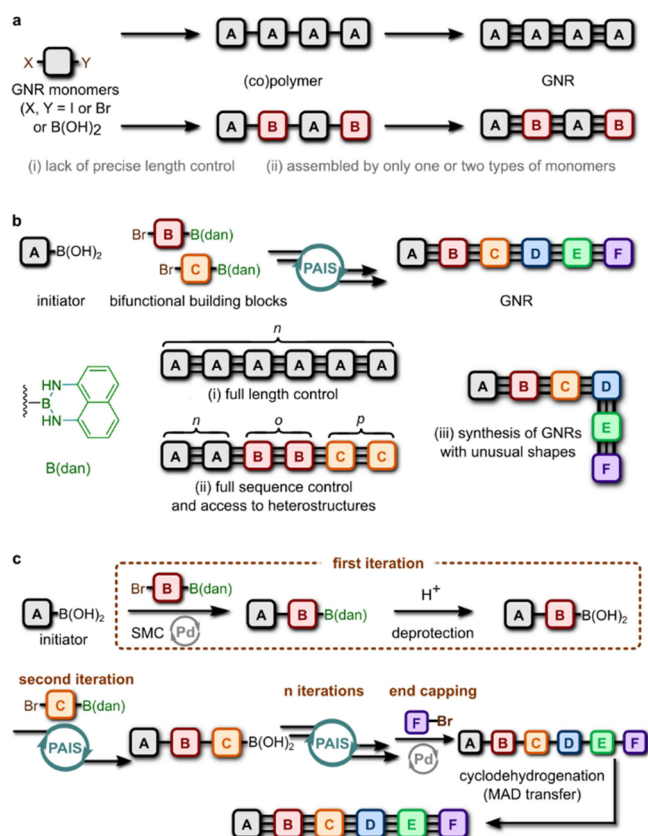


Figure 1. Bottom-up GNR synthesis strategies. (a) Conventional GNR synthesis via polymerization or copolymerization of monomers. (b) This work: a new programmable fabrication strategy for obtaining structurally diverse and monodisperse “designer” GNRs, which is enabled by PAIS. dan: 1,8-diaminonaphthalene. (c) In this PAIS process, the Suzuki–Miyaura coupling and B(dan) deprotection constitute one operative iteration, and only one GNR monomer is introduced to the chain per iteration.

by a protecting-group-aided iterative synthesis (PAIS) strategy (Figure 1b).

Inspired by advanced preparation strategies for oligonucleotides in which protecting groups play a key role in providing programmability and length control,^{50,51} an important question is whether a similar approach can be adopted for the synthesis of GNR polymer or oligomer precursors. Considering the effectiveness of Suzuki–Miyaura coupling (SMC) in solution-phase GNR synthesis,^{9,10,15,16,20,23} our PAIS strategy capitalizes on the use of bifunctional building blocks (BBBs) containing a halide and a masked boronic acid to achieve controlled iterative couplings (Figure 1c). Specifically, 1,8-diaminonaphthalene (dan) is used to protect the boronic acid group of our BBBs because [B(dan)] is stable and unreactive under SMC conditions and can be easily deprotected to reveal the reactive boronic acid moiety upon treatment with an acid, based on Sugimoto’s seminal work.⁵² We were motivated by the idea that a BBB containing both a bromo and B(dan) substituent could first couple with an initiating monomer (i.e., the “initiator”) that only contains a boronic acid via SMC. Acid hydrolysis of the B(dan) moiety could then be performed to deprotect the boronic acid, activating it for the next cross-coupling step. The resulting boronic acid intermediate could then be cross-coupled with the second (either the same or different) BBB for chain propagation. In this PAIS process, the

SMC and acid hydrolysis constitute one operative iteration, and *only one GNR monomer is introduced to the chain per iteration*. This is the key to realizing programmability and length/sequence control. The GNR polymer or oligomer chain can be terminated at any stage by SMC with an end-capping monomer that only contains a bromo group. The final GNR product is then obtained through cyclodehydrogenation (CDH), either in solution or on-surface.

RESULTS AND DISCUSSION

Length Control. To test this hypothesis, we first set out to prepare chevron-type GNRs⁸ with exactly six repeating units (Figure 2a). To achieve this goal, we began with phenylboronic acid and performed six iterations of solution-based cross-coupling and hydrolysis with a chevron-type bifunctional building block (BBB_{ch}) prepared via borylation of the corresponding dibromo monomers and protection of the resulting boronic acid moiety with dan (for details, see Supporting Information, Figure S1). SMC was realized in high yield with 1 mol % Pd(dppf)Cl₂ as the catalyst, K₃PO₄ as the base, H₂O as the additive, and THF as the solvent. In each SMC step, one chevron-type BBB was added to the oligomer; because the BBB contains an unreactive B(dan) group, no further coupling occurred afterward. Hydrolysis was realized with HCl under the N₂ atmosphere at 60 °C, which turned the unreactive B(dan) terminus into reactive B(OH)₂, effectively activating it for the next coupling reaction with another BBB. The two-step SMC-deprotection process was iterated a total of six times to introduce six chevron repeating units, and the synthesis of the oligomer (GNR) precursor **pre-chGNR(6)** was completed by terminating coupling with PhBr.

The resulting monodisperse **pre-chGNR(6)** sample was then transferred to a precleaned Au(111) surface via the recently established matrix-assisted direct (MAD) transfer technique using pyrene as the matrix⁵³ (for details, see the Supporting Information). The Au(111) sample was then heated to $T_1 = 80$ °C for $t = 10$ h to sublime the pyrene matrix and induce diffusion of the polymers over the surface, followed by heating to $T_2 = 360$ °C for $t = 20$ min to induce CDH of the oligomers into fully planar **ch-GNR(6)**. The resulting GNRs were characterized via bond-resolved scanning tunneling microscopy (BRSTM) imaging,²⁶ revealing the expected structure with exactly six repeating units (Figure 2b). Some defects were seen, such as an occasional incomplete CDH, as well as an occasional phenyl ring ejection, which are known to occur in on-surface CDH of chevron-type GNRs.^{54,55} Larger-scale STM scans (Figures 2c and S8a) show that about 75% of the observed GNR structures are consistent with the **ch-GNR(6)** target structure. This is also corroborated by the MALDI-TOF mass spectrum (Figure 2d), which reveals peaks corresponding precisely to the desired molecular weights of the GNR oligomer precursor. This suggests that the phenyl ejection defects observed in the surface-cyclized GNRs were introduced during the CDH step and are not likely to be present in the GNR precursor.

Heterostructure Control. In addition to the length control described above, the PAIS method can also generate heterostructures with precise, predefined monomer sequences of different building blocks. To illustrate this point we have synthesized precise, monodisperse $N = 9$ armchair (9-AGNR)/chevron-GNR heterostructures (Figure 3a). These heterostructures exhibit useful “straddling-gap” heterojunction electronic structure because the 9-AGNR band gap is smaller

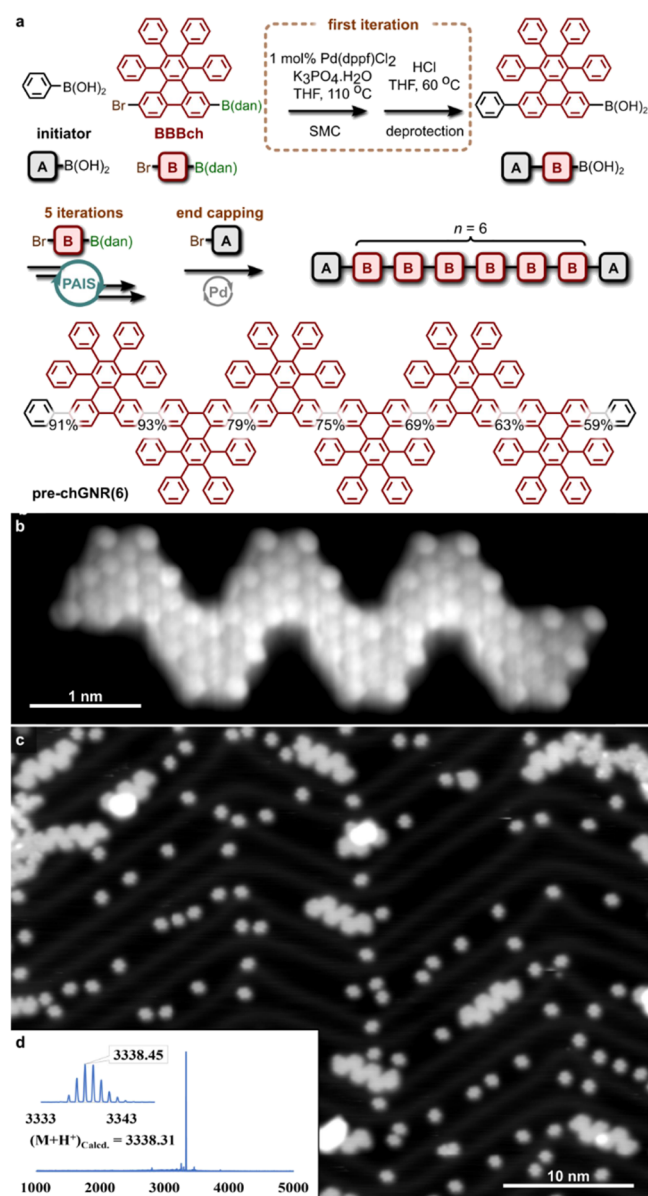


Figure 2. Length control: synthesis of **chGNR(6)**. (a) Synthesis of the oligomer (GNR) precursor **pre-chGNR(6)** demonstrating GNR length control. Yields for each iteration in the oligomer synthesis are provided at the corresponding connection positions. (b) BRSTM image (constant height dI/dV at $V = 0$ V) of **chGNR(6)**. (c) Large-scale STM topograph ($V = -1.8$ V, $I = 50$ pA) shows monodisperse **chGNR6** on Au(111) after the CHD step. (d) MALDI-TOF-MS spectrum of **pre-chGNR(6)**.

than the band gap of the chevron-GNR.^{56,57} The synthesis here was started with the same phenylboronic acid initiator as before, after which five repeating units of para-terphenylene were added through five successive SMC/deprotection cycles utilizing the para-terphenylene building block (**BBB_{p3p}**). Three chevron monomers (**BBB_{ch}**) were then added to the chain afterward, at which point, the synthesis was completed by end-capping the oligomer with PhBr (**Figure 3a**). The resulting oligomer (GNR) precursor (**pre-9-chGNR**) was then transferred to the gold surface via the MAD-transfer protocol, after which CDH was performed to yield the final, fully planar **9-chGNR** heterostructure.

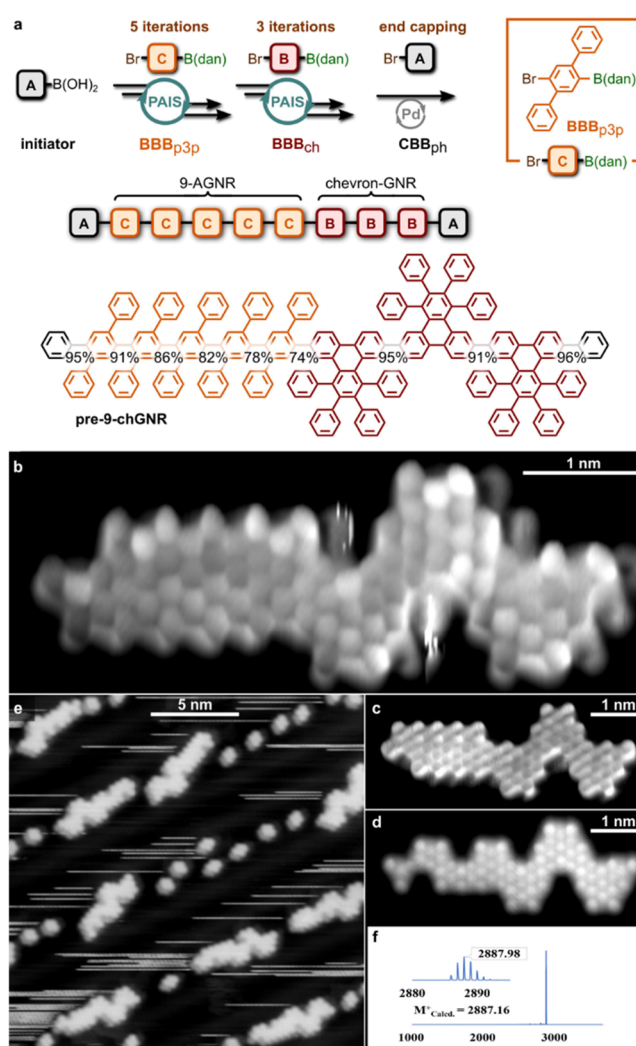


Figure 3. Heterostructure control: synthesis of **9-chGNRs**. (a) Synthesis of the oligomer (GNR) precursor **pre-9-chGNR** demonstrating a precise two-component GNR heterostructure. Yields for each iteration in the oligomer synthesis are provided at the corresponding connection positions. (b) BRSTM image (constant height dI/dV at $V = 0$ V) of **9-chGNR** after CHD. (c, d) BRSTM images (constant height dI/dV at $V = 0$ V) of **9-chGNRs** showing phenyl ejection defects. (e) Large-scale STM topograph ($V = -0.8$ V, $I = 50$ pA) shows monodisperse **9-chGNRs** on Au(111). (f) MALDI-TOF-MS spectrum of **pre-9-chGNR**.

Figure 3b shows a BRSTM image of the final **9-chGNR**, which has the exact intended GNR structure. We do observe that this GNR heterostructure often suffers from defect formation (such as phenyl ejection) upon on-surface CDH (**Figure 3c,d**). This is likely caused by the relatively free rotation of para-terphenyl groups around the GNR axis, leading to undesired stacking between neighboring phenyl rings and subsequent cleavage under CDH conditions. Regardless of these defects, the backbone of each GNR on the surface clearly shows the intended structure (**Figure 3e**). The large area image shows that about 80% of observed GNRs have the expected sequence and the desired overall shape (**Figure S8c**). The MALDI-TOF mass spectrum also reveals a set of sharp peaks at the intended molecular weights (**Figure 3f**), indicating that the observed defect formation is likely a consequence of the on-surface CDH process and not the chemical synthesis.

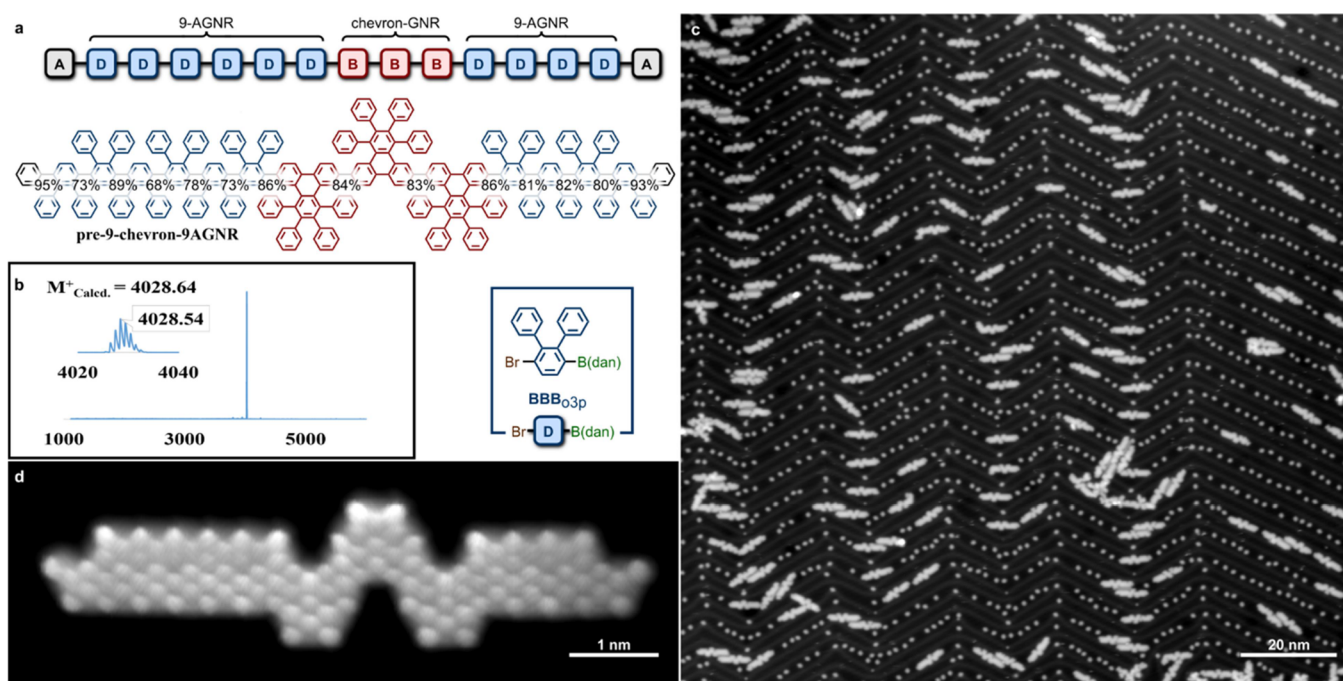


Figure 4. Double-junction heterostructures: synthesis of **9-chevron-9AGNRs**. (a) Synthesis strategy to obtain oligomer GNR precursor **pre-9-chevron-9AGNR** exhibiting a double-junction heterostructure. Yields for each iteration in the oligomer synthesis are shown at the corresponding connection positions. (b) MALDI-TOF-MS spectrum of **pre-9-chevron-9AGNR**. (c) Large-scale STM topograph ($V = -1.4$ V, $I = 20$ pA) of fully cyclized **9-chevron-9AGNRs**. (d) BRSTM image (constant height dI/dV at $V = 0$ V) of a **9-chevron-9AGNR** after CHD.

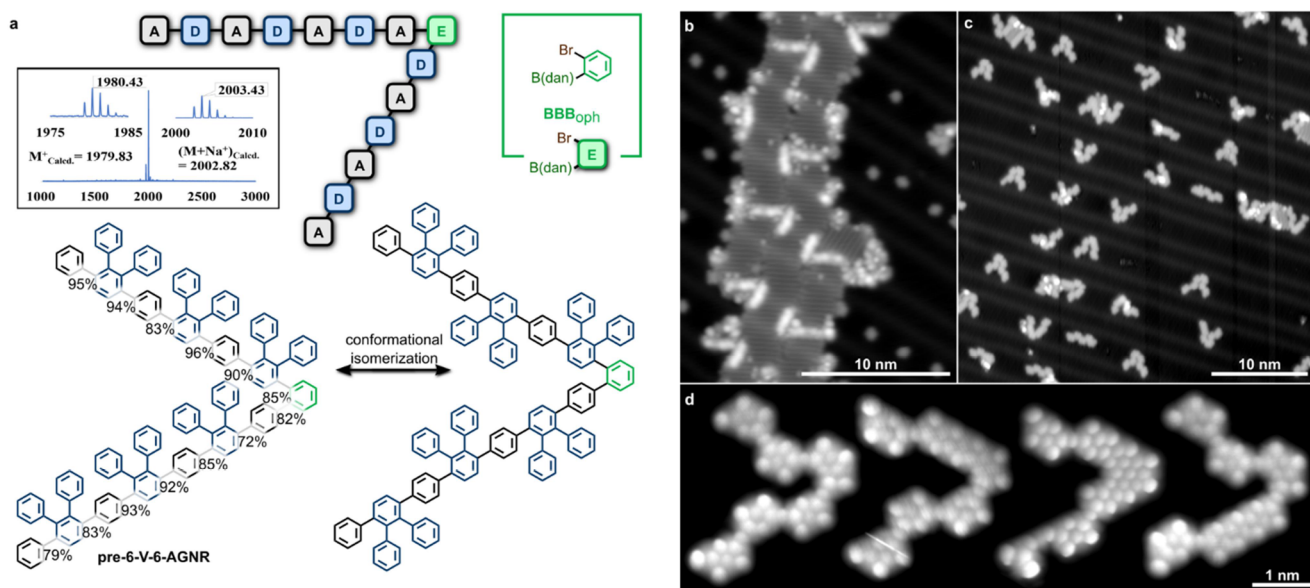


Figure 5. Kinked GNRs: synthesis of **6-V-6-AGNRs**. (a) Synthesis of oligomer (GNR) precursor **pre-6-V-6-AGNR** demonstrating a kinked GNR structure. Yields for each iteration in the oligomer synthesis are provided at the corresponding connection positions. The inset shows a MALDI-TOF-MS spectrum of **pre-6-V-6-AGNRs**. (b) STM topograph ($V = -1.4$ V, $I = 100$ pA) of the oligomer (GNR) precursor (**pre-6-V-6-AGNR**). (c) Large-scale STM topograph ($V = -1.6$ V, $I = 50$ pA) showing monodisperse **6-V-6-AGNRs** after CDH. (d) BRSTM images (constant height dI/dV at $V = 0$ V) of **6-V-6-AGNRs**.

In order to explore the effectiveness of the PAIS strategy to create precise nonperiodic GNR structures with multiple interfaces, we fabricated a double heterojunction composed of two 9-AGNR segments surrounding a single chevron segment (Figure 4a shows a sketch of the intended structure). Like para-terphenyl, polymers with ortho-terphenyl units are known to yield 9-AGNRs.^{58,59} The synthesis was achieved via sequential introduction of six ortho-terphenyl units, three

chevron monomers, and then four ortho-terphenyl BBBs (Figure 4a). After end-capping, the **9-chevron-9AGNR** heterojunction oligomer precursor (**pre-9-chevron-9AGNR**) having 18 phenylene units in its backbone was isolated in high purity, as supported by the MALDI-TOF mass spectrum (Figure 4b).

The resulting **pre-9-chevron-9AGNR** was then transferred to the gold surface via the MAD-transfer protocol, after which

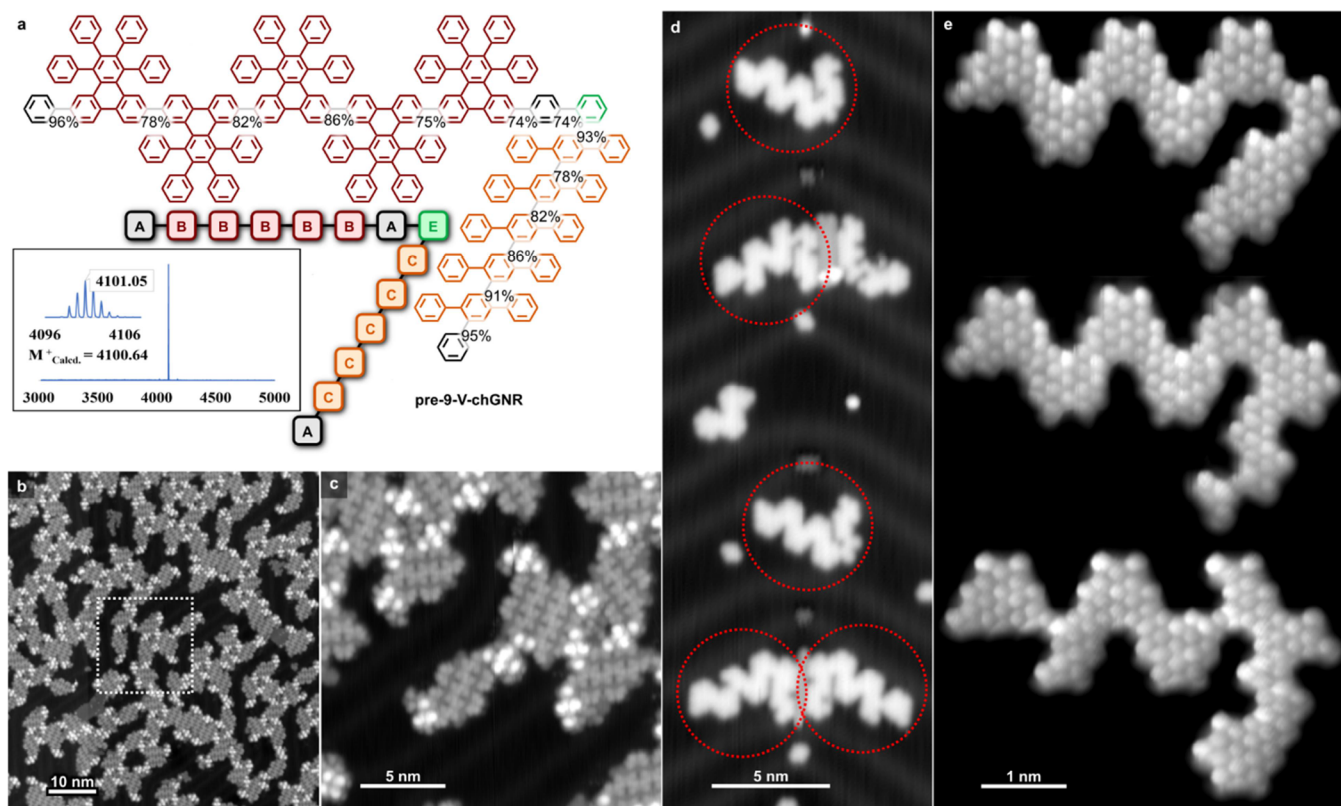


Figure 6. Kinked heterojunctions: synthesis of 9-V-chGNRs. (a) Synthesis of oligomer (GNR) precursor **pre-9-V-chGNR** demonstrating a kinked, two-component GNR heterostructure. Yields for each iteration in the oligomer synthesis are provided at the corresponding connecting positions. The inset shows the MALDI-TOF-MS spectrum of **pre-9-V-chGNR**. (b) Large-scale STM topograph ($V = -2$ V, $I = 50$ pA) of oligomer (GNR) precursor (**pre-9-V-chGNRs**). (c) Close-up STM image ($V = -2$ V, $I = 50$ pA) of **pre-9-V-chGNR** (boxed area in b). (d) Large-scale STM topograph ($V = -1.8$ V, $I = 50$ pA) of monodisperse 9-V-chGNRs after CHD (each GNR is labeled by a red circle). (e) BRSTM images (constant height dI/dV at $V = 0$ V) of 9-V-chGNRs.

CDH was performed to yield the final, fully planar double heterojunction GNR. Larger-scale STM scans (Figure 4c) clearly show high uniformity of this sample, as about 94% of GNRs observed on the surface exhibit the expected structure. The undesired GNR products were mainly generated by intermolecular reactions (i.e., GNRs landing on top of each other during the MAD transfer). The BRSTM image further confirms that the precise targeted GNR structure was obtained experimentally (Figure 4d). This further confirms the extensive programmability of the PAIS strategy, including control of the length, sequence, shape, and size.

Kinked GNRs. Having established that the PAIS method can give access to length-controlled GNRs and precise sequence-defined GNR heterostructures, the potential of PAIS to generate GNRs with previously inaccessible shapes was investigated next. Our starting hypothesis was that GNRs with controlled angular turns could be obtained by selecting a BBB that has the bromine and B(dan) substituents at an angle relative to each other. “Kinked” GNRs termed **6-V-6-AGNR** (where the V represents the kink) were designed and synthesized by merging the **6-AGNR** scaffold with an ortho-phenylene unit (BBB_{oph}) (Figure 5a). The ortho linkage between the bromine and the B(dan) groups in BBB_{oph} introduces an abrupt 120° growth direction change. After synthesis, the oligomer (GNR) precursor (**pre-6-V-6-AGNR**) was transferred onto Au(111) using MAD for CDH and STM imaging. STM images (Figure 5b) and MALDI-TOF mass spectrum (Figure 5a inset) confirm the correct V-shaped

scaffold of the GNR oligomer precursors produced using PAIS. Figure 5c shows a large-scale image of monodisperse **6-V-6-AGNRs** on Au(111) after CDH, in which $\sim 84\%$ of the observed GNRs have the expected sequence with the desired angular turn. Close-up BRSTM images can be seen in Figure 5d, which confirm that the majority of GNRs found on the surface have the expected 120 -degree kink in their backbone, as well as the correct sequence and length. The observed conformational rotation of ortho-terphenyl units in the **6-AGNR** segments took place during the CDH stage, leading to “flip” isomers (this was not seen in the liquid-phase preparation of **6-AGNRs** by Scholl oxidation in our previous work²³). The isomerization seen here is likely due to slight steric repulsion between neighboring terphenyl units, which lowers the activation barrier for cyclization into nonstraight shapes.

Lastly, to show the full range of structural flexibility afforded by PAIS, the kinked structural motif was integrated into a two-component GNR heterostructure. This was accomplished by fabricating a kinked heterojunction using chevron and 9-AGNR building blocks. The new oligomeric precursor (**pre-9-V-chGNR**) was successfully prepared using the PAIS strategy (Figure 6a), involving the use of four different BBBs. Figure 6b, c shows the GNR oligomer precursor after MAD deposition to the Au(111) surface. The chevron-GNR segments are in good agreement with previous images of regular chevron-GNR precursors,⁸ while the 9-AGNR segments appear as bright lobes. Figure 6d shows a large-scale

image of the resulting 9-V-chGNRs after CDH. The close-up BRSTM images in Figure 6e show 120° kinked heterojunctions with a thick chevron arm bonded to a thinner 9-AGNR arm. Phenyl ejection defects are visible (similar to what was seen for ch-GNR(6) and 9-chGNR), but the BRSTM images confirm that the GNRs exhibit the exact sequence and length that they were designed to have.

CONCLUSIONS

In conclusion, we have developed a programmable approach to fabricate structurally diverse monodisperse GNRs with a predetermined length, shape, and monomer sequence. This approach is enabled by the PAIS strategy, as well as subsequent MAD-transfer and on-surface CDH. The effectiveness and precision of the approach are supported by BRSTM characterization of diverse GNR structures that could not be fabricated using more conventional GNR synthesis techniques. The GNRs accessible to this technique are not limited to the lengths shown here because much longer GNRs could, in principle, be prepared by adding more iterations so long as the corresponding oligomer or polymer remains soluble. Utilization of this method for liquid-phase fabrication of longer and more complex monodisperse GNR structures is ongoing in our laboratories and is focused on addressing the scalability and defect issues that arise from on-surface synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.2c05670>.

Additional experimental details, materials, methods and spectral data (PDF)

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Notes

The authors declare the following competing financial interest(s): A provisional patent application on the PAIS method has been filed.

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