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Bottom-up synthesis of graphene nanoribbons on surfaces

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# 1 **Bottom-Up Synthesis of Graphene Nanoribbons on Surfaces**

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21

22 **Abstract** The review discusses the progress in the synthesis of atomically precise graphene  
23 nanoribbons from molecularly defined precursors on surfaces. It covers the literature from 2010  
24 through 2016.

25

26 **Keywords** Graphene nanoribbon, bottom-up synthesis, surface catalysis, scanning tunneling  
27 microscopy/spectroscopy

28

29 **Abbreviations**

30	AFM	atomic force microscopy
31	AGNR	armchair graphene nanoribbon
32	CB	conduction band
33	CeGNR	cove edge graphene nanoribbon
34	CGNR	chevron graphene nanoribbon
35	DOS	density of states
36	GNR	graphene nanoribbon
37	HREELS	high-resolution electron energy loss spectroscopy
38	IPES	inverse photoemission spectroscopy
39	LDOS	local density of states
40	ncAFM	non-contact atomic force microscopy
41	STM	scanning tunneling microscopy
42	STS	scanning tunneling spectroscopy
43	UHV	ultra high vacuum
44	UPS	ultraviolet photoemission spectroscopy
45	VB	valence band
46	XPS	X-ray photoemission spectroscopy
47	ZGNR	zig-zag graphene nanoribbon
48		

## 49 **1 Introduction**

50 The outstanding transformative potential of graphene, an infinite sheet of carbon atoms tightly  
51 packed into a honeycomb lattice, has been recognized mostly due to its exceptionally high  
52 charge-carrier mobility, thermal conductivity, tensile strength, and mechanical stiffness [1-3]. Yet,  
53 these undeniably very desirable properties represent only a very small facet of the true potential  
54 of all-sp<sup>2</sup> carbon materials and its potential to revolutionize the field of molecular electronics. The  
55 electronic properties of graphene itself can be described as a gapless semiconductor or  
56 semimetal (Figure 1) [4, 5]. Its valence and conductance band overlap in a single point. Graphene  
57 shows a strong ambipolar electric field effect. The charge carriers can be tuned continuously  
58 between holes and electrons reaching densities as high as 10<sup>13</sup> cm<sup>-1</sup> and mobilities in excess of  
59 15000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The charge mobility in graphene is largely dominated by impurity scattering  
60 effects and is almost independent of the temperature. Even at ambient conditions the charge  
61 carriers in graphene move ballistically over submicron distances covering a typical gap between  
62 the source and drain electrodes of a transistor in less than 1 ps [1, 2, 6].

63 Over the last decade an overwhelming variety of applications for graphene have been  
64 proposed ranging from fillers for composite plastic materials, graphene based batteries, super  
65 capacitors, and field emitters [7, 8], transparent electrodes in optoelectronics [9, 10], carbon-  
66 based environmental sensors [11], spin-valves [12, 13], and field-effect transistors [1]. The  
67 research in the field of all-sp<sup>2</sup> carbon-based materials has largely been motivated by its  
68 applications in advanced functional electronics. Due to its unique properties graphene has been  
69 identified as one for the most promising materials for post-silicon integrated circuit architectures  
70 [14]. The seamless integration of graphene into advanced electronic circuits, however, calls for  
71 semiconductors, rather than semimetals, featuring well-defined and tunable band gaps and large  
72 on-off current ratios at ambient conditions. This can be achieved by reducing the infinite two-  
73 dimensional carbon sheet to a narrow one-dimensional graphene nanoribbon (GNR) [5, 15]. This  
74 quantum mechanical confinement alters the electronic band structure and gives rise to a well-  
75 defined gap between the conductance and the valence band [16, 17]. In fact, GNRs most unusual  
76 properties, e.g. the theoretically predicted edge-magnetism, the exceptionally high spin-  
77 coherence, and the highly tunable band gap, are intimately linked to quantum mechanical  
78 boundary conditions dictated by the dimension, symmetry, and the edge-structure [18].  
79 Unfortunately, these complex structure-function relationships remain poorly understood. The  
80 exploration, realization, and implementation of these truly exotic properties rely on the  
81 development of innovative synthetic strategies, that provide atomically precise control over the



82 assembly of functional nanographene.

83 Superior synthetic strategies toward atomically defined and tunable GNRs must overcome  
84 several longstanding challenges. First and foremost is the reliable control of the absolute  
85 dimensions, i.e. length and width. Cutting-edge top-down lithographic patterning techniques have  
86 been successfully used to fabricate individual GNR featuring widths as narrow as 10 nm. The  
87 process however is exceedingly laborious, relies on the availability of sophisticated  
88 instrumentation, and is limited to the fabrication of individually unique samples. Synthetic bottom-  
89 up approaches instead have the potential to yield rationally designed GNRs in highly  
90 homogeneous batch synthesis. Structural variation of the small-molecule building blocks, the  
91 precursors for the GNRs, represents a reliable strategy to dial-in a desired width and edge  
92 symmetry. Pure samples of hydrogen terminated zig-zag (ZGNRs) or armchair GNRs (AGNRs)  
93 with homogeneous widths and highly reproducible physical properties can be obtained.  
94 Furthermore, this rational approach paves the way for the assembly of GNRs featuring designer-  
95 edges tailored to a variety of very specific application requirements. The extraordinary control  
96 over the structure of GNRs can also be applied to rational defect engineering or doping. The  
97 chemical synthesis of small-molecule precursors allows the introduction of functional groups or  
98 heteroatoms into the edges or into the carbon lattice of the GNR itself. The exact position of these  
99 dopants and the highly regular pattern along the length of the ribbons can easily be predicted and  
100 can be used to tune e.g. the Fermi energy, the band gap, or the number and the nature of charge  
101 carriers in the GNR.

## 102 **2 Top-Down Synthetic Strategies**

103 The controlled synthesis of GNR based functional materials is a field still in its infancy. The  
104 techniques used to synthesize GNRs can be broadly categorized into two complementary  
105 approaches: classical top-down patterning of two dimensional graphene sheets, and the  
106 controlled bottom-up growth of graphene nanostructures from small-molecule precursors. Early  
107 top-down approaches relied on lithographic techniques to pattern mechanically exfoliated sheets  
108 of graphene (Figure 2). Han et al. used e-beam lithography to pattern etch masks on single sheets  
109 of graphene [5]. Oxygen plasma etching of the unprotected graphene yielded individual GNRs  
110 with widths ranging from 10–100 nm and lengths of 1–2  $\mu\text{m}$ . The electronic properties of these  
111 structures, however, suffer from harsh reaction conditions. Using this technique, it is difficult to  
112 control both the edge symmetry and the substitution pattern of the GNRs. Tapasztó et al.  
113 combined the surface modification and atomic resolution imaging capabilities of STM techniques

114 to engineer graphene nanostructures [15]. Current etching of a single sheet of graphene at the  
115 surface of multilayer graphite yielded GNRs ranging in widths between 2.5–10 nm and lengths up  
116 to 120 nm. This technique represents a significant improvement, however, the low throughput and  
117 edge irregularities or roughness in the narrower ribbons remain a common problem of top-down  
118 approaches.

119 Naturally occurring defect structures in graphene have been used by Li et al. to fabricate sub  
120 10 nm wide and  $\sim 1 \mu\text{m}$  long GNRs by sonication of exfoliated graphene sheets suspended in  
121 organic solvents [19]. While this approach yields GNRs with well-defined edges, the random  
122 distribution of defects can not be used to control the absolute dimensions of the ribbon. Kosynkin  
123 at al. and Jiao et al. have unzipped single-walled and multi-walled carbon nanotubes along the  
124 longitudinal axis to yield narrow graphene nanoribbons [17, 20, 21]. Both techniques rely on the  
125 use of exceptionally harsh reaction conditions, large excess of strong oxidants like  $\text{KMnO}_4$  or  
126 plasma etching, to induce and propagate defects along the longitudinal axis of the nanotubes.  
127 The edge structure of the resulting unfolded GNRs can directly be correlated to the chirality of the  
128 initial carbon nanotube. The use of harsh reaction conditions and the inherent inhomogeneity of  
129 carbon nanotubes, however, lead to irregularities in the substitution pattern and unpredictable  
130 edge symmetries. Carbon atoms exposed during the unzipping process can easily be oxidized to  
131 e.g. alcohols, ketones, or carboxylic acids. This irregular substitution negatively and unpredictably  
132 affects the conductive properties of narrow GNRs.

### 133 **3 Rational Bottom-Up Synthesis**

134 A significant advance in the rational synthesis of GNRs has been demonstrated by Müllen,  
135 Fasel, and coworkers [22]. Pioneering work related to the surface supported assembly of  
136 molecular wires and covalent organic networks sparked the rational design of polymers that could  
137 be converted into GNRs through surface catalyzed cyclodehydrogenation strategies [23-25]. The  
138 general concept is illustrated for the rational synthesis of  $N = 7$  (where  $N$  is the integer number of  
139 carbon atoms counted across the width of the GNR) AGNRs from 10,10'-dibromo-9,9'-bianthryl  
140 (**1**) in Figure 3. The brominated small-molecule precursors is evaporated onto a clean noble metal  
141 (e.g. Au, Ag, Cu) surface held at a constant temperature ( $T_1$ ) under ultra-high vacuum (UHV). The  
142 intimate interaction with the catalytically active metal surface induces the homolytic cleavage of  
143 the carbon–halogen bond to give a diradical intermediate. These intermediate carbon-centered  
144 diradicals diffuse along the surface and recombine in a step-growth polymerization to yield linear  
145 *poly*-anthracene chains. Thermal annealing of these precursors at an elevated temperature ( $T_2$ )

146 induces a cyclodehydrogenation sequence [26] that yields fully conjugated GNRs ranging in  
147 length from 12–60 nm [27]. This surface-based self-assembly technique yields 7-AGNRs with  
148 atomically defined hydrogen substituted armchair edges. The width and the crystallographic  
149 symmetry of bottom-up fabricated GNRs is primarily determined by the structure of the small-  
150 molecule precursor. The length of the ribbon largely depends on the surface coverage, the  
151 average diffusion length of monomers and growing polymer chains on the surface, and the  
152 competition between chain-extension, chain-termination and radical-transfer processes. While  
153 this technique yields superior GNRs with hydrogen terminated edges it is limited by the growth  
154 conditions. The efficient incorporation into devices demands GNRs with lengths in excess of 100  
155 nm. Particularly for electronic applications it is essential that the GNR is supported by an insulator  
156 rather than by a highly conductive metal to prevent competing conduction pathways.

### 157 **3.1 Bottom-Up Synthesis on Surfaces: Mechanism and Design Strategies**

158 A central aspect to the rational bottom-up synthesis of GNRs lies in the design of the  
159 molecular precursors. The precursor molecules are required to meet a series of thermodynamic,  
160 kinetic, and structural criteria imposed by the dimensions and the symmetry of the desired GNR,  
161 the nature of the surface used as the growth substrate, and technical limitations imposed by the  
162 UHV system used in the fabrication. Figure 4 summarizes a selection of building blocks used in  
163 the synthesis of AGNRs, chevron GNRs (CGNRs), and ZGNRs on surfaces. Initial work has  
164 largely focused on the synthesis of AGNRs ranging in width from  $N = 5$  to  $N = 13$ . A common  
165 structural feature of most molecular precursors is a mirror symmetry perpendicular to the long  
166 axis of the GNR. This preferred structure, an A–A building block, ensures that the rate of radical  
167 recombination at either end of the growing polymer chain is comparable. The inherent symmetry  
168 further circumvents structural defects that could emerge from asymmetric radical recombination  
169 of A–B building blocks featuring, for example, different steric demands at either end of the  
170 monomer. A second important structural consideration is the placement of aryl rings that undergo  
171 cyclodehydrogenation during the thermal annealing on the surface. As a post-polymerization step  
172 the successful defect free cyclodehydrogenation rests on a clear preference of the aryl rings to  
173 undergo exclusively the desired cyclization that leads to the extended conjugated  $\pi$ -system of  
174 GNRs. Careful structural considerations ensure that the appended aryl rings form the desired C–  
175 C bonds rather than participating in side reactions that could lead to kinks or defects along the  
176 GNR backbone. Conceptually this is illustrated in the design of the precursor for 13-AGNRs  
177 (Figure 5). The *ortho*-substitution of the bond between the biphenyl wing and the anthracene core  
178 gives access to only one distinct cyclodehydrogenation product as opposed to two potentially

179 accessible orientations for the alternative *meta*-substitution pattern.

180 Further consideration has to be given to the choice of activating substituents. The large  
181 majority of successful building blocks feature either C–Br or C–I bonds that undergo homolytic  
182 cleavage to generate halogen radicals and the desired Csp<sup>2</sup> centered radicals that participate in  
183 the step growth polymerization. The preferential selection of Br and I substituents for the synthesis  
184 of GNRs on precious metal surfaces is not arbitrary but meets very specific kinetic and  
185 thermodynamic requirements. The key challenges are the choice of a functional group that is  
186 compatible with the sublimation conditions used during the deposition of molecular precursor on  
187 the target substrate, a bond that can be selectively activated through an external stimuli (e.g. heat,  
188 light) on the surface under conditions that do not cleave other labile bonds (C–H, C–C) in the  
189 molecule, and a homolytic fragmentation pattern that leaves a Csp<sup>2</sup> centered radical and  
190 preferably a small molecule behind that either irreversibly desorbs from the surface or is  
191 sufficiently deactivated to not interfere during the radical chain propagation step. These conditions  
192 are largely met in the activation of labile C–Br and C–I bonds over the omnipresent C–H bonds  
193 on Au, Ag and Cu surfaces. DFT calculations by Björk et al. have demonstrated that the highly  
194 exothermal bond dissociation of phenylbromide or phenyliodide (317 kJ mol<sup>-1</sup> and 321 kJ mol<sup>-1</sup>  
195 respectively) turns into an endothermal process on Au(111), Ag(111), and Cu(111) surfaces [28,  
196 29]. This unusual thermodynamic stabilization can be explained by covalent interactions between  
197 the Csp<sup>2</sup> centered radical on the phenyl ring and the free valences of the metal surface.  
198 Chemisorption of the high energy phenyl radical drives the reaction towards the dissociated  
199 products. The ability for stabilizing the phenyl radical follows a trend in the series Au, Ag, Cu with  
200 the latter being the most reactive surface. Along with the overall reversion of the thermodynamic  
201 parameters, the kinetic barrier for the homolytic cleavage of the C–Br or C–I bond follows a similar  
202 trend. The activation energy for the dissociation of the C–Br and C–I bonds is highest on Au (97  
203 kJ mol<sup>-1</sup> and 69 kJ mol<sup>-1</sup>) and lowest on Cu (64 kJ mol<sup>-1</sup> and 38 kJ mol<sup>-1</sup>). These theoretical  
204 results are largely corroborated by experiments. Batra et. al and Simonov et al. followed the  
205 thermal activation of the C–Br bonds in **1** on a Au(111) surface using X-ray photoemission  
206 spectroscopy (XPS) [30, 31]. At temperatures below 100 °C the XPS of molecule decorated  
207 substrates indicates that **1** is only physisorbed on the surface (Figure 6). As the temperature is  
208 raised to 120–130 °C new signals for both C1s and Br3d appear that are consistent with the  
209 formation of a chemisorbed carbon and bromine radical. At 180 °C the reaction is complete and  
210 only the chemisorbed C and Br species can be observed. Further heating leads to the desorption  
211 of bromine (Br3d doublet at 68/69 eV disappears) while the carbon centered radical later  
212 undergoes recombination to form the polyanthracene precursor. Experimental data indicates that

213 the radical step growth polymerization precedes the desorption of Br from the Au(111) surface by  
214 a few degrees [32]. The subtle difference between Br desorption and C–C bond formation energy  
215 is important, as omnipresent Br atoms on the surface can act as chain termination or radical  
216 transfer reagents during the step-growth polymerization phase. While Br and I groups are  
217 privileged motifs among molecular GNR precursors the structural scope is not limited to carbon–  
218 halogen bonds. Recent encouraging examples include thermally induced isomerization of  
219 enediynes that efficiently and regioselectively generate  $Csp^2$  centered radicals that can  
220 recombine to form new C–C bonds [33, 34].

221 A more complex factor that has to be considered in the design of competent molecular  
222 precursors lies in the sample preparation procedure itself. Surface mediated GNR growth is  
223 commonly performed in a UHV system as the nature of the radical recombination that leads to  
224 the extended polymer precursors requires an atomically clean surface. The molecular building  
225 blocks for GNRs are commonly evaporated from a crucible onto the face of a single crystal of  
226 metal thin film. This step mandates a thermal stability that is compatible with the sublimation  
227 temperature, and preferably below the uncatalyzed activation of the thermally labile groups.  
228 Furthermore, an exceptionally high purity of the molecular sample is instrumental to the formation  
229 of extended polymers, as even trace impurities ( $< 0.1\%$ ) or decomposition products can readily  
230 sublime and form a monolayer coverage on the metal substrate before the desired building blocks  
231 can evaporate. Finally, even at  $10^{-9}$  Pa, sublimation itself places an upper limit on the size of  
232 molecular precursors that can be deposited efficiently, and restricts the nature, the position, and  
233 the size of substituents that can be incorporated into the structure of the resulting GNR.

234 Even if all the above criteria are met through the rational design of a molecular building block,  
235 a series of less predictable factors remain. These include for example the preferred adsorption  
236 geometry and adsorption energy of the molecules on the substrate. Predicting the self-assembly  
237 of molecules on a surface solely based on routine DFT calculations in the gas phase is a daunting  
238 challenge and increases exponentially with any additional degree of freedom or decrease in  
239 symmetry inherent to the molecule itself. Aside from the numerous orientations a molecule can  
240 adopt with respect to the crystallographic axes and the unit cell of the underlying substrate, any  
241 non-planar molecule inherently has multiple surfaces that can adsorb to the substrate. When  
242 approaching monolayer coverages additional intermolecular interactions can induce the formation  
243 of long range ordered molecular islands. Since the step growth polymerization relies on a formal  
244 radical recombination, the physisorbed or chemisorbed intermediates have to come close enough  
245 to form a covalent C–C bond. During this critical step the relative orientation of reaction centers

246 and the steric demand imposed by the immediate surrounding both contribute to the height of the  
247 activation barriers and thus the product distribution. This is illustrated in the fact that two molecules  
248 of the non-planar dibromobisanthrene **1** adsorbed on a Au(111) surface (dihedral angle between  
249 anthracenes  $\sim 80^\circ$ ) can approach one another in a staggered conformation that allows for the  
250 fusion of both radical centers. If instead a planar 9,10-dibromoanthracene were used the repulsive  
251 interaction between *peri*-hydrogens would effectively prevent the formation of a new C–C bond.  
252 As important as the relative orientation is a well-balanced molecule surface interaction.  
253 Adsorbates that interact too weakly with the substrate tend to form irregular clusters along  
254 crystallographic defects and step edges or desorb prematurely during the thermal activation  
255 steps. If instead the adsorption energy is too large the diffusion of activated species across the  
256 surface can become a rate limiting step. While molecular designs greatly benefit from structural  
257 analogies to proven systems, even in these cases the sheer complexity inherent to balancing the  
258 multitude of intermolecular forces along with the significant variability that comes with different  
259 metal substrates and crystallographic faces has thus far prevented the development of any  
260 practical predictive model. An illustrative example is the growth of GNRs from **1** on Au(111) vs  
261 Cu(111) (Figure 7). On Au(111) substrates **1** grows 7-AGNRs as expected based on the design  
262 considerations [22]. On the more active Cu(111) surface however the resulting GNRs feature a  
263 planar chiral (3,1) edge pattern resulting from the lateral fusion of molecular building blocks at an  
264 angle of  $77^\circ$  with respect to the intended axis of propagation [35-38].

265 The last and arguably more controllable step is the cyclodehydrogenation of the GNR  
266 polymer precursor on the metal substrate. If the molecular building blocks have been carefully  
267 designed every aryl ring can only fuse in one unique and predictable position. Extensive DFT  
268 calculations based on the cyclization of a 9,9'-bianthracene model on Au(111) performed by Björk  
269 et al. demonstrate that the precious metal surface plays a key role in the cyclodehydrogenation  
270 step [26]. While a number of plausible stepwise processes were considered the lowest activation  
271 barrier is associated with a concerted mechanism that sees the aryl rings rotate towards one  
272 another to form a new C–C bond while the *ipso* H-atoms at the corresponding positions are  
273 transferred to the Au(111) substrate as atomically chemisorbed hydrogen. The metal substrate  
274 thus acts as a catalyst that facilitates the dissociation of H-atoms. An additional cooperative effect  
275 has been observed in the study of extended *oligo*-anthracene model systems. The planarization  
276 and the strain induced by a first random cyclodehydrogenation drastically decreases the activation  
277 barrier for the cyclization of immediately adjacent rings. On Au(111) surface the  
278 cyclodehydrogenation proceeds in a cascade emanating in both directions from an initial arbitrary  
279 starting point. While this special case of positive cooperativity is rather unique to the synthesis of

280 7-AGNRs form **1** and related structures, the lowering of the activation barrier for adjacent  
281 cyclizations induced by the distortion imparted by the initial C–C bond formation is a commonly  
282 observed phenomenon in surface catalysis with on Au, Ag, and Cu.

### 283 **3.2 Rationally Tuning the Energy Structure in Bottom-Up Fabricated GNRs**

284 Quantum mechanical calculations have proven to be a valuable tool to predict the band  
285 structure of functional organic materials. A variety of theoretical models e.g. tight binding, density  
286 functional theory, and *GW* approximations that include the self-energy of a many-body system of  
287 electrons, have been applied to GNRs reflecting varying levels of accuracy [39, 40]. While the  
288 absolute numbers reflecting e.g. the magnitude of the band gap, the density of states of the energy  
289 of the valence (VB) and the conductance band (CB) edges diverge significantly between various  
290 theoretical models the underlying general trends are consistent throughout a family of structurally  
291 related GNRs. For consistency and to avoid confusions we will herein refer to calculations based  
292 on the *GW* approximation wherever possible.

293 Hydrogen terminated GNRs featuring an armchair pattern along the edges are predicted to  
294 be intrinsic semiconductors. The magnitude of the band gap between the valence and the  
295 conductance band edges roughly scales inversely width of the GNR (Figure 8) [40]. This general  
296 trend is consistent within all three families of armchair GNRs: the width is expressed as the  
297 number of atoms  $N = 3p$ ,  $N = 3p+1$ , and  $N = 3p+2$  counted in a straight chain across a ribbon ( $p$   
298 = 0, 1, 2, 3, ...). The smallest band gaps have been predicted for the  $3p+2$  series, whereas the  
299 largest band gaps are expected for members of the  $3p+1$  family. The width dependence of  
300 semiconducting AGNRs allows to rationally dial-in a desired band structure by tightly controlling  
301 the structure of the molecular precursor. Experimental determination of the band gaps in a family  
302 of AGNRs adsorbed on Au(111) supports this general trends. The quasi-particle band gaps of 7-  
303 AGNRs, 9-AGNRs, and 13-AGNRs determined by scanning tunneling spectroscopy (STS) are  
304 2.3 eV, 1.4 eV and 1.4 eV respectively. While 7-AGNRs and 13-AGNRs, derived from **1** and **2**  
305 respectively, belong to the same family ( $3p+1$ ) and serve to illustrate the reduction in band gap  
306 for wider ribbons, 9-AGNRs derived from **3** fall into the intermediate  $3p$  series and only  
307 coincidentally feature a band gap that is comparable to the significantly wider 13-AGNRs. Figure  
308 9 depicts and overlay of  $dI/dV$  spectra of 7-AGNRs and 13-AGNRs recorded on a Au(111) crystal  
309 [41]. The smaller intrinsic band gap of 13-AGNR (blue), corresponding to a peak to peak distance  
310 in a density of states plot, is straddled by the significantly larger gap of the 7-AGNRs (red). It is  
311 worth noting that theoretical models based on the DFT *GW* approximation do generally not include  
312 a discrete interaction between the GNRs and the underlying metal substrate. A direct comparison

313 between the calculated quasi-particle band gap of isolated GNRs (3.8 eV, 2.0 eV and 2.4 eV for  
314 7-AGNRs, 9-AGNRs and 13-AGNRs, respectively) and the experimentally determined band gaps  
315 is thus restricted by limitations in the accuracy of the models describing the hybridization of the  
316 GNR with the surface states. Zhang et al. and Kimouche et al. have expanded the series of  
317 AGNRs to include a member of the  $3p+2$  family associated with the smallest theoretically  
318 predicted band gaps. Both tetrabromonaphthalene **4** and the isomeric dibromoperylenes **5** serve  
319 as molecular precursors for 5-AGNRs [42, 43]. While initial STS on Au(111) appeared to indicate  
320 an unusually large bandgap (2.8 eV) a careful study of a series of oligomers derived from 5-  
321 AGNRs ranging in length between 2 to 14 monomer units (**5**) revealed a more detailed picture.  
322 Aside from the dominant signals previously assigned to the CB and VB edges the study revealed  
323 a series of smaller peaks in the  $dI/dV$  spectrum that fall within the assumed band gap (Figure 10).  
324 Reassignment of the CB and VB states led to a reinterpretation of the DOS and revealed an  
325 exceptionally small band gap of 0.1 eV for ribbons featuring more than five monomer units [43].  
326 This lower band gap is consistent with the expected trend for the  $3p+2$  family (1.7 eV for 7-  
327 AGNRs)

328       Aside from varying the width of GNRs the unique structural control inherent to a rational  
329 bottom-up synthesis offers a variety of alternative strategies to tailor the electronic structure.  
330 CGNRs derived from the dibromotriphenylene precursor **6** for example can be thought of as a  
331 GNR comprised of hexabenzocoronenes laterally fused at an angle of ( $\sim 104^\circ$ ) [22]. STS on  
332 Au(111) reveals an intermediate band gap of 2.0 eV [44]. For comparison, the theoretically  
333 predicted band gap calculated using the *GW* approximation is 3.5 eV. Optical spectroscopy of  
334 identical CGNRs shows a still unresolved departure from these values. High-resolution electron  
335 energy loss spectroscopy (HREELS) and ultraviolet photoemission/inverse photoemission  
336 spectroscopy (UPS/IPES) show band gaps of 2.8 eV and 1.3 eV respectively [45, 46]. A resolution  
337 of this apparent contradiction is pending further detailed investigation.

338       Liu et al. introduced a class of planar chiral GNRs derived from dibromobischrysene **7** [47].  
339 The structure of these cove-edge GNRs (CeGNRs) resembles a zig-zag edge in which every  
340 fourth carbon atom has been replaced by hydrogen. Deposition of **7** on Au(111) followed by  
341 thermal annealing and cyclodehydrogenation yields GNRs ranging in length between 5–20 nm.  
342 The unique edge structure of these chiral GNRs however is unusually susceptible to unselective  
343 C–H activation. Concurrent hydrogen abstraction during the cyclodehydrogenation step leads to  
344 ubiquitous radical centers along the edges that undergo recombination or uncontrolled radical  
345 transfer processes. As a result of this insufficient selectivity, CeGNRs tend to fuse into larger



346 irregular GNR aggregates at temperatures commensurate with the cyclodehydrogenation step.  
347 Optical spectroscopy along with ab initio DFT calculations (not including the *GW* approximation)  
348 indicate a potentially small band gap of 1.7–1.9 eV.

349       Narrow ZGNRs featuring a zig-zag pattern of hydrogen terminated carbon atoms along the  
350 longitudinal edge feature a series of unique properties among bottom-up fabricated GNRs.  
351 Theoretical calculations predict that the edge states are ferromagnetically coupled along one zig-  
352 zag edge and antiferromagnetically with respect to the other edge. These spin polarized electronic  
353 states are of great interest for advanced functional materials for spintronics. Ruffieux et al.  
354 demonstrated the bottom-up synthesis of  $N = 6$  ZGNRs (where  $N$  is the number of carbon zig-zag  
355 chains counted across the width of the ribbon) from the unusual molecular precursor **8** (Figure  
356 11) [48]. While all AGNRs and CGNRs feature a long axis that is aligned parallel to the armchair  
357 edge, the long axis in ZGNRs is perpendicular to the preferred growth direction of halogen-based  
358 surface polymerizations. The anchor shaped design of molecular precursor **8** elegantly resolves  
359 this challenge by arranging in an alternating head-to-toe orientation that aligns the long axis of  
360 the GNR with the zig-zag edge while retaining the preferred relative orientation of the new C–C  
361 bond formed during the radical step growth polymerization. Lastly the two additional methyl  
362 groups were incorporated into the structure of **8** to close the remaining gaps along the zig-zag  
363 edges of 6-ZGNRs. STS of 6-ZGNRs that have been transferred from the Au(111) gold substrate  
364 onto an insulating NaCl layer show a band gap of 1.5 eV. As the 6-ZGNR is mechanically  
365 decoupled from the interaction with the Au surface states the experimental values superbly match  
366 the theoretically predicted band gap (1.4 eV) calculated using the single particle Green's function  
367 and a screened Coulomb interaction (*GW* approximation). Further investigation of the exotic  
368 electronic and magnetic properties of ZGNRs along with a redoubled effort to stabilize the  
369 chemically reactive zig-zag edges is ongoing and holds great promise for the development of  
370 graphene based spintronic devices.

### 371 **3.3 Substitutional Doping in Bottom-Up fabricated GNRs**

372       While the extraordinary structural control innate to a rational bottom-up synthesis of functional  
373 graphene nanomaterials is superior to classical inorganic semiconductors, the rising complexity  
374 of structure-function relationships are at present a critical limitation to a robust performance-driven  
375 materials design. Instrumental tools and strategies to tailor the band structure and the Fermi level  
376 of GNRs require a deeper understanding of how atomistic structure guides the alignment of  
377 energy states. In particular, the concept of doping in atomically defined nanoscale graphene  
378 structures extends beyond the bounds of classical theories derived for inorganic semiconductors

379 and has been the topic of extensive exploration. Theoretical models predict that the energy of the  
380 VB and CB of semiconducting GNRs can be tuned by introducing a highly regular pattern of  
381 electron donating or electron withdrawing functional groups or atoms along the edges of GNRs  
382 (Figure 12). Early on this edge-doping has been at the center of investigation as it represents the  
383 least intrusive chemical modification that can readily be incorporated into the structure of  
384 molecular precursors. Bronner et al., Cai et al., and Vo et al. demonstrated that the introduction  
385 of nitrogen atoms in the form of pyrimidine and pyridine rings into the edges of CGNRs induces a  
386 rigid band shift (Figure 13) [44, 45, 49]. Theoretical calculations indicate the magnitude of the  
387 band gap shift correlates with the number and only to a lesser extent with the position of the  
388 heteroatoms. Electronic HREELS spectra of CGNRs derived from **6** (0 N-atoms), **9** (1 N-atom),  
389 and **10** (2 N-atoms) reveal that the overall magnitude of the band gap remains largely unchanged  
390 (2.8 eV, 2.8 eV, and 2.7 eV respectively). UPS spectroscopy shows a rigid shift of the entire band  
391 structure to lower energy with increasing number of N-atoms (~0.1 eV per N-atom). STS of  
392 CGNRs grown on Au(111) from dipyrimidine precursor **11** (4 N-atoms) show a band gap of 2.0  
393 eV that is comparable to the parent unsubstituted CGNRs. Yet, both VB and CB of CGNRs  
394 derived from **11** are shifted by 1.1 eV to lower energy. This general trend is supported by DFT  
395 calculations and extends the series of nitrogen edge-doping patterns in CGNRs up to 8 N-atoms.  
396 Based on theory an average shift of ~0.13 eV can be attributed to each N-atom. Computationally  
397 this concept has been applied to the introduction of boron atoms along the edges of CGNRs. As  
398 expected the direction of the rigid band shift is inverted (toward higher energy) while the  
399 magnitude amounts only to ~0.06 eV per boron atom.

400 Examples of edge doping are not restricted to the family of CGNR. Nguyen et al.  
401 demonstrated that a similar concept can not only be applied to the structurally more diverse family  
402 of AGNRs, but can also be extended to include group VI elements [50]. The molecular precursors  
403 for sulfur doped AGNRs (**12**) were derived from the structure of **2** by replacing one phenyl ring on  
404 each side by a thiophene. Even though the Pauling electronegativity of S-atoms is only marginally  
405 different from C-atoms (2.55 vs. 2.58), the hybridization of the heteroatom lone-pair with the  
406 conjugated  $\pi$ -system enhances the energy splitting between the CB (VB) and CB+1 (VB-1),  
407 respectively (Figure 14). The reorganization of the energy band structure leads to an overall  
408 reduction of the intrinsic band gap when compared to the parent 13-AGNRs. A notable distinction  
409 between nitrogen-doping in CGNRs and sulfur-doping in AGNRs is the overlap of the filled lone  
410 pair on sulfur (p-symmetry) with the p-orbitals on carbon that form the backbone of the GNR. The  
411 nitrogen lone pair in CGNRs instead is orthogonal and cannot interact directly with the GNR  $\pi$ -  
412 system. This previously unappreciated distinction opens entirely new avenues to tailor the density

413 of states proximal to the band edges, a feature particularly relevant to tuning optical transitions in  
414 GNRs.

415 An indispensable technology required for the development of GNR based electronic devices  
416 is the ability to tune the local charge carrier density by introducing shallow donor (n-type) and  
417 acceptor states (p-type) proximal to the CB and VB edges, respectively. Edge-doping, as outlined  
418 above, however, only shifts the energy of band edges without introducing dopant states within the  
419 band gap. Substitutional n-/p-doping, that is, the introduction of filled/empty donor or acceptor  
420 states into the intrinsic gap of atomically defined GNRs, instead requires the incorporation of  
421 dopant heteroatoms at deterministic positions preferably along the backbone of the ribbon where  
422 the filled/empty p-orbitals are forced into conjugation with the extended  $\pi$ -system. Cloke et al.  
423 and Kawai et al. were the first to demonstrate rational backbone doping in AGNRs by using 5,10-  
424 bis(10-bromoanthracene-9-yl)-5,10-dihydroboranthrene (**13**) as a molecular precursor for  $N = 7$   
425 AGNRs [51, 52]. Non-contact atomic force microscopy (ncAFM) with carbon monoxide  
426 functionalized tips reveals a characteristic pattern of anthracene/boranthrene/anthracene units  
427 along the backbone of the GNR. In figure 15 the contrast at the position of the boron atoms  
428 appears darker due to the strong interaction of the empty p-orbitals with the surface states of the  
429 underlying metal. First-principles calculations based on the *GW* approximation including the  
430 screening effects from the underlying Au(111) substrate show a new empty state in the middle of  
431 the band gap of 7-AGNRs. The DOS of both the VB and this new CB bands show significant  
432 contributions ( $\sim 10\%$ ) from B-atoms. Substitutional boron-doping along the backbone of 7-AGNRs  
433 thus introduces a deep lying acceptor band approximately 0.9 eV above the VB maximum. The  
434 theoretically predicted quasiparticle band gap is significantly smaller than that for the undoped  
435 pristine 7-AGNRs ( $\sim 2.1$  eV) calculated at same level of theory. The interpretation of  $dI/dV$  of  
436 boron-doped 7-AGNRs on Au(111) is challenging as the peak corresponding to the VB coincides  
437 with the surface states of the Au(111) substrate. A clearer signal can be obtained for the CB and  
438 CB+1 states at 1.0 eV and 1.6 eV. Better results have recently been obtained by growing boron-  
439 doped 7-AGNRs on Ag(111) surfaces. The surface state of Ag(111) is shifted with respect to  
440 Au(111) and allows for the unambiguous identification of all four VB-1 ( $-1.0$  eV), VB ( $-0.3$  eV),  
441 CB (1.1 eV), and CB+1 (1.5 eV) states for boron-doped 7-AGNRs. As expected the experimental  
442 band gap  $\sim 1.4$  eV is significantly smaller than the corresponding gap of pristine 7-AGNRs (2.3  
443 eV).

### 444 **3.4 Spatial Isolation of Energy States in Segmented GNRs**

445 Rectification, resonant tunneling, and light harvesting are just a few examples of dynamic

446 processes that are intimately linked to the transport of charge carriers across a boundary between  
447 materials with dissimilar energy band structures. While harnessing the corresponding  
448 performance in a single GNRs holds great promise for further device miniaturization and superior  
449 energy efficiency, the microscopic structure and the underlying physics of energy band alignment  
450 at intraribbon heterojunction interfaces is still a topic of intense investigation. The unique control  
451 inherent to the rational bottom-up synthesis along with high resolution imaging (STM, ncAFM)  
452 and spectroscopic (STS) tools provide a path to a deterministic design of single GNR functional  
453 heterostructures devices. While the preparation of segmented polymers through traditional  
454 solution based methods is well established in the literature the surface facilitated synthesis  
455 described herein imposes a series of new challenges. The design of segmented GNRs featuring  
456 e.g. two distinctive molecular precursors, two different band structures, or two unique doping  
457 patterns requires that both building blocks A and B are structurally compatible. This requirement  
458 guarantees that the cyclodehydrogenation at the interface between to segments proceeds  
459 efficiently and the resulting heterojunctions are atomically defined. The second, arguably more  
460 challenging problem, is the development of new synthetic strategies that provide control over the  
461 sequence and the segmentation in GNR heterostructures. As discussed in section 3.1 the step-  
462 growth polymerization of activated molecular building blocks on a precious metal surface relies  
463 formally on a radical recombination mechanism. The sequence at which monomers are  
464 incorporated into the growing polymer chain is largely random and current strategies lack the  
465 exquisite control developed for block-copolymer synthesis in solution.

466 Cai et al. demonstrated the assembly of CGNR heterojunctions formed from molecular  
467 building blocks **6** and **11** [53]. Alternating evaporation both precursors onto a Au(111) surface  
468 held at 200 °C followed by standard cyclodehydrogenation leads to CGNRs featuring an  
469 alternating pattern of segments composed of **6** and **11**. While a sequential deposition offers a  
470 rudimentary control over the concentration of activated building blocks on the surface the random  
471 nature and the unfavorable kinetics of the step growth process do not provide GNRs with a  
472 reproducible sequence of heterojunctions. While CGNR segments formed from **6** and **11** are  
473 structurally almost indistinguishable by topographic STM the difference in their composition  
474 becomes apparent in STS mapping (Figure 16).  $dI/dV$  maps recorded at  $-0.35$  V and  $-1.65$  V  
475 show a distinctive alternating contrast characteristic for the VB of CGNRs formed from **6** and **11**  
476 respectively. The band gap in the nitrogen edge-doped segments is rigidly shifted to lower energy  
477 with respect to the undoped CGNRs. DFT calculations (Figure 17) reveal that the electronic  
478 structure of a seamlessly fused **6/11** CGNR interface resembles a staggered gap type II  
479 heterojunction. Both the VB and the CB are offset by 0.45 eV and 0.55 eV respectively. The band

480 bending at the interface is exceptionally sharp. The band respective band structures reach  
481 essentially bulk properties within only 2nm from the interface. The significant electrostatic  
482 potential across the **6/11** CGNR heterojunction has promising implications for the device  
483 applications that require an efficient charge separation such as GNR based photovoltaics.

484 Chen et al. successfully assembled intraribbon heterojunctions comprised of fused segments  
485 of 7- and 13 AGNRs [54]. Co-deposition of molecular precursors **1** and **3** onto a Au(111) surface  
486 held at 24 °C followed by stepwise annealing at 200 °C and 400 °C leads to extended AGNRs  
487 featuring alternating widths (Figure 18). The narrower segments (~1.3 nm) are comprised of 7-  
488 AGNRs while the wider segments (~1.9 nm) correspond to 13-AGNRs.  $dI/dV$  spectra recorded at  
489 the highlighted positions above the respective GNR segments reflect the expected band structure  
490 for 7- and 13-AGNRs; a large band gap (2.7 eV) for the 7-AGNR segment and a small band gap  
491 (1.5 eV) for the 13-AGNR segment respectively. The respective band structures are highly  
492 localized in their respective segments and do not significantly extend beyond the heterojunction.  
493 If the STM tip is placed immediately above a 7-13 junction two additional highly localized states  
494 (1.25 V and 1.15 V) can be observed in the  $dI/dV$  spectrum. These states are unique to the  
495 interface and lie just below the CB of the 13-AGNRs. The relative band alignment is reminiscent  
496 of a straddling gap type I semiconductor junction. The lowest unoccupied (highest occupied) state  
497 in the  $N = 13$  segment is lower (higher) than that in the  $N = 7$  segment. In this unique band  
498 arrangement, a 7-13-7-AGNR sequence can be thought of as a quantum well for charge carriers  
499 trapped in the 13-AGNR segment. This architecture provides opportunities for designing  
500 graphene quantum-dot devices with sub nanometer feature size.

501 While the above examples highlighted the functional complexity that can be integrated into a  
502 single GNR, the limited control over the length and the sequence of individual segments within  
503 bottom-up fabricated GNR remains a grand challenge in the field. An alternative to the sequential  
504 co-deposition strategy outlined above has been proposed by Blankenburg et al. [55]. They noticed  
505 that the cyclodehydrogenation of *poly*-anthracene, the intermediate resulting from the radical  
506 polymerization of **1** on Au(111) surfaces, can be stopped at an intermediate stage. As the  
507 cyclodehydrogenation proceeds through a cooperative mechanism (see section 3.1) along the  
508 backbone of the GNR, the reaction can be stopped at a stage where segments of fully cyclized  
509 and partially cyclized 7-AGNRs coexist within the same ribbon. STM images of 7-AGNRs  
510 featuring partially cyclized 5<sup>+</sup>-AGNR segments are depicted in figure 19. While this method  
511 formally yields GRN heterojunctions, there is no control over the sequence or the position of the  
512 junction within the ribbon. If the cyclodehydrogenation is induced by STM tip pulsing, segments

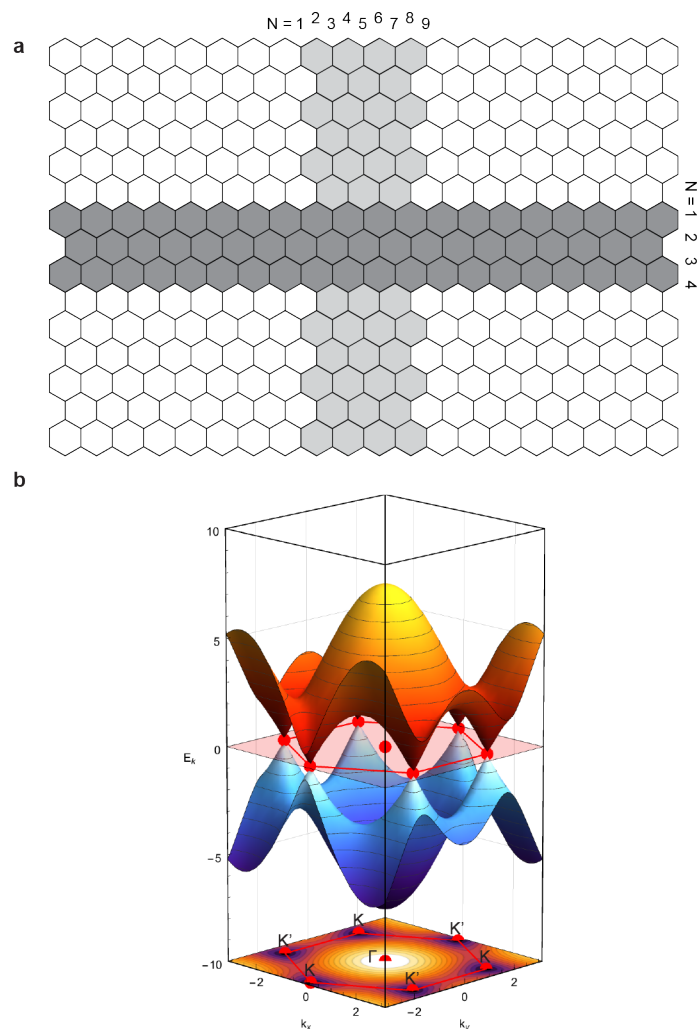
513 of partially cyclized 5<sup>+</sup>-AGNR could selectively be converted into 7-AGNRs. While STM tip  
514 manipulation of individual GNRs certainly is not a viable strategy for bulk fabrication the use of a  
515 secondary patterning step would overcome the challenges inherent to the uncontrolled step  
516 growth polymerization.

517 Marangoni et al. demonstrated an alternative edge-doping strategy toward segmented  
518 CGNRs that relies on a late stage interconversion of a reactive functional group.[56] Rather than  
519 relying on the co-polymerization of two dissimilar molecular precursors, the structure of  
520 dibromotriphenylene **14** incorporates a 9-methyl-9*H*-carbazole substituent as an internal reactive  
521 moiety along the convex protrusions of CGNR. Thermal activation of 9-methyl-9*H*-carbazole  
522 interconverts the functional group into either an electron rich carbazole, by cleavage of the N–  
523 CH<sub>3</sub> bond, or an electron deficient phenanthridine group, through a radical ring expansion  
524 mechanism. ncAFM images (Figure 20) clearly show the segmented structure in CGNRs featuring  
525 either five membered or six membered rings along the edges of the GNR. Late stage  
526 functionalization strategies hold great promise in the context of rational GNR heterostructure  
527 engineering as they potentially allow the site specific doping of prefabricated GNRs through a  
528 secondary activation step, e.g. light, heat, current.

## 529 **4 Conclusion**

530 The rational bottom-up synthesis of GNRs on solid supports has been instrumental in  
531 developing the fundamental understanding of the exotic physical properties emerging from lateral  
532 quantum confinement effects in graphene nanostructures. The unique insight gained from width  
533 modulation, edge-doping, backbone doping and the deterministic design of intraribbon GNR  
534 heterojunctions has demonstrated the potential and inspired new perspectives for their  
535 implementation in future generations of electronic devices. An implication of these visionary  
536 concepts still faces a multitude of technical challenges that require a coordinated interdisciplinary  
537 approach including the development of novel synthetic tools and techniques associated with the  
538 chemistry of molecular precursors, the exploration of the reactivity and the physical processes  
539 governing the self-assembly on surfaces, the access to high resolution and high throughput  
540 physical characterization techniques, and ultimately the integration with current electronic circuit  
541 architectures.

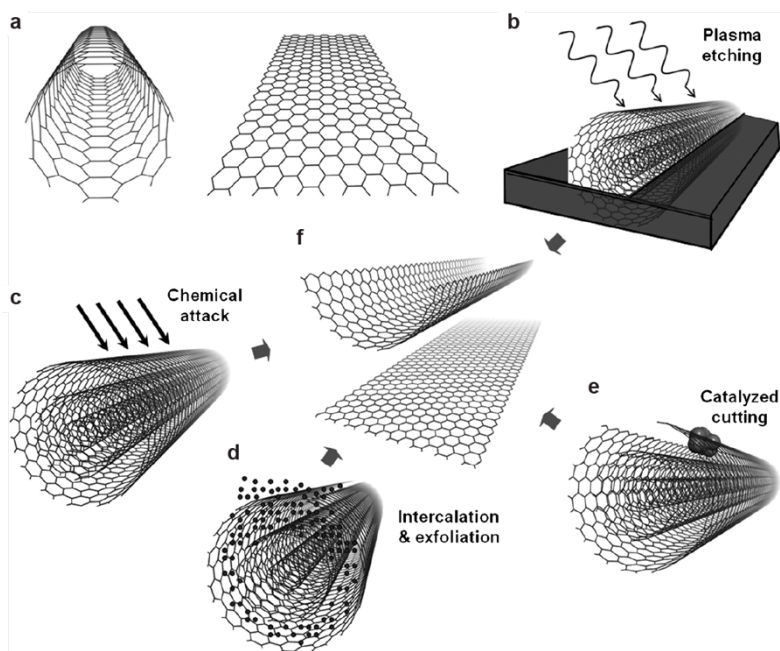
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543

544 **Figure 1** a) Schematic representation of graphene and graphene nanoribbons with armchair  
 545 edges (vertical) and zig-zag edges (horizontal). The numbering used to define the width of the  
 546 armchair GNRs (AGNRs) and zig-zag GNRs (ZGNRs) is denoted along the edges. b) Schematic  
 547 representation of the electronic band structure in graphene featuring a linear dispersion at the  
 548 Dirac points  $K$  and  $K'$ .

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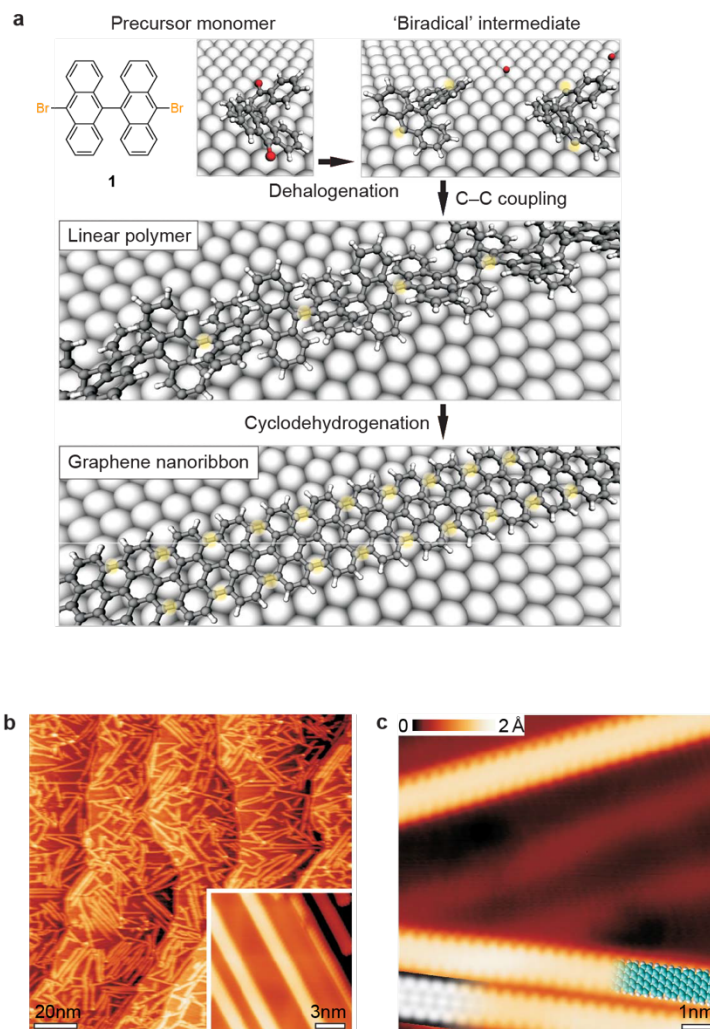


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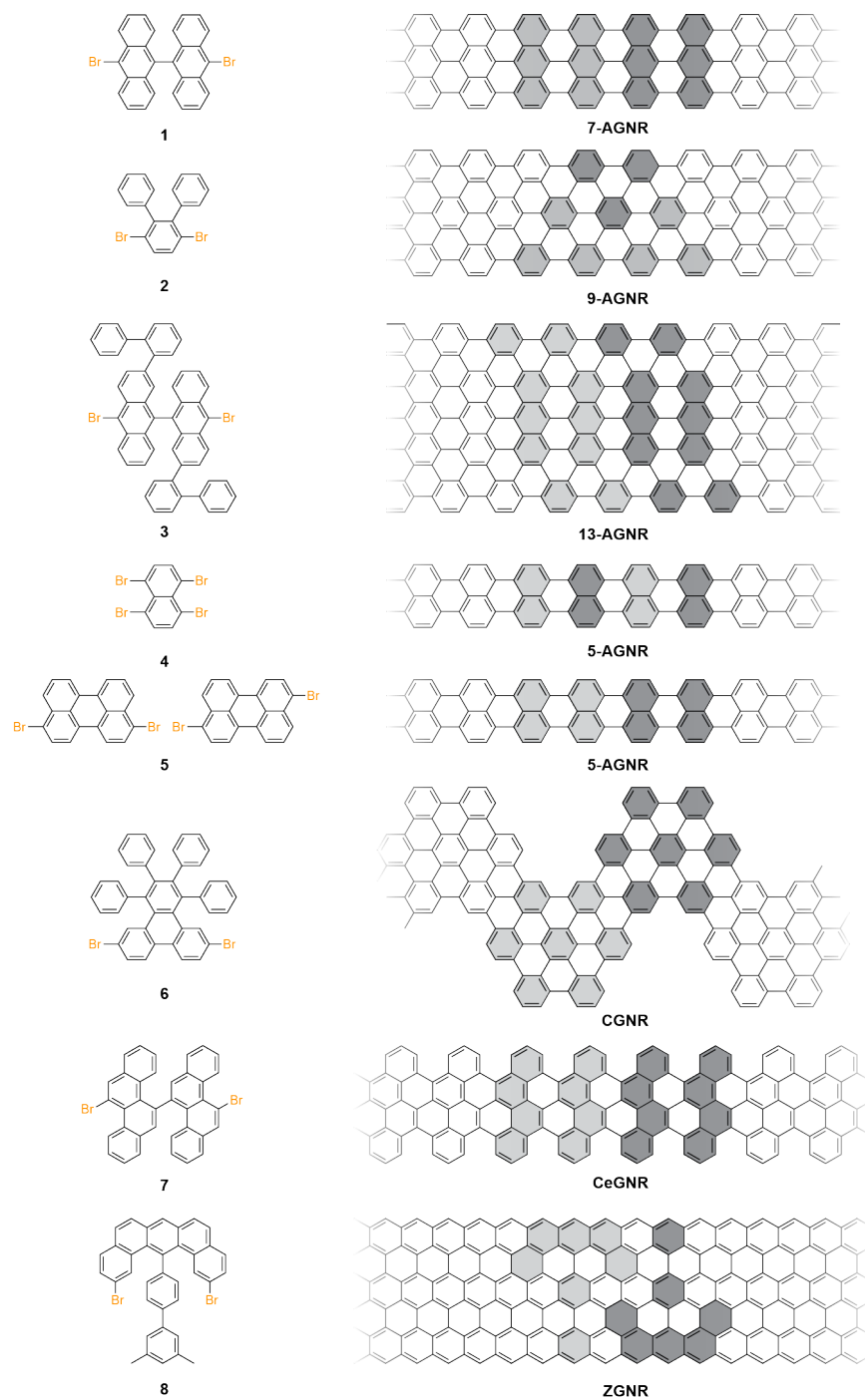
551 **Figure 2.** a) single walled carbon nanotubes (SWCNT) and graphene nanoribbon (GNR). Top-  
552 down synthetic approaches toward GNRs: b) plasma etching [20], c) longitudinal unzipping  
553 through chemical attack [17], d) intercalation of alkali metals followed by exfoliation of CNTs [57],  
554 e) metal nanoparticle catalyzed unzipping of CNTs [58], f) unfolded GNRs. Reproduced with  
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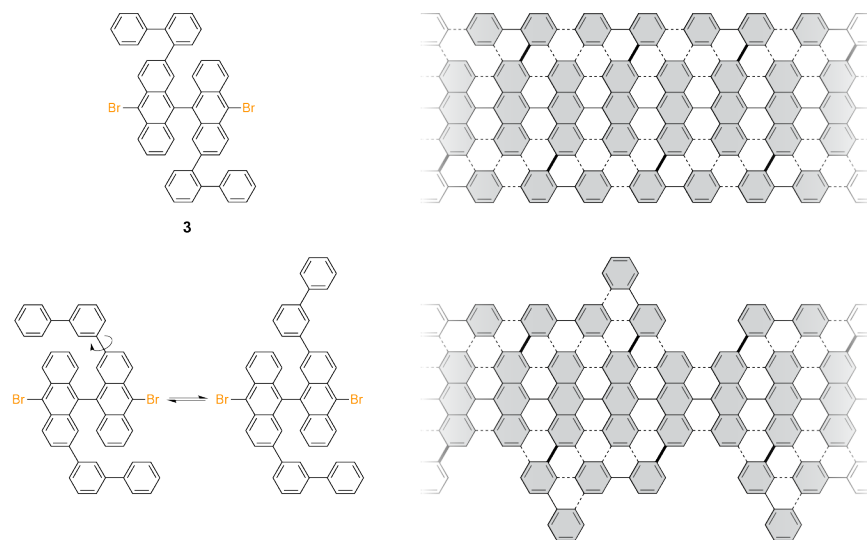
557  
 558 **Figure 3.** a) General scheme for the stepwise bottom-up synthesis of GNRs on Au(111). Key  
 559 steps are the activation of the monomer precursor through dehalogenation, recombination to form  
 560 a new C–C bonds, and cyclodehydrogenation to form fully extended 7-AGNRs. b) Large area  
 561 STM image of 7-AGNRs on Au(111). c) magnified image of 7-AGNRs showing the smooth  
 562 hydrogen terminated armchair edges. A CPK model of 7-AGNR nanoribbons is overlaid as a  
 563 guide to the eye. Reproduced with permission from ref. [22], Copyright (2010) Nature Publishing  
 564 Group.  
 565



566

567 **Figure 4.** Schematic representation of AGNRs [22, 41-43], CGNRs [22], CeGNRs [47], ZGNRs  
568 [48] and the respective molecular precursors used in their synthesis on Au, Ag, or Cu surfaces.

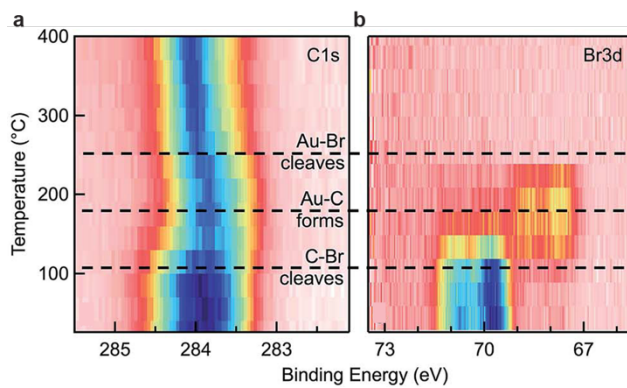
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570

571 **Figure 5.** Two possible designs for 13-AGNR precursors. Only precursor **3** is set up to exclusively  
572 cyclize to form the desired defect free armchair edge. Rotation around the anthracene biphenyl  
573 C–C bond in the *meta* substituted precursor can lead to two possible cyclodehydrogenation  
574 patterns.

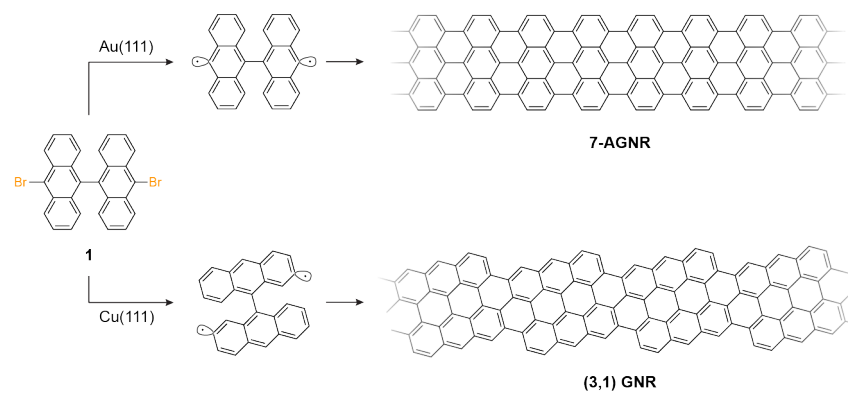
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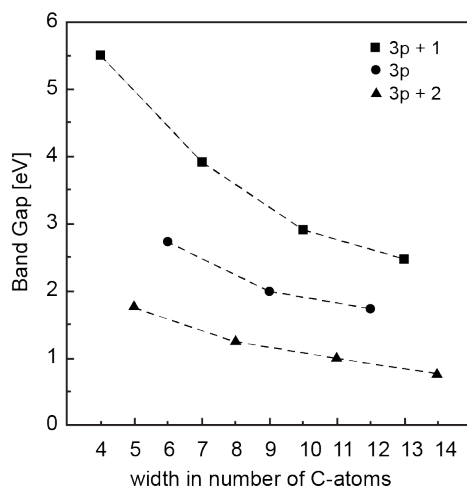
577 **Figure 6.** Temperature dependent XPS for a) C1s and b) Br3d for **1** on Au(111). The three dashed  
578 lines correspond to the onset of the homolytic C–Br cleavage, the surface stabilized radical  
579 intermediates, and the desorption of Br from Au(111). Reproduced with permission from ref. [30],  
580 Copyright (2014) Royal Society of Chemistry.

581



582 **Figure 7.** 7-AGNR and chiral GRNs featuring a (3,1) edge pattern formed from the same  
 583 precursor **1** on Au(111) and Cu(111) surfaces respectively[35-37].

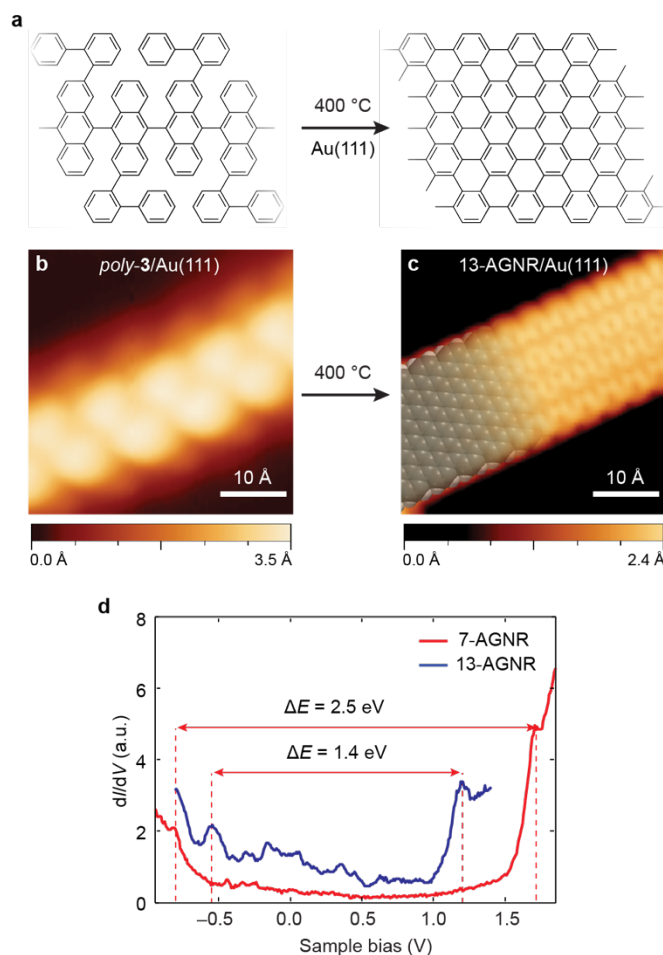
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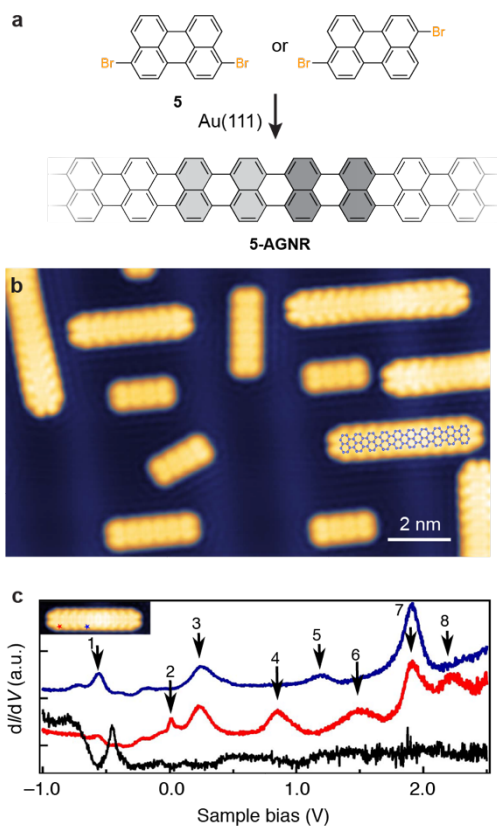
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586 **Figure 8.** Correlation of *GW* band gaps with the number of carbon atoms across the width of  
587 AGNRs. The three families of AGNRs are represented by filled squares ( $3p+1$ ), circles ( $3p$ ), and  
588 triangles ( $3p+2$ ). AGNRs belonging to the same family are connected by dotted lines as a guide  
589 to the eye. [40]

590



591  
 592 **Figure 9.** a) Schematic representation of the synthesis of 13-AGNRs from **3**. At 400 °C a  
 593 cyclodehydrogenation sequence converts *poly-3* into 13-AGNRs. b) STM image of the *poly-3*.  
 594 The polymers are nonplanar with an apparent height of 3.5 Å. c) STM image of 13-AGNRs formed  
 595 after annealing *poly-3* at 400 °C. A CPK model of a 13-AGNR has been overlaid onto the STM  
 596 image as a guide to the eye. d)  $dI/dV$  spectra of 13-AGNR (blue) and 7-AGNR (red) on Au(111).  
 597 Adapted with permission from ref. [41], Copyright (2013) American Chemical Society.  
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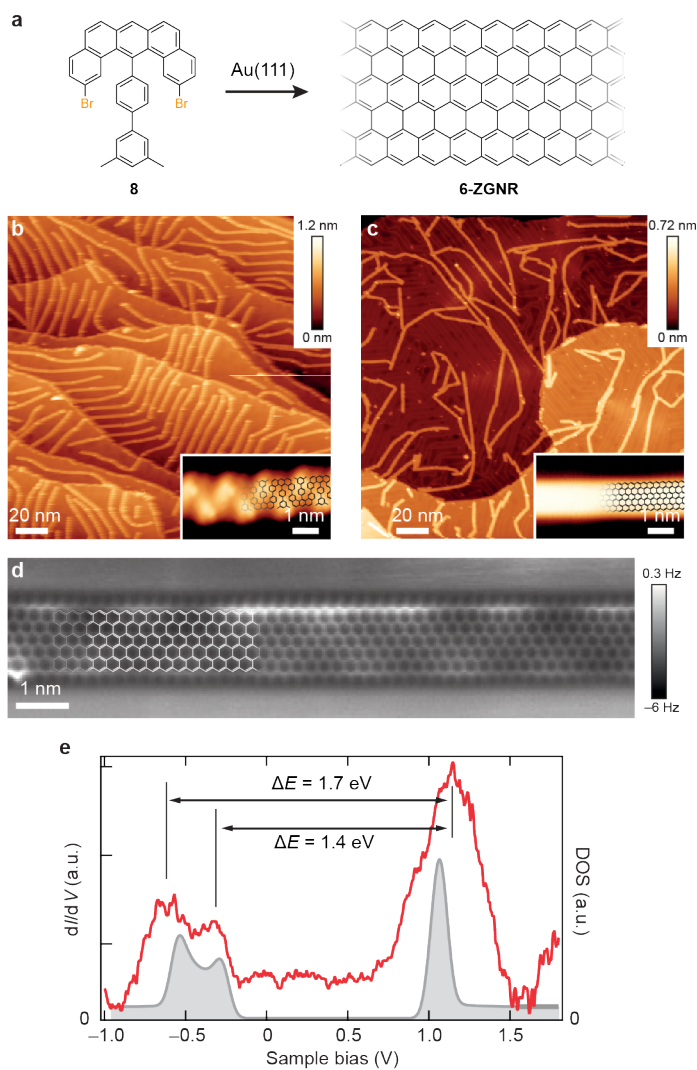
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600 **Figure 10.** a) Schematic representation of the synthesis of 5-AGNRs from **5**. b) STM image of 5-  
601 AGNRs on Au(111). c)  $dI/dV$  spectra acquired on five monomer 5-AGNR are the positions (red  
602 and blue star) marked in the STM inset. Reproduced from ref. [43].

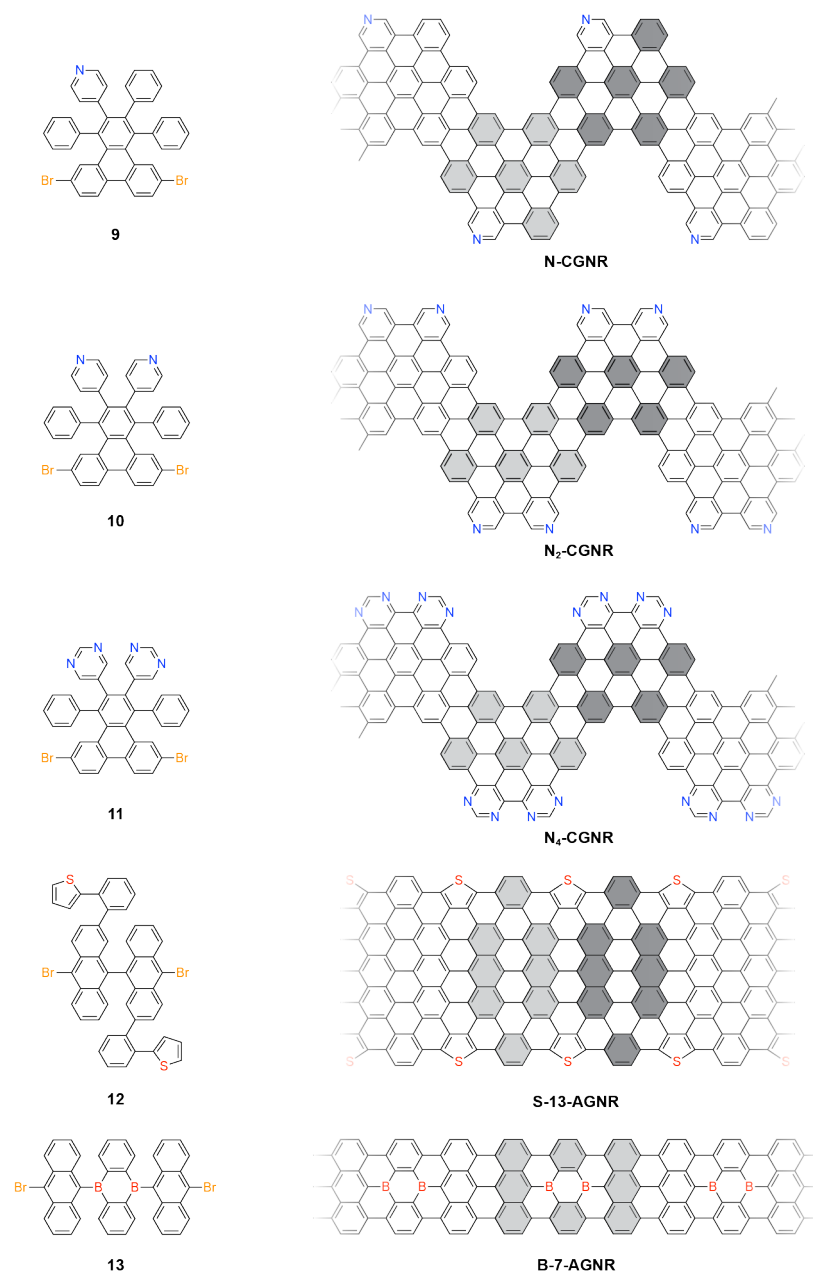
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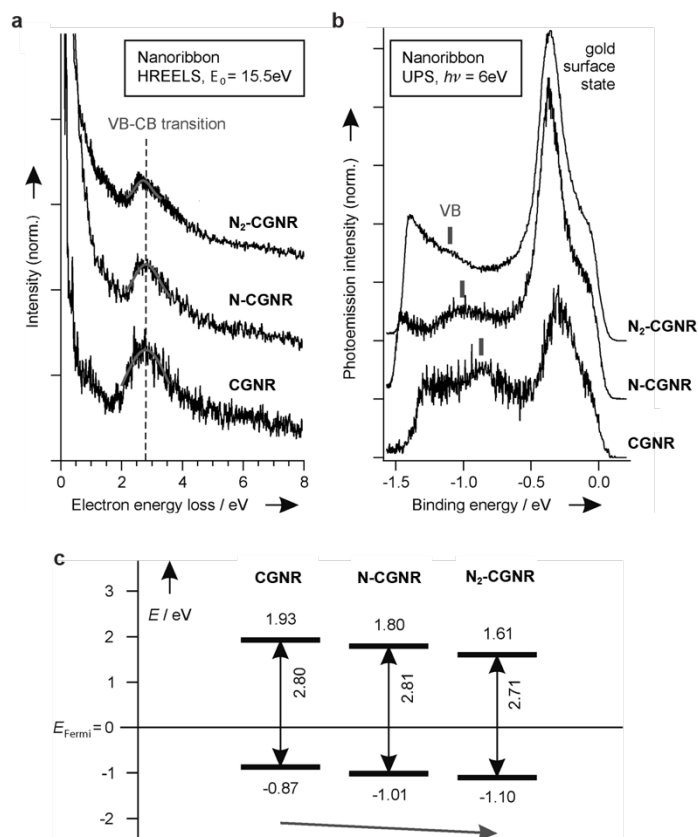
605  
 606 **Figure 11.** a) Schematic representation of the synthesis of 6-ZGNRs from **8**. b-c) Large area STM  
 607 image of *poly-8* and 6-ZGNRs on Au(111). d) ncAFM of 6-ZGNRs showing the hydrogen  
 608 terminated zig-zag edge. e)  $dI/dV$  spectrum (red) recorded at the zig-zag edge of a 6-ZGNR  
 609 partially suspended on a NaCl monolayer island on Au(111) and calculated DOS (gray).  
 610 Reproduced with permission from ref. [48], Copyright (2016) Nature Publishing Group.  
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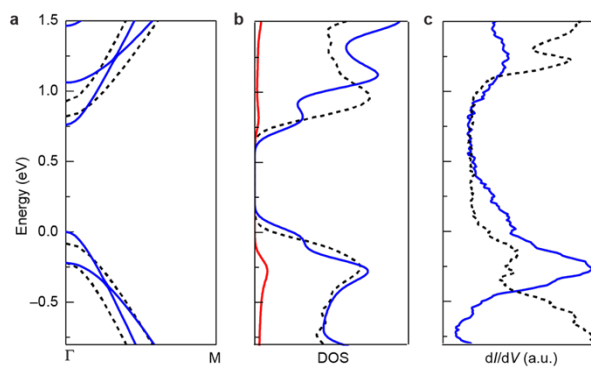
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613 **Figure 12.** Schematic representation of examples for nitrogen edge-doping in CGNRs [44, 45,  
614 49], sulfur edge-doping in 13-AGNRs [50], and backbone boron doping in 7-AGNRs [51, 52].

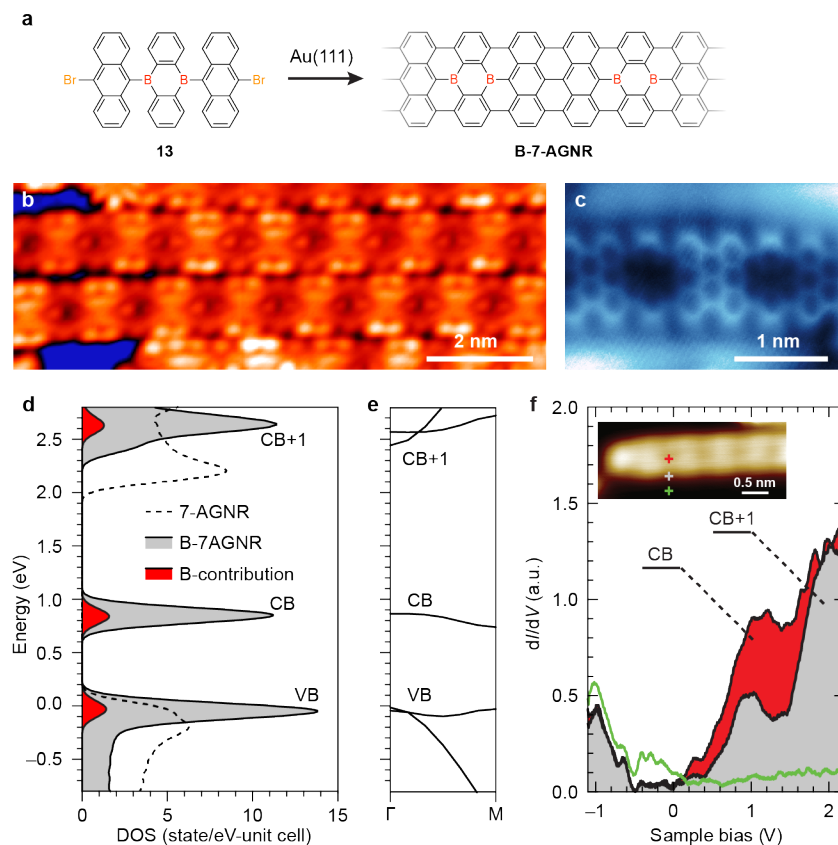
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 617 **Figure 13.** a) Electronic HREELS spectra for CGNRs edge doped with zero, one and two nitrogen  
 618 atoms. The VB–CB transition is essentially unperturbed by the doping. b) UPS spectra of CGNRs,  
 619 N-CGNRs, and N<sub>2</sub>-CGNRs on Au showing the shift in the VB edge towards lower energy. c)  
 620 Summary of the band gap, VB and CB alignment derived from HREELS and UPS spectroscopy.  
 621 Reproduced with permission from ref. [45], Copyright (2013) John Wiley and Sons.  
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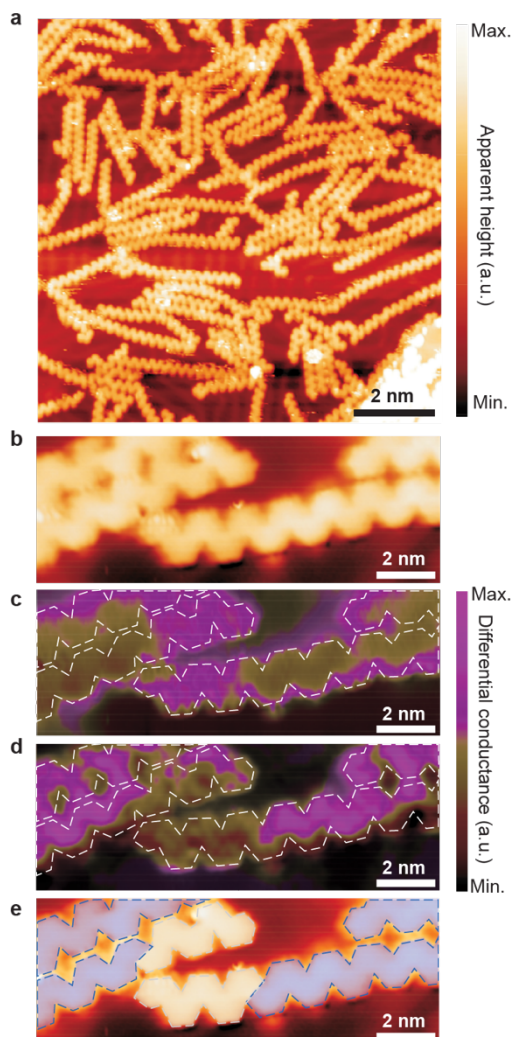


623  
624 **Figure 14.** Calculated band structure of a) S-13-AGNR (blue) and undoped 13-AGNR (black). b)  
625 Calculated DOS of a S-13-AGNR (blue), the partial density of states (PDOS) of sulfur orbitals  
626 (red), and the DOS of a undoped 13-AGNR (black). c) Experimental  $dI/dV$  spectrum for S-13-  
627 AGNR (blue) and undoped 13-AGNR (black). Reproduced with permission from ref. [50],  
628 Copyright (2016) American Chemical Society.  
629



630  
 631 **Figure 15.** a) Schematic representation of the bottom-up synthesis of B-7-AGNRs on Au(111). b)  
 632 STM topographic image of fully cyclized B-7-AGNRs. c) ncAFM image of B-7-AGNRs. The  
 633 position of boron dopants appears darker in the frequency shift image as the empty p-orbital on  
 634 B-atoms strongly interacts with the free valences of the underlying Au substrate. d) Calculated  
 635 total DOS for B-7-AGNRs (gray) and the contribution from B-atoms to the DOS (red) using the  
 636 *GW* approximation and including screening effects from Au(111) substrate. For comparison the  
 637 DOS for undoped 7-AGNRs is plotted as a dotted line. VB maximum is set to 0 eV. e) Calculated  
 638 quasiparticle band structure of B-7-AGNRs (using *GW* approximation). f)  $dI/dV$  spectrum of B-7-  
 639 AGNRs recorded at the positions marked in the inset. While CB and CB+1 can clearly be identified  
 640 in the spectrum the position of the VB coincides with the surface state of the Au(111) substrate.  
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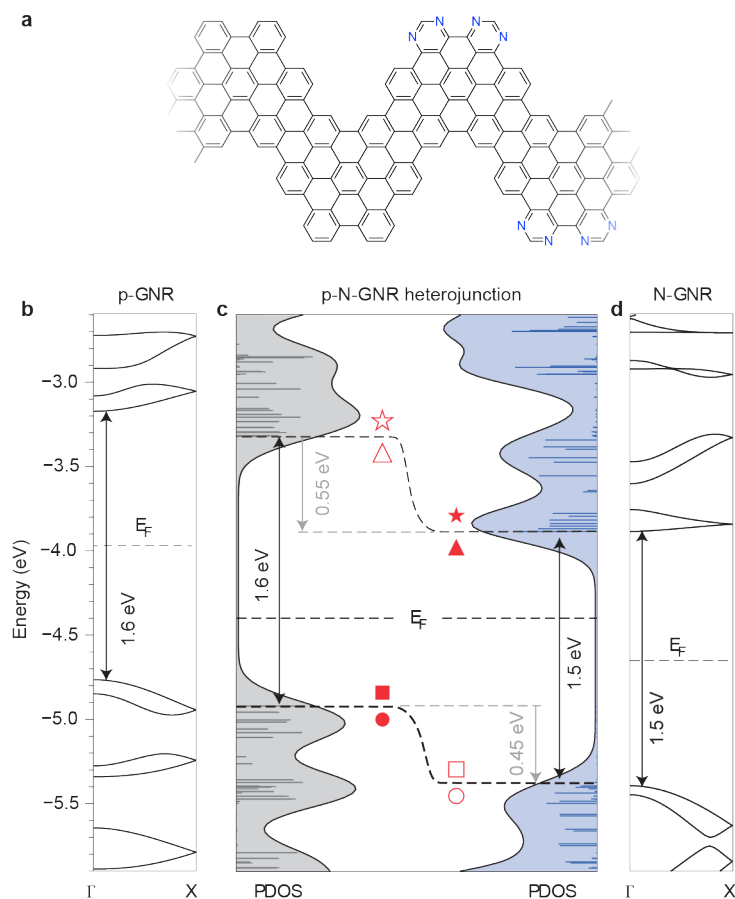
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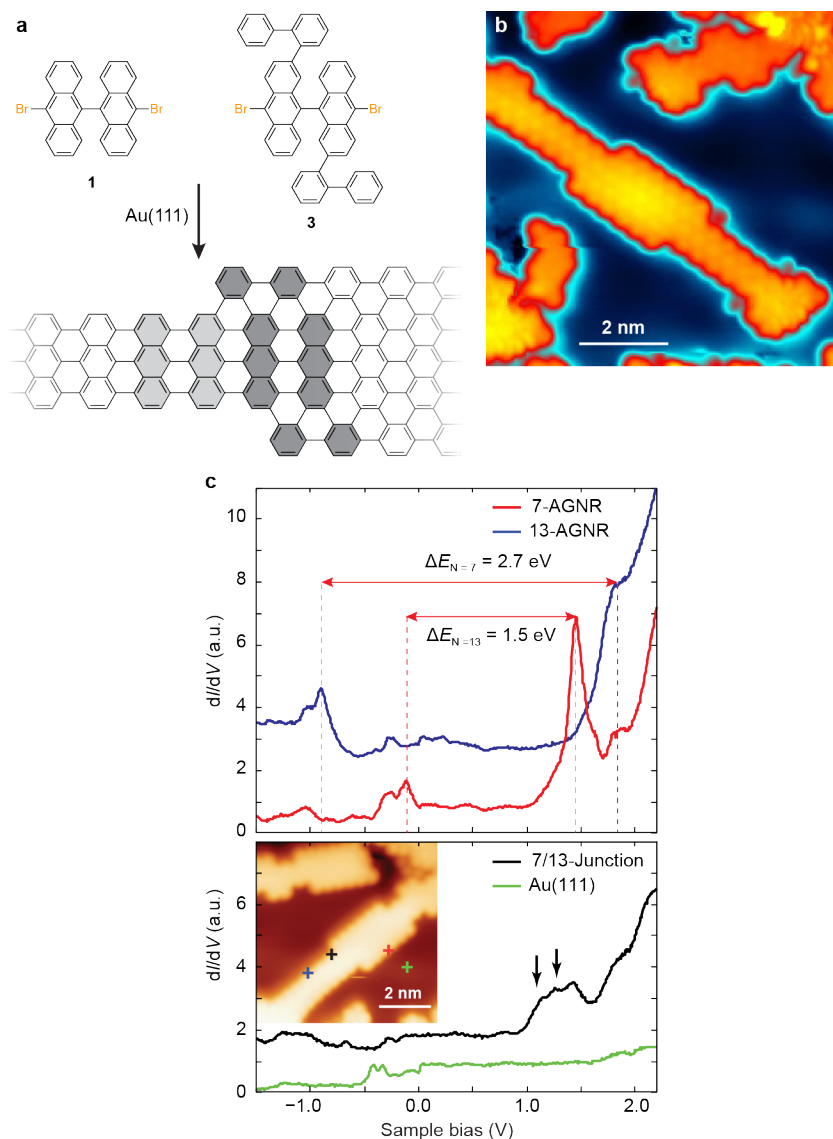
644

645 **Figure 16.** a) Large area STM image of segmented CGNRs formed by sequential co-deposition  
646 of **6** and **11**. b) STM topographic image of a **6/11** CGRN interface. c-d)  $dI/dV$  maps recorded at -  
647 0.35 V and -1.65 V, respectively. e) Overlay of topographic STM image illustrating the  
648 segmentation pattern in **6/11** CGNRs. Reproduced with permission from ref. [44], Copyright  
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651  
 652 **Figure 17.** a) Schematic representation of the structure of a **6/11** CGNR heterojunction interface.  
 653 b,d) DFT calculated band structure of pristine CGNRs (b) and nitrogen doped CGNR (d). c) PDOS  
 654 of the p-GNR segment (left, grey) and the N-GNR segment (right, blue) of the heterojunction  
 655 shown in a). The p-N-GNR heterojunction exhibits a staggered gap configuration with band offsets  
 656 of 0.45 eV (VB) and 0.55 eV (CB). Reproduced with permission from ref. [44], Copyright (2014)  
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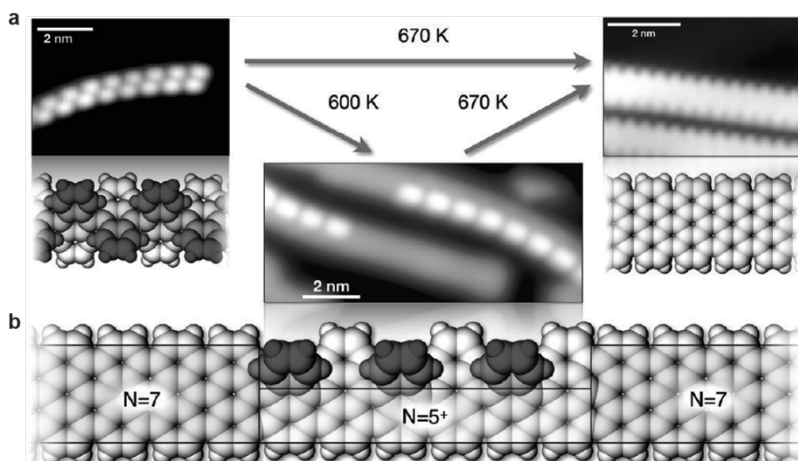


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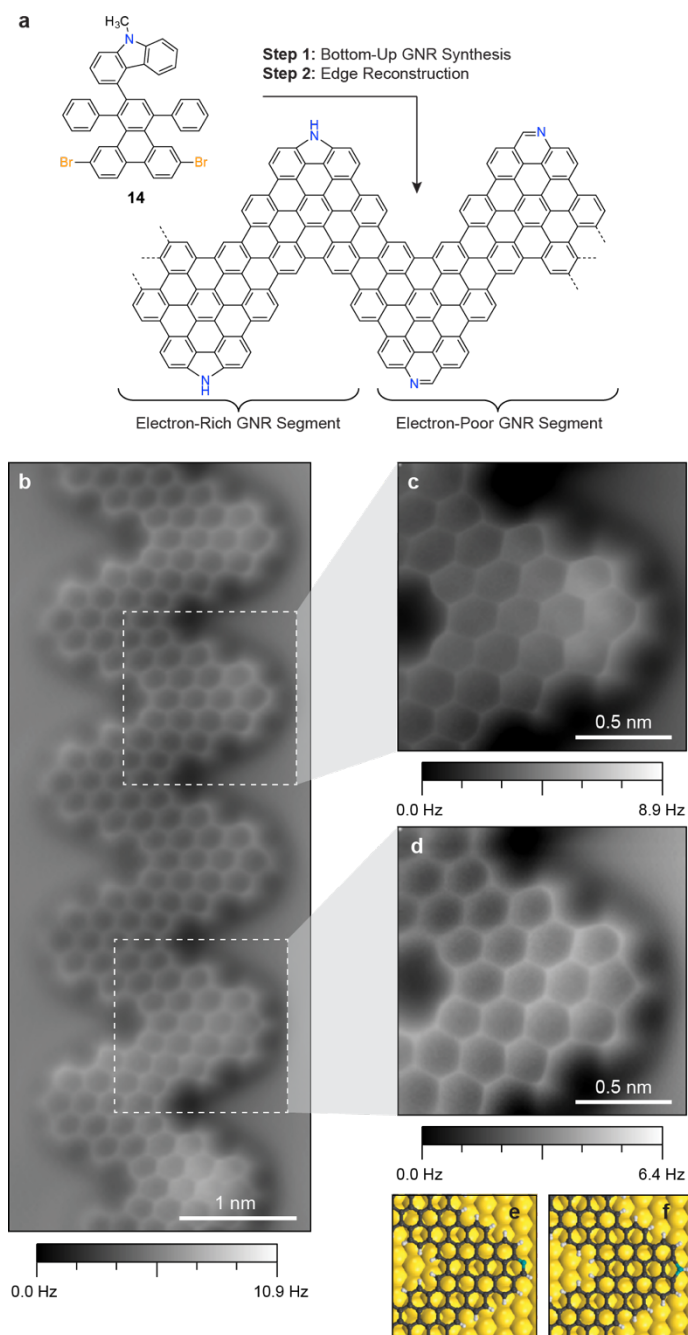
660 **Figure 18.** a) Synthesis of 7/13-AGNR heterojunctions from molecular building blocks **1** and **2**. b) STM topographic image of a 7/13-AGNR heterojunction. c)  $dI/dV$  spectroscopy of 7/13-AGNR heterojunction electronic structure recorded on a 7-AGNR segment (blue), a 13-AGNR segment (red), at the 7/13-AGNR heterojunction (black), and on the Au(111) surface. Reproduced with permission from ref. [54], Copyright (2015) Nature Publishing Group.

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666  
 667 **Figure 19.** GNR heterojunctions by partial cyclodehydrogenation of polyanthrylene oligomers. (a)  
 668 STM images and CPK models demonstrating the synthesis of AGNRs starting from *poly-1* on a  
 669 Au(111) substrate. b) Annealing at a reduced temperature of 600 K results in partial  
 670 cyclodehydrogenation and produces intraribbon 7/5<sup>+</sup>/7-AGNR heterojunctions. Reproduced with  
 671 permission from ref. [55], Copyright (2012) American Chemical Society.  
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673  
 674 **Figure 20.** a) Schematic representation of the bottom-up synthesis of segmented nitrogen-doped  
 675 CGNRs through edge reconstruction. Electron-rich carbazole and electron-poor phenanthridine  
 676 subunits along the edges emerge from a thermal rearrangement of the 9-methyl-9*H*-carbazole in  
 677 building block **1**. b) nc-AFM image CGNR heterostructure on Au(111) featuring discrete segments  
 678 of fused phenanthridine and carbazole groups. c-d) nc-AFM image of phenanthridine and  
 679 carbazole fused CGNR. e-f) Ball and stick model of phenanthridine and carbazole fused GNRs

680 serves as a guide to the eye. Reproduced with permission from ref. [56], Copyright (2016) John  
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