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Engineering Edge States of Graphene Nanoribbons for Narrow-Band Photoluminescence

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ABSTRACT: Solid-state narrow-band light emitters are on-demand for quantum optoelectronics. Current approaches based on defect engineering in low-dimensional materials usually introduce a broad range of emission centers. Here, we report narrow-band light emission from covalent heterostructures fused to the edges of graphene nanoribbons (GNRs) by controllable on-surface reactions from molecular precursors. Two types of heterojunction (HJ) states are realized by sequentially synthesizing GNRs and graphene



nanodots (GNDs) and then coupling them together. HJs between armchair GNDs and armchair edges of the GNR are coherent and give rise to narrow-band photoluminescence. In contrast, HJs between the armchair GNDs and the zigzag ends of GNRs are defective and give rise to nonradiative states near the Fermi level. At low temperatures, sharp photoluminescence emissions with peak energy range from 2.03 to 2.08 eV and line widths of 2-5 meV are observed. The radiative HJ states are uniform, and the optical transition energy is controlled by the band gaps of GNRs and GNDs. As these HJs can be synthesized in a large quantity with atomic precision, this finding highlights a route to programmable and deterministic creation of quantum light emitters.

KEYWORDS: graphene nanoribbons, graphene nanodots, mixed-dimensional heterojunctions, quantum-well-like states, scanning tunneling microscopy, first-principles calculations, narrow-band photoluminescence

ngineering interfacial coupling offers a significant opportunity to achieve hybrid dimensionality systems, with functionalities beyond those possessed by individual constituent components. To engineer interfaces with prescribed functionalities, an essential first step is to understand the nature of interfacial coupling and its effect on interfacial electronic properties. Compared to the weak van der Waals coupling, covalent coupling ensures the stability of heterostructures possessing well-defined interface structures.²⁻⁵ In the pursuit of controllable and uniform covalent coupling at an interface, the edge and surface structures of constituent units need to be synthesized with atomic precision. The surface-assisted synthesis under ultrahigh vacuum conditions is a promising pathway toward atomically precise covalent sp² nanostructures. Many graphitic nanostructures have already been synthesized, such as fullerenes,⁶ graphene nanodots (GNDs),^{7,8} graphene nanoribbons (GNRs),^{9–13} and carbon nanotubes (CNTs),14 which provide well-defined platforms to realize coupled interfaces with exceptional functionalities.^{15–19} For example, functionalized GNDs²⁰ and

 $CNTs^{21-23}$ have been explored as single-photon emitters (SPEs). However, a significant challenge remains in engineering interfacial coupling with well-controlled and defined emitting states to confine the emission in a narrow band.²³

Precisely defining a narrow band of emission energies necessitates atomic control of not only the emitter itself but also the environment that confines the emission states.^{24,25} A bottom-up approach to the synthesis of molecular covalent nanostructures with atomic precision benefits from the combination of reproducible fabrication, the extraordinary programmability and tunability by chemical design, and the ability to order emission states into large-scale arrays. It was previously shown that anchor groups in CNTs can be used to

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Figure 1. On-surface synthesis of the GNR–GND heterojunctions. (a) Schematic of synthesis of GNR–GND HJs from molecular building precursors 1' and 2'. Both the 7-aGNR (1) and the BN–GND (2) are synthesized by a two-step annealing process with surface-assisted reactions, respectively, at T1 = 470 K, T2 = 670 K and T3 = 520 K, T4 = 640 K. Armchair and zigzag edges in both structures are highlighted. Further annealing at T5 = 770 K creates GNR–GND mixed-dimensional HJs, where conjugation occurs between the armchair edges (AA conjugation) or one armchair edge and one zigzag edge (AZ conjugation). The interface structures are highlighted with red. (b) Large-area STM image of the GNR–GND HJs (sample voltage $V_s = -2.0$ V, tunneling current $I_t = 20$ pA). Two representative GNDs coupled to the 7-aGNRs, one to the edge and one to the end, are marked with red and white dashed circles, respectively. (c) High-resolution STM image of the GNR–GND HJ formed at the GNR edge ($V_s = -0.2$ V, $I_t = 100$ pA) and (d) same image with superimposed structural model. (e) High-resolution STM image showing two GNDs bonded to the GNR edge and the end ($V_s = -2.5$ V, $I_t = 150$ pA) and (f) same image with superimposed structural model.

locally introduce sp³ hybridization and generate splitting of the doubly degenerate frontier orbitals of bright and dark states,²⁶ which can create SPEs with high photon purity.^{21–23} By taking advantage of the development of on-surface synthesis of GNRs and GNDs, a promising route emerges toward atomically precise mixed-dimensional heterostructures with well-defined junction states to achieve deterministic narrow-band photon emitters.

Herein, we use surface-assisted synthesis to create interfacial quantum-well-like (QWL) states in covalent GNR-GND heterojunctions (HJs) and realize ultra-narrow-band photoluminescence (PL). The atomic structures and electronic properties of HJs are examined by combining scanning tunneling microscopy/spectroscopy (STM/STS) with density functional theory (DFT) calculations. Two kinds of characteristic GNR-GND HJs are revealed that, respectively, generate QWL interface states and localized defect states near the Fermi level ($E_{\rm F}$). After transferring the HJs to a SiO₂/Si substrate, sharp-line PL with a narrow-band energy range from 2.03 to 2.08 eV is observed at 4 K. It can be attributed to light emission from QWL junction states, whereas the deep defect states near the $E_{\rm F}$ are nonradiative. The atomically uniform GNR-GND HJs with a narrow-band photon emission provide a promising avenue for deterministic creation of photon emitters for quantum optoelectronics applications.^{27,28}

RESULTS AND DISCUSSION

On-Surface Synthesis of GNR-GND HJs. Covalent graphitic mixed-dimensional HJs are formed by sequentially synthesizing GNRs and GNDs and then fusing them together, as illustrated in Figure 1a. Following previous studies,^{9,29–33} we synthesize armchair GNRs with a width of seven carbon atoms (7-aGNRs, 1) by depositing and annealing molecular building block 10,10'-dibromo-9,9'-bianthryl (DBBA) (1') at 470 and 670 K on a Au(111) surface (see Methods for details). To synthesize the GND component, molecular precursor N, N', N''-tris(2-biphenylyl)borazine (2') is deposited on the same Au(111) surface held at room temperature after the growth of the 7-aGNRs. The sample is then sequentially annealed at 520 and 640 K to form hexa-peri-hexabenzoborazinocoronene (BN-HBC, 2), a B₃N₃-doped GND with a hexagonal BN core and six short armchair edges (see Supporting Information (SI) Figure S1). Further annealing at 770 K leads to the fusion of 7-aGNRs and GNDs, resulting in GNR-GND mixed-dimensional HJs. The GNDs can conjugate either to the armchair edges of 7-aGNRs or to the short zigzag ends. The fusion between the GNR and GND armchair edges, named as AA conjugation, gives rise to a seamless interface structure, whereas that between the armchair edge of the GND and the zigzag end of the GNR, named as AZ conjugation, gives rise to a defective interface with 5-7-4rings. The formation of the mixed-dimensional HJs is facilitated by fusions between polycyclic hydrocarbon structures similar to those between GNRs,³⁴ indicating that

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Figure 2. Electronic properties of the GNR–GND HJ via AA conjugation. (a) Topographic STM image of a GNR–GND HJ formed via AA conjugation ($V_s = -2.0$ V, $I_t = 50$ pA). (b) Normalized (dI/dV)/(I/V) curves acquired at the marked sites of 1–18 in (a) ($V_s = -2.0$ V, $I_t = 100$ pA). (c) Color-coded 2D map plotted with curves 1–18 in (b). (d) Normalized (dI/dV)/(I/V) curves acquired at the marked sites of 1'–20' in (a) ($V_s = -2.0$ V, $I_t = 100$ pA). (e) Color-coded 2D map plotted with curves 1'–20' in (d). States 1–7 are marked with dashed lines in (b–e), where the spectra in different segment are shown in different colors. The narrow regions near the E_F (zero bias) are not shown, where uncertainties can be induced to the normalizations in (b–e). (f) Supercell used to simulate the LDOS map of GNR–GND HJ. (g) Simulated LDOS map 3 Å above the HJ plane along the red shadow marked region in (f) (line 1) and (h) along the blue shadow marked region in (f) (line 2). The same color bar is used in (g) and (h). HOMOs and LUMOs for the GNR and GND components along with interface states 3–5 are marked.

the observed fusion is a universal phenomenon between polyaromatic hydrocarbons, regardless of their dimensionalities.

With a relatively low GND coverage (<0.05 monolayer, ML), most GNDs are connected on the GNR edges and ends individually, as shown in Figure 1b. Figure 1c shows a high-resolution STM image of a GNR–GND HJ with AA conjugation, well consistent with the seamless interface structural model depicted in Figure 1d. The orientation of the GNDs due to the existence of the BN core can be determined by high-resolution STM images (see SI Figure S2). Figure 1e shows the case of two individual GNDs conjugated to the edge and the end of a 7-aGNR. Based on a comparison of atomic resolution STM images (see SI Figure S3) with models of different possible configurations (see SI Figure S4), we find that the interface structure consists of 5–7–4 rings for AZ conjugation (Figure 1f). Moreover, the formation of the tetragon is expected to create a local strain, as evident from the

observation of lattice distortion at the edge near the GNR end (Figures 1e and S4).

Electronic Properties of the GNR-GND HJs. We first study the GNR-GND HJ formed via AA conjugation (Figure 2a). Figure 2b shows normalized (dI/dV)/(I/V) curves (curves 1-18) taken along the GNR edge and across the left side of the HJ until the top edge of the GND. Away from the junction (green curves), the 7-aGNR edge shows the highest occupied and lowest unoccupied molecular orbital (HOMO_R and LUMO_R) at $V_s = -1.0$ V (state 1) and $V_s = 1.7$ V (state 2), respectively, and a band gap of about 2.7 eV, typical of the 7aGNR as previously reported.³⁴⁻³⁸ The GND edge (blue curves) exhibits a larger band gap of about 4.0 eV, with HOMO_D and LUMO_D at $V_s = -1.7$ V (state 6) and $V_s = 2.3$ V (state 7) (see SI Figure S5), respectively. Near the junction (red curves), all states related to the HOMO and LUMO in the GNR and GND segments are suppressed, and new states 3-5 emerge at $V_s = -0.7$, 1.3, and 1.9 V. The right side of the HJ displays similar electronic states and therefore is not further analyzed (see SI Figure S6). A two-dimensional (2D) colorcoded local density of states (LDOS) map is shown in Figure 2c to visualize the spatial distributions of the LDOS at the HJ. It can be seen that, whereas the interface states 3 and 4 can penetrate the GNR section for about 1.5 nm, state 5 is localized at the interface.

Figure 2d shows the (dI/dV)/(I/V) curves (curves 1'-20') taken from the opposite edge side of the ribbon with the corresponding 2D color-coded plot shown in Figure 2e. Similarly, away from the junction region (green curves), characteristic electronic structures for the bulk 7-aGNR can be resolved. Interestingly, the interface states 3 and 4 are also seen at the opposite GNR edge within a length of about 3 nm (red curves) near the junction region (see SI Figure S6). Compared to the states at the HJ side (Figure 2b,c), state 3 is even more pronounced at the opposite edge site (Figure 2d,e). The spatial distributions of the observed states are further presented by their dI/dV mapping in SI Figure S7.

Figure 2f-h shows the simulation results based on firstprinciples calculations, which well reproduce the experimental results in Figure 2c,e. Note that there are finite DOS in the band gap region in Figure 2c,e, which are from the Au(111)^{4,36,37} whereas the simulations do not include the surface,³ substrate. For example, the interface state 3 is more intense at the opposite edge side of the HJ (Figure 2h) than at the conjugated side (Figure 2g). The interface states 3-5 originate from hybridization between the seamlessly conjugated GNR and GND. States 3 and 4 are confined by the wider band gaps of the GNR and GND, forming a quantum well at the interface with states 3 and 4 corresponding to the valence and conduction bands of the quantum well. The presence of these QWL states is different from previously reported seamless GNR heterostructures,^{34,37,39} where no interface states were observed. At higher GND coverage (>0.1 ML), multiple GNDs can be coupled together through single C-C bonds and seamlessly conjugate to the GNR edge (see SI Figure S8). Nevertheless, the electronic properties of the GNR, GND, and the junction remain nearly the same as those of isolated GNR-GND HJs in Figure 2b.

We next characterize the electronic behaviors of the defective junction with 5-7-4 rings formed via AZ conjugation. Along the edge of the conjugated end (Figure 3a), 32 dI/dV curves are acquired and shown in Figure 3b. The junction state (state 8; see below) is observed very close to the $E_{\rm F}$, and thus we use the dI/dV instead of the normalized (dI/ dV/(*I*/*V*) curves to compare with the simulated LDOS. Away from the junction region, the characteristic electronic properties of the GNR (green) and GND (blue) are observed, like those in Figure 2b,c. Near the junction (pink curves), a peak appears at about 0.25 V (state 8) along both the upper and the lower sides, with a broad tail extending to higher bias. It is more clearly resolved in the 2D color-coded map (Figure 3c), which shows an interface state localized within a length scale of about 1 nm. The state 8 is slightly more intense at the lower edge (tetragon side, sites 21-26) than at the upper edge (pentagon side, sites 7-12), consistent with the structure asymmetry, which is different from the nearly symmetric AA junction in Figure 2. Further details of spatial distributions of states 1, 2, 6, 7, and 8 are shown in SI Figure S9. Figure 3d shows the simulated LDOS map along the arrowed shadow line 3 marked in Figure 3e, confirming that an interfacial state appears in the vicinity of the $E_{\rm F'}$ well consistent with the experimental results in Figure 3c. Note that the slight shift of



Figure 3. Electronic properties of the GNR-GND HJ via AZ conjugation. (a) Topographic STM image of a GND coupled to the 7-aGNR end ($V_s = -2.0 \text{ V}$, $I_t = 20 \text{ pA}$). (b) dI/dV curves acquired from the marked sites 1-32 in (a) ($V_s = -2.0 \text{ V}$, $I_t = 100 \text{ pA}$). The typical spectra in different segments are shown in different colors. (c) Color-coded 2D map plotted with curves 1-32 in (b). States 1-2 and 6-8 are marked with dashed lines in (b) and (c). (d) Simulated LDOS map 3 Å above the HJ along the edge as marked in (e). HOMOs and LUMOs for the GNR and GND components along with interface states 8 are marked. (e) Sketch of HJ with an arrowed pink shadow marked region where the LDOS map is acquired.

state 8 from zero energy in the experiment can be attributed to the effect of *p*-type doping of the Au substrate, as seen for the HOMO and LUMO of the 7-aGNR (Figures 2b,d and 3b).

Optical Properties of the GNR-GND HJs. The QWL states at the GNR-GND junction can act as light emission centers. The band alignment of the HJ is depicted in Figure 4a,b, where photogenerated excitons, electron-hole pairs bound by Coulomb interactions, in the GNR and GND can migrate into the QWL states. Due to the greater size of GNR compared to the size of GND and the much smaller band gap of the GNR (2.7 eV) compared to that of the GND (4.0 eV), excitons are mainly generated in the GNRs and then transferred to the QWL junction states. At the AA junction, excitons recombine radiatively to emit photons (Figure 4a). However, at the AZ junction, due to the defective "trap" states nearly at the $E_{\rm F}$, the excitons annihilate nonradiatively through a trap-assisted Shockley-Read-Hall recombination^{40,41} (Figure 4b). Considering that the mean free path of the long-lived excitons in GNRs⁴² is on the order of micrometers,⁴³ photogenerated excitons in GNRs (<100 nm long) can migrate ballistically to the interface states and recombine radiatively with photon wavelength defined by the junction states (Figure 4c).

To measure the PL behaviors of the GNR–GND HJs, we transfer the as-grown samples to SiO_2/Si substrates using a bubbling transfer method^{44,45} (see details in Methods). Figure 4d is an optical microscopy image of the transferred GNR–GND HJs on a SiO_2/Si substrate, showing a uniform monolayer of GNR–GND HJs. The Raman spectrum (Figure 4e) of the GNR–GND HJs on SiO_2/Si shows the character-



Figure 4. Optical behaviors of the GNR-GND HJs. (a) Energy band alignment of the AA HJ with the band energy positions from STS data, as shown in Figure 2. (b) Energy band alignment of the AZ HJ with the band energy positions from STS data, as shown in Figure 3. The generation, diffusion, and recombination of excitons in the 7-aGNR and the different light emission behaviors in the two kinds of HJs are schematically illustrated in (a) and (b). (c) Sketch of an exciton in the GNR formed after excitation with photon energy of $h\nu$, which is mobile in the semiconducting 7aGNR. The recombination of exciton at the AA junction emits a photon with an energy of $h\nu'$, whereas the exciton annihilates at the AZ junction nonradiatively. (d) Optical image of the GNR-GND HJs after transferred onto a SiO₂/Si substrate. (e) Raman spectrum (532 nm laser) of the transferred GNR-GND HJs, with main peaks labeled as the breathing-like mode (BLM), the Si substrate vibration mode (Si), and the D and G band-like modes. (f) Room-temperature and low-temperature PL curves acquired from the pristine GNR sample (black) and the GNR-GND HJ sample (red and pink) with a 405 nm (3.1 eV) laser. The main peak positions are marked with black and red arrows.

istic breathing-like mode (BLM) at 396 cm⁻¹, D-like band at 1345 cm⁻¹, and G-like band at 1609 cm⁻¹, with the Si vibration mode at 521 cm⁻¹, which are nearly the same as those in pristine GNRs after transfer to the SiO₂/Si substrate (see SI Figure S10). The Raman peaks, especially the BLM peak, display a symmetric shape, similar to those in pristine 7-aGNRs,^{9,34} indicating the absence of additional bonding induced by the bubbling transfer.³⁰ The D band is more intense than the G band in the GNR–GND HJs, with a D-to-G ratio about 1.11, as compared to the ratio of about 0.77 in pristine 7-aGNRs (see SI Figure S10). The slight enhancement of the D band signal can be ascribed to the coupling of GNDs to GNRs.

Figure 4f compares the PL of the pristine GNR sample and the GNR–GND HJ sample (see SI Figure S11) measured with a 405 nm (3.1 eV) laser at both 300 and 4 K. The spectra are obtained by subtracting the background signal taken on the bare SiO₂ substrate on the same sample surface (see SI Figure S12). At 300 K, a broad PL peak is observed at around 1.8 eV

in the pristine GNR sample, which is consistent with previous observations and attributed to the exciton recombination at defect sites induced by laser exposure.⁴⁶⁻⁴⁸ Here, we do not observe direct PL intensity at the energy of its optical photon gap (2.1 eV),⁴⁶ as the energy of E_{11} corresponds to an optically forbidden (dark) electronic state in the 7-aGNR.49,50 Highorder multiphonon Raman modes are also observed from the 7-aGNRs in the high-energy region.⁵¹ In comparison, the 300 K PL spectrum of the GNR-GND HJ sample shows a broad PL peak around 2.1 eV that exists neither in the pristine GNR sample nor in the pristine GND sample even with a high coverage (see SI Figure S13) and thus is attributed to the recombination at the QWL states of the AA HJ (Figure 4a). At 4 K, PL shows sharp peaks on top of a broad background from the GNR-GND HJ sample (pink curve). For example, a sharp peak appears at 2.08 eV with a line width of about 5 meV. Note, the PL peak energy corresponds well to the quasiparticle band gap of the QWL states measured by STS on the Au(111) (Figure 2), and the reduction of quasi-particle band gap of 7-aGNR induced by the screening of the Au is believed comparable to the exciton binding energy of 7-aGNR on the $SiO_2/Si.^{52}$

The spatial distribution of the PL measured with a 532 nm (2.3 eV) laser at 4 K is shown in Figure 5a for the GNR-GND HJ sample. Compared to a pristine GNR sample (Figure 5b), the PL is clearly enhanced in the GNR-GND HJs. Three typical PL curves representing three spatial positions marked in Figure 5a,b are shown in Figure 5c, one from the GNR-GND HJs and two from the GNR sample with different intensities. Broad PL peaks are found at around 1.8 eV (green shade) in the pristine GNR sample, with the same energy position as that measured with a 405 nm laser (Figure 4f). All curves display similar Raman peaks of the 7-aGNRs (see SI Figure S14). In the region of 2.02–2.07 eV (orange-shaded region), where no Raman peaks exist, a sharp PL peak at ~2.06 eV (601.6 nm) emerges in GNR-GND HJ sample, with a narrow width of about 3.0 meV. Note that a few strong PL patches are also found in the pristine GNR sample, but there are no sharp PL lines, such as the gray curve in Figure 5c.

Figure 5d shows four representative PL spectra from 400 measurements on the GNR-GND HIs (see SI Figure S15 for more PL spectra). Four distinct PL peaks can be resolved within a narrow range of 2.03 to 2.07 eV. Figure 5e shows the statistic percentage of occurrence of sharp PL peaks among the 400 measured spectra, indicating that the peaks mostly appear around 2.06 and 2.07 eV, in an ultranarrow energy range. The narrow distribution range of the emission energy confirms the uniformity of the junction structures. The PL peaks in such a narrow energy range all have a narrow line width between 2 and 5 meV. The variations of the occurrence and the energy positions for the sharp PL peaks reflect the changes of the local sample environment. This behavior is obviously different from the Raman modes as these sharp PL peaks exist at nearly the same energies when excited with different laser wavelengths (405 nm in Figure 4e and 532 nm in Figure 5).

CONCLUSION

By controlling on-surface reactions, we have demonstrated a strategy to engineer interface states of mixed-dimensional GNR-GND HJs with atomic precision. Two different conjugation sites are observed. QWL junction states are revealed when the HJ is formed at the GNR edge *via* AA conjugation, whereas deep-level defect states are formed *via*

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Figure 5. Narrow-band PL in the GNR-GND HIs at 4 K excited with a 532 nm (2.3 eV) laser: (a) $20 \times 20 \ \mu m^2$ PL maps (20×20 pixels) of the GNR-GND HJs and (b) pristine GNR sample, with the same energy range from 2.02 to 2.07 eV (i.e., 613 to 598 nm in wavelength) and the integration time of 1 s for each pixel. The maps are plotted with the same color bar. (c) Three PL curves from the red-box-marked pixel in (a) and black- and gray-boxmarked pixels in (b). The Raman peaks are marked with dashed lines and arrows. A sharp PL peak at 2.07 eV is observed in the red curve acquired from the GNR-GND HJs, with a width of about 3.0 meV. The orange shade marks the mapping range for (a) and (b). The green shade marks a broad PL peak at around 1.8 eV for the black curve. (d) Four representative PL curves taken at the corresponding boxed pixels in (a), with the coordinates marked for each curve. Dominant PL peaks are at 2.03, 2.05, 2.06, and 2.07 eV. Spectra in (c) and (d) are vertically shifted for clarity. (e) Statistic percentage of occurrence of the PL peaks at different energies.

AZ conjugation at the GNR end. Light-generated excitons can recombine at the GNR–GND AA HJs and give rise to PL with a narrow peak energy range of 2.03–2.08 eV and an ultranarrow line width of 2–5 meV at low temperature, indicative of possible single-photon emission. As the energy gap of the interfacial quantum well greatly depends on the band gaps of the defining GNRs and GNDs, the PL wavelength can be tuned by controlling the structures of the GNRs and GNDs with choices from a vast pool of molecular precursors. The observed conjugation formats and electronic states in HJs should be applicable to other graphitic nanostructures. The QWL interfacial states at the HJs point to an alternative approach to single-photon emitters. The interfacial structures of GNR–GND HJs are tunable with atomic precision and can be synthesized in a large quantity. If the spatial resolution can be improved in the antibunching measurement, the single-photon emission behavior can be verified by using, for example, Hanbury Brown–Twiss interferometry.^{53,54} Although the 7-aGNRs and the GNR–GND HJs can be stable in air,⁵⁵ further work is needed to evaluate the potential damage and the possible effects of laser illumination on the hetero-structures, which has been observed for the pristine 7-GNRs,^{46–48} giving defect-induced broad light emission at 1.8 eV (Figures 4f and 5c). From this standpoint, a single molecular level^{56,57} of single-photon emission is suggested for future work.

METHODS

Sample Preparation. The Au(111) single crystal is cleaned by repeated cycles of argon ion bombardment and annealing to 740 K. Molecular precursors are well degassed in ultrahigh vacuum conditions at temperatures slightly lower than the evaporation temperatures. DBBA molecules (1') are used as precursors to synthesize the 7-aGNRs (1) by following our previous recipes.²⁹ While evaporated at 485 K from a Knudsen cell (SVT Associates, Inc.) with the Au substrate held at 470 K, the molecules undergo dehalogenation upon adsorption. The sample is subsequently annealed at 470 and 670 K for 30 min to induce polymerization (at 470 K) and cyclodehydrogenation/graphitization (at 670 K), resulting in the 7-aGNRs. Then N, N', N''-tris(2-biphenylyl)borazine (2') crystalline flakes are evaporated at 430 K from a different Knudsen cell, while the same Au substrate is held at room temperature. With subsequent annealing at 520 and 640 K for 20 min, intramolecular cyclodehydrogenation can be induced, giving the BN-GNDs (2). After a further annealing at 770 K, the GNR-GND HJs can be achieved.

STM Measurements. The STM characterizations are performed with a homemade variable-temperature system at 105 K under ultrahigh vacuum conditions. A cleaned commercial PtIr tip is used. All STM images are acquired in a constant-current mode. The dI/dV spectra are recorded using a lock-in amplifier with a sinusoidal modulation (f = 731 Hz, $V_{mod} = 20$ mV) by turning off the feedback loop-gain. The polarity of the applied voltage refers to the sample bias with respect to the tip.

Sample Transfer. After the growth of the pristine GNR and the GNR–GND HJ samples on ~100 nm Au(111)/mica, they are transferred to 90 nm SiO₂/Si substrates following an electrochemical bubbling method.^{44,45} First, the GNR/Au/mica sample is spin-coated with poly(methyl methacrylate) (PMMA) and then baked at 395 K for 5 min. Second, in an electrochemical cell with a KOH aqueous solution (1 mol/L) as electrolyte, a piece of W foil as anode, and the GNR/Au/mica sample as cathode, a constant voltage of 3.0 V is applied between these two electrodes. In a water-splitting reaction, the H₂ microbubbles are produced at the cathode. The bubbles help detach the PMMA/GNR membrane from the Au surface. Finally, the floating PMMA/GNR film is cleaned by deionized water and transferred to the target substrate, which is 90 nm SiO₂/Si. After drying, the PMMA layers are removed by a well-established acetone bath process.

PL Measurements. The Raman/PL spectra are measured in a custom-built micro-Raman/PL setup. The samples are excited with a continuous wave diode-pumped solid-state laser (Excelsior, Spectra Physics, 405 or 532 nm, 100 mW) through an upright microscope using a 50× long-working distance objective with NA (numeric aperture) = 0.5. The typical incident laser power on a sample is maintained at ~100 mW to reduce possible laser heating and damaging of the samples during Raman/PL spectra acquisition. The scattered Raman or PL light is analyzed by a spectrometer (Spectra

Pro 2300i, Acton, f = 0.3 m) that is coupled to the microscope and equipped with a 1800 grooves/mm grating and a CCD camera (Pixis 256BR, Princeton Instruments). The low-temperature Raman/PL spectra are measured using a liquid He cryostat (MicrostatHiResII, Oxford Instruments) with a temperature controller (MercuryiTC, Oxford Instruments) that allows precise temperature control from 3.6 to 300 K. The cryostat is mounted on a motorized XY microscope stage (Marzhauser) under the microscope of the micro-Raman/PL setup. The cryostat is evacuated to the base pressure of 7×10^{-7} mbar prior to cooling.

Calculation Methods. The ab initio calculations are performed with the Quantum Espresso package,⁵⁹ using ultrasoft pseudopotentials⁶⁰ and Perdew-Burke-Ernzerhof (PBE) exchange correlation functional.⁶¹ The energy cutoff for the plane wave basis of Kohn-Sham wave functions is 30 Ry, and that for the charge density is 300 Ry. The structures are relaxed until forces on atoms reach a threshold of 0.001 Ry bohr⁻¹. The STM images are simulated based on Tersoff's method.^{62'} The AA-conjugated GNR-GND HJ is modeled with a periodic boundary condition along the GNR length, in order to eliminate the effect of zigzag edge. The supercell length is 5.5 nm, consisting of 13 anthryl units for the GNR. The AZ-conjugated GNR-GND HJ is modeled with a finite GNR chain with 10 anthryl units. The vacuum size normal to the HJ plane is 20 Å for both AA and AZ HJs. The in-plane distances between periodic images is >20 Å along the nonperiodic directions. The LDOS values are calculated for boxes localized along the route of experimental scanning.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c01737.

On-surface synthesis of the BN-GNDs, additional STM images of the pristine GNRs and GNR–GND HJs, simulated STM image and model structures of the GNR–GND HJs, additional dI/dV curves and mapping of the GNR–GND HJs, Raman spectra of the pristine 7-aGNR sample before and after transfer, room-temperature PL spectra from the pristine GNRs and the GNR–GND HJs, PL spectra on the pristine BN-GND sample, assignment of the Raman peaks in PL spectra, more representative PL curves on the GNR–GND HJ sample acquired at 4 K (PDF)

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Author Contributions

A.-P.L. conceived the project and designed the experiments. J.B. designed the theory tasks. C.M. and A.-P.L. synthesized GNRs and GNDs and performed STM characterizations; Y.L. and K.H. conducted molecular precursor synthesis; A.M., H.W., and G.G. transferred the as-grown samples onto SiO₂/Si substrates; C.M., B.J.L., and A.A.P. performed the PL and Raman measurements; Z.X., L.L., J.H., W.L., and J.B. performed the theoretical calculations. C.M. and A.-P.L. wrote the paper with contributions from all authors.

Notes

The authors declare no competing financial interest.

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