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Synthesis and Applications of Graphene Nanoribbons and Heterostructures from Molecular Precursors

by

Wade Scott Perkins

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate Division of the University of California, Berkeley

Committee in charge:

Professor Felix Fischer, Chair
Professor K. Peter Vollhardt
Professor Richmond Sarpong
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Synthesis and Applications of Graphene Nanoribbons and Heterostructures from Molecular Precursors

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Wade Scott Perkins
Abstract

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University of California, Berkeley

Professor Felix Fischer, Chair

Graphene nanoribbons (GNRs), nanometer wide strips of graphene with extraordinary electronic and physical properties, represent the cutting edge of post-silicon electronics development. These nanomaterials boast potential solutions to downsizing of future electronics in both size and energy consumption, as well as opening the door to faster processing. Novel GNRs of varied width and heteroatom incorporation were synthesized in a surface assisted bottom-up fashion from novel small molecule precursors (Chapter 2). The advancement of GNR based technologies to new and advanced architectures requires the controlled formation of functional GNR heterostructures, and to this end, a GNR-porphyrin-GNR heterostructure was designed and developed which is shown to self-assemble on functionalized surfaces (Chapter 3). Furthermore, bulk GNRs are shown to have practical applications beyond the single ribbon scale, acting as functional support materials for inorganic nanoparticles (Chapter 4). This work advances both the development and applications of bottom-up synthesized GNRs.
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Chapter 1

Introduction

In the first chapter of this thesis graphene, synthetic methods, and applications are introduced. Motivation for confinement of graphene into atomically precise narrow graphene nanoribbons is provided, and existing synthetic methods and characterization tools are explored. This provides a literature foundation for the novel synthetic methods, heteromaterials, and applications that will make up Chapters 2–4.
CHAPTER 1. INTRODUCTION

1.1 Graphene

Prior to its isolation in 2004, graphene, a single atom layer of hexagonally arranged carbon atoms, was thought by many researchers to be too unstable for isolation due to the tendency to roll into other carbon allotropes such as fullerenes and carbon nanotubes (CNTs). Since the discovery of the so called “Scotch-tape method” of repeated mechanical exfoliation of graphite flakes that first produced single-layer graphene, it has become one of the most intensely researched topics in materials, prompting the 2010 Nobel Prize in physics for Novoselov and Geim. Among the properties that have drawn significant attention for future electronics and materials applications are its outstanding charge carrier mobility (250,000 cm\(^2\)/Vs, orders of magnitude higher than silicon), high specific surface area (2630 m\(^2\)/g), thermal conductivity (5,000 W/mK), high Young’s modulus (1.0 TPa), and remarkably high optical transparency (97.7%) which make it an attractive material for flexible and optical electronics.

Today, a variety of synthetic methods for single- and few-layer graphene sheets exist. In addition to mechanical exfoliation via scotch tape, exfoliation of graphite using a ball mill, as well as surfactant mediated electrochemical exfoliation, have been shown to be viable options. Graphene can also be grown epitaxially on metal substrates, among other methods. However, synthesis by chemical vapor deposition on various transition metal surfaces using solid, liquid, or gaseous starting materials is the most commercially viable synthetic method for large, well controlled sheets.

Many electronic applications of graphene hinge on two main factors besides quality and scale of the synthesis. The first is the need to transfer the graphene sheet off of the metal surfaces that are commonly used for its synthesis onto a dielectric substrate such that the electronic properties of the graphene are not overshadowed by the metal substrate. This has been addressed in a variety of ways including polymer-assisted transfer, roll-to-roll transfer methods, and even direct growth on dielectrics. The second is the need for a bandgap for semiconducting applications. Because graphene is intrinsically semi-metallic in its conductance due to a lack of bandgap, new methods are required to modify the electronic structure of graphene. The most promising of which is lateral confinement of graphene into high aspect ratio strips of graphene called graphene nanoribbons (GNRs) that feature a tunable bandgap due to quantum confinement.

1.2 Graphene Nanoribbons

Graphene nanoribbons (GNRs) are semiconducting quasi-one dimensional strips of graphene whose electronic and magnetic properties depend heavily on their width and edge structure. Three of the most commonly investigated types of GNR edge structures (armchair or AGNRs, zig-zag or ZGNRs, and cove type GNRs) are shown in Figure 1.1. Due to the extremely sensitive relationship between the physical and electronic structures, high precision and reproducibility are key factors to be considered when developing a GNR synthetic method.
Researchers round the world have investigated synthetic methods that fall into two main categories: top-down and bottom-up synthesis.

**Top-Down Synthesis**

Top-down syntheses of GNRs start with larger graphitic structures (graphene, graphite, carbon nanotubes), and laterally confine them using a variety of methods. These methods commonly boast advantages in generation of commercially viable amounts of material, however confinement down to the sub 10 nm width scale and control over edge structure remain major challenges in the field.

**GNRs by Sonication of Graphite**

One method of top-down GNR fabrication that excels in smooth edges, high aspect ratios, and bulk production is the sonochemical cutting of graphite flakes. This method commonly makes use of dispersing a graphite flake in an aqueous solution using surfactants (such as sodium dodecyl sulfate or SDS) and strong oxidizing acids (H$_2$SO$_4$ or HNO$_3$) along with a templating polymer [PVP,$^{51}$ PmPV,$^{50}$ or self assembled flavin monocucleotide (FMV)$^{49}$]. The primary challenges associated with using this methodology are the need to overcome the strong van der Waals forces between graphene sheets and the directional unzipping, which are addressed by the use of varied surfactants and templates.
Figure 1.2: A) Representation of non-covalently templated sonication cutting of graphite. [Reproduced from reference \textsuperscript{49}] B-D) AFM images of GNRs produced by sonication displaying a variety of defects. [Reproduced from references \textsuperscript{50,51}] E) Histogram of GNR widths produced by sonication. [Reproduced from reference \textsuperscript{51}] F) Raman spectra of GNRs produced by sonication showing broad peaks and high D/G ratio. [Reproduced from reference \textsuperscript{49}]

However, the smooth edges touted by this method are commonly defined by having edge roughness smaller than the ribbon width, and do not have edges aligned with a crystallographic axis, which would lead to the atomically defined A- or ZGNRs. Indeed, examples of AFM topographical images include, in addition to edge roughness, defects such as kinks or wedge shaped ribbons as seen in Figure 1.2B, C, and D.\textsuperscript{50,51} Furthermore, while this technique has been shown to produce ribbons that are sub 10 nm in width, the control is such that ribbons are always produced as a wide assortment of widths as seen in Figure 1.2E, which leads to large variability in electrical properties. Evidence for defects, which can include vacancies, edge functionalization, and topological defects, can be readily seen in the Raman spectra of the materials which tend to feature broad G peaks, as well as high D/G or D’/G ratios (Figure 1.2F).

While impressive device measurements have been obtained using GNRs produced in this method, such as the $I_{on}/I_{off}$ ratios of up to $10^7$ in a GNR FET,\textsuperscript{50} the reproducibility is sufficiently low that these methods are inadequate for reliable fabrication of electronic devices.
CHAPTER 1. INTRODUCTION

GNRs by Unzipping Carbon Nanotubes

Figure 1.3: A) 3D representation of partial longitudinal unzipping of a CNT triggered by a sidewall modification. [Reproduced from reference\textsuperscript{52}] AFM images of GNRs made by electrochemical unzipping of MWCNTs at B) 0.7V and C) 0.5V [Reproduced from reference\textsuperscript{53}] D) Width distribution of GNRs produced by intercalation assisted oxidative unzipping of MWCNTs. [Reproduced from reference\textsuperscript{54}] E) and F) Representative Raman spectra of GNRs produced by laser induced unzipping of MWCNTs. [Reproduced from reference\textsuperscript{55}]

One of the most explored top-down methods of GNR synthesis that performs well in terms of bulk production and length is from the longitudinal unzipping of CNTs as shown in Figure 1.3A. This has been accomplished using both single-walled and multi-walled CNTs (SWCNT and MWCNT respectively), with unzipping derived from chemical oxidation, high pressure reduction with H\textsubscript{2}, laser pulses, intercalation of ions (Li\textsuperscript{+}, K\textsuperscript{+}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, and others) in strong acid (H\textsubscript{2}SO\textsubscript{4}), followed by exfoliation with KMnO\textsubscript{4}.

The harsh oxidative conditions commonly employed in chemical unzipping are well known to lead to a variety of edge oxidation products and disorder.\textsuperscript{54} Other methods, including reductive unzipping,\textsuperscript{56} electrochemical unzipping,\textsuperscript{53} laser-induced unzipping,\textsuperscript{55} and unzipping through a combination of other chemical reactivity and STM tip manipulation\textsuperscript{52} are capable of limiting the amount of edge oxidation, but do not reduce the edge disorder and still lead to ribbons with highly defective edges, as seen in example AFM images (Figure 1.3B and C). A primary shortcoming of using CNTs as a starting material, is that the as-synthesized CNTs are always a mixture of various chiralities, with $\frac{1}{3}$ being metallic conductors. This means
that regardless of the unzipping method, the edge chirality of the produced GNR will always be an uncontrolled mixture leading to inconsistent electronic properties. Furthermore, the width of the GNR will always be limited by the diameter of the CNT, leading to GNRs far larger than the desirable < 10 nm width (Figure 1.3D).

**GNRs by Etching Graphene**

![Figure 1.4](image)

Figure 1.4: A) Schematic representation of a device based on GNRs etched from graphene with a nanowire mask. [Reproduced from reference 57] B) SEM image of device with GNRs etched in a parallel arrangement. [Reproduced from reference 58] C) STM topograph of GNRs made from chemically unzipped CNTs followed by H\textsubscript{2} plasma etching. [Reproduced from reference 59] D) Scaling of GNR width with mask size under O\textsubscript{2} plasma treatment. [Reproduced from reference 57] E) Comparison of Raman signal of a pristine graphene sheet and the GNR after etching. [Reproduced from reference 60]

Fabrication of GNRs by etching graphene sheets is a synthetic method with advantages in both generating aligned GNRs (Figure 1.4B) and in making integrated interconnects by patterned cutting. This gives etched GNR devices an advantage over other methods with regards to avoiding the Schottky barrier dominated performance common in CNT devices due to the crystallographic continuity of the GNR and electronic connections. 57,58

Most etch methods follow a scheme similar to that seen in Figure 1.4A, whereby metal electrodes are patterned onto a sheet of graphene using electron beam lithography (EBL), and a lithography resistant mask (commonly either a polymer or nanowire) is patterned onto the sheet to define the desired GNR. The extraneous, surrounding graphene is then etched away using O\textsubscript{2} plasma, 57,58,61 H\textsubscript{2} plasma, 59 or reactive ion etching (Ga\textsuperscript{+}, He\textsuperscript{+}, etc.). 60
However, these harsh treatments cause significant defects along the edges of the GNRs, including oxidation from the O_2 plasma and roughness and disorder, as can be seen in the high resolution STM topograph in Figure 1.4C. In addition, while some methods have successfully produced GNRs in the sub-10 nm regime,\textsuperscript{57} such examples are uncommon and still lack the control to generate such ribbons reproducibly (Figure 1.4D). Devices fabricated from etched GNRs of width > 20 nm tend to suffer from low transport gap values arising from the wide ribbons.\textsuperscript{58,61,62} Transistors based on etched GNRs also suffer from low $I_{on}/I_{off}$, with ratios on the order of $10^2$ being considered impressive.\textsuperscript{57,63}

**Bottom-Up Synthesis**

In order to preserve the predicted properties of GNRs in a realized ribbon, complete atomic precision over the width and edge structure are required. Where the previous top-down fabrication methodologies all failed in this endeavor, bottom-up synthesis of molecular precursors succeeds. By utilizing a two step sequence of polymerization followed by cyclodehydrogenation starting from molecular precursors defined by organic synthesis, the precise width, edge structure, and doping pattern of a GNR can be controlled. This has been accomplished both on metal surfaces in UHV, as well as in solution. These two complementary methods have their own advantages with regards to available characterization, scale, and unique functionalization given the different reaction pathways.

**On Surface Bottom-Up Synthesis of GNRs**

The first example of on-surface bottom-up synthesis of atomically precise GNRs was published in 2010, when Cai et al. reported the synthesis of both $N = 7$ AGNRs (where $N$ is the width of the ribbon in number of carbon atoms) and Chevron type GNRs as shown schematically in Figure 1.5.\textsuperscript{64} In this precedent setting report, a dibrominated monomer was deposited on a Au(111) surface and annealed to enable a surface catalyzed homolytic bond cleavage, resulting in a diradical species that can diffuse about the surface and recombine to form the C-C bonds that make up the precursor polymer backbone. At an elevated annealing temperature, the precursor polymer is cyclodehydrogenated to planarize and graphitize the material, resulting in a GNR whose width and edge structure are perfectly controlled. Due to the hermetic environment, issues such as incorporation of oxidation products or dangling bonds are excluded. This is confirmed by high resolution STM as well as XPS. Furthermore, single ribbon electronic characterization is possible with this technique, although the experimental results differ from those previously calculated due to an effect of screening and hybridization due to the gold surface. This can best be compensated for in calculations using an image charge model.

This biradical polymerization technique was then utilized in reports that expand upon the number and type of GNRs available. In 2013, the first example of a wider, controlled AGNR was published.\textsuperscript{65} By modifying the bisanthracene core to include biphenyl substituents, the resulting GNR is instead 13 atoms across, lowering the observed bandgap by 1.2 eV from
Figure 1.5: On-surface synthesis of $N = 7$ AGNRs from dibromobisanthracene monomer. [Reproduced from reference 64] A) The dihalogenated monomer is deposited on a Au(111) surface under UHV and annealed to induce homolytic bond cleavage, resulting in a biradical intermediate. This diffuses about the surface and recombines to form the linear precursor polymer. At a higher annealing temperature, the precursor polymer is cyclodehydrogenated to produce the desired GNR. B) STM image of $N = 7$ AGNRs imaged at room temperature and C) High resolution STM of $N = 7$ AGNRs taken at 5 K.

The $N = 7$ case to 1.4 eV (Figure 1.6A and B). While in the case of $N = 7$ AGNRs the authors observe ribbon lengths of $\sim 30$ nm, in the case of $N = 13$ AGNRs the ribbons observed are significantly shorter (11 nm). The authors claim this length decrease is due to a length limiting quenching of the aryl radicals via hydrogen abstraction. Additionally, it can be observed that there are electronic states associated with the ends of ribbons that extend $\sim 30$ Å from the edges, at which point the bulk electronic structure is reached.

The first reported member of the lowest predicted bandgap $N = 3p + 2$ family came in 2015 when Zhang et al. synthesized $N = 5$ AGNRs starting from tetrabromonaphthalene. An important insight into the mechanism of ribbon formation was found, when Au-organic hybrid polymers were observed that then collapse to the desired GNR at a higher temperature (Figure 1.6C and D). This is in contrast to the previous reports that claim the polymer formation step is carried out by free radicals recombining. However, while Cu- and Ag-organic hybrids are more commonly observed, there have only been rare reports of Au-organic hybrids as observed here, so it is currently unclear how general this mechanism is likely to be. An advantage of this particular monomer is that there is no cyclodehydrogenation step...
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Figure 1.6: A) High resolution STM image of $N = 13$ AGNR on Au(111) with partial model overlay. B) STS of $N = 13$ AGNR compared to $N = 7$ AGNR. [Reproduced from reference\textsuperscript{65}] C) High resolution STM image and D) DFT model of Au-organic hybrid polymer precursor to $N = 5$ AGNRs. [Reproduced from reference\textsuperscript{66}]

required, thus allowing for milder temperatures to be used.

In addition to synthesizing AGNRs of different widths, surface assisted synthesis has been used to generate ribbons of varying edge construction, including chevron\textsuperscript{64} and zig-zag (Figure 1.7).\textsuperscript{71} ZGNRs are of particular interest due to the predicted spin-polarized edge states. This study produced ZGNRs of $\sim 50$nm, paving the way for future research on the unique edge magnetic properties. The authors find that when the ZGNRs are directly on the Au surface, no edge states are observed due to strong interaction of the ribbon with the metal surface. However, when the ribbons are dragged onto islands of insulating NaCl, they become electronically decoupled from the surface, allowing for the observation of two different electronic edge states.

Further tuning of the electronic structure of GNRs beyond width and edge structure modifications has been accomplished through the site selective replacement of carbon atoms with heteroatom dopants, including N,\textsuperscript{75–78} B,\textsuperscript{72,73,79} and S (Figure 1.8).\textsuperscript{74} The synthesis and characterization of chevron type GNRs incorporating 1,\textsuperscript{76} 2,\textsuperscript{76,77} and 4\textsuperscript{78} nitrogen atoms replacing edge carbon atoms has shown that the effect of incorporating a pyridine-like nitrogen with the lone pair orthogonal to the $\pi$-system of the ribbon is to rigidly realign the bandgap to lower energies via inductive effects. This is in contrast to the cases where B atoms were incorporated in the center of the ribbon, with the empty $p$-orbital in conjugation with the $\pi$-system.\textsuperscript{72,73,79} In this case, an effect more analogous to traditional semiconductor doping is observed, where new electronic dopant states are introduced into the bandgap.

More advanced modulation of GNR electronic structure has been accomplished through the fabrication of GNR heterostructures where a single ribbon contains varying size or dopant profiles along its axis. Heterostructures thus far reported include an all carbon type-I heterojunction made by copolymerizing monomers used for $N = 7$ and $N = 13$ AGNRs (Figure
1.9A), a type-II heterojunction made by combining chevron monomers of varied nitrogen incorporation (Figure 1.9B), chevron type GNRs with interspersed electron rich and electron deficient heterocycles made from a single monomer with a divergent on-surface rearrangement, and an embedded quantum dot system by copolymerization of $N = 7$ and B-doped $N = 7$ monomers. Similar to the penetration of end states $\sim 30\text{Å}$ into the ribbon noted previously, it was observed through STS that in the case of the type-II heterojunction the band bending between segments occurs over a short distance (Figure 1.9B), being complete after $\sim 2\text{nm}$, reaching the bulk electronic structure only one monomer away from the junction. This sharp interface should lead to an electrostatic field about 2 orders of magnitude greater than in a traditional semiconductor $p-n$ junction which one would expect to lead to higher charge carrier separation efficiency in photovoltaic systems.

**Solution Phase Bottom-Up Synthesis of GNRs**

While surface assisted synthesis of GNRs gives access to atomically defined structural characterization and in depth single ribbon electronic characterization, solution phase synthesis of GNRs has the advantage of bulk production and does not require a metal surface, making it ideal for device fabrication. A notable disadvantage of solution phase processing of GNRs is the tendency to form large $\pi$-stacked aggregates, that need to be disrupted to perform any single ribbon characterization or device fabrication. As such, solution synthesized GNRs will commonly have alkyl side chains regularly decorating the periphery of the ribbon.
Figure 1.8: A) B atom dopants in $N = 7$ AGNRs produce localized mid-gap dopant states in the electronic structure. [Reproduced from references $^{72,73}$] B) S doped GNR STM and calculated electronic structure. [Reproduced from reference $^{74}$] C) Divergent N doping of chevron GNRs through a common precursor. [Reproduced from reference $^{75}$]
to interfere with ribbon-ribbon packing and allow for greater solution dispersability. Precursor polymers are formed through a variety of polymerization reactions including Suzuki copolymerization, Yamamoto, and Diels-Alder polymerization.

Both 9- and 18-AGNRs have been synthesized in solution. Suzuki co-polymerization of appropriate monomers yielded the $N = 9$ AGNR precursor polymer with lengths of about 12 nm (Figure 1.10A). This polymerization has been found to suffer in length due to the extreme steric crowding around the reactive sites. By switching instead to a nickel mediated AA type Yamamoto homopolymerization, significantly longer precursor polymers were obtained for the $N = 18$ AGNRs (Figure 1.10B). In both cases, the precursor polymers were converted to the desired GNRs by FeCl$_3$ mediated Scholl reaction, which cyclodehydrogenates the polymers, graphitizing the material.

Chevron GNRs are also available via solution phase synthesis. Unique to chevron GNRs, the same monomer that is used in UHV on surface synthesis can be used in solution by utilizing the Yamamoto polymerization. This has allowed for the production of gram quantities of chevron GNR, as well as the measurement of the optical band gap (1.33 eV). Scanning probe microscopy of samples prepared by dropcasting a suspension of the GNRs

Figure 1.9: A) A type-I heterojunction made by fusing $N = 7$ and 13 AGNRs. [Reproduced from reference$^{80}$] B) A type-II heterojunction made by combining chevron GNRs of different N doping and the observed sharp band bending. [Reproduced from reference$^{78}$]
CHAPTER 1. INTRODUCTION

Figure 1.10: A) 9-AGNRs synthesized in solution by first palladium catalyzed Suzuki polymerization, followed by FeCl₃ mediated cyclodehydrogenation. R is a solubilizing branched alkyl chain. B) 18-AGNRs synthesized by first nickel mediated Yamamoto polymerization, followed by FeCl₃ mediated cyclodehydrogenation with one monomer unit highlighted in red for clarity. R=C₁₂H₂₅.

Figure 1.11: A) Solution synthesize of chevron GNRs by first nickel mediated Yamamoto polymerization followed by FeCl₃ mediated cyclodehydrogenation. B) STM image of chevron GNRs synthesized in solution and dropcast onto Au(111) showing preferred side-by-side alignment with one ribbon highlighted in green for clarity. [Reproduced from reference 86] C) Experimental setup for measuring bulk conductance of chevron GNR powder compressed into a disk. [Reproduced from reference 85]
in organic solvent reveal that ribbons, as when synthesized on surface, tend to have a preferential side-by-side alignment. Bulk conductivity measurements on a pellet of chevron GNRs between cylindrical aluminum contacts give values of $\sim 30 \, \mu A$ at $\pm 5 \, V$.\textsuperscript{85} This evidence of bulk conductivity is promising for future electronic applications, but does not indicate the conductivity of single ribbons and likely suffers from defects, such as inefficient ribbon-to-ribbon junctions and low packing density.

An edge structure that is more readily available from solution synthesis than on surfaces is the cove type GNR.\textsuperscript{87,89–91} The polymer precursors for these ribbons are synthesized by using a heterobifunctional monomer that contains both a terminal alkyne and cyclopentadienone that undergo a thermal Diels-Alder cycloaddition followed by cheletropic extrusion of CO to yield new benzene rings (see Figure 1.12A). Because this reactivity is not known on metal surfaces, this method of producing cove-type GNRs is currently unique to the solution phase, preventing atomic resolution imaging or single ribbon spectroscopy. However, due to the ability to include long and/or branched alkyl chains regularly along the periphery of the ribbon, their solution processability is significantly higher than that of other ribbons. This development has allowed for characterization of charge carrier mobility by THz spectroscopy,\textsuperscript{87,91} and has prompted studies on the most effective ways of depositing ribbons onto insulating surfaces both isolated and as thin films (Figure 1.12B and C).\textsuperscript{89,90}
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Applications of Bottom-Up Synthesized GNRs

Once GNRs have been synthesized, there arises the further challenge of incorporating a single atom thick, 1 nm wide material into an electronic device. Among the primary issues associated with using surface synthesized GNRs is the need to transfer them from the metal surface to an insulating substrate such as SiO$_2$ or Al$_2$O$_3$, as well as the random alignment of the transferred ribbons. Devices fabrication using solution synthesized GNRs is likewise complicated by the need to overcome the strong $\pi$−stacking between ribbons to isolate and manipulate a single ribbon, guide its placement onto the substrate, and make contact with it.

The first reported use of bottom-up synthesized GNRs in a functioning FET made use of $N = 7$ AGNRs synthesized on a Au(111) surface.$^{92}$ The transfer process involved first coating the GNR on Au on mica stack with poly(methyl methacrylate) (PMMA), then delaminating the mica with an aqueous solution of 40% HF an removal of the gold with a gold etchant to leave GNRs on PMMA (Figure 1.13A). This was pressed onto a target SiO$_2$ on Si substrate and the PMMA was washed away with acetone and Pd contacts were fabricated onto the surface to yield a device shown schematically in Figure 1.13B. Raman spectroscopy was used to confirm the presence of GNRs on the substrate, however no further techniques were used to locate individual GNRs and, as such, the GNRs are arranged randomly under the contacts. This fact, along with the length of the ribbons (average 10–15 nm, up to 40 nm) being shorter than the contact channel length (20–30 nm), led to a low device yield. After annealing the devices under vacuum ($300 ^\circ$C, $3 \times 10^{-7}$ Torr) to remove adsorbed oxygen and water, they show impressive $I_{on}/I_{off}$ ratios of $3.6 \times 10^{3}$ at a source-drain voltage of $V_{sd} = 1$ V. However, transport through the device was dominated by Schottky junction contacts due in part to band alignment between the GNR and Pd, and in part to the short contact overlap.
CHAPTER 1. INTRODUCTION

Figure 1.13: Methods of fabricating FETs from bottom-up synthesized GNRs include A) a wet transfer method off of Au on mica films for surface synthesized GNRs. B) A representative GNR FET schematic. [Reproduced from reference 92] C) submersion of a SiO$_2$ surface with a hydrophobic SAM in a dispersion of GNRs with prepatterned markers used to locate GNRs during contact deposition. [Reproduced from reference 93] D) electrospray deposition of a GNR dispersion to form a thin film on graphite electrodes. [Reproduced from reference 94]

Solution synthesized GNRs were integrated into a transistor two years later, when highly dispersible alkylated cove-type GNRs with a nominal length of $\sim 600$ nm were deposited on an Al$_2$O$_3$ based substrate and contacted with Ti/AuPd electrodes. In this case, the GNRs were suspended in an aqueous dispersion using 1% sodium dodecylsulfate (SDS) as a surfactant and the substrate (8 nm Al$_2$O$_3$ on 100 nm SiO$_2$ on doped silicon) was capped with a monolayer of tetradecyl phosphonic acid before submersion in the GNR dispersion. The GNRs were then located using AFM with reference to prepatterned markers on the surface (shown in Figure 1.13C) and contacted with the Ti/AuPd electrodes with 100 nm channel length. While the authors claim that in their case the current is not limited by the metal contact junction, their $I_{on}/I_{off}$ ratio suffers greatly when compared to the previous report, reaching only $I_{on}/I_{off} = 2$ with $I_{on}$ up to 70 $\mu$A. The authors acknowledge that the
low $I_{on}/I_{off}$ ratio could be due to having contacted not one ribbon, but several in a bundle, which their calculations show could lower the band gap to as low as 30% of a single GNR.

A very different approach to solution phase GNR device fabrication designed to yield a transistor not consisting of a single ribbon, but of a thin film yielded devices with slightly better $I_{on}/I_{off}$ up to 5, but only by reducing $I_{on}$ to the nA range and at the very high $V_G =40\,\text{V}$.\textsuperscript{94} While the GNRs used both in this report and in the previous are the same, the fabrication methods are quite unique. Here, the authors prepattern graphite electrodes on a SiO$_2$ substrate and form a film of GNRs in the channel by an electrospray deposition method from a dispersion in THF/MeCN (Figure 1.13D). This results in the need for significant amounts of inter-ribbon charge transport, the inefficiency of which could be partially to blame for the low current passing through the device.

GNRs have also been used in chemical sensing applications. By dropcasting a thin film of cove GNRs from suspension onto prepatterned Ti/Au electrodes and annealing the device to 500 °C to thermally remove alkyl chains and improve ribbon-ribbon contact, a sensor that shows conductivity change on exposure to NO$_2$ was made that is sensitive down to 50 ppb.\textsuperscript{89} An alternative use of GNRs is not to use them as active device materials on their own, but to use them combined with another active material. Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a conductive polymer commonly used in the development of organic field effect transistors (OFETs), among other organic electronic applications. By creating a blend of solution synthesized $N=18$ AGNRs and P3HT, researchers were able to improve the charge carrier mobility by a factor of three over a pure P3HT device without sacrificing high $I_{on}/I_{off}$ as happens when a similar blend is made with sheet graphene or CNTs instead.\textsuperscript{83} The resultant device was also functional as an organic phototransistor (OPT) with increased photoresponse.

**Characterization of GNRs by Raman Spectroscopy**

While microscopies that provide atomic resolution imaging of GNRs (AFM, STM) are extremely valuable characterization tools, they are not immediately viable in many scenarios and do not provide any information on the electronic or vibronic nature of the materials. A spectroscopic technique that has become one of the most valuable and ubiquitous in the GNR literature is Raman spectroscopy.

Raman spectroscopy is a type of vibrational spectroscopy whereby the energies of vibrational modes in a molecule are probed by scattering light from the sample. Characterization by Raman spectroscopy has become a staple technique for all graphitic materials, including graphene, graphite, CNTs, and GNRs due to the ability to acquire information about phonons, electron-phonon, magneto-phonon, and electron-electron interactions, as well as strain, doping, disorder, and functional groups.\textsuperscript{95} Vibrational characterization is particularly important in conjunction with optical and electronic characterization in graphitic systems, due to the strong electron-phonon coupling in graphene.\textsuperscript{96}

A monochromatic laser is used to illuminate the sample with energy, typically below the energy of an electronic excitation, to a virtual excited state. In the majority of cases, this virtual excited state relaxes to its original ground state and emits a photon with the
same wavelength as the incident photon. This elastic scattering is referred to as Rayleigh scattering. However, about $10^{-5}\%$ of the incident photons are scattered inelastically in a process referred to as Raman scattering. In this case, the virtual excited state relaxes not to the ground state, but to a vibrationally excited state due to interaction of the photon with the polarizability ellipsoid of a vibrating molecule. This relaxation results in the emission of a photon of lower energy than the incident photon. All of the scattered light is detected and plotted as a difference in incident and detected light with the Raman shift defined as in Equation 1.1. This sets the elastically scattered light to $0\text{ cm}^{-1}$ and makes the resultant spectrum independent of excitation wavelength.

$$\bar{\nu} = \frac{1}{\lambda_{\text{incident}}} - \frac{1}{\lambda_{\text{scattered}}} \quad (1.1)$$

The first order Raman spectrum of graphitic materials is dominated by two signals resulting from in-plane vibrations. The G peak ($\approx 1600\text{ cm}^{-1}$) corresponds to the primary transverse- and longitudinal-optical modes (TO and LO respectively) seen in Figure 1.14. In graphene these modes are degenerate, thus resulting in a single sharp peak. However, this is not the case in CNTs where the two modes are inequivalent resulting in a split G peak, or in GNRs where only one G peak is observed due to one of the two modes being inactive in backscattering depending on the edge chirality of the ribbon. This makes the G peak a particularly diagnostic feature when distinguishing between allotropes.

Figure 1.14: Primary in plane lateral (A) and transverse (B) optical vibrational modes in graphene. [Reproduced from reference]

The other primary first order feature in the Raman spectrum of graphitic materials is the D peak, appearing around $1300\text{ cm}^{-1}$. This is due to an in-plane double resonance where the electron is elastically scattered off of a lattice defect. Because a lattice defect is necessary for this peak, it is not present in pristine single layer graphene. However, in GNRs it is multicomponent due again to the inequivalence of the TO and LO phonons. Because the two primary subcomponents of the D peak show different responses at different $\lambda_{\text{ex}}$, it can appear as either broadened or bifurcated depending on instrument resolution and excitation wavelength.

Finally, in the higher wavenumber region, primarily for GNRs and large PAHs, we have the overtone and combination peaks. The first is a broad feature around $2600\text{ cm}^{-1}$ corresponding to the 2D and $D_j + D_k$ resonances. This multicomponent peak is the result of multiphonon processes combining the aforementioned D peak components. Around $2900\text{ cm}^{-1}$ is the D+G peak, a bifurcated peak arising from multiphonon interactions between

\[ A \quad 0\text{-LO} \quad 1595\text{ cm}^{-1} \quad B \quad 0\text{-TO} \quad 1607\text{ cm}^{-1} \]
the G and D peak subcomponents. Finally, the sharper 2G resonance appears around 3200 cm$^{-1}$. In defective graphene, similar features can be seen that instead result from interaction with the D’ peak not generally observed in GNRs.

1.3 Conclusion

Due to the extensive limitations of top-down methodology and the inherent advantages of bottom-up synthesis of GNRs, future GNR based technologies must be based on bottom-up synthesized GNRs to ensure quality and reproducibility. As such, new synthetic methods are required to expand the library of GNRs available through bottom-up synthesis. The remainder of this dissertation will focus on the synthesis and characterization of novel GNRs and GNR-heterostructures (requisite for the development of advanced device architectures), as well explore novel applications of bottom-up synthesized GNRs.
Chapter 2

Synthesis of Novel Armchair GNRs by Surface Assisted Synthesis

In this chapter the syntheses of novel organic small molecule precursors to graphene nanoribbons are shown. The on-surface behaviors of the precursors are then characterized using high resolution scanning tunneling and non-contact atomic force microscopies. Electronic structure calculations performed using density functional theory in the Quantum Espresso package are provided for two of the ribbons explored in this chapter.
CHAPTER 2. SYNTHESIS OF NOVEL ARMCHAIR GNRS BY SURFACE ASSISTED SYNTHESIS

2.1 $N = 9$ Armchair GNR and Derivatives

![Graph showing LDA and GW predictions of AGNR bandgap dependence on width of ribbon.](image)

Figure 2.1: LDA and GW predictions of AGNR bandgap dependence on width of ribbon.\textsuperscript{103}

First principles calculations on narrow armchair GNRS calculated at two different levels of theory, in the local density approximation (LDA) and with the GW approximation, predict a non-linear dependence of the bandgap on width of the ribbon. Instead, three distinct families exist with monotonically decreasing bandgap within them (Figure 2.1). In order to confirm the theoretical predictions and tune the bandgap of device materials, it is necessary to develop methods for the synthesis of GNRs that span the possible range of widths.

The first AGNR explored here is the $N = 9$ AGNR, a member of the middle bandgap $N = 3p$ family. To gain a better understanding of the electronic structure of the GNR beyond the published bandgap, first-principles calculations are performed. The synthesis of a novel monomer is then described, followed by characterization of the different methods of graphitization.

Calculations

First-principles calculations of $N = 9$ AGNRs were performed using DFT in the Quantum Espresso package.\textsuperscript{104} The pseudopotentials used were norm-conserving with a plane wave energy cutoff of 70 Ry. The structure was relaxed until the force on each atom was smaller than 0.014 eV. The unit cell dimension along the ribbon axis was relaxed, and 20 Å in the two orthogonal directions to avoid ribbon-ribbon interactions. The Gaussian broadening used in plotting the DOS was 0.04 eV. The resultant band structure and density of states (DOS) can be seen in Figure 2.2A and B respectively. The calculated bandgap of 0.675 eV is consistent with calculations performed at the same level of theory,\textsuperscript{105} giving credence to
Figure 2.2: A) Band structure with bandgap = 0.675 eV, consistent with previous calculations at the same level of theory, but not calculations utilizing GW correction and B) densities of states of $N = 9$ AGNR.

the validity of the results. In addition to the value of the bandgap, the clear dispersion of the valence and conduction bands indicates facile transport through the ribbon.

**Synthesis**

The synthesis of diiodosexiphenyl 4 was accomplished in four steps from 4,4′-dinitrobiphenyl as in Scheme 2.1. Selective 2,2′ diiodination by first forming a bridged iodonium intermediate with NaIO₃ in H₂SO₄, then ring opening with CuI and NaI yielded 1 in 50% yield. Reduction of the nitro groups with SnCl₂ under acidic conditions followed by recrystallization from EtOH yielded 5 in 50% yield. Installation of the biphenyl substituents onto the diaminobiphenyl core was accomplished using Suzuki-Miyaura cross coupling, and final installation of the requisite halogens was done using a modified Sandmeyer reaction to yield 4 in 25% yield from 3.

**Surface Characterization**

Monomer 4 was sublimed under UHV onto a room temperature Au(111) surface. Initial characterization of 4 on Au(111) (Figure 2.3 A and B) showed amorphous coverage of the surface. An important observation is that even at sub-monolayer coverage of 4, the molecules tended to form multilayer islands, indicating a preferential adsorption of new monomers onto already deposited monomers instead of onto clean Au(111). Annealing the islands to 150 °C (Figure 2.3C and D) and higher did not lead to any appreciable change in the coverage.
or morphology of the sample. We attribute this apparent lack of polymerization to the aforementioned lack of Au-monomer interaction.

In an attempt to circumvent the apparently difficult surface assisted polymerization of 4, a hybrid route utilizing solution phase polymerization and surface cyclodehydrogenation was devised (Scheme 2.2). The precursor polymer 6 was synthesized in solution by Yamamoto polymerization of 4 with Ni. MALDI-MS of 6 (Figure 2.4B) clearly showed one family of
peaks separated by the expected repeat unit (456 D). GPC of the sample produced with these conditions (Figure 2.4A) showed the presence of lower molecular weight oligomers at higher retention time that appear as sharp individual peaks, as well as longer polymers that form a more even distribution.

We then synthesized 9AGNR 7 in two ways. The first is the all solution route, in which the Scholl oxidation with FeCl₃ is used. Analysis of this sample by Raman spectroscopy (Figure 2.4D) showed the characteristic D and G peaks, as well as the expected overtones. We then dropcast a solution of 6 in DCM onto a freshly cleaned Au(111) surface, which was rapidly reintroduced to UHV. Annealing the sample to 400 °C both helped remove contaminants introduced by exposing the sample to air, and enabled the surface assisted cyclodehydrogenation to yield 9AGNR 7. Figure 2.4C shows an STM topography image, wherein several extended structures of uniform height and width consistent with 7 can be readily identified. Performing Raman spectroscopy on this sample and comparing it to the solution prepared sample (Figure 2.4D) showed that the two samples match nicely with regard to peak positioning, with differences arising mostly in the intensity of the higher order peaks and FWHM of the D and G peaks.

Figure 2.3: A and B) STM images of 4 as deposited on Au(111) at room temperature. C and D) 4 after annealing to 150 °C.
CHAPTER 2. SYNTHESIS OF NOVEL ARMCHAIR GNRS BY SURFACE ASSISTED SYNTHESIS

Figure 2.4: A) GPC trace of 6  B) Raman spectrum of 6  C) STM image of \(N = 9\) AGNR obtained by dropcasting a solution of 6 in \(\text{CH}_2\text{Cl}_2\) onto a freshly cleaned Au(111) surface and annealing to \(400\) °C in UHV, inset: close up of two \(N = 9\) AGNRs. B) Raman spectra obtained for 7 prepared both by solution synthesis with the Scholl oxidation and by surface assisted cyclodehydrogenation.

The modularity of the synthesis of \(N = 9\) AGNR monomer 4 creates the possibility of generating a variety of different GNRs from monomers that can be made by cross coupling of intermediate 2 with the appropriate substituent instead of biphenyl boronic acid as was used in the synthesis of 4. Monomers for which synthetic progress has been made are depicted in Figure 2.5. This allows access to GNRs of different width (8), edge construction (9), doping patterns (10, 11, 12), and solubility (13, \(R = \text{alkyl}\)). The syntheses of these monomers were stalled at the difficult, highly sterically crowded cross coupling needed to create the full backbone, and at the time of writing require further optimization.
Figure 2.5: Alternative monomers considered to make use of modularity of synthesis for 4, available via cross coupling of 2 with the appropriate substituent.

2.2 $N = 11$ Armchair GNR

As a member of the lowest predicted bandgap $N = 3p + 2$ family, $N = 11$ AGNR is an attractive target for expanding the available toolbox. To date, only one member of the $3p + 2$ family has been reported, and the bandgap observed by STS was significantly higher than that predicted by first-principles calculations.

Calculations

First-principles calculations of $N = 11$ AGNRs were performed using DFT in the Quantum Espresso package. The pseudopotentials used were norm-conserving with a plane wave energy cutoff of 70 Ry. The structure was relaxed until the force on each atom was smaller than 0.014 eV. The unit cell dimension along the ribbon axis was relaxed, and 20 Å in the two orthogonal directions to avoid ribbon-ribbon interactions. The Gaussian broadening used in plotting the DOS was 0.01 eV.

Synthesis

The synthesis of 20 was accomplished in seven steps from commercially available 1,3-dicyano benzene (Scheme 2.3). The starting material was selectively iodinated by directed ortho
metallation using LDA, followed by quenching with I₂ to give 15 in moderate yield, followed by bromination with NBS under acidic conditions to produce 16. A double reduction of the cyano groups to aldehydes using Raney-Nickel yielded 17. Ortho-tolyl groups were installed by nucleophilic addition of an o-tolyl Grignard reagent to the aldehydes, followed by PCC oxidation of the resulting diol intermediate to give 18 in 94% over two steps. Isolation of the intermediate diols was found to result in lower overall yield. Dimerization of 18 using Ullman coupling was directed both by known increased activity of iodine over bromine, as well as the direction afforded by having electron withdrawing groups ortho to the desired halogen, yielding 19 in good yield. Final cyclization of 19 to produce the desired monomer 20 was accomplished by heating with P₂S₅, which proceeds through the tetrathione analogue of 19.

Surface Characterization

The results of surface studies of monomer 20 on Au(111) are shown in Figures 2.7 and 2.8. In Figure 2.7 A and B we see that at room temperature, 20 forms well ordered monolayer islands at submonolayer coverage. This is in stark contrast to the formation of amorphous, thick islands formed by 4. We attribute this to the larger planar π-system present in 20 due to the pyrene core that can interact more strongly with the surface, as well as the decreased flexibility of the monomer, allowing for efficient on-surface packing. We anticipate that this preorganization is likely to positively influence the polymerization. After annealing the sample to 150 °C (Figure 2.7C), we continue to observe the presence of well ordered islands with apparent striations. Annealing to 250 °C results in the breaking up of the islands (Figure 2.7D), leaving isolated extended segments that can be attributed to precursor polymer 21.

Further annealing of the precursor polymers to 400 °C efficiently planarized the observable
CHAPTER 2. SYNTHESIS OF NOVEL ARMCHAIR GNRS BY SURFACE ASSISTED SYNTHESIS

Scheme 2.3: Synthesis of 20.

Scheme 2.4: Surface assisted synthesis of 14.
Figure 2.7: STM of 20 as deposited at room temperature on Au(111) (A and B), after annealing to 150 °C (C), and after annealing to 250 °C (D).

features (Figure 2.8). In Figure 2.8A we note the presence of fairly long, planar features of constant width and height consistent with 11AGNR 14. Zooming in on one such structure as seen in Figure 2.8B reveals that sections of the observed features are indeed the desired GNRs. However, also observable at the end of the shown ribbon are segments that appear to be more defective. Focusing on a section of material that appears to be very defect rich in both STM (Figure 2.8C) and NC-AFM (D) reveals that the defect sites appear to be the result of unwanted side reactivity at the site of the methyl groups.

2.3 N-Doped $N = 7$ Armchair GNR

Syntheses
The synthesis of dibromophenazine 25 was accomplished in three isolated steps (Scheme 2.5). Bromination of benzothiadiazole with NBS under acidic conditions to yield 22, followed by NaBH$_4$ reduction of the heterocycle yielded diamine 23 in good yield. Condensation of diamine 23 with quinone 24 generated by K$_2$Cr$_2$O$_7$ oxidation of catechol yielded the target
Figure 2.8: STM of 20 after annealing to 400 °C (A-C), and NC-AFM of the same sample (D).

Scheme 2.5: Synthesis of 25.
25. Tetrabromophenazine 26 was synthesized by extensive bromination of phenazine under acidic conditions.

**Surface Characterizations**

Sublimation of 25 onto a Au(111) surface at room temperature resulted in the planar, lacy pattern observable in Figure 2.9A and B. Annealing the sample to 130 °C at a rate of 5 °C/min to induce homolytic dehalogenation and polymerization to 27, followed by further annealing to 450 °C at the same rate to induce graphitization to GNR 28, yields the structures seen in Figure 2.9C and D. From the larger area scan in Figure 2.9C it is immediately clear that the initial self-assembled structure is gone, replaced by extended high aspect ratio structures as would be expected from successful polymerization. Upon closer inspection (Figure 2.9D), we can see that we do not have the smooth edge structure that would be associated with successful graphitization to GNR 28, but rather a regularly spaced saw-tooth type structure. We attribute this to precursor polymer 27, indicating successful polymerization of 25 to 27 without further reaction. This result indicates that the planarity of 27 on Au(111) allows for strong interaction of each subunit with the surface and prevents the necessary rotation of every other unit that would allow for cyclodehydrogenation.
2.4 Heavily N-Doped $N = 7$ Armchair GNR

Synthesis

To further modify the electronic structure of $N = 7$ AGNR, heavily N-doped GNR 31 was designed, expected to be synthesizable from monomer 29. Polymerization of 29 to yield precursor polymer 30 is expected to occur at temperatures typical of other monomers, $< 200 ^\circ C$. However, unique to this case, the final graphitization step required is not a cyclodehydrogenation reaction, but rather a cyclic N-N bond forming reaction along both sides of the polymer. This reactivity is less understood, and as such the temperature required to effect it is currently unknown.

The synthesis of monomer 29 was performed in five steps from previously synthesized dibromobenzothiadiazole 22. First, dinitration with fuming nitric acid in triflic acid gave 32. Attempts to perform complete reduction of both nitro groups as well as the thiadiazole ring with Zn in AcOH to produce the free tetraamine and condensation with glyoxal to yield
Scheme 2.8: Proposed surface synthesis of heavily N-doped $N = 7$ AGNR 31 to proceed in two steps. First, surface assisted homolytic cleavage of C-Br bonds and diffusion to allow for formation of polymer 30, then further annealing to fully conjugate the polymer to yield GNR 31.

Scheme 2.9: Synthesis of heavily N-doped GNR monomer 29
29 in one sequence were unsuccessful. Instead, the reduction and condensation steps had to be separated and performed in sequence. Reduction of the nitro groups with Fe powder yielded the free diamine 33 in moderate yield, which was then condensed with glyoxal to yield quinoxaline derivative 34. A similar two-step reduction-condensation was performed on the thiadiazole ring by reaction first with LiAlH$_4$ to yield the diaminoquinoxaline 35, then condensation with glyoxal to yield monomer 29.
Chapter 3

Embedding Porphyrin Quantum Dots in Bottom-Up Synthesized GNRs

Quantum dots (QDs) embedded within semiconducting graphene nanoribbons (GNRs) represent a promising class of material for the realization of solid-state quantum computing. In this chapter, the synthesis of an atomically defined and highly tunable GNR-QD-GNR heterostructure is explored. The inclusion and control over the QD placement are confirmed by mass spectrometry and $^{13}\text{C}-\text{NMR}$, and electronic communication and charge transfer between subunits are investigated using UV-Vis and EEM fluorescence spectrosopies. Site selective deposition of the GNR-QD-GNRs onto insulating surfaces is accomplished through coordination of the QDs to amine functionalized sites on the surface, crucial for further device fabrication studies.
CHAPTER 3. EMBEDDING PORPHYRIN QUANTUM DOTS IN BOTTOM-UP SYNTHESIZED GNRS

3.1 Introduction

GNR-QDs

Semiconducting quantum dots (QDs) are considered attractive candidates for solid-state qubits, the fundamental building block of quantum computing. In particular, the use of spin in QDs to be the holder of quantum information has been investigated. For this application, carbon-based QDs are most highly desirable because the low spin-orbit coupling and weak hyperfine interaction in carbon leads to significantly longer spin coherence lifetimes than in other semiconducting QD systems (i.e., GaAs). Among carbon-based materials, graphene’s two-dimensional nature suits it well for integrated quantum nanodevice systems, however the gapless nature of graphene prevents its use directly. For these reasons, quasi one-dimensional semiconducting GNRs are prime candidates for investigating semiconducting QDs.

Experimentally, however, the lithographic methods used to define these confined QDs in GNRs introduce sufficient defect density that the performance of the device is dominated by roughness, obscuring the materials intrinsic properties. Recent progress in the bottom-up synthesis of GNRs allows for the generation of GNRs with atomic control over the width, edge structure, and heteroatom dopants. The extension of the bottom-up synthesis of GNRs to include in-line QDs requires the ability to form atomically controlled heterojunctions within the ribbon. Experimental realizations of this technique have been accomplished by the randomized copolymerization of compatible monomers, meaning that while each junction is well defined, the placement and number of junctions within the ribbon are not. Therefore, extending the control over atomic placement that bottom-up synthesis affords to include control over QD incorporation, new strategies are required.

To ensure perfect control over the number and placement of QDs incorporated into any GNR, a strategy involving heteroditopic monomer and a series of homoditopic linker molecules was developed (Figure 3.1). By utilizing a dialkyne linker unit, the Diels-Alder polymerization guarantees that the active ends of the growing polymer chain express alkynes, thus allowing only the incorporation of more monomer and preventing the incorporation of more linkers.

Cove GNR Synthesis

Alkylated cove-type precursor monomer was synthesized in a modification of a previous literature report (Scheme 3.1). The synthesis is centered on the Knövenagel condensation between diphenylketone, synthesized in two steps from hexadecylbenzene, and 3-bromobenzil to yield the key tetraphenyl cyclopentadienone core. Installation of the terminal alkyne used in polymerization was accomplished by first Sonogashira cross coupling of and TMS-acetylene, followed by silyl deprotection with KF to yield the monomer.
3.2 Pyrene Based QD Linker

Synthesis
Synthesis of $^{13}$C labelled dipropynyl pyrene linker molecule 45, shown in Scheme 3.2 begins with dibromination of pyrene and separation of the 1,4- and 1,6-dibromopyrene isomers. Installation of the two terminal triple bonds is accomplished in two steps from 42 by first Sonogashira cross coupling with TMS-acetylene to yield 43, followed by silyl deprotection with K$_2$CO$_3$ in MeOH to yield diyne 44. Finally, introduction of the $^{13}$C methyl group by deprotonation of the terminal alkynes with BuLi and quenching with $^{13}$C-MeI to give 45.

Incorporation of 45 into the desired polymer 46 was attempted in two ways. First, in the hopes of incorporating 45 between two pre-formed polymer chains, polymerization of 36 was conducted in the absence of 45 for three hours, followed by addition of 45 and further polymerization for 24 h. However, more significant incorporation was achieved by beginning the polymerization in the presence of 47 as in Scheme 3.3 to yield polymer 46 ($M_n=17,000$, PDI=1.3 by GPC). Notable in Figure 3.2B is the presence of a second feature in the GPC trace at higher retention time. This feature has been noted in previous reports of AB type Diels-Alder polymerizations and has been attributed to the formation of cyclic oligomers due to intramolecular head-tail reactivity.$^{87,91}$
CHAPTER 3. EMBEDDING PORPHYRIN QUANTUM DOTS IN BOTTOM-UP SYNTHESIZED GNRS

Scheme 3.1: Synthesis of cove type GNR precursor monomer 36.

UV-Vis

Incorporation of 45 into polymer 46 is evidenced by comparison of distinctive features in the UV-Vis absorption spectra of 45, 46, and poly-36 (Figure 3.2A). The distinctive three peak structure of 45 (red) is mirrored in 46. However, while the features are similar they are notably blue shifted, indicating that the absorption is not due to unreacted 45 present in the mixture, but rather to a reaction of the unit. While this evidence does support the introduction of 45 into the polymer, it does not immediately prove that we have achieved the desired central location. To prove centrality, we turn to $^{13}$C-NMR spectroscopy.

Quantitative $^{13}$C-NMR

Figure 3.3, shows the alkyl region of the $^{13}$C-NMR spectrum of labeled 45 (red) displaying a clear isolated signal at $\delta \approx 5$ ppm. When comparing poly-36 to 46, in the ideal case we
Scheme 3.2: Synthesis of $^{13}$C-labelled pyrene linker 45.

Figure 3.2: A) UV-Vis absorption spectroscopy of 45 (red), 46 (blue), and poly-36 confirming incorporation of the pyrene unit into the polymer. B) GPC trace of 46 ($M_\text{n}=17,000$, PDI = 1.3), displaying a smaller, higher retention peak due to cyclic oligomers ($M_\text{n}=5,400$, PDI=1.0).
would note the complete disappearance of the resonance associated with the propyne methyl group, and appearance of a downshifted benzyl methyl resonance. However, instead, it is obvious that we see incomplete conversion of peak A to B. This would indicate that the produced structure is not the intended, symmetrically functionalized 46, but rather a monofunctionalized 45 acting as a capping agent on poly-36. Quantitative $^{13}$C-NMR analysis reveals that the ratio of symmetrically functionalized 36 to monofunctionalized 36 is 15:1.

This low degree of incorporation at the propyne groups indicates that the internal triple bonds are not kinetically competitive during the polymerization. This is likely due to the increased steric hindrance surrounding the triple bonds of 45 when compared to the triple bonds of monomer 36 (Figure 3.4). This results from two structural changes: replacing a terminal hydrogen with a methyl group, and the added bulk of the fused pyrene ring. Because of this congestion the rate of reaction of the monomer is so much greater than that of the linker that while inclusion is not completely excluded, it is low enough to prevent its use in this system. To explore this hypothesis and remedy the problem, tetrphenyl linker
Figure 3.3: $^{13}$C-NMR of 45 (red), 46 (blue), and poly-36 (black) demonstrating incomplete, asymmetric reactivity of linker 45.

48 was designed to have terminal triple bonds with steric bulk more comparable to that of 36.

### 3.3 Tetraphenyl Based QD Linker

**Synthesis**

Tetraphenyl linker candidate 48 was designed to have more kinetically competitive triple bonds than the predecessor 45. To increase steric bulk while maintaining the analytical handle that $^{13}$C labeling affords, the isotopic enrichment was moved from a methyl group to the terminal triple bond carbon. Synthesis begins with 2 (Scheme 3.4), which was previously synthesized for the production of $N = 9$ AGNR monomer 4. Suzuki-Miyaura cross coupling of 2 with phenylboronic acid yielded tetraphenyl core 49. Conversion of the amines to labelled alkynes was accomplished in four steps. First, a modified Sandmeyer reaction replaced the amines with iodine atoms yielding 50. Lithium-halogen exchange, followed by quenching with DMF then afforded dialdehyde 51. Installation of the isotopically en-
Figure 3.4: Increased steric bulk around the internal alkynes of 45 as compared to monomer 36 results in lower inclusion. Tetraphenyl linker 48 is designed to be more kinetically competitive.

Scheme 3.4: Synthesis of $^{13}$C-labelled tetraphenyl linker 48.
riched carbons was then achieved via Wittig reaction with $^{13}$C-MePPh$_3$I, followed by one-pot tetrabromination-elimination to yield labelled diyne 48. Incorporation of 48 into polymer 53 was accomplished analogously to 46 (Scheme 3.5). Analysis by GPC (Figure 3.5B) shows a main peak ($M_n=11,000$, PDI=1.3), with the secondary peak noted in Figure 3.2B appearing as a shoulder instead of an isolated peak due to greater overlap.

$^{13}$C-NMR

Figure 3.5A shows a comparison of the aryl regions in the $^{13}$C-NMR spectra of poly-36 and 53. As in the case of the $^{13}$C-NMR analysis of 46, all of the resonances present in the aryl region of poly-36 find matches in 53. The important distinction to be made between this system and the previous one is the complete disappearance of the alkyne resonance associated with 48, indicating that the decreased steric hindrance of 48 has indeed made
CHAPTER 3. EMBEDDING PORPHYRIN QUANTUM DOTS IN BOTTOM-UP SYNTHESIZED GNRS

![Graph](image)

Figure 3.5: A) $^{13}$C-NMR comparison between poly-$^{36}$ and $^{53}$, displaying a prominent new peak corresponding to the isotopically enriched carbons. B) GPC trace of $^{53}$, $M_n=11,000$; PDI=1.3.

...the alkynes more kinetically competitive, enabling symmetric placement of the linker within the polymer.

### 3.4 Porphyrin Based QD Linker

With this information regarding effective design of the linking moieties, a more electronically interesting and tunable system was designed for inclusion in the GNR-QD-GNR architecture. Porphyrins have been the subject of many molecular electronics studies, due in part to their propensity for electronic communication both in plane and, in the case of various metalloporphyrins, axially. Their highly tunable metal centers allow for fine tuning their magnetic and electronic properties, as well as their interaction with axially coordinated ligands. For these reasons, porphyrins are an attractive candidate for incorporation into a GNR-QD-GNR system.

**Synthesis**

To ensure symmetric, approximately linear incorporation into the precursor polymer, as well as to allow for continued monitoring by $^{13}$C-NMR, $A_2B_2$ tetraaryl porphyrin $^{57}$ was chosen as a QD candidate. Synthesis of $^{57}$ is best accomplished by coupling aldehyde $^{56}$ with presynthesized meso-phenyldipyrrromethane to reduce scrambling and formation of other, undesired porphyrin species as in Scheme 3.6. Aldehyde $^{56}$ was synthesized in three steps from monoprotected para-phthalaldehyde by first the two-step conversion of the aryl aldehyde to isotopically enriched alkyne $^{55}$ by Wittig reaction with $^{13}$C-MePPh$_3$I, followed by bromination and elimination. Deprotection of the remaining acetal yields the requisite coupling partner $^{56}$. Macrocyclization yields $A_2B_2$ porpyrin $^{57}$ in 11% yield.
Scheme 3.6: Synthesis of $^{13}$C-labelled porphyrin linker 57.

Figure 3.6: $^{13}$C NMR of 57 showing clear $^{13}$C enrichment of the terminal alkyne carbon, poly-36, and 58, demonstrating clear consumption of labeled alkynes and replacement by a new aromatic peak B.

Synthesis of 58 was performed analogous to 53 and 46 by copolymerization of 36 and 57 in Ph$_2$O at 230 °C (Scheme 3.7). $^{13}$C-NMR (Figure 3.6) confirms that the sterically unhindered terminal triple bonds of 57 are as kinetically competent as those of 36 and 48. Complete disappearance of the isotopically enriched terminal alkyne carbon labelled A in 57 and the presence of peak B at $\delta = 130$ ppm supports complete, symmetric incorporation.

An unavoidable side product of the polymerization is homopolymer poly-36. While not readily detectable by analytical techniques like NMR or GPC, this impurity can be detected
with MALDI-MS as shown in Figure 3.7A. The spectrum shows two clear families of peaks that have the repeat unit of the monomer (829 D), separated from each other by the mass of the porphyrin (662 D). Fractionation of the polymer mixture was accomplished via silica gel chromatography, eluting with 10% DCM in hexanes. With this, isolated samples of 58 and poly-36 were obtained, as evidenced by MALDI-MS in Figure 3.7C and 3.7E respectively. This technique is most effective for smaller lengths of functionalized polymer, due to the increased contribution of the porphyrin to the overall polarity of the polymer, which can be seen when comparing the GPC traces of the resulting samples (Figure 3.7B, D, F). While the fractionated sample of poly-36 (Figure 3.7F) is similar in length to the crude mixture (B), the isolated sample of 58 is notably shorter (D).
Figure 3.7: A) MALDI-MS and (B) GPC trace of crude mixture of 58 and poly-36 (C) MALDI-MS and (D) GPC trace of fractionally isolated 58 (E) MALDI-MS and (F) GPC trace of the remaining, fractionally isolated poly-36.
Figure 3.8: A) Raman spectrum of GNR-QD-GNR 60. B) UV-Vis absorption spectra of precursor polymer 58 (black), cove type GNR 59 (blue), and GNR-QD-GNR 60 (red).

Graphetization and Raman

Porphyrin functionalized precursor polymer 58 was converted to GNR-QD-GNR 60 using Scholl oxidation conditions with FeCl₃ in DCM and MeNO₂. The resulting black powder was characterized by Raman spectroscopy (Figure 3.8A), which displays features consistent with unfunctionalized cove type GNRs, with notably narrow G band and well defined higher order peaks, indicating an efficient conversion.

UV-Vis

Both cGRNs 59 and GNR-QD-GNR heterostructures 60 featuring solubilizing hexadecyl side chains form stable dispersions after sonication and centrifugation in THF. The respective UV-vis absorption spectra are depicted in Figure 3.8B. A broad absorption at \( \lambda_{\text{max}} = 556 \) nm characteristic for cove-type GNRs dominates the spectrum of 60. The \( \lambda_{\text{max}} \) of GNR-QD-GNR heterostructures 60 is only slightly shifted (\( \approx 6 \) nm) to shorter wavelength when compared to the absorption of pristine cGNRs. A second prominent absorption at \( \lambda = 433 \) nm in the spectrum of 60 can be attributed to the corresponding \( S_0 \rightarrow S_2 \) transition (Soret band) in the porphyrin core, while the characteristic Q-bands are obscured by the dominant absorption of the cove-type GNR segments. The bathochromic shift (\( \approx 10 \) nm) of the Soret band in 60, compared to the A₂B₂ precursor 57 (\( \lambda_{\text{max}} = 423 \) nm), can be attributed to an efficient electronic coupling with the extended \( \pi \)-system of the adjacent cove-type GNRs.

Fluorescence

Figure 3.9A,B shows the excitation emission matrix (EEM) fluorescence spectra for cGNRs 59 and GNR-QD-GNR heterostructures 60, respectively. Excitation of both pristine cGNRs
and 60 at $\lambda_{Ex} = 560$ nm leads to a broad fluorescence centered around $\lambda_{Em} = 705$ nm. If however the GNR-QD-GNR heterostructure 60 is excited at $\lambda_{Ex} = 425$ nm, close to the Soret band of the porphyrin core, a very broad emission $\lambda_{Em} = 650–720$ nm featuring characteristics of both the porphyrin and cove-type GNRs is observed. This indicates that the porphyrin $S_2$ excited state is able to relax either by fluorescing, or by transferring the excited state energy to the GNRs, which then fluoresce. The exchange between excited states in the porphyrin and the GNR further support a limited electronic communication between the central porphyrin quantum dot and the extended GNR segments.

**Surface Functionalization and Raman Mapping**

Fabrication of devices from isolated GNRs has been a major difficulty due to non-selective deposition and the tendency to form bundles. An ideal deposition technique would utilize a means of increasing the strength of the interaction between the substrate surface being deposited onto and individual GNRs. The open axial coordination sites of Zn@60 provide just such an opportunity. By functionalizing the target metal oxide surface with a self assembled monolayer (SAM) containing a coordinating group (in this case amines) as shown in Figure 3.10, deposition of Zn@60 followed by removal of non-adhered material can yield even coverage without bundling.

Samples were prepared by patterning an Al$_2$O$_3$ on Si surface with Pt strips. After cleaning the exposed Al$_2$O$_3$ with O$_2$ plasma, the wafers were functionalized with aminated silane (MeO)$_3$Si(CH$_2$)$_3$NH(CH$_2$)$_6$NH$_2$ in refluxing toluene. The now aminated surfaces were submerged in a well dispersed sample of Zn@60, and then thoroughly rinsed to remove any non-adhered material. Mapping the intensity of the G peak in the Raman spectra on the resultant surface shows clear differentiation between areas that did and did not contain the coordinating SAM (Figure 3.11B), mirroring the same pattern seen in the optical image.
Scheme 3.8: Metallation of 60 to form metalloporphyrin GNR-QD-GNR heterostructure Zn@60.
Figure 3.10: Functionalization of insulating surfaces (SiO$_2$ or Al$_2$O$_3$) with a coordinating aminosilane guides selective deposition of Zn@60.
Figure 3.11: Optical microscopy image of Pt patterns on functionalized Al$_2$O$_3$ and Raman mapping of the G band of substrates after B) amine functionalization and Zn@60 C) hydrocarbon functionalization and Zn@60 D) amine functionalization and 59.

(Figure 3.11A). In order to ensure that the selectivity seen is a result of axial coordination to the Zn metalloporphyrin, control experiments were undertaken. In the case of using Zn@60 and a strictly non-coordinating hydrocarbon SAM, as well as in the case of the coordinating SAM with unfunctionalized cGNR, no contrast was observed in the Raman maps (Figure 3.11C and D respectively). It is worth noting that any minor features seen in Figure 3.11C or D are the result of inconsistent baseline, and not from observable G peaks (Figure 5.1).

**Conclusion**

In conclusion, a novel GNR-QD-GNR heterostructure with well defined stoichiometry and connectivity has been synthesized. Electronic characterization by UV-Vis absorption and EEM fluorescence spectroscopies reveals electronic communication between the constituent moieties. Selective, site specific deposition of the metal functionalized GNR-QD-GNR onto
insulating surfaces functionalized with a coordinating SAM was performed and confirmed by mapping the G peak intensity in the Raman spectra. Future efforts will focus on device fabrication and characterization.
Chapter 4

GNRs as a Support Material for Inorganic Nanoparticles

In this chapter, bulk solution synthesized graphene nanoribbons are explored as conductive support materials for inorganic nanoparticles of two different applications: Au nanoparticles for electrocatalytic reduction of CO$_2$ to CO and SnO$_2$ nanoparticles as an anode material in lithium ion batteries. In both cases it is demonstrated that the GNRs form a flexible conductive matrix that stabilize the nanoparticles while allowing efficient electron and mass transport through the composite. Composite materials are additionally characterized by SEM, TEM, STEM, and Raman spectroscopy.

Parts of this chapter have been published in:
CHAPTER 4. GNRS AS A SUPPORT MATERIAL FOR INORGANIC NANOPARTICLES

While previous chapters have focused on the development of synthetic methods for novel GNRs and GNR heterostructures intended for single ribbon devices and applications, this chapter focuses on use of GNRs as a bulk material. The inherent tunability, conductivity, and tendency to form porous aggregates make GNRs an attractive replacement for other graphitic materials commonly used in the support of inorganic nanoparticles. Two types of nanoparticles in particular will be explored here: Au nanoparticles used in the electrocatalytic reduction of CO$_2$ to CO, and SnO$_2$ nanoparticles used in potential next-generation lithium ion batteries.

4.1 Au Nanoparticles for CO$_2$ Reduction

Inorganic nanostructured materials, primarily realized in the form of nanoparticles (NPs), have emerged as competent heterogeneous catalysts for challenging chemical transformations.\textsuperscript{110–113} While nanostructured catalysts promote the industrial scale production of value added chemicals, more recently their characteristics have inspired NP-based water splitting, fuel cell, and carbon dioxide (CO$_2$) reduction catalysts, relevant to a sustainable clean energy cycle.\textsuperscript{114,115} While traditional catalyst design has focused on intrinsic structural parameters like size, shape, and composition of NPs,\textsuperscript{116–122} the more complex variables of the nanostructured catalytic environment and the dynamic mass- and energy-transport processes at the solid/liquid or solid/gas interface remain insufficiently understood.\textsuperscript{123} A more inclusive model that embraces the multifaceted role of the support along with the demonstrated tunability of NPs themselves offers new opportunities for the design and performance optimization of heterogeneous catalyst systems.\textsuperscript{124} Indeed, the structural diversity of chemical environments surrounding catalytically active sites at the surface of NPs are typically described by ensemble measurements,\textsuperscript{59,125,126} and this analytical challenge is further convoluted by the inherent inhomogeneity of common support materials such as carbon black (C$_{\text{black}}$), reduced graphene oxide (rGO), carbon nanotubes (CNTs), or inorganic metal oxides (MO$_x$) at the nanometer scale, preventing the development of instructive structureperformance relationships. By rational bottom-up design of a functional GNR support material it is possible to boost key performance parameters such as stability, selectivity, and activity, thereby enhancing the electrocatalytic reduction of CO$_2$ by gold nanoparticles (AuNPs) in aqueous solution. Electrochemical measurements further reveal that this molecular-materials support can influence the mechanism for CO$_2$ reduction at the nanoparticle interface.

AuNPs are appealing CO$_2$ reduction electrocatalysts as they offer aqueous compatibility and reasonable selectivity for CO$_2$ reduction to CO, together with the high surface area inherent to metal nanoparticles.\textsuperscript{117,127} As electrocatalytic reduction of CO$_2$ at the surface of metal NPs follows a proton-coupled mechanism, it necessarily faces competing proton reduction, limiting the Faraday efficiency (FE) for CO production.\textsuperscript{128,129} Moreover, competent nanoparticle catalysts frequently contend with low activity or prohibitively high overpotential for bulk applications.\textsuperscript{115,119,130,131} Most pressing, however, is the issue of catalyst stability, as many nanoparticle electrocatalyst systems deliver strong performance for only minutes
Figure 4.1: Design and bottom-up synthesis of GNR-AuNP composite materials. (A) Synthesis of chevron GNRs from molecular precursors. (B) Synthesis of cove GNRs from molecular precursors. Schematic representation of 63, and 66 composite materials is not to scale.

before degrading under harsh electrocatalytic conditions. Efforts to mitigate premature catalyst deactivation have highlighted the role of the support material in stabilizing nanodispersed metals. Graphitic support materials in particular have drawn significant interest, largely because their structure and electronics facilitate strong interaction between the carbon support and metal nanoparticles. These strong d-π interactions lead to enhanced dispersion and stabilization of metal NPs and can serve to modulate the electronic structure at the NP surface. As such, graphene, GO, rGO, and CNTs have been investigated as nanoparticle support materials, particularly in the contexts of fuel cells and thermal catalysis. While each of these graphitic materials carries certain inherent strengths and limitations, all of them notably lack rational tunability and structural homogeneity on the nanometer scale.

GNRs offer structural precision and tunability unrivaled among graphitic materials, since their structure follows deterministically from small-molecule precursors readily modified through organic synthesis. Electronic homogeneity follows from structural homogeneity, and as such, bottom-up GNRs do not contend with the variable band gaps and metallicity found in CNTs as previously discussed. With the combination of structural and electronic tunability with mechanical flexibility and a high aspect ratio graphitic topology, bottom-up GNRs are appealing materials for enhancing support-NP interaction and thereby exerting control over catalytic performance and stability. The potential enhancement is not restricted to the mechanical immobilization of metallic NPs within an inert matrix, but takes advantage of charge transfer at the GNR-metal NP interface, a Mott-Schottky heterojunction, that can
 CHAPTER 4. GNRS AS A SUPPORT MATERIAL FOR INORGANIC NANOPARTICLES

Figure 4.2: Electron microscopy of AuNPs and AuNP-GNR composites. (A) HAADF-STEM images of oleylamine-capped AuNPs show a narrow size distribution centered around an average NP diameter of 8 nm. (B) HAADF-STEM of unannealed 66a composite shows the uptake of a high density of AuNPs into the GNR aggregate. (C) HAADF-STEM and (D) TEM images of 63 composite after annealing. (E) HAADF-STEM and (F) TEM images of 66a composite after annealing. (G) HAADF-STEM and (H) TEM images of 66b composite after annealing.

give rise to superior catalytic performance. Inspired by the use of graphitic support materials (e.g., graphene, rGO, CNTs, mesoporous carbon), we explored structurally defined bottom-up synthesized GNRs as a functional support for AuNP electrocatalysis.

Chevron GNRs (62) and cove GNRs (65a) were synthesized following the bottom-up strategy outlined in Figure 4.1. While chevron GNR precursor 61 was prepared following a reported procedure, the synthesis of molecular precursors for cove GNRs 64a and 64b is depicted in Scheme 4.1, following a general structure similar to the alkylated cove GNR precursor 36 discussed in previous chapters. Knoevenagel condensation of 67 with 1,3-diphenylpropan-2-one yielded the brominated cyclopentadienone 68. Sonogashira cross-coupling of 68 with ethynyltrimethylsilane followed by deprotection of the TMS group gave the heterobifunctional molecular building block 64a. The inherent flexibility of a rational bottom-up synthesis of graphene nanoribbons from molecular precursors is illustrated by the synthesis of a 64b, a derivative of 64a featuring methyl esters along its edges (Scheme 4.1). Knoevenagel condensation of 69 with 1,3-bis(4-bromophenyl)propan-2-one gave cyclopentadienone 70, featuring both iodide and bromide substituents on the aromatic rings. Selective Sonogashira crosscoupling of 70 with ethynyltriisopropylsilane yielded the dibromo-cyclopentadienone 71. Pd-catalyzed carbonylation of 71 in MeOH followed by deprotection...
of the TIPS group with AgF gave the molecular precursor for methyl-ester-functionalized cove GNRs 64b.\textsuperscript{166,167}

Step-growth polymerization of 2,7-dibromophenanthrene\textsuperscript{61} or cyclopentadienone 64a, followed by oxidative cyclodehydrogenation, yields structurally homogeneous samples of GNRs 62 and 65a, respectively.\textsuperscript{84,89,168} Notably, these syntheses are scalable, and can afford grams of GNR at a time. Raman spectroscopy of 62 and 65a shows the characteristic signatures for D, G, and radial breathing like modes (RBLM) that are consistent with the formation of extended GNRs (Figure 5.2).\textsuperscript{86,88,99} The successful removal of trace metals (Fe, Ni) used in the bottom-up synthesis of GNRs was confirmed by X-ray photoelectron spectroscopy (XPS) (Figure 5.3).

### Table 4.1: Physical and Electrocatalytic Characterization of AuNP Composites.

<table>
<thead>
<tr>
<th></th>
<th>BET Surface area\textsuperscript{a} (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>AuNP electrochemically active SA\textsuperscript{b} (cm\textsuperscript{2}mg\textsuperscript{-1} AuNP)</th>
<th>onset potential\textsuperscript{c} (mV vs RHE)</th>
<th>CO\textsubscript{2} reduction activity\textsuperscript{d} j\textsubscript{co}(A g\textsuperscript{-1})</th>
<th>ECSA-normalized CO\textsubscript{2} reduction activity\textsuperscript{d} j\textsubscript{co} (mA cm\textsuperscript{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>63</td>
<td>19.8</td>
<td>2.87</td>
<td>-0.36</td>
<td>22.6</td>
<td>7.87</td>
</tr>
<tr>
<td>66a</td>
<td>5.9</td>
<td>4.60</td>
<td>-0.14</td>
<td>36.8</td>
<td>8.00</td>
</tr>
</tbody>
</table>
| C
| 64b    | 26.8                            | 1.70                            | -0.54                           | 6.4 g                            | 3.76                            |
| black–AuNP | 26.8                            | 1.70                            | -0.54                           | 6.4 g                            | 3.76                            |

\textsuperscript{a}Measured by N\textsubscript{2} sorption at 77 K. \textsuperscript{b}Measured by lead underpotential deposition. \textsuperscript{c}Potential at which total CV activity exceeded 0.5 mA cm\textsuperscript{2}, measured in 0.5 M aqueous KHCO\textsubscript{3} saturated with CO\textsubscript{2} (pH 7.3). \textsuperscript{d}Total CV activity at -0.87 V vs RHE, measured in 0.5 M aqueous KHCO\textsubscript{3} saturated with CO\textsubscript{2} (pH 7.3).

Oleylamine-capped monodisperse AuNPs were synthesized following a procedure derived from a previously reported method.\textsuperscript{130,169} High-angle annular dark field scanning transmis-
Figure 4.3: Characterization of AuNP-GNR composite materials. (A) IR spectroscopy of 63 composite materials prior to (black) and after (red) annealing. The characteristic vibronic signature associated with the oleylamine capping ligand is absent after the annealing at 185 °C for 10 h. (B) Raman spectra of 63 (blue) and 66a (red) exhibit unaltered characteristic GNR peaks. (C) PXRD patterns of GNR- and C_{black}-AuNP composite powders exhibit the characteristic signals of AuNPs. (D) 298 K CO\textsubscript{2} adsorption experiment for GNR- and C_{black}-AuNP composites. Despite having lower BET surface areas, GNR composites uptake more CO\textsubscript{2} than the comparable C_{black} composite, reflecting their greater microporosity. (E) PXRD of composite AuNP electrodes prepared by depositing 66b (black), 66a (red), 63 (blue), and C_{black}-AuNP (green) on conductive carbon paper (gray) followed by annealing at 185 °C for 10 h.
CHAPTER 4. GNRS AS A SUPPORT MATERIAL FOR INORGANIC NANO Particles

sion electron microscopy (HAADF-STEM) of AuNPs shows the expected narrow size distribution centered around an average NP diameter of 8 nm (Figure 4.2A). GNR-AuNP composite materials were prepared by sonicating a dispersion of equal mass of AuNPs and the respective GNRs 62 or 65a in hexane. The high affinity of AuNPs for the GNR support is immediately evident as the red AuNP solution loses its characteristic color upon sonication with GNRs, becoming a dark suspension. HAADF-STEM of the isolated black powder, rinsed with hexane and drop cast onto TEM grids, shows the uptake of the AuNPs into large nanoribbon aggregates (Figure 4.2B). GNR-AuNP composites commonly range in size from 0.2 to 1.0 µm and feature a substantial concentration of nanoparticles; STEM images of GNR samples prepared without AuNPs show aggregates of comparable size and morphology (Figure 5.4). The high density of AuNPs and the lateral overlap observed in transmission mode images suggest the AuNPs are embedded within a threedimensional GNR network, rather than perched on its surface.

Following incorporation of AuNPs into the GNR matrix, the oleylamine capping ligands decorating the surface of AuNPs were removed by annealing GNR-AuNP composites in air at 185 °C for 10 h.127 STEM and TEM images of annealed samples show that composite aggregates remain intact and are comparable in size and morphology to those observed prior to annealing (Figure 4.2C–F). IR spectra of samples prior to and immediately after annealing confirm that the oleylamine ligands have been removed, leaving pristine AuNPs behind (Figure 4.3A).169 Raman spectra of annealed GNR-AuNP composites show no shift or broadening of the diagnostic D, G, and RBLM modes (Figure 4.3B), indicating that the integral structure of the GNRs remains unaltered. Powder X-ray diffraction (PXRD) of the black GNR-AuNP composite shows the characteristic broadened signals of AuNPs (Figure 4.3C).130,170 Although the NPs have been stripped of their stabilizing ligand shell, only minimal coalescence of the nanoparticles during the annealing process is observed by STEM, indicating an efficient stabilization of uncapped AuNPs through dispersion interactions with the GNR matrix.

Traditionally, NP support materials emphasize high surface area as a crucial factor to dynamic mass transport to and from the catalytically active surface.114,171,172 However, surface area measurements derived from N2 adsorption at 77 K (BET model, Table 4.1 showed that both 66a (5.9 m2 g−1) and 63 (19.8 m2 g−1) composites present lower surface areas than a reference composite prepared from Cblack-AuNP (26.8 m2 g−1). This behavior is not unexpected in aggregates of a graphitic material, for which strong dispersion interactions between graphene planes lead to stacking and low BET surface area.173 Furthermore, it has been shown that N2 adsorption at 77 K does not appreciably capture ultramicroporosity (pore size < 0.7 nm) due to restricted diffusion of N2 into micropores at low temperature.174–178 CO2 absorption at 298 K is not restricted by micropore diffusion and provides a better approximation for the transport of small gas molecules through the GNR matrix.179,180 AuNP composites of 62 and 65a show more than twice the CO2 uptake measured for the Cblack-AuNP reference (Figure 4.3D), reversing the trend in BET surface area observed for N2 adsorption. These results suggest a significant microporosity for the GNR aggregates in comparison to the Cblack composite, and is an indication that GNRS, despite their inherently
CHAPTER 4. GNRS AS A SUPPORT MATERIAL FOR INORGANIC NANOPARTICLES

Figure 4.4: (A) Lead underpotential deposition experiments to determine the AuNP electrochemically active surface area (ECSA) of AuNP composite electrodes. Pb-UPD experiments for 63 composite electrodes (blue), 66a composite electrodes (red), and 66b composite electrodes (black) indicate much higher ECSA for the GNR composites than for C\textsubscript{black}-AuNP composite electrodes (green). The active surface area was determined on the basis of a reference Au foil electrode (black). (B) Cyclic voltammograms of 63 (blue), 66a (red), and 66b (black) composite materials in 0.5 M aqueous KHCO\textsubscript{3} saturated with CO\textsubscript{2} (pH 7.3). The performance of C\textsubscript{black}-AuNP (green) serves as a standard reference. (C) Cyclic voltammograms of 62 (blue), 65a (red), and 65b (black) electrodes, prepared without AuNPs, in 0.5 M aqueous KHCO\textsubscript{3} (pH 7.3) saturated with CO\textsubscript{2} (full lines) and N\textsubscript{2} (dotted lines). (D) Cyclic voltammograms of 63 composite electrodes (blue) and 66a composite electrodes (red) in 0.5 M aqueous KHCO\textsubscript{3} (pH 7.3) saturated with Ar. (E) Faradaic efficiencies for CO production (FE\textsubscript{CO}) by 63 (blue triangles), 66a (red circles), 66b (black squares), and C\textsubscript{black}-AuNP (green diamonds) composite electrodes. Electrolysis performed at potentials from -0.37 to -0.87 V vs RHE in 0.5 M aqueous KHCO\textsubscript{3} saturated with CO\textsubscript{2} (pH 7.3). (F) Partial current for CO production (\textit{j}_\textit{CO}) by 63 (blue triangles), 66a (red circles), 66b (black squares), and C\textsubscript{black}-AuNP (green diamonds) composite electrodes. Electrolysis performed at regular potentials from -0.37 to -0.87 V vs RHE in 0.5 M aqueous KHCO\textsubscript{3} saturated with CO\textsubscript{2} (pH 7.3).
low surface area, can facilitate mass transport within NP composite aggregates.

We determined the electrochemically active surface area (ECSA) of AuNP composites using lead underpotential deposition experiments (Pb-UPD) (Figure 4.4A and Table 4.1. All samples display two characteristic signals in the Pb-UPD voltammograms, corresponding to lead deposition on the Au(111) and Au(110) faces, respectively. Integration of the peaks in comparison to a Au foil standard provides a quantitative measure of the accessible surface area of the AuNPs. Electrodes fabricated from GNR-AuNP composites have greater ECSA values (2.87 and 4.60 cm$^2$/mg AuNP for composites, respectively) than the corresponding C$_{black}$-AuNP reference (1.70 cm$^2$/mg AuNP) at the same nanoparticle loading. ECSA is a direct quantitative measure for the ability of a support material to disperse and immobilize nanoparticles without obstructing the transport of reactants and products to and from the nanoparticle surface. The significantly higher ECSA measured for GNR-AuNP composites indicates that GNRs, and in particular GNR 65a, facilitate the dispersion of AuNPs and do not obstruct access to the catalytically active metal surface.

In an effort to benchmark the performance of GNR-AuNP composite materials with respect to traditional supports like C$_{black}$, we studied the electrocatalytic reduction of CO$_2$ in aqueous KHCO$_3$ buffered solution. AuNP composites with single-walled carbon nanotubes (SWCNTs) were examined as a second point of reference, but the comparatively poor performance of the SWCNT composites made them an unsuitable standard (Figure 5.5). GNR-AuNP composite electrodes were fabricated by drop casting a sonicated dispersion of AuNPs and the respective GNRs (1:1 by mass with either or 65a; composites made using GNR 65b are discussed later) in hexane onto conductive carbon paper, followed by thermal annealing in air at 185 °C for 10 h. The characteristic PXRD pattern of AuNPs in these annealed electrodes matches that of the composite bulk powders characterized above (Figure 4.3E). Cyclic voltammetry of the resulting composite electrodes (Figure 4.4B) in 0.5 M aqueous KHCO$_3$ saturated with CO$_2$ (pH 7.3) reveals a strong synergistic effect between nanoparticles and GNRs. Composite electrodes formed from GNRs or 65a and AuNPs deliver significantly more current than corresponding electrodes made from AuNPs alone, or AuNPs supported by a C$_{black}$ matrix. Notably, electrodes fabricated from GNRs without any added AuNPs produce minimal current across the entire examined potential window (Figure 4.4C), indicating that the GNRs themselves are not electrochemically active. The current enhancement observed in GNR-AuNP composite electrodes disappears in the absence of CO$_2$ (Figure 4.4D), suggesting the excess current drives CO$_2$ reduction.

When compared to a C$_{black}$-AuNP reference, GNR composites exhibit a catalytic onset (defined here as the potential at which current density exceeds 0.5 mA cm$^2$) at significantly positively shifted potentials (0.36 V for 63 and 0.14 V for 66a composites, versus 0.54 V for C$_{black}$- AuNP, all potentials versus reversible hydrogen electrode (RHE), Table 4.1, indicating the catalytic environment created by the GNR support significantly lowers the required overpotential for CO$_2$ reduction on AuNPs. This shift in catalytic onset is consistent with the formation of a Mott Schottky heterojunction at the GNR-AuNP interface. Lower work function materials promote charge migration across the semiconductorNP inter-
Figure 4.5: (A) Faraday efficiencies for CO production ($\text{FE}_{\text{CO}}$) by 63 (blue triangles), 66a (red circles), 66b (black squares), and $\text{C}_{\text{black}}$-AuNP (green diamonds) composite electrodes. Electrolysis performed in 0.5 M aqueous KHCO$_3$ saturated with CO$_2$ (pH 7.3). (B) Total volume (at STP) of CO produced by 63 (blue triangles), 66a (red circles), 66b (black squares), and $\text{C}_{\text{black}}$-AuNP (green diamonds) composite electrodes. Electrolysis performed in 0.5 M aqueous KHCO$_3$ saturated with CO$_2$ (pH 7.3). (C) Total current density for 66a (red line) and 66b (black line) over 24 h. Faraday efficiency for CO production with 66a (red circles) and 66b (black squares) over 24 h. Both current density and Faraday efficiency show little change between 10 and 24 h of fixed potential electrolysis at -0.47 V vs RHE. (D–F) Cyclic voltammograms for lead underpotential deposition experiments on AuNP composite electrodes following extended controlled-potential electrolysis at -0.47 V vs RHE, to measure the change in AuNP ECSA. Cyclic voltammetry was performed in 0.1 M aqueous KOH containing 1 mM Pb(OAc)$_2$ and purged with Ar. (D) $\text{C}_{\text{black}}$-AuNP composite electrodes exhibit a significant decline in ECSA following fixed potential electrolysis experiments. (E) 63 composites and (F) 66a composites retain almost all of their ECSA following fixed potential electrolysis experiments.
face toward the high work function AuNPs, increasing electron density at the metal surface and shifting the catalytic onset.\textsuperscript{139,150,152,153,183–188} Theory and experiment indicate that the semiconducting GNRs employed here, and particularly cove-type GNRs, feature appreciably lower work functions than other carbon supports like graphene or C\textsubscript{black}, consistent with the positively shifted onset potentials observed Table 4.1.\textsuperscript{86,145,154,187,189–193}

One hour controlled-potential electrolysis experiments over a potential range from 0.87 to 0.37 V underline the synergy between AuNPs and GNRs. Both Faraday efficiency (FE\textsubscript{CO}, Figure 4.4E) and partial current (\(j\textsubscript{CO}\), Figure 4.4F) for CO\textsubscript{2} reduction to CO by GNR-AuNP composites dramatically exceed those of C\textsubscript{black}-AuNP across a broad potential window. Selectivity in particular was starkly improved for GNR composites, with increased \(j\textsubscript{CO}\) leading to FE\textsubscript{CO} values exceeding 80%, as much as 29 percentage points higher than those of C\textsubscript{black}-AuNP composites across the entire potential window. \textit{66a} composites deliver the highest activity and selectivity, consistent with a larger ECSA and lower CO\textsubscript{2} reduction onset potential.

Notably, at potentials distant from their catalytic onsets, the activity of GNR composites is closely proportional to their measured ECSAs (Table 4.1). While GNRAuNP composites do not suppress hydrogen evolution, as the partial current for proton reduction (\(j\textsubscript{H2}\)) is comparable to C\textsubscript{black}-AuNP composites (Tables 5.1–5.4), the observed increase in selectivity reflects a greatly enhanced activity of GNR-AuNPs toward CO\textsubscript{2} reduction.

We performed bulk electrolysis experiments to evaluate the ability of GNRs to stabilize AuNPs overextended reaction times (Figure 4.5A). AuNPs supported by C\textsubscript{black} degrade rapidly, delivering only 22% FE\textsubscript{CO} after 3 h. Electrodes instead fabricated from GNR-AuNP composites maintain superior performance for more than 10 h of continuous electrolysis. At -0.47 V, \textit{66a} composites retained 88% of their original FE\textsubscript{CO} after 10 h of catalysis, and produced more than 33 mL CO/mg of AuNP, compared with only 0.4 mL CO/mg AuNP for the C\textsubscript{black} composite electrodes prepared from the same AuNPs (Figure 4.5B). Longer controlled-potential experiments indicated that the \textit{66a} composite in particular had reached a plateau of stability; with over 24 h of uninterrupted catalysis at -0.47 V, the composite delivered 87% of its original FE\textsubscript{CO}, nearly unchanged from the 10 h experiment (Figure 4.5C).

We interrogated the origin of nanoparticle stabilization in GNR-AuNP composites. PbUPD experiments at selected time points during bulk electrolysis reveal the change in the ECSA of the AuNPs. During the electrolysis with C\textsubscript{black}-AuNP composites (-0.47 V), a significant reduction in active Au surface area, that correlates with the loss of catalytic activity, can be observed within hours (Figure 5D). After 4 h of catalysis, only 48% of the original Au surface area remains, and only 15% is retained after 10 h. TEM images of C\textsubscript{black}-AuNP composites recorded following 3 h of bulk electrolysis suggest that a plausible mechanism of deactivation relies on the coalescence of AuNPs to form larger aggregates with significantly reduced active surface area (Figure 5.6).\textsuperscript{132} \textit{63} (Figure 4.5E) and \textit{66a} (Figure 4.5F) composites effectively prevent NP coalescence and the associated reduction in ECSA. \textit{66a} composites in particular lose only 4% of their active Au surface area over 4 h of catalysis (10% over 10 h). We suggest that the effective immobilization of the NPs through strong
dispersion interactions with the matrix of narrow, flexible GNRs effectively precludes NP mobility and prevents coalescence into larger structures.

A unique advantage of bottom-up synthesized GNRs as functional nanoparticle supports, unmatched by other graphitic support materials, lies in their inherent molecular-level tunability. The rational synthesis from small-molecule precursors provides an absolute control over key functional parameters such as shape, dimension, and electronic structure, and enables the deterministic introduction of functional groups. GNR 65b, a cove-type GNR bearing methyl carboxylate groups along its edges, was synthesized from the ester-functionalized cyclopentadienone 73b (Scheme 4.1). Raman spectroscopy of 65b shows characteristic peaks for the D, G, and RBLM peaks reminiscent of the unsubstituted 65a, while IR spectroscopy confirms the presence of methyl carboxylate groups in the fully cyclized GNR (Figure 5.7). AuNP composites prepared from the ester-modified 65b resembled those of 65a by STEM and TEM (Figure 4.2G,H), and displayed a similar low surface area (12.6 m² g⁻¹) and CO₂ uptake behavior at 298 K (Figure 4.3D). The ECSA of 66b as measured by Pb-UPD (4.4 cm²/mg AuNP) was very similar to that of the parent 66a composite (Figure 4.4A). The electrocatalytic performance of 66b composites, however, was found to be strikingly different from that of the unfunctionalized composite (Figure 4.4E,F). A significantly increased CO₂ reduction activity is reflected in both an increased jₐ and a higher FEₐ, and can only be attributed to the functionalization of the GNR support. A 1 h controlledpotential experiment at −0.66 V revealed a 92% FEₐ for the 66b composite, a remarkable improvement over the 53% FEₐ observed for the C_black-AuNP composite under the same conditions. In comparison to composites of the unfunctionalized GNR 65a, the rate of hydrogen production is nearly unchanged, but FEₐ is improved across the potential window owing to an approximately 50% increase in the rate of CO production (Tables 5.1–5.4).

The improved performance is retained throughout long-term experiments; for a 10 h experiment at −0.47 V, 66b electrodes deliver an overall FEₐ of 71%, retaining 91% of the FEₐ performance (78%) exhibited in the first hour at that potential (Figure 4.5A). A 24 h experiment at the same potential delivered a total FEₐ of 67% (86% of the FEₐ recorded for the first hour), with the composites characteristic increased activity remaining nearly constant for the duration (Figure 4.5C). Over the course of 10 h, the ester-functionalized composite produced more than 50 mL of CO/mg AuNP, representing a 137-fold increase in total catalytic output over the same nanoparticles embedded in a C_black matrix (Figure 4.5B). The overall efficiency performance of 65b composite after 10 h of electrocatalysis is comparable to the first hour of composite 65a, and exceeds the initial performance of any other material tested.

To better understand the source of the marked increase in performance exhibited by 66b composites, the kinetics of CO₂ reduction for each composite were studied using Tafel analysis. Figure 4.6 shows that the functionalization of cove GNRs with methyl carboxylates alters the mechanistic pathway for CO₂ reduction at the Au nanoparticle surface. A Tafel slope of 141 mV/decade for C_black-AuNP is consistent with the expected value for a rate-limiting single-electron transfer to adsorbed CO₂ to generate the radical anion. This observation and proposed mechanism conform with previous studies of aqueous CO₂ reduc-
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Figure 4.6: Tafel study of CO\textsubscript{2} reduction by GNR- and C\textsubscript{black}-AuNP composite materials. A Tafel analysis shows the CO\textsubscript{2} reduction behavior of AuNP composites with 62 (blue triangles) and 65a (red circles). Tafel slopes are comparable to that of the C\textsubscript{black} (green diamonds) composite, indicating no shift in the mechanism of CO\textsubscript{2} reduction for those materials. For the 66b composite (black squares), however, the Tafel slope is markedly different, indicating that the catalytic environment created by the support material changed the mechanism of CO\textsubscript{2} reduction at the AuNP surface.

4.2 SnO\textsubscript{2} Nanoparticles as Anode Material in Lithium Ion Batteries

In addition to CO\textsubscript{2} reduction as previously discussed, an alternative use of inorganic nanoparticles is for use as anode materials for lithium ion batteries (LIBs).\textsuperscript{196-201} Similar to the pre-
previous case, stabilizing the nanoparticles during the harsh working conditions is a crucial and challenging issue for which GNRs are fit to address. For lithium ion batteries in particular, the support material and its defect structure have been shown to play a major role in device performance, inspiring us to move towards a next-generation graphitic support material.

SnO$_2$ batteries have been the subject of longstanding interest because of their high theoretical Li$^+$ storage capacity (~1480 mAh/g), low cost, material abundance, and low charge/discharge potential vs. Li$^+$/Li.$^{202-206}$ However, they are beset by stability challenges of the sort which support materials are best suited to address; in the process of alloying lithium (overall reaction SnO$_2$ + 8.4 Li $\rightarrow$ Li$_3$O + Li$_{4.4}$Sn), the material undergoes volume expansion of as much as 360%. This frequently leads to pulverization of the tin material, disrupts the stability of the solid electrolyte interphase (SEI) layer, saps faradaic efficiency, and eventually leads to loss of electrical contact and device function.$^{204,205,207-211}$ As such, SnO$_2$ batteries have been the subject of a great deal of research into graphitic support materials, which finds that defects, edges and dopant atoms, play an important role in battery performance. Defect sites have been shown to play a key role not only in storing lithium directly, but also in immobilizing tin nanoparticles, controlling nanoparticle growth, facilitating mass transport, and contributing to composite flexibility.$^{212-215}$ Unfortunately, modern support materials introduce defects by harsh chemical treatment or pyrolysis, with minimal control over defect concentration or morphology. Such an approach limits detailed investigation of defects role and inhibits rational design of improved support materials. GNRs, with their

Scheme 4.2: Bottom-up synthesis of narrow GNRs from small molecule precursors and device fabrication.
high edge to surface ratio and precise, synthetically controlled structure, meet this challenge to a degree unparalleled by other graphitic materials.216

We therefore synthesized a composite of SnO2 nanoparticles grown in-situ on a support of bottom-up synthesized GNRs, and investigated it as an anode material for LIBs. Performance of the material was characterized by galvanostatic cycling, which revealed a high first charge capacity of 1233 mAh/g, indicating excellent transport of Li through the material. The composite material displayed coulombic efficiency as high as 98% after 20 cycles, with stable capacity exceeding 900 mAh/g together with strong rate capability. In addition, when the GNR-SnO2 composite material was tested in a more limited potential range to isolate the performance of lithium alloying, the composite exhibited exceptional stability performance together with high capacity, coulombic efficiency and rate capability. These results demonstrate narrow GNRs suitability as a nanoparticle support material for battery applications.

Atomically precise chevron-type GNRs 62 were synthesized as discussed in the previous section (Figure 4.1). The SnO2 nanoparticles were synthesized in-situ by hydrolysis of SnCl2 in the presence of a surfactant-supported aqueous suspension of GNRs, followed by annealing in air. Powder X-ray diffraction (PXRD) of the composite (Figure 4.7A) confirmed the formation of nanocrystalline SnO2, with average crystal size of 3.9 nm as calculated by the Scherrer equation. Raman spectroscopy of the GNR/SnO2 composite (Figure 4.7B) revealed the characteristic peaks of narrow GNRs, including D and narrow G bands, together with the higher order 2D, D+D, and 2D peaks, indicating preservation of GNR structural integrity during nanoparticle synthesis. X-ray photoelectron spectroscopy (XPS) of the electrode (Figure 4.7C) shows elemental composition of the composite used in cell production, including prominent peaks corresponding to SnO2 and graphitic carbon, and notably indicating the complete removal of residual Ni and Fe from the GNR synthesis. Thermogravimetric analysis (TGA) indicated that the composite was comprised of 69% SnO2 by mass, consistent with the expected mass balance and suggesting complete incorporation of the GNRs.

Figures 4.8A and B show SEM micrographs for the GNR-SnO2 nanocomposite under different, highlighting the rough microstructure of the GNR composite, with SnO2 nanoparticles dispersed throughout the larger composite structure. Following synthesis, the GNR/SnO2 composite was wet ball milled, mixed with carbon black (8 wt%) and PVDF binder (10 wt%), and printed on a nickel current collector foil to give an electrode with thickness of ~15 µm. SEM of the electrode surface (Figure 4.8C) illustrates its smooth morphology, a product of the ball milling done prior to printing. Electrodes prepared without this milling step appeared far rougher by SEM, and exhibited inferior battery performance (Figure 5.9). TEM of the composite (Figure 4.8D) indicated the SnO2 consists of discrete nanoparticles with an average size of 4-5 nm, and confirmed they are well dispersed within aggregates of GNR. This structure, with nanoparticles immobilized within aggregates of flexible GNRs, is ideal for stabilizing nanoparticles and accommodating their volume expansion while also facilitating Li mass transport to the SnO2 surface.

To gain an initial understanding of lithium storage by the GNR-SnO2 nanocomposite, we performed cyclic voltammetry (CV) for the first three cycles between 0.005 and 3.0 V vs.
Figure 4.7: (A) XRD pattern of the GNR/SnO$_2$ nanocomposite. The particle size estimated using the Scherrer equation was 3.9 nm. (B) Raman spectroscopy of the GNR/SnO$_2$ composite exhibits the characteristic signals of narrow GNRs. (C) XPS spectroscopy of printed GNR/SnO$_2$ nanocomposite electrode, including prominent signals characteristic of SnO$_2$. (D) TGA under air of the GNR/SnO$_2$ composite (red) and GNRs alone (black) using a 20 °C min$^{-1}$ ramp to 550 °C followed by 15 minutes at that temperature.
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Figure 4.8: (A, B) SEM micrographs of the GNR/SnO$_2$ nanocomposite under different magnification. (C) SEM micrograph of the electrode prepared with GNR/SnO$_2$ nanocomposite with carbon black as conductive additive and PVDF as binder. (D) TEM micrograph of the GNR/SnO$_2$ nanocomposite.

Li$^+$/Li (Figure 4.9A, 0.1 mV s$^{-1}$). When SnO$_2$ is discharged in presence of a lithium source, it is known to reduce in a two-step process:

SnO$_2$ + 4 Li$^+$ + 4e$^-$ → Sn + 2 Li$_2$O \hspace{1cm} (4.1)

Sn + 4.4Li$^+$ + 4.4e$^-$ → Li$_{4.4}$Sn \hspace{1cm} (4.2)

In bulk SnO$_2$, the conversion of SnO$_2$ to Sn and Li$_2$O (Eq. 4.1) is irreversible, but the reaction is reversible if nanocrystals of SnO$_2$ are used the starting material. For our GNR composite, the first cycle in the cathodic direction exhibits a reaction up to 1.0 V corresponding to Equation 4.1, as well as the formation of a solid electrolyte interphase (SEI) layer. In the second cycle, the broad peak due to formation of the SEI layer disappeared, indicating the formation of a stable SEI layer during the first cycle. The rapid formation of a stable SEI is a crucial property often associated with graphene, and the ability of the GNR composite to maintain the SEI through multiple expansive cycles demonstrates its functionality as a flexible support material.

Below 1.0 V in CV of the GNR-SnO$_2$ nanocomposite, we observe current corresponding to Equation 4.2, the alloying of Sn with Li$^+$ to form Li$_{4.4}$Sn. The peak at 0.10 V can therefore
be ascribed to the formation of Li$_4$·4Sn. Recent studies have shown that the formation of Li$_2$O continues until the electrode reaches $\sim$0 V vs. Li$^+$/Li, and Sn formed during this process alloys with Li as soon as it is formed.$^{211,217}$ In the anodic direction, the peaks at 0.57 and 1.24 V are assigned to the delithiation of Li$_x$Sn, and the reconversion of Sn to SnO$_2$, respectively. The peak at 1.24 V and the non-zero current between 1.5 to 3.0 V indicate that the reaction (4.1) is reversible to some extent. In later cycles, the new peaks at 1.24 and 0.87 V are can be ascribed to the conversion of SnO$_2$ to Sn, and alloying of Sn, respectively. The location of the peaks for the formation of Li$_4$·4Sn alloy, dealloying of Li$_4$·4Sn to Sn and the conversion of Sn to SnO$_2$ remained constant. The third cycle overlapped with the second cycle, demonstrating excellent reversibility of the GNR-SnO$_2$ nanocomposite.

To better understand the full lithium storage capabilities of the GNR-SnO$_2$ nanocomposite, we undertook galvanostatic charge/discharge cycling experiments between 0.005 to 3.0 V vs. Li$^+$/Li (Figure 4.9C, 100 mA g$^{-1}$). The first cycle discharge and charge capacities of the GNR/SnO$_2$ electrode were $\sim$2028.9 and $\sim$1233 mAh/g, respectively, corresponding to
a coulombic efficiency (CE) of 60.8%. The loss in capacity during the first cycle was due to the consumption of lithium ions during formation of the SEI layer. The coulombic efficiency increased to 97% within 10 cycles, and exceeded 98% after 20 cycles. The high first cycle charge capacity of ∼1233 mAh/g indicate that both reaction (4.1) and (4.2) are taking part in storage, as it exceeds the theoretical limit of either individually. The synergistic effect between nano-sized SnO₂ particles and bottom up synthesized graphene nanoribbons with high edge-to-surface ratio facilitated the conversion of Sn to SnO₂ and prevented aggregation during cycling, maintaining the few-nanometer sized NPs and thus allowing both reaction (4.1) and (4.2) to take part in reversible Li ion storage. Capacity of the electrode stabilized to ∼961 mAh/g after 10 cycles and the capacity at the end of 30 cycle was ∼900 mAh/g. Additionally, the composite showed excellent rate capability of 1170, 767, 663, 502 and 360 mAh/g at 100, 250, 500, 1000 and 2000 mA/g, respectively (Figure 4.9D). In Figure 4.9B we see that the charging curve up to ∼1.0 vs. Li⁺/Li lay on the same plane demonstrating excellent reversibility of the alloying/dealloying process. The loss in capacity during initial cycles is due to incomplete conversion of Sn to SnO₂.

While taking advantage of the Li⁺ storing reactions of both Eq. 4.1 and 4.2 maximizes reversible storage capacity, it requires a wide voltage range (3.0 to 0.005 V vs Li⁺/Li), a full cell making use of both reactions together with a typical high voltage transition metal oxide based cathode would have to be discharged below 1 V, well below the input battery voltage of most consumer electronic devices. For this reason, we chose to focus on a cell using only reaction 4.2, the alloying and de-alloying of Sn with Li; because this process takes place between 0 and 1.2 V vs Li⁺/Li, a full cell making use of this reaction only would operate at a much more desirable voltage. Furthermore, we find the GNR-SnO₂ nanocomposite displays exceptional stability behavior when cycled in this potential range. Figures 4.10A and B show the galvanostatic charge/discharge curves and charge/discharge capacities of GNR/SnO₂ nanocomposite cycled between 0.005 to 1.2 V vs. Li⁺/Li for 30 cycles. The first cycle charge capacity of the electrode was ∼601 mAh/g, and more than 90% of this capacity is retained after 30 cycles. The coulombic efficiency of the electrode was above 98% after 15 cycles. Notably, although limiting the electrode to the alloying/dealloying process of course limits its capacity, it still exhibits a capacity higher than the theoretical limit of a conventional graphite electrode (∼372 mAh/g), and with excellent stability. The charge/discharge curves lay on the same plane, indicating a highly reversible process. (Figure 4.10B). The composite showed excellent rate capability of 600, 492, 400, 324 and 245 mAh/g at 100, 250, 500, 1000 and 2000 mA/g, respectively (Figure 4.10C). Figure 4.10D shows the galvanostatic charge/discharge capacity of the electrode cycled at 100 mA/g for 25 cycles then at 250 mA/g for 125 cycles. The capacity at the start of cycling at 250 mA/g was ∼497 mAh/g and at the end of 125 cycles, the capacity was ∼458 mAh/g, demonstrating excellent capacity retention when the electrode was operating between 0 to 1.2 V.
Figure 4.10: Galvanostatic charge/discharge curves (A) and charge/discharge capacity (B) of GNR/SnO$_2$ nanocomposite cycled between 1.2 and 0.005 V vs. Li$^+$/Li at 100 mA/g for 30 cycles, respectively. (C) Capacity retention of the electrode cycled between 1.2 and 0.005 V vs. Li$^+$/Li at 100, 250, 500, 1000 and 2000 mA/g. (D) Charge/discharge capacity of GNR/SnO$_2$ nanocomposite cycled between 1.2 and 0.005 V at 100 mA/g and 250 mA/g.
Chapter 5

Supporting Information

5.1 Materials and General Methods

Unless otherwise stated, all manipulations of air and/or moisture sensitive compounds were carried out in oven-dried glassware, under an atmosphere of Nitrogen. All solvents and reagents were purchased from Alfa Aesar, Spectrum Chemicals, Acros Organics, TCI America, and Sigma-Aldrich and were used as received unless otherwise noted. Organic solvents were dried by passing through a column of alumina and were degassed by vigorous bubbling of N₂ through the solvent for 20 min. Flash column chromatography was performed on SiliCycle silica gel (particle size 4063 µm). Thin layer chromatography was carried out using SiliCycle silica gel 60 ÅF-254 precoated plates (0.25 mm thick) and visualized by UV absorption. All ¹H and ¹³C NMR spectra were recorded on a Bruker AV-600, AV-500, DRX-500, AVB-400, AVQ-400, or AV-300 spectrometer and are referenced to residual solvent peaks (CDCl₃ ¹H NMR = 7.26 ppm, ¹³C NMR = 77.16 ppm; CD₂Cl₂ ¹H NMR = 5.32 ppm, ¹³C NMR = 53.84 ppm). ESI mass spectrometry was performed on a Finnigan LTQFT (Thermo) spectrometer in positive ionization mode. Gel permeation chromatography (GPC) was carried out on a LC/MS Agilent 1260 Infinity set up with a guard and two Agilent Polypore 300 x 7.5 mm columns at 35 °C. All GPC analyses were performed on a 0.2 mg/mL solution of polymer in chloroform. An injection volume of 25 µL and a flow rate of 1 mL/min were used. Calibration was based on narrow polydispersity polystyrene standards ranging from Mw = 100 to 4,068,981. UV-Vis spectroscopic measurements were conducted in a Varian Cary 50 spectrophotometer (Agilent, USA). 3-bromobenzil, ¹³C-MePPh₃I, ²¹⁸ 5-phenyldipyrrromethane, ²¹⁹ 4-(1,3-dioxolan-2-yl)benzaldehyde, ²²⁰ 5,15-bis(4-ethynlphenyl)-10,20-diphenyl-21H,23H-porphine and 3-bromobenzil were synthesized according to literature procedures.
5.2 Synthetic Procedures

2,2'-Diiodo-4,4'-dinitrobiphenyl (1): A 100 mL flask was charged with 4,4'-dinitrobiphenyl (1.03 g, 4.23 mmol), NaIO$_3$ (0.87 g, 4.38 mmol), and H$_2$SO$_4$ (10 mL). The reaction mixture was heated to 110 °C for 2 h. The reaction mixture was poured over crushed ice and the precipitate filtered and collected. A 100 mL flask was charged with NaI (1.85 g, 12.355 mmol), CuI (0.10 g, 0.54 mmol), and DMF (10 mL). The previously collected precipitate was added to this reaction mixture and heated to 110 °C for 5 h. The reaction mixture was poured into water and extracted with EtOAc. The combined organics were dried with MgSO$_4$, filtered, and the solvent was removed under reduced pressure. Recrystallization from EtOH yielded 1 as yellow needles (1.06 g, 2.131 mmol, 50%). $^1$H NMR (400 MHz, CDCl$_3$, 22 °C): $\delta$ = 8.82 (s, 2 H), 8.34 (d, $J$ = 10.7 Hz, 2 H), 7.36 (d, $J$ = 8.4 Hz, 2 H) ppm. ESI-HR-MS (m/z): calcd for C$_{12}$H$_6$N$_2$O$_4$I$_2$ [M]$^+$ 495.8417, found 495.8424. Matches previous reports.

2,2'-Diiodo-4,4'-diaminobiphenyl (2): A 250 mL roundbottom flask was charged with 1 (3.26 g, 6.57 mmol), SnCl$_2$·2H$_2$O (17.94 g, 79.5 mmol), EtOH (40 mL), and conc. HCl (37 mL). The reaction mixture was heated to 40 °C for 1 h. The reaction mixture was basified with 200 mL 6 M NaOH and extracted with Et$_2$O. The combined organics were dried with MgSO$_4$, filtered, and the solvent was removed under reduced pressure. Recrystallization from EtOH yielded 2 as yellow needles (1.88 g, 4.32 mmol, 66%). $^1$H NMR (300 MHz, CDCl$_3$, 22 °C): $\delta$ = 7.25 (d, $J$ = 2.4 Hz, 2 H), 6.94 (d, $J$ = 8.2 Hz, 2 H), 6.69 (dd, $J$ = 8.1 Hz, 2.2 Hz, 2 H), 3.71 (s, 4 H) ppm; ESI-HR-MS (m/z): calcd for C$_{12}$H$_{11}$N$_2$I$_2$ [M]$^+$ 436.9012, found 436.9006. Matches previous reports.
[1,1' : 2', 1 '' : 2 '', 1‴′:2‴′, 1‴‴:2‴‴, 1″‴:2″‴, 1″″‴:2″″‴, 1″″″:2″″″‴-Sexiphenyl]-4‴″, 5‴″-diamine (3): An oven dried 50 mL Schlenk roundbottom flask was charged with 2 (315 mg, 0.687 mmol), 2-biphenylboronic acid (302 mg, 2.53 mmol, 2.2 eq), toluene (8 mL), and 1M K₂CO₃ (aq.). The reaction mixture was sparged with N₂ for 1 h, at which point Pd(PPh₃)₄ (99 mg, 0.086 mmol, 0.13 eq) was added under flow of N₂. A reflux condenser was attached, and the mixture was stirred at 100 °C under N₂ for 4 h. After cooling to 22 °C the mixture was filtered and the filtrate was diluted with CH₂Cl₂ (10 mL) and H₂O (10 mL). The mixture was extracted with CH₂Cl₂ (2 × 10 mL). The combined organics were washed with sat. NaHCO₃ (10 mL), H₂O (10 mL), dried with MgSO₄, filtered, and the solvent removed under reduced pressure. Column chromatography (SiO₂: 4:1 hexanes/EtOAc) yielded 3 (91 mg, 0.19 mmol, 27%) as a colorless solid. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 7.23–7.08 (m, 8H), 7.08–6.91 (m, 8H), 6.63 (d, J=6.1 Hz, 2H), 6.42 (s, 2H), 6.31 (d, J=6.4 Hz, 2H), 6.13 (d, J=6.6 Hz, 2H), 3.51 (s, br, 4H) ppm; ¹³C {¹H} NMR (125 MHz, CDCl₃, 22 °C): δ = 143.6, 141.5, 140.5, 140.2, 131.6, 129.3, 128.7, 127.2, 126.0, 125.4, 118.5, 117.4, 114.4 ppm; ESI-HRMS (m/z): calcd for C₃₆H₂₉N₂ [M+H]⁺ 489.2325, found 489.2327.

4‴″, 5‴″-Diiodo-1,1′:2′, 1″′:2″′, 1‴‴′:2‴‴′, 1‴‴‴:2‴‴‴, 1″‴‴:2″‴‴‴-sexiphenyl (4): A 50 mL roundbottom flask was charged with 3 (91 mg, 0.19 mmol), H₂O (10 mL), and H₂SO₄. The reaction mixture was cooled to 5 °C and a solution of NaNO₂ (30 mg, 0.43 mmol, 2.3 eq) in H₂O (1 mL) was added dropwise over 5 min, and stirred at 5 °C for 45 min. To this was added KI (128 mg, 0.77 mmol, 4.2 eq) portionwise over 5 min and the reaction mixture was stirred at 22 °C for 5 h. The mixture was then extracted with EtOAc (2 × 15 mL). The combined organics were washed with 2M NaOH (30 mL) and brine (30 mL), dried with MgSO₄, filtered, and the solvent was removed under reduced pressure. Column chromatography (SiO₂: 1:2 hexanes/EtOAc) yielded 4 (33 mg, 0.047 mmol, 25%). ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 7.47 (s, 2H), 7.24–7.14 (m, 4 H), 7.13–7.02 (m, 8H), 7.02–6.92 (m, 6H), 6.51–6.40 (m, 4H)
ppm; $^{13}$C $\{^1$H$\}$ NMR (125 MHz, CDCl$_3$, 22 °C): $\delta$ = 141.9, 141.2, 139.4, 139.2, 138.1, 136.5, 132.9, 131.5, 131.1, 129.9, 128.8, 128.0, 127.2, 126.1, 92.3 ppm; EI-HRMS ($m/z$): calcd for C$_{36}$H$_{24}$I$_2$ [M]$^+$ 709.9968, found 709.9959.

5-Bromo-2-iodoisophthalonitrile (16): A 100 round bottom flask was charged with 15 (5.00 g, 19.7 mmol) in sulfuric acid (22 mL). The reaction mixture was heated to 50 °C. N-bromosuccinimide (3.89 g, 21.9 mmol) was added portionwise over 3 min and the reaction mixture stirred for 10 min at 50 °C. The reaction mixture was poured over ice/water (200 mL), filtered, and the precipitate washed with water. Recrystallization from EtOAc (500 mL) yielded 16 (4.12 g, 12.4 mmol, 63%) as a colorless crystalline solid. $^1$H NMR (400 MHz, CDCl$_3$, 22 °C): $\delta$ = 7.89 (s, 2H) ppm; $^{13}$C $\{^1$H$\}$ NMR (151 MHz, CDCl$_3$, 22 °C): $\delta$ = 140.0, 124.9, 122.9, 117.1, 101.8 ppm; EI-HRMS ($m/z$): calcd for C$_8$H$_2$N$_2$Br$_1$I$_1$ [M]$^+$ 331.8446, found 331.8450.

5-Bromo-2-iodoisophthalaldehyde (17): A 500 mL round bottom flask was charged with 16 (4.65 g, 14.0 mmol) in formic acid (210 mL). Raney-Nickel (50% slurry in H$_2$O, 17 mL, 136 mmol) was added quickly via syringe. The reaction mixture was heated to 100 °C and stirred for 1.5 h. The reaction mixture filtered hot and the grey precipitate washed with CH$_2$Cl$_2$. The filtrate was diluted with H$_2$O, and extracted with CH$_2$Cl$_2$ (3 × 200 mL). The combined organic phases were washed with saturated aqueous NaCl (400 mL), dried over MgSO$_4$, and the solvent removed under reduced pressure. Column chromatography (SiO$_2$; 40% CH$_2$Cl$_2$ in hexanes) yielded 17 (1.06 g, 3.13 mmol, 22%) as a colorless solid. $^1$H NMR (500 MHz, CDCl$_3$, 22 °C): $\delta$ = 10.25 (s, 2H), 8.18 (s, 2H) ppm; $^{13}$C $\{^1$H$\}$ NMR (150 MHz, CDCl$_3$, 22 °C): $\delta$ = 193.5, 138.1, 137.4, 124.5, 103.3 ppm; EI-HRMS ($m/z$) cald for C$_8$H$_4$O$_2$IBr [M]$^+$ 337.8439, found 337.8438.
(5-Bromo-2-iodo-1,3-phenylene)bis(o-tolylmethanone) (18): A 200 mL Schlenk round bottom flask was charged under N\textsubscript{2} with 17 (1.01 g, 2.98 mmol), in dry THF (35 mL). The reaction mixture was cooled to \(-78\) °C. o-tolylmagnesium chloride (1.0 M in THF, 6.5 mL, 6.5 mmol) was added dropwise over 5 min and the reaction mixture stirred for 16 h with gradual warming to 24 °C. The reaction mixture was acidified with 1 M aqueous HCl (5 mL), diluted with H\textsubscript{2}O (100 mL) and extracted with CH\textsubscript{2}Cl\textsubscript{2} (4 × 100 mL). The combined organic phases were washed with saturated aqueous NaCl (200 mL), dried over MgSO\textsubscript{4}, and the solvent removed under reduced pressure. To the crude reaction product was added CH\textsubscript{2}Cl\textsubscript{2} (500 mL), celite (2.43 g), and PCC (2.16 g, 10.0 mmol). The reaction mixture was stirred at 24 °C for 4 h. The reaction mixture was filtered and the brown precipitate washed with CH\textsubscript{2}Cl\textsubscript{2} (500 mL), and the combined filtrates concentrated under reduced pressure. Column chromatography (SiO\textsubscript{2}; 1:1 hexanes/CH\textsubscript{2}Cl\textsubscript{2}) yielded 18 (1.46 g, 2.81 mmol, 94%) as a colorless solid. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 22 °C): \(\delta = 7.50\) (s, 2H), 7.50-7.46 (m, 2H), 7.36 (dd, \(J = 7.8, 1.3\) Hz, 4H), 7.25 (t, \(J = 7.6\) Hz, 2H), 2.67 (s, 6H) ppm; \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (150 MHz, CDCl\textsubscript{3}, 22 °C): \(\delta = 197.5, 148.7, 141.2, 134.5, 133.1, 132.7, 132.5, 132.2, 126.0, 122.9, 88.7, 21.9\) ppm; EI-HRMS (m/z): calcd for C\textsubscript{22}H\textsubscript{16}O\textsubscript{2}Br\textsubscript{1}I\textsubscript{1} [M]\textsuperscript{+} 517.9378. found 519.9380.

\begin{center}
\includegraphics[width=0.3\textwidth]{18.png}
\end{center}

(4,4′-Dibromo-[1,1′-biphenyl]-2,2′,6,6′-tetracyl)tetrakis(o-tolylmethanone) (19): A 5 mL Schlenk tube was charged under N\textsubscript{2} with 18 (78 mg, 0.15 mmol) and copper powder (70 mg, 1.1 mmol), in DMF (0.4 mL). The reaction mixture was heated to 120 °C and stirred for 14 h. The reaction mixture was cooled to 24 °C and filtered through celite, washing with EtOAc. The filtrate was washed with 0.5 M aqueous HCl (2 × 5 mL), and saturated aqueous NaCl, dried over MgSO\textsubscript{4}, and the solvent removed under reduced pressure. Column chromatography (SiO\textsubscript{2}; 1:1 hexanes/toluene) yielded 19 (53 mg, 0.068 mmol, 91%) as a colorless solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 22 °C): \(\delta = 7.61\) (s, 4H), 7.45 (d, \(J = 7.7\) Hz, 4H), 7.30 (t, \(J = 7.5\) Hz, 4H), 7.20 (d, \(J = 7.6\) Hz, 4H), 7.08 (t, \(J = 7.6\) Hz, 4H), 2.34 (s, 12H) ppm; \textsuperscript{13}C \{\textsuperscript{1}H\} NMR (150 MHz, CDCl\textsubscript{3}, 22 °C): \(\delta = 196.8, 140.6, 139.2, 138.6, 137.7, 136.9, 131.4, 131.2, 130.9, 125.2, 120.1, 20.29\) ppm; ESI-HRMS (m/z): calcd for C\textsubscript{44}H\textsubscript{32}O\textsubscript{4}Br\textsubscript{2} [M]\textsuperscript{+} 782.0667, found 782.0667.
2,7-Dibromo-4,5,9,10-tetra-o-tolylpyrene (20): A 100 Schlenk round bottom flask was charged under N₂ with 19 (362 mg, 0.461 mmol), and phosphorus pentasulfide (2.27 g, 5.1 mmol), in dry o-xylene (20 mL). A reflux condenser was attached and the reaction mixture was heated to 150 °C and stirred for 48 h. The reaction mixture was cooled to 22 °C and filtered through celite, washing with toluene. The filtrate was concentrated under reduced pressure. Column chromatography (SiO₂; 9:1 hexanes/CH₂Cl₂) yielded 20 (120 mg, 0.17 mmol, 36%) as a colorless solid. ¹H NMR (600 MHz, CD₂Cl₂, 22 °C): δ = 7.71 (s, 4H), 7.28–7.24 (m, 8H), 7.16–7.12 (m, 8H), 7.15–7.03 (m, 12H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 138.2, 137.7, 136.6, 132.6, 130.2, 130.0, 128.9, 128.0, 127.4, 125.8, 125.2, 20.6, 20.5 ppm; ESI-HRMS (m/z): calcd for C₄₄H₃₂Br₂ [M]+ 718.0871, found 718.0872.

4,7-Dibromobenzo[c][1,2,5]thiadiazole (22): A 25 mL roundbottom flask was charged with a magnetic stir bar, benzo[c][1,2,5]thiadiazole (1.00 g, 7.34 mmol), NBS (2.75 g, 15.5 mmol, 2.1 eq), and conc. H₂SO₄ (10 mL) under air. The mixture was stirred at 60 °C for 3 h. After cooling room temperature, the reaction was quenched with aq. Na₂S₂O₄ (100 mL), extracted with toluene (3 × 100 mL), the combined organics were dried with MgSO₄, filtered, and the solvent removed to yield 22 as an off-white solid (2.09 g, 7.1 mmol, 97%). ¹H NMR (400 MHz, CDCl₃, 22 °C): δ = 7.73 (s, 2H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 153.1, 132.5, 114.0 ppm; EI-HRMS (m/z): calcd for C₆H₂N₂S²⁻Br⁻¹⁺Br⁻¹ [M]+ 293.8291, found 293.8289. Matches previous reports.??

3,6-Dibromobenzene-1,2-diamine (23): An oven dried 500 mL Schlenk roundbottom flask was charged with a magnetic stir bar, 22 (2.01 g, 6.83 mmol), and EtOH (250 mL) under N₂.
The mixture was cooled to 0 °C in an ice water bath and NaBH₄ (4.65 g, 134 mmol, 19.6 eq) was added portionwise over 6 minutes. The mixture was stirred at 0 °C for 20 min, at which point the ice bath was removed and stirring continued under N₂ for 24 h. The mixture was then cooled to 0 °C and quenched with H₂O (150 mL). The EtOH was removed via rotavap and the mixture extracted with Et₂O (3 × 200 mL). The combined organics were dried with MgSO₄, filtered, and concentrated to yield 23 (1.816 g, 6.83 mmol, 100%) as an off-white solid. ¹H NMR (300 MHz, CDCl₃, 22 °C): δ = 6.84 (s, 2H), 3.89 (br, s, 4H) ppm. Matches previous reports.

1,4-Dibromophenazine (25): A 1 L roundbottom flask was charged with a magnetic stirbar, K₂Cr₂O₇ (7.06 g, 24 mmol, 12 eq), H₂SO₄ (30 mL), and H₂O (270 mL). To this was added a solution of catechol (1.32 g, 12.0 mmol, 6 eq) in CH₂Cl₂ (300 mL) and the biphasic mixture was stirred vigorously for 15 min. The organic layer was transferred to a 500 mL roundbottom flask containing 23 (532 mg, 2.0 mmol) in AcOH (2 mL) and a magnetic stirbar. A reflux condensor was attached and the mixture stirred at 50 °C for 7 h. Solvent removed under reduced pressure. Column chromatography (SiO₂: CH₂Cl₂:hexanes 1:1) yielded 25 (59 mg, 0.17 mmol, 9%) as a yellow solid. ¹H NMR (600 MHz, CDCl₃, 22 °C): δ = 8.41 (dd, J=6.7, 3.4 Hz, 2H), 8.06 (s, 2H), 7.95 (dd, J=6.8, 3.4 Hz, 2H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 144.0, 141.2, 133.4, 132.1, 129.9, 124.3 ppm; EI-HRMS (m/z): calcd for C₁₂H₆N₂ ⁷⁹Br₁⁸¹Br₁ [M]+ 337.8877, found 337.8880. Matches previous reports.

1,4,6,9-Tetrabromophenazine (26): A 25 mL roundbottom flask was charged with a magnetic stirbar, phenazine (662 mg, 3.68 mmol), and NBS (2.75 g, 15.5 mmol, 4.2 eq), and H₂SO₄ (10 mL). The mixture was stirred at 60 °C for 3 h. After cooling to 22 °C the mixture was diluted with H₂O (100 mL) and extracted with CH₂Cl₂ (3 × 100 mL). The combined organics were washed with aq. Na₂S₂O₃ (200 mL) and sat. NaCl (200 m), dried with MgSO₄, filtered, and concentrated. Column chromatography (SiO₂: CH₂Cl₂:hexanes 1:1) yielded 26 (100 mg, 0.20 mmol, 5.5%) as a yellow solid. ¹H NMR (600 MHz, CDCl₃, 22 °C): δ = 8.14 (s, 4H) ppm. ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 141.6, 134.8, 124.3 ppm; EI-HRMS (m/z): calcd for C₁₂H₄N₂ ⁷⁹Br₂⁸¹Br₂ [M]+ 495.7067, found 495.7070.
4,7-Dibromo-5,6-dinitrobenzo[c][1,2,5]thiadiazole (32): An oven dried 250 mL 2-neck round-bottom flask was charged with a magnetic stir bar and TfOH (60 mL) and cooled to 0 °C. Fuming nitric acid (6 mL) was added via needle and syringe, followed by 22 (10.14 g, 34.5 mmol) portionwise over 10 min. After stirring at 0 °C for 10 min after addition the mixture was heated to 50 °C and stirred for 21 h. After cooling to room temperature the mixture was poured carefully into 700 mL crushed ice water and filtered to give a colorless precipitate that was washed with a further 1 L of H₂O. The precipitate was suspended in and filtered from MeOH twice. Recrystallization from toluene yielded 32 as pale yellow needles (5.60 g, 14.7 mmol, 43%). ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 155.9, 151.5, 110.4 ppm; EI-HRMS (m/z): calcd for C₆N₄O₄S²Br₁¹¹Br₁ [M]⁺ 383.7987, found 383.7991. Matches previous reports.

4,7-Dibromo-5,6-diaminobenzo[c][1,2,5]thiadiazole (33): A 1 L Schlenk roundbottom flask was charged with a magnetic stir bar and AcOH (500 mL) and sparged with N₂ for 38 min. A solid mixture of 32 (2.57 g, 6.73 mmol) and Fe powder (6.03 g, 108 mmol, 16 eq) was added under flow of N₂. The flask was fitted with a reflux condensor and the mixture was stirred at 100 °C for 3 h. The mixture was then poured into 1.4 L of 5% aq. NaOH and filtered. The yellow precipitate was taken up in 500 mL hot EtOAc, dried with MgSO₄, filtered, and the solvent removed to yield 33 as a yellow solid (1.12 g, 3.45 mmol, 51%). GCMS (m/z): calcd for C₆N₄S²Br₁¹¹Br₁ [M]⁺ 323.9, found 323.9. Matches previous reports.

4,9-Dibromo-[1,2,5]thiadiazolo[3,4-g]quinoxaline (34): A 500 mL 2-neck roundbottom flask was charged with a magnetic stir bar, 33 (1.12 g, 3.45 mmol), EtOH (250 mL), THF (100 mL), and AcOH (20 mL) and sparged with N₂ for 15 min. Glyoxal (40 % in H₂O, 1.0 mL, 8.3 mmol, 2.4 eq) was added via needle and syringe and the mixture was stirred for 24 h. The solvents were then removed at reduced pressure and the residue taken up in EtOAc (300 mL) and washed with sat. NaHCO₃ (3 × 200 mL) and brine (200 mL). The combined
organics were dried with MgSO$_4$, filtered, and the solvent removed to yield 34 as an orange solid (560 mg, 1.62 mmol, 47%). $^1$H NMR (600 MHz, CDCl$_3$, 22 °C): $\delta = 9.03$ (s, 2H) ppm. Previously reported.??

5,8-Dibromoquinoxaline-6,7-diamine (35): An oven dried 500 mL Schlenk roundbottom flask was charged with a magnetic stirbar, 34 (560 mg, 1.62 mmol), and dry Et$_2$O (250 mL) and sparged with N$_2$ for 15 min. The solution was cooled to 0 °C and solid LiAlH$_4$ (1.04 g, 27.4 mmol, 17 eq) was added portionwise. After addition the cold bath was removed and the mixture stirred at room temperature for 18 h. The reaction was quenched with sat. NH$_4$Cl and extracted with Et$_2$O (3 × 200 mL). The combined organics were dried with MgSO$_4$, filtered, and the solvent removed. Column chromatography (Al$_2$O$_3$: EtOAc:hexanes 1:1 to EtOAc) yielded 35 as a red solid (37 mg, 0.12 mmol, 7.2%). GCMS (m/z): calcd for C$_8$H$_6$N$_4$Br$_1^+$ 317.9, found 317.9.

5,10-Dibromopyrazino[2,3-g]quinoxaline (29): A 50 mL Schlenk roundbottom flask was charged with a magnetic stirbar, 35 (36 mg, 0.11 mmol), and EtOH (25 mL) and sparged with N$_2$ for 20 min. Glyoxal (40 % in H$_2$O, 0.9 mL, 7.4 mmol, 68 eq) was added via needle and syringe and the solution was stirred at room temperature for 18 h. The solvent was removed at reduced pressure and the red residue was taken up in CH$_2$Cl$_2$ (20 mL) and washed with sat. NaHCO$_3$ (3 × 20 mL) and brine (20 mL). The combined organics were dried with MgSO$_4$, filtered, and the solvents removed at reduced pressure. Preparative TLC (Al$_2$O$_3$: EtOAc:hexanes 1:1) yielded 29 as an orange solid (7.5 mg, 0.022 mmol, 20%). $^1$H NMR (300 MHz, CDCl$_3$, 22 °C): $\delta = 9.17$ (s, 4H) ppm; EI-HRMS (m/z): calcd for C$_{10}$H$_4$N$_4$Br$_1^+$ 339.8782, found 339.8784. Previously reported.??

1-(Bromomethyl)-4-hexadecylbenzene (37): A 100 mL heavy wall pressure vessel was charged under N$_2$ with hexadecylbenzene (24.85 g, 82.1 mmol) and paraformaldehyde (3.02 g, 100.6
mmol) in acetic acid (30 mL). HBr (33% in AcOH, 24 mL) was added with stirring. The reaction mixture was stirred for 15 h at 120 °C. The reaction mixture was cooled to 24 °C and diluted with CH₂Cl₂ (150 mL). The combined organic phases were washed with saturated aqueous NaHCO₃ (150 mL), water (150 mL), saturated aqueous NaCl (150 mL), dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Column chromatography (SiO₂; hexanes) followed by recrystallization from hexanes yielded 37 (14.51 g, 36.7 mmol, 45%) as a colorless solid. ¹H NMR (400 MHz, CDCl₃, 22 °C): δ = 7.30 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 4.49 (s, 2H), 2.59 (t, J = 7.8 Hz, 2H), 1.22–1.33 (m, 26H), 0.88 (t, J = 6.6 Hz, 3H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 143.6, 135.1, 129.1, 129.0, 35.9, 34.0, 32.1, 31.5, 29.9 (2C), 29.8 (2C), 29.7, 29.6, 29.5, 29.5, 22.9, 14.3 ppm; EI-HRMS (m/z): calcd for C₂₃H₃₉Br [M]⁺ 394.2235, found 394.2233. Matches previous report.

1,3-Bis(4-hexadecylphenyl)propan-2-one (38): A 150 mL heavy wall pressure vessel was charged under N₂ with NaOH (4.02 g, 100.5 mmol) and benzyltriethylammonium chloride (187.3 mg, 0.82 mmol) in water (2.3 mL). 37 (7.62 g, 19.3 mmol) and CH₂Cl₂ (57 mL) added with stirring. Reaction mixture heated to 40 °C. Fe(CO)₅ (1.4 mL, 10.4 mmol) was added and the reaction mixture was stirred at 40 °C for 18 h. The reaction mixture was cooled to 24 °C, diluted with CH₂Cl₂ (100 mL), and filtered through celite. The filtrate was diluted with water (100 mL) and extracted with CH₂Cl₂ (3 × 100 mL). The combined organic phases were washed with saturated aqueous saturated aqueous NaCl (200 mL), dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Column chromatography (SiO₂; 2:1 hexanes/CH₂Cl₂), followed by recrystallization from hexanes yielded 38 (3.99 g, 6.05 mmol, 63%) as a colorless solid. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 7.12 (d, J = 7.9 Hz, 4H), 7.05 (d, J = 7.9 Hz, 4H), 3.67 (s, 4H), 2.57 (t, J = 7.8 Hz, 4H), 1.62–1.55 (m, 4H), 1.34–1.22 (m, 52H), 0.88 (t, J = 6.9 Hz, 6H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 206.4, 141.9, 131.3, 129.5, 128.9, 48.8, 35.7, 32.1, 31.6, 29.9 (2C), 29.8 (2C), 29.7 (2C), 29.5, 29.5, 22.9, 14.3 ppm; EI-HRMS (m/z): calcd for C₄₇H₇₈O [M]⁺ 658.6053, found 658.6044.

3-(3-Bromophenyl)-2,5-bis(4-hexadecylphenyl)-4-phenylcyclopenta-2,4-dienone (39): A 500 mL three neck round bottom flask with reflux condensor was charged under N₂ with 38
(5.48 g, 8.31 mmol) 1-(3-bromophenyl)-2-phenylethane-1,2-dione (2.41 g, 8.34 mmol) and in t-BuOH (250 mL). The reaction mixture was heated to 80 °C. Tetraethylammonium hydroxide (20 wt% in H2O, 2.8 mL) was added all at once. The reaction mixture was stirred at 80 °C for 50 min. The reaction mixture was cooled to 24 °C, quenched with 1M HCl (15 mL), diluted with water (150 mL) and extracted with CH2Cl2 (3 × 150 mL). The combined organic phases were washed with saturated aqueous NaCl (300 mL), dried over MgSO4, filtered, and concentrated on a rotary evaporator. Column chromatography (SiO2; 4:1 hexanes:CH2Cl2) yielded 39 (4.60 g, 5.04 mmol, 61%) as a purple solid. 1H NMR (500 MHz, CD2Cl2, 22 °C): δ = 7.38 (d, J = 8.8 Hz, 1H), 7.28 (t, J = 7.4 Hz, 2H), 7.21 (t, J = 7.5 Hz, 2H), 7.14–7.09 (m, 5H), 7.09–7.04 (m, 5H), 6.95 (d, J = 7.1 Hz, 2H), 6.89 (d, J = 7.6 Hz, 1H), 2.61–2.53 (m, 4H), 1.62–1.56 (m, 4H), 1.34-1.24 (m, 52H), 0.88 (t, J = 6.9 Hz, 6H) ppm; 13C {1H} NMR (126 MHz, CDCl3, 22 °C): δ = 200.7, 153.7, 152.0, 142.9, 142.6, 135.6, 133.2, 132.3, 131.4, 130.0, 129.6, 129.4, 128.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.6, 125.9, 125.1, 122.0, 35.9, 32.1, 31.4, 29.9 (2C), 29.8 (2C), 29.7 (2C), 29.7, 29.5, 29.5, 29.5, 22.9, 14.3 ppm; EI-HRMS (m/z): calcd for C61H83O79Br [M]+ 910.5622, found 910.5621.

2,5-bis(4-Hexadecylphenyl)-3-phenyl-4-(3-((trimethylsilyl)ethynyl)phenyl)cyclopenta-2,4-dienone (40): A 500 mL Schlenk round bottom flask was charged under N2 with 39 (4.53 g, 4.96 mmol) and CuI (102 mg, 0.54 mmol) in triethylamine (275 mL). The reaction mixture was degassed. Trimethylsilylacetylene (2.25 mL, 15.9 mmol) and Pd(PPh3)4 (275 mg, 0.24 mmol) were added and the reaction mixture was stirred at 80 °C for 17 h. The reaction mixture was cooled to 24 °C and the solvent removed under reduced pressure. The purple residue was taken up in CH2Cl2 (300 mL) and washed with saturated aqueous NH4Cl (200 mL) and saturated aqueous NaCl (200 mL), dried over MgSO4, filtered, and concentrated on a rotary evaporator. Column chromatography (SiO2; 6:1 hexane/CH2Cl2) yielded 40 (3.79 g, 4.08 mmol, 82%) as a purple solid. 1H NMR (500 MHz, CD2Cl2, 22 °C): δ = 7.32 (m, 1H), 7.28–7.23 (m, 1H), 7.21–7.18 (m, 2H), 7.17–7.11 (m, 5H), 7.11–7.04 (m, 5H), 6.96–6.93 (m, 2H), 6.90–6.88 (m, 1H), 2.62–2.54 (m, 4H), 1.66–1.54 (m, 4H), 1.41–1.09 (m, 52H), 0.88 (t, J = 6.9 Hz, 6H), 0.19 (s, 9H) ppm; 13C {1H} NMR (151 MHz, CDCl3): δ 201.0, 153.9, 152.9, 142.7, 142.5, 134.0, 133.3, 132.6, 131.9, 130.1, 130.0, 129.5, 129.4, 128.6, 128.3, 128.3, 128.2, 128.1, 127.8, 125.5, 125.0, 123.2, 104.6, 94.9, 36.0, 35.9, 32.1, 31.4, 31.3, 29.9,
29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 22.8, 14.3, 0.0 ppm; EI-HRMS (m/z): calcd for C_{66}H_{93}OSi [M+H]^+ 929.6990, found 929.6990.

3-(3-Ethynylphenyl)-2,5-bis(4-hexadecylphenyl)-4-phenylcyclopenta-2,4-dienone (36): A 1000 mL three neck round bottom flask was charged under N₂ with 40 (3.68 g, 3.96 mmol) in THF (350 mL) and MeOH (350 mL). Solid KF (1.39 g, 23.9 mmol) was added and the reaction mixture was stirred at 40 °C for 7 h. The reaction mixture was concentrated on a rotary evaporator. Column chromatography (SiO₂; 6:1 hexane/CH₂Cl₂) yielded 36 (2.77 g, 3.23 mmol, 82%) as purple solid. ¹H NMR (600 MHz, CD₂Cl₂, 22 °C): δ = 7.36 (dt, J = 7.8, 1.4 Hz, 1H), 7.28–7.24 (m, 1H), 7.22–7.18 (m, 2H), 7.15 (t, J = 7.8 Hz, 1H), 7.13–7.10 (m, 4H), 7.10–7.05 (m, 5H), 6.96–6.92 (m, 3H), 3.04 (s, 1H), 2.59–2.52 (m, 4H), 1.63–1.54 (m, 4H), 1.35–1.11 (m, 52H), 0.88 (t, J = 7.0 Hz, 6H) ppm; ¹³C {¹H} NMR (151 MHz, CDCl₃, 22 °C): δ = 200.9, 153.8, 152.7, 142.7, 142.5, 134.0, 133.3, 132.9, 132.1, 130.1, 130.0, 129.9, 129.4, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 125.7, 125.1, 122.1, 83.2, 77.7, 35.9, 32.1, 31.3, 31.3, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 22.8, 14.3 ppm; EI-HRMS (m/z): calcd for C_{63}H_{85}O [M+H]^+ 857.6595, found 857.6591.

Poly-36 A 5 mL Schlenk tube was charged under N₂ with 36 (32 mg, 0.037 mmol) and diphenyl ether (167 mg, 0.98 mmol). The reaction mixture was degassed, the vessel sealed under N₂, and the reaction mixture was stirred at 230 °C for 6 h. After cooling to 24 °C the residue was taken up in THF and precipitated in MeOH (1:2 by volume) and centrifuged. The pellet was reprecipitated 4× to yield polymer poly-36 as a yellow solid (28 mg, 91%). 42 was prepared according to a literature procedure.²²²
1,6-Bis((trimethylsilyl)ethynyl)pyrene (43): A 50 mL Schlenk tube was charged with 42 (379 mg, 1.0 mmol), CuI (18 mg, 0.096 mmol, 0.10 eq), magnetic stirbar, THF (7 mL), and NEt$_3$ (2.5 mL) under N$_2$. The reaction mixture was degassed freeze-pump-thaw. Pd(PPh$_3$)$_4$ (69 mg, 0.059 mmol, 0.06 eq) and TMSA (0.85 mL, 6.0 mmol, 6 eq) were added under N$_2$ and the reaction mixture was stirred at 50 °C for 43 h. The solvent was removed under reduced pressure and the residue was extracted with Et$_2$O. The combined organics were washed with 1M HCl (20 mL), and sat. NaCl (20 mL), dried with MgSO$_4$, filtered, and the solvent removed under reduced pressure. Column chromatography (SiO$_2$: 9:1 hexanes/EtoAc) yielded 43 (347 mg, 0.88, 88%) as a yellow solid. $^1$H NMR (500 MHz, CDCl$_3$, 22 °C): δ = 8.54 (d, J=8.9 Hz, 2H), 8.14 (d, J=7.7 Hz, 2H), 8.12–8.05 (m, 4H), 0.42 (s, 18H) ppm; $^{13}$C {$^1$H} NMR (126 MHz, CDCl$_3$, 22 °C): δ = 132.2, 131.1, 130.1, 128.1, 126.2, 125.0, 123.9, 118.2, 103.8, 100.6, 0.18 ppm; EI-HRMS (m/z): calcd for C$_{26}$H$_{26}$Si$_2$ [M]$^+$ 394.1573, found 394.1577. Matches previous report.

1,6-Diethynylpyrene (44): A 25 mL roundbottom flask was charged with 43 (347 mg, 0.88 mmol), MeOH (5 mL) and CHCl$_3$ (10 mL) under N$_2$. Solid K$_2$CO$_3$ (506 mg, 3.67 mmol, 4.2 eq) was added and the reaction mixture was stirred at 22 °C for 1 h. The reaction mixture was diluted with CHCl$_3$ (20 mL) and washed with 1M HCl (10 mL) and brine (10 mL), dried over MgSO$_4$, filtered, and the solvent removed under reduced pressure. Recrystallization from CHCl$_3$ yielded 44 as a brown solid (120 mg, 0.48 mmol, 55%). $^1$H NMR (500 MHz, CDCl$_3$, 22 °C): δ = 8.63 (d, J=9.0 Hz, 2H), 8.24–8.12 (m, 6H), 3.64 (s, 2H) ppm; $^{13}$C {$^1$H} NMR (126 MHz, CDCl$_3$, 22 °C): δ = 132.5, 131.3, 130.5, 128.2, 126.2, 125.1, 123.8, 117.2, 93.0, 82.5 ppm; EI-HRMS (m/z): calcd for C$_{20}$H$_{10}$ [M]$^+$ 250.0783, found 250.0783. Matches previous report.
1,6-Di(prop-1-yn-1-yl-3-$^{13}$C)pyrene (45): An oven-dried 50 mL Schlenk tube was charged with 44 (9 mg, 0.036 mmol), dry THF (6 mL), and a magnetic stir bar under N$_2$. The reaction mixture was cooled to –78 °C and n-BuLi (2.5M in hexanes, 0.1 mL, 0.25 mmol, 7 eq) was added and stirred for 1 h. $^{13}$C-MeI (0.1 mL, 1.6 mmol, 45 eq) was then added and stirred for 14 h with gradual warming to 22 °C. The reaction was quenched with addition of sat. NH$_4$Cl (10 mL), extracted with Et$_2$O (10 mL). The combined organics were washed with sat. NaCl (10 mL), dried with MgSO$_4$, filtered, and the solvent removed under reduced pressure. Column chromatography (SiO$_2$: hexanes) yielded 45 as a yellow solid (6 mg, 0.02 mmol, 59%). $^1$H NMR (400 MHz, CDCl$_3$, 22 °C): δ = 8.56 (d, $J$=9.1 Hz, 2H), 8.13–8.03 (m, 6H), 2.30 (d, $J$=131.7 Hz, 6H) ppm.

[1,1′:2′,1″:2″,1‴-Quaterphenyl]-4″,5′-diamine (49): A 250 mL 3-neck roundbottom flask was charged with 2 (3.23 g, 7.41 mmol), Ph-B(OH)$_2$ (3.67 g, 30.1 mmol, 4.1 eq), K$_2$CO$_3$ (8.43 g, 61 mmol, 8.2 eq), Pd(PPh$_3$)$_4$ (147 mg, 0.13 mmol, 0.018 eq), THF (80 mL), H$_2$O (60 mL), and a magnetic stir bar under N$_2$. The reaction mixture was degassed by freeze-pump-thaw and stirred at 75 °C for 24 h. After cooling to 22 °C the crude mixture was filtered through celite and washed with sat. NaHCO$_3$ (2 × 50 mL), sat. NaCl (2 × 50 mL), and the combined organics were dried with MgSO$_4$, filtered, and the solvent removed under reduced pressure. Column chromatography (SiO$_2$: 40% EtOAc in hexanes) yielded 49 (319 mg, 0.95 mmol, 13%). $^1$H NMR (600 MHz, CDCl$_3$, 22 °C): δ = 7.12 (d, $J$=8.1 Hz, 2H), 7.06 (t, $J$=7.3 Hz, 2H), 6.99 (t, $J$=7.5 Hz, 4H), 6.68–6.62 (m, 6H), 6.49 (d, $J$=2.0 Hz, 2H), 3.67 (s(br), 4H) ppm; EI-HRMS (m/z): calcd for C$_{24}$H$_{20}$N$_2$ [M]$^+$ 336.1626, found 336.1622. Matches previous report.??
4",5'-Diiodo-1,1':2',1"':2",1""'-quaterphenyl (50): A 100 mL roundbottom flask was charged with 49 (283 mg, 0.84 mmol) and a magnetic stirbar. The reaction vessel was submerged in an ice water bath and to it were added sequentially H<sub>2</sub>O (20 mL), conc. HCl (6 mL), and H<sub>2</sub>SO<sub>4</sub> (20 mL). When the reaction mixture had reached 0 °C a solution of NaNO<sub>2</sub> (125 mg, 1.81 mmol, 2.2 eq) in H<sub>2</sub>O (14 mL) was added dropwise over 17 min, maintaining an internal temperature <10 °C, and stirred for 1 h at 0 °C. The reaction mixture was then poured quickly into a solution of KI (1.50 g, 9.04 mmol, 10.8 eq) at 0 °C and stirred for 16 h with gradual warming to 22 °C. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL) and the combined organics were washed with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (aq), and sat. NaCl, dried over MgSO<sub>4</sub>, filtered, and the solvent removed under reduced pressure. Column chromatography (SiO<sub>2</sub>: hexanes) yielded 50 (219 mg, 0.39 mmol, 47%) as a colorless solid. ¹H NMR (500 MHz, CDCl<sub>3</sub>, 22 °C): δ = 7.66 (dd, J=8.2, 1.6 Hz, 2H), 7.51 (t, J=1.9 Hz, 2H), 7.12 (t, J=7.3 Hz, 2H), 7.07 (d, J=8.1 Hz, 2H), 7.03 (t, J=7.6 Hz, 4H), 6.56 (d, J=7.6 Hz, 4H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl<sub>3</sub>, 22 °C): δ = 143.0, 139.2, 138.9, 138.6, 136.3, 133.2, 129.1, 127.9, 126.8, 93.6 ppm; EI-HRMS (m/z): calcd for C<sub>24</sub>H<sub>16</sub>I<sub>2</sub> [M]⁺ 557.9342, found 557.9346.

[1,1':2',1"':2",1""'-Quaterphenyl]-4",5'-dicarbaldehyde (51): An oven dried 25 mL Schlenk roundbottom flask was charged with 50 (182 mg, 0.33 mmol), a magnetic stirbar, and dry THF (10 mL). The reaction mixture was cooled to −78 °C and n-BuLi (2.5M in hexanes, 0.30 mL, 0.75 mmol, 2.3 eq) was added dropwise over 2 min. The reaction mixture was stirred under N<sub>2</sub> at −78 °C for 1 h, then dry DMF (3 mL) was added and the reaction mixture was stirred for 16 h with gradual warming to 22 °C. yielded 51 as a colorless solid (36 mg, 0.10 mmol, 30%). ¹H NMR (500 MHz, CDCl<sub>3</sub>, 22 °C): δ = 10.05 (s, 2H), 7.90 (dd, J= 8.2, 1.9 Hz, 2H), 7.70 (d, J= 2.0 Hz, 2H), 7.59 (d, J=8.2 Hz, 2H), 7.14 (t, J=7.25 Hz, 2H), 7.04 (t, J=7.5 Hz, 4H), 6.60 (d, J=8.7 Hz, 4H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl<sub>3</sub>, 22 °C):
$\delta = 192.0, 145.2, 142.0, 139.1, 136.1, 132.3, 131.9, 129.2, 128.1, 128.0, 127.1$ ppm; EI-HRMS ($m/z$): calcd for C$_{26}$H$_{18}$O$_2$ [M$^+$] 362.1307, found 362.1312.

$4'',5''$-Di(vinyl-$^{13}$C)-1,1'':2',1'':2'',1'':-quaterphenyl (52): An oven dried 25 mL Schlenk round-bottom flask was charged with $^{13}$C-MePPh$_3$I (36 mg, 0.089 mmol, 3.2 eq), dry THF (3.5 mL), and a magnetic stirbar under N$_2$. The reaction mixture was cooled to 0 °C and t-BuOK (11.5 mg, 0.10 mmol, 3.7 eq) was added. The reaction mixture was stirred at 0 °C for 1 h, then 51 (10 mg, 0.028 mmol) was added. The mixture was stirred at 0 °C for 1 h, and then for a further 16 h at 22 °C. The crude mixture was diluted with Et$_2$O (10 mL) and washed with sat. NH$_4$Cl (10 mL) and sat. NaCl (10 mL). The combined organics were dried over MgSO$_4$, filtered, and the solvent removed under reduced pressure. Column chromatography (SiO$_2$: hexanes) yielded 52 (8 mg, 0.022 mmol, 79%) as a colorless solid. $^1$H NMR (500 MHz, CDCl$_3$, 22 °C): $\delta =$ 7.41 (d, $J$=7.5 Hz, 2H), 7.35 (d, $J$=7.9 Hz, 2H), 7.21 (s, 2H), 7.10 (t, $J$=7.2 Hz, 4H), 6.73 (dd, $J$=17.6 , 11.0 Hz, 2H), 6.65 (d, $J$=7.4 Hz, 4H), 5.77 (dd, $J$=154.4, 17.6 Hz, 2H), 5.26 (dd, $J$=160.3, 10.9 Hz, 2H) ppm; $^{13}$C ($^1$H) NMR (126 MHz, CDCl$_3$, 22 °C): $\delta =$ 141.3, 140.9, 139.4, 136.8, 136.3, 132.0, 129.2, 128.3, 127.7, 126.2, 124.9, 114.1 ppm.

$4'',5''$-Di(ethynyl-$^{13}$C)-1,1':2',1'':2'',1'':-quaterphenyl (48): An oven dried 50 mL Schlenk tube was charged with 52 (8 mg, 0.022 mmol), dry CH$_2$Cl$_2$ (3 mL), and a magnetic stirbar. The reaction mixture was cooled to 0 °C and a solution of Br$_2$ in CH$_2$Cl$_2$ (0.6M, 0.1 mL, 0.06 mmol, 2.7 eq) was added dropwise over 10 min. The reaction was stirred at 0 °C for 30 min, then stirred at 22 °C for a further 2 h. Volatiles were removed at reduced pressure and dry Et$_2$O (3 mL) was added to the reaction vessel, at which point t-BuOK (70 mg, 0.62
mmol, 28 eq) was added with stirring over 1 h, then stirred at 22 °C for 5 h. The mixture was washed with H₂O (2 × 2 mL) and sat. NaCl (2 mL), the combined organics were dried over MgSO₄, filtered, and the solvent removed at reduced pressure. Column chromatography (SiO₂: hexanes:toluene 95:5) yielded 48 (3 mg, 0.008 mmol, 36%) as a colorless solid. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 7.47 (d, J = 8.5 Hz, 2H), 7.36–7.30 (m, 4H), 7.10 (t, J = 6.8 Hz, 2H), 7.01 (t, J = 7.8 Hz, 4H), 6.57 (d, J = 8.1 Hz, 4H), 3.10 (d, J = 251.6 Hz, 2H) ppm.

2-(4-[2-¹³C]Vinylphenyl-1,3-dioxolane) (54): A 200 mL Schlenk round bottom flask was charged under N₂ with methyl-¹³C-triphenylphosphonium iodide (219 mg, 0.54 mmol) in dry THF (12 mL). The reaction mixture cooled to 0 °C, followed by addition of t-BuOK (72 mg, 0.64 mmol). The reaction mixture was stirred at 0 °C for 1 h. After darkening the flask with aluminum foil, a solution of 4-(1,3-dioxolan-2-yl)benzaldehyde (99 mg, 0.55 mmol) in dry THF (3 mL) was added to the yellow reaction mixture at 0 °C. The reaction mixture was stirred for 24 h at 24 °C in the dark. The reaction mixture was diluted with EtOAc (50 mL) and washed with saturated aqueous ammonium chloride. The aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic phases were dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Column chromatography (SiO₂; 9:1 hexane/ EtOAc) yielded 54 (87 mg, 0.49 mmol, 88%) as a colorless oil. ¹H NMR (600 MHz, CDCl₃, 22 °C): δ = 7.48–7.36 (m, 4H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.81 (s, 1H), 5.77 (ddd, J = 154.6, 17.6, 0.9 Hz, 1H), 5.26 (ddd, J = 160.5, 10.9, 0.9 Hz, 1H), 4.18–4.09 (m, 2H), 4.08–3.99 (m, 2H) ppm; ¹³C {¹H} NMR (126 MHz, CDCl₃, 22 °C): δ = 138.6, 137.5, 136.6 (d, J = 69.7 Hz), 126.8, 126.3 (d, J = 4.9 Hz), 114.6, 103.7, 65.4 ppm; EI-HRMS (m/z): calcd for [M]+ 177.0871, found 177.0871.

2-(4-[2-¹³C]Ethynylphenyl)-1,3-dioxolane (55): A 100 mL Schlenk round bottom flask was charged under N₂ with 54 (219 mg, 1.24 mmol) in dry CH₂Cl₂. Br₂ (0.1 mL, 1.94 mmol) was added dropwise over 2 min at 0 °C and the reaction mixture was stirred at 0 °C for 3 h. Solvent and excess Br₂ were removed at reduced pressure. The residue was dissolved in
dry THF (60 mL) and cooled to 0 °C, followed by addition of t-BuOK (497 mg, 4.43 mmol). The reaction mixture was stirred for 1 h at 0 °C, and then 15 h at 24 °C. The reaction mixture was quenched with saturated aqueous ammonium chloride (60 mL), and extracted with EtOAc (3×60 mL). The combined organic phases were dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Column chromatography (SiO₂; 9:1 hexane/ EtOAc) yielded 55 (84 mg, 0.48 mmol, 39%) as a colorless solid; ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 7.51 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 5.81 (s, 1H), 4.16–4.09 (m, 2H), 4.09–4.01 (m, 2H), 3.09 (d, J = 251.5 Hz, 1H) ppm; ¹³C ¹H NMR (126 MHz, CDCl₃, 22 °C): δ = 138.6, 132.2, 126.5, 123.0 (d, J = 12.7 Hz), 103.3, 83.5 (d, J = 176.3 Hz), 77.8, 65.4 ppm; ESI-HRMS (m/z): calcd for C₁₂H₁₀O₂ [M]+ 175.00714, found 175.0709.

4-[2-¹³C]Ethynylbenzaldehyde (56): A 25 mL round bottom flask was charged with 55 (72 mg, 0.41 mmol), in MeOH (6 mL). Aqueous HCl (1 M, 6 mL) was added and the reaction mixture stirred for 3 h at 30 °C. The reaction mixture was quenched with saturated aqueous NaHCO₃ (10 mL) and extracted with CH₂Cl₂ (3×15 mL). The combined organic phases were washed with saturated aqueous NaCl (30 mL), dried over MgSO₄, filtered, and concentrated on a rotary evaporator. Column chromatography (SiO₂; 2:1 hexane/ CH₂Cl₂) yielded 56 (42 mg, 0.32 mmol, 78%) as a colorless solid. ¹H NMR (500 MHz, CDCl₃, 22 °C): δ = 10.02 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 3.29 (d, J = 253.1 Hz, 1H) ppm; ¹³C ¹H NMR (126 MHz, CDCl₃, 22 °C): δ = 191.6, 136.0, 132.8, 129.6, 128.4 (d, J = 12.7 Hz), 82.0 (d, J = 8.2 Hz), 81.22 ppm; ESI-HRMS (m/z): calcd for C₈H₆O₁ [M]+ 131.0452, found 131.0449.

5,15-bis(4-[2-¹³C]Ethynlphenyl)-10,20-diphenyl-21H,23H-porphine (57): A 100 mL Schlenk round bottom flask was charged under N₂ with 56 (40 mg, 0.305 mmol) and
5-phenyldipyrromethane (68 mg, 0.306 mmol) in dry CH$_2$Cl$_2$ (32 mL). The reaction vessel was darkened with aluminum foil. TFA (0.02 mL, 0.26 mmol) was added and the reaction mixture was stirred at 24 °C for 3 h, at which point DDQ (144 mg, 0.63 mmol) was added and the reaction mixture stirred at 24 °C for an additional 1 h. The reaction mixture was quenched with NEt$_3$ (1 mL) and filtered through a plug of silica, eluting with CH$_2$Cl$_2$, and concentrated on a rotary evaporator. Column chromatography (SiO$_2$; 1:1 hexane/CH$_2$Cl$_2$) yielded 57 (11 mg, 0.17 mmol, 11%) as a purple solid. $^1$H NMR (500 MHz, CDCl$_3$, 22 °C): $\delta$ = 8.89–8.79 (m, 8H), 8.23–8.17 (m, 8H), 7.90 (d, $J = 7.7$ Hz, 4H), 7.80–7.72 (m, 6H), 3.32 (d, $J = 251.4$ Hz, 2H), -2.81 (s, br, 2H) ppm; $^{13}$C $\{^1$H$\}$ NMR (226 MHz, CDCl$_3$, 22 °C): $\delta$ = 142.9, 142.8, 142.2, 142.1, 134.6 (d, $J = 18.3$ Hz), 130.7, 128.0, 127.9, 126.9, 125.0, 121.8, 120.6, 120.4, 119.4, 78.5, 78.4 (d, $J = 88$ Hz) ppm; ESI-HRMS ($m/z$): calcd for $^{12}$C$_{46}^{13}$C$_2$H$_{31}$N$_4$ [M+H]$^+$ 665.2610, found 665.2609.

58: A 5 mL Schlenk tube was charged under N$_2$ with 36 (62 mg, 0.072 mmol), 57 (2.0 mg, 0.003 mmol) and diphenyl ether (280 mg, 1.65 mmol). The reaction mixture was degassed, the vessel sealed under N$_2$, and the reaction mixture was stirred at 230 °C for 16 h. After cooling to 24 °C the residue was taken up in THF and precipitated in MeOH (1:2 by volume) and centrifuged. The pellet was reprecipitated 4× to yield polymer 58 as a red solid (53.4 mg, 86%), Mn = 29 000, PDI = 1.8 based on SEC analysis. Fractionation by chromatography over SiO$_2$ (10% DCM in hexanes, followed by DCM) yielded poly-36 (28 mg), Mn = 27 000, PDI = 2.2, and 58 (25 mg) Mn = 11 000, PDI = 1.2.
60: A 500 mL Schlenk round bottom flask was charged under N\textsubscript{2} with polymer 58 (50 mg) in dry CH\textsubscript{2}Cl\textsubscript{2} (200 mL). To this was added a solution of FeCl\textsubscript{3} (3.923 g, 24.2 mmol) in dry MeNO\textsubscript{2} (8 mL). Nitrogen was bubbled through the reaction mixture with stirring at 24 °C for 66 h. The reaction mixture was then poured into MeOH (800 mL) and filtered. The dark precipitate was washed sequentially with MeOH (500 mL), THF (500 mL), 1M HCl (500 mL), H\textsubscript{2}O (500 mL), 15% NaOH (500 mL), and MeOH (500 mL) to yield 60 as a dark purple powder (48 mg, 97%).

60@Zn: A 25 mL heavy wall pressure vessel was charged with GNR 60 (10 mg) and Zn(OAc)\textsubscript{2} (18 mg, 0.098 mmol), in toluene (6 mL). The reaction mixture was sonicated for 5 min., and then stirred at 120 °C for 42 h. The reaction mixture was filtered and the precipitate washed sequentially with toluene, MeOH, 1M HCl, H\textsubscript{2}O, 15% NaOH, H\textsubscript{2}O, and MeOH to yield 60@Zn as a dark purple powder (9 mg, 90%).

Figure 5.1: Collected line scans of the Raman mapping experiments (Figure 3.11) for A) Zn@60 on aminated SAM, B) cGNR on aminated SAM, and C) Zn@60.
Table 5.1: Controlled potential electrolysis experiments at $-0.47$ V using coveester GNR-AuNP composite electrodes. Results of controlled potential electrolysis experiments at $-0.47$ V to explore the stability and CO$_2$ reduction performance of the coveester GNR-AuNP composite electrodes. Note: The TCD channel of the GC has a high detection limit for H$_2$ and the internal standard C$_2$H$_4$, leading to some uncertainty in the quantification of H$_2$. As a result, the Faradaic efficiency for H$_2$ and the overall Faradaic efficiency have an error of up to $\pm 10\%$. However, the CO quantification by GC (FID) is accurate, and therefore so are the corresponding Faradaic efficiencies.

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Table 5.2: Controlled potential electrolysis experiments at $-0.47$ V using cove GNR-AuNP composite electrodes. Results of controlled potential electrolysis experiments at $-0.47$ V to explore the stability and CO$_2$ reduction performance of the cove GNR-AuNP composite electrodes. Note: The TCD channel of the GC has a high detection limit for H$_2$ and the internal standard C$_2$H$_4$, leading to some uncertainty in the quantification of H$_2$. As a result, the Faradaic efficiency for H$_2$ and the overall Faradaic efficiency have an error of up to $\pm 10\%$. However, the CO quantification by GC (FID) is accurate, and therefore so are the corresponding Faradaic efficiencies.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Total Charge (C)</th>
<th>Volume CO (mL)</th>
<th>FE$_{CO}$ (%)</th>
<th>Volume H$_2$ (mL)</th>
<th>FE$_{H2}$ (%)</th>
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### Table 5.3: Controlled potential electrolysis experiments at $-0.47$ V using chevron GNR-AuNP composite electrodes.

Results of controlled potential electrolysis experiments at $-0.47$ V to explore the stability and CO$_2$ reduction performance of the chevron GNR-AuNP composite electrodes. Note: The TCD channel of the GC has a high detection limit for H$_2$ and the internal standard C$_2$H$_4$, leading to some uncertainty in the quantification of H$_2$. As a result, the Faradaic efficiency for H$_2$ and the overall Faradaic efficiency have an error of up to $\pm 10\%$. However, the CO quantification by GC (FID) is accurate, and therefore so are the corresponding Faradaic efficiencies.

<table>
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<tr>
<th>Time (h)</th>
<th>Total Charge (C)</th>
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<th>FE$_{CO}$ (%)</th>
<th>Volume H$_2$ (mL)</th>
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### Table 5.4: Controlled potential electrolysis experiments at $-0.47$ V using Cblack-AuNP composite electrodes.

Results of controlled potential electrolysis experiments at $-0.47$ V on Cblack-AuNP composite electrodes to serve as a standard reference for GNR composite performance and stability. Note: The TCD channel of the GC has a high detection limit for H$_2$ and the internal standard C$_2$H$_4$, leading to some uncertainty in the quantification of H$_2$. As a result, the Faradaic efficiency for H$_2$ and the overall Faradaic efficiency have an error of up to $\pm 10\%$. However, the CO quantification by GC (FID) is accurate, and therefore so are the corresponding Faradaic efficiencies.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Total Charge (C)</th>
<th>Volume CO (mL)</th>
<th>FE$_{CO}$ (%)</th>
<th>Volume H$_2$ (mL)</th>
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Figure 5.2: Raman spectra of GNRs. Chevron GNRs (62) (blue), cove GNRs (65a) (red), and coveester GNR (65b) (black).
CHAPTER 5. SUPPORTING INFORMATION

Figure 5.3: X-ray photoelectron spectroscopy (XPS) characterization GNRs. XPS of chevron GNRs (62) (blue), cove GNRs (65a) (red), and coveester GNRs (65b) (black). Samples were prepared by sonicating 0.5 mg of the respective GNR in THF (0.5 mL) and dropcasting onto a Si wafer held at 80 °C. All samples show prominent C 1s signals from the deposited GNR, as well as Si and O signals from the underlying substrate. While adventitious Ca was observed in some samples, prominent signals associated with Ni (2p3/2, 853 eV; 2p1/2, 870 eV) and Fe (2p3/2, 707 eV; 2p1/2, 720 eV) used as reagents or catalysts in the GNR synthesis could not be detected in purified GNR.

Figure 5.4: Structural characterization of GNRs. (A,B) STEM of chevron GNR (62) aggregates.
CHAPTER 5. SUPPORTING INFORMATION

Figure 5.5: Electrocatalytic performance of SWCNT-AuNP composites. SWCNT-AuNP composites serve as an additional point of reference for the performance of GNR-AuNP composites. The SWCNT-AuNP composite materials exhibit drastically inferior performance, even in comparison to Cblack composites. In a direct comparison with GNR composites, CO$_2$ reduction activity was significantly reduced at mildly reducing potentials, and correspondingly FECO is reduced across the entire potential window. SWCNT-AuNP composites were prepared following the same procedure described for GNR and Cblack composites, but using SWCNTs as support material. All electrochemical experiments were performed in 0.5 M aqueous KHCO$_3$ solution saturated with CO$_2$ (pH 7.3). (A) Cyclic voltammogram of SWCNT-AuNP composite material. (B) Faradaic efficiencies for CO production (FECO) by SWCNT-AuNP composite electrodes. Electrolysis performed at potentials from $-0.47$ V to $-0.77$ V vs. RHE. (C) Total current density for SWCNT-AuNP composite over 4 h at $-0.77$ V vs. RHE. Note that this potential is more negative than that used for long-term controlled potential electrolysis experiments using GNR or Cblack support materials ($-0.47$ V vs. RHE); at $-0.47$ V the SWCNT composite showed minimal CO$_2$ reduction activity. Across the 4 h experiment, FECO for the SWCNT-AuNP composite fell to 27% from its initial value of 61%.
Figure 5.6: (A) HAADF-STEM image of Cblack-AuNP composites after annealing show a narrow size distribution centered around an average NP diameter of 8 nm. (B) HAADF-STEM image of Cblack-AuNP composites after 3 h of bulk electrocatalysts in 0.5 M aqueous KHCO$_3$ saturated with CO$_2$ (pH 7.3) show a significant broadening of the AuNP size distribution as a result of sintering of AuNPs.

Figure 5.7: IR spectrum of coveester GNRs. The carbonyl CO stretch of the coveester GNR (65b) following the Scholl reaction matches that of the ester-functionalized poly-73, indicating that the esters remain intact. A partially saponified sample of poly-73 shows a significant shift of the CO stretching frequency that is absent in the IR spectrum of coveester GNR (65b). We thus conclude that the methyl esters in coveester GNR (65b) have not been saponified under the reaction conditions.
Figure 5.8: MALDI of GNR precursor polymers. MALDI mass spectrometry of (A) chevron GNR precursor poly-61, (B) cove GNR precursor poly-64a, (C) covester GNR precursor poly-64b.
Figure 5.9: SEM comparison of ball milled and hand ground GNR/SnO$_2$ composite electrodes.
Chapter 6

Appendix

This chapter includes the Quantum Espresso input files for electronic calculations on $N = 9$ and $N = 11$ AGNRs, unfuctionalized, ester functionalized, and carboxylic acid functionalized cove GNRs, and chevron GNRs.
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CHAPTER 6. APPENDIX

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C 0.748149245 1.442585426 0.000000000
C 4.439402382 2.197861526 0.000000000
C 5.681927119 1.441592235 0.000000000
K_POINTS automatic

8 1 1 0 0 0
Non Self-Consistent Input

&CONTROL

  calculation = 'nscf',
  outdir = '/home/wsperkins/Quantum_Pyrene/Carboxycove/262680',
  pseudo_dir = '/usr/software/espresso-5.1.1/pseudo',
  prefix = 'AcidCove',
  forc_conv_thr = 1.0D-3,

/&

&SYSTEM

  ibrav = 8,
  celldm(1) = 14,
  celldm(2) = 20,
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  nat = 44,
  ntyp = 3,
  ecutwfc = 20.0,
  ecutrhop = 80.0,
  nbnd = 85,

/&

&ELECTRONS

  conv_thr = 0.000001,

/&

ATOMIC_SPECIES

  O 15.99940 O.pbe-mt_fhi.UPF
  C 12.01070 C.pbe-mt_fhi.UPF
  H  1.00794 H.pbe-mt_fhi.UPF

ATOMIC_POSITIONS angstrom

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K_POINTS automatic
Density of States Input

&DOS

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   outdir = '/home/wsperkins/Quantum_Pyrene/Carboxycove/262680',
    fildos = 'CarboxyCove_fildos',
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    degauss = 0.00073499,
    DeltaE = 0.01,

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Band Structure Input

&BANDS

    prefix = 'AcidCove',
    outdir = '/home/wsperkins/Quantum_Pyrene/Carboxycove/262680',
    filband = 'CarboxyCove_bands_filband',

/

6.4 Ester Functionalized Cove GNR Quantum Espresso Code

Relax Calculation Input

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    prefix = 'estercove',
    verbosity = 'high',
    forc_conv_thr = 1.0D-3,
&SYSTEM

ibrav = 8,
celldm(1) = 14,
celldm(2) = 20,
celldm(3) = 20,
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ntyp = 3,
ecutwfc = 20,
ecutrho = 80,
occupations = 'smearing',
degauss = 0.05D0,
smearing = 'marzari-vanderbilt',

&ELECTRONS

conv_thr = 0.000001,

&IONS

ATOMIC_SPECIES

C 12.01070 C.pbe-mt_fhi.UPF
H 1.00794 H.pbe-mt_fhi.UPF
O 15.99940 O.pbe-mt_fhi.UPF

ATOMIC_POSITIONS angstrom

C 10.854400000 -2.247400000 1.213200000
C 10.862200000 -3.666200000 1.220600000
C 10.850100000 2.007400000 1.220700000
C 10.853400000 0.588700000 1.213200000
C 9.617100000 -1.539100000 1.215800000
C 8.378700000 -2.243200000 1.220600000
C 8.376500000 -3.659400000 1.222800000
C 9.618900000 -4.330200000 1.220300000
C 9.616400000 -0.120700000 1.215800000
C 9.616400000 2.670900000 1.219900000
K_POINTS automatic
8 1 1 0 0 0

6.5 Unfunctionalized Cove GNR Quantum Espresso Code

Relax Calculation Input

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    prefix = 'cove',
    verbosity = 'high',
    forc_conv_thr = 1.0D-3,

/
&SYSTEM

    ibrav = 8,
    celldm(1) = 14,
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    celldm(3) = 20,
    nat = 38,
    ntyp = 2,
    ecutwfc = 20,
    ecutrho = 80,
    occupations = 'smearing',
    degauss = 0.05D0,
    smearing = 'marzari-vanderbilt',

/
&ELECTRONS

    conv_thr = 0.000001,

/
&IONS
/
ATOMIC_SPECIES
CHAPTER 6. APPENDIX

C 12.01070 C.pbe-mt.fhi.UPF
H 1.00794 H.pbe-mt.fhi.UPF

ATOMICPOSITIONS angstrom

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K_POINTS automatic

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6.6 Chevron GNR Quantum Espresso Code

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calculation = 'relax',
pseudo_dir = '/usr/software/espresso-5.1.1/pseudo/',
prefix = 'C_chevron',
verbosity = 'high',
forc_conv_thr = 1.0D-3,
/
&SYSTEM

ibrav = 8,
celldm(1) = 32.31,
celldm(2) = 5,
celldm(3) = 20,
nat = 108,
ntyp = 2,
ecutwfc = 5,
ecutrho = 20,
occupations = 'smearing',
degauss = 0.05D0,
smearing = 'marzari-vanderbilt',
/
&ELECTRONS

conv_thr = 0.000001,
CHAPTER 6. APPENDIX

/ &IONS
/
ATOMIC_SPECIES

C  12.01070  C.pbe-mt_fhi.UPF
H  1.00794  H.pbe-mt_fhi.UPF

ATOMIC_POSITIONS angstrom

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### 6.7 List of Abbreviations Used

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BIBLIOGRAPHY


