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Inserting Porphyrin Quantum Dots in Bottom-Up Synthesized Graphene Nanoribbons

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Abstract: Diels-Alder copolymerization of tetraphenylecyclopenta-dieneone, a precursor for cove graphene nanoribbons (cGNRs), with bifunctional porphyrins yields defined nanostructures comprised of a single cGNR-porphyrin-cGNR heterojunction within each ribbon. 13C-NMR labeling and high-resolution mass spectrometry of solubilized polymer intermediates indicates that every porphyrin is covalently linked to two extended segments of cGNRs. UV-Vis absorption and fluorescence emission spectroscopy reveal a strong electronic correlation between the porphyrin and the adjacent cGNR segments that can be attenuated through reversible metalation of the porphyrin core. Our versatile bottom-up synthetic strategy provides access to structurally well defined, functional GNR-quantum dot-GNR heterostructures within a single graphene nanoribbon.

The design and implementation of carbon-based functional nanoelectronic materials into device architecture relies on the development of synthetic tools capable of providing a precise and reproducible control over the structure of materials at the nanometer scale. Recent advances in the bottom-up synthesis of semiconducting graphene nanoribbons (GNRs), quasi-one dimensional strips of single-layer graphene, have enabled the preparation of carbon-based nanomaterials with exquisite control over the width,[1-5] the crystallographic symmetry (e.g. armchair,[1-13] zig-zag[14]), and the edge structure (cove,[15-16] chevron[17-20]) both in solution and on metal surfaces. While bottom-up synthesized GNRs have been touted for their intrinsic exotic electronic,[21-31] magnetic,[25, 29-32] and optical properties,[18, 27, 28, 33-34] examples for the deterministic assembly of functional bottom-up synthesized GNRs heterostructures have thus far been limited to uncontrolled copolymerization of molecular precursors on metal surfaces[6, 13, 18, 20] or the study of small-molecule model systems in solution.[35-37]

We herein report the solution-based bottom-up synthesis and characterization of a GNR heterostructure comprised of two segments of solubilized cove GNRs (cGNRs) linked by a substituted tetraphenylporphyrin core (1, Scheme 1) acting as a highly tunable molecular quantum dot (QD). While our synthetic strategy can be extended to a variety of bifunctional linkers (see Supporting Information), we herein focus on the integration of a disubstituted tetraphenylporphyrin (H2(TPP)) and its metal complexes into a cGNR-H2(TPP)-cGNR heterostructure. Mass spectrometry (MS) and 13C-NMR spectroscopy of 13C-labeled poly-phenylene intermediates underscores the exquisite structural control over monomer sequence in the cGNR-H2(TPP)-cGNR heterojunction. Electronic characterization of the resulting metalloporphyrin-cGNR hybrid materials by UV-Vis absorption and fluorescence emission spectroscopy shows strong electronic communication between the porphyrin and cGNR segments. We further demonstrate that reversible binding of primary amine ligands to the axial coordination site of the metalloporphyrin core can serve as a tool to direct the assembly of cGNR-Zn(TPP)-cGNR heterostructures on photolithographically patterned substrates.

[Scheme 1. Synthesis of cove-type GNRs featuring a single porphyrin at the center of the ribbon. Reaction conditions: a) Ph2O, 230 °C, 24 h, 40% b) FeCl3, CH3Cl2, CH3NO2, 24 °C, 2 h, 55%. * 99.5% 13C isotopically labelled.]

The deterministic bottom-up synthesis of cGNR-porphyrin-cGNR heterojunctions is depicted in Scheme 1. 5,15-bis(4-ethynylphenyl)-10,20-diphenylporphyrin (2) serves as the precursor for the porphyrin core in 1. The solubilized cGNR
segments are derived from tetraphenylcyclopentadienone monomer 3. Diels-Alder polymerization of 3 in the presence of 2 (19:2) yields the GNR polymer precursor 4 featuring a central porphyrin core extended on either side by chains of poly-3 along with the expected homopolymer poly-3. Size exclusion chromatography (SEC) analysis of the crude polymer mixtures (calibrated to polystyrene standards) show a monomodal size-distribution centered around $M_n = 29000$, a polydispersity index $D_{0.4} = 1.8$, and an average degree of polymerization $X_n = 35$ (determined by $^1$H-NMR end-group analysis of the characteristic porphyrin resonances at ~2.8 ppm). Matrix-assisted laser desorption/ionization (MALDI) mass spectrometry (Figure 1a) reveals the presence of two distinctive families of polymers separated by $\Delta m/z = 662$ g mol$^{-1}$, the mass of the tetraarylporphyrin 2. The repeat unit within both polymer families ($\Delta m/z = 829$ g mol$^{-1}$) corresponds to the mass of the monomer unit resulting from the Diels-Alder reaction and chelotropic extrusion of CO from 3. To gain insight into the efficiency of the functionalization of both alkynes in the tetraarylporphyrin 2 we followed the copolymerization of 3 with 99.5% $^{13}$C labeled 2. Characteristic $^{13}$C NMR resonances for the isotopically enriched terminal alkyne C-atom shift from $\delta = 79$ ppm in 2 to $\delta = 131$ ppm upon lateral extension of both ends of the porphyrin core with segments of poly-3. The absence of $^{13}$C labeled alkyne resonances ($\delta = 79$ ppm) in the crude polymerization mixture indicates that both functional ends of 2 have reacted and were efficiently incorporated into the extended polymer backbone. The crude polymerization mixture is thus comprised of only two distinctive polymeric species, the homopolymer poly-3 and the copolymer 4 featuring a single porphyrin core extended on both sides by chains of poly-3.

Fractionation of the crude polymer mixture through column chromatography over SiO$_2$ yields poly-3 and 4 in 45% and 40% isolated yield, respectively. While the MALDI mass spectrometry of poly-3 (Figure 2b) shows only one characteristic family of peaks separated by the monomer mass ($\Delta m/z = 829$ g mol$^{-1}$), the corresponding MALDI of 4 (Figure 1c) contains predominantly (> 95%) the desired copolymer alongside trace amounts of poly-3. Figure 1d shows the aromatic region of the $^{13}$C NMR spectra of fractionated poly-3 and copolymer 4. The diagnostic resonance associated with the 99.5% $^{13}$C labeled terminal alkyne in 2 appears at $\delta = 131$ ppm. Oxidative cyclodehydrogenation of both poly-3 and 4 with an excess of FeCl$_3$ gave solubilized cGNR and cGNR-porphyrin-cGNR heterostructure 1 in 96% and 97% isolated yield, respectively. Raman spectroscopy ($\lambda_R = 532$ nm) of fully cyclodehydrogenated 1 features characteristic radial breathing like mode (RBLM) ($194$ cm$^{-1}$ FWHM = 78 cm$^{-1}$), D ($1322$ cm$^{-1}$ FWHM = 62 cm$^{-1}$), and G ($1600$ cm$^{-1}$ FWHM = 38 cm$^{-1}$) peaks with a ratio $I_D/I_G = 1.2$ reminiscent of pristine cGNRs along with higher order 2D, D+G and 2G peaks (Figure 2a). We conclude that the incorporation of a single porphyrin core at the center of a cove-type GNR does not perturb the structure of the parent cGNR segments in 1.

Both cGNRs and cGNR-H$_2$(TPP)-cGNR heterostructure 1 feature solubilizing hexadecyl side chains and form stable dispersions after sonication and centrifugation in THF. The respective UV-Vis absorption spectra are depicted in Figure 2b. A broad absorption at $\lambda_{max} = 556$ nm characteristic for cGNRs dominates the spectrum of 1. The $\lambda_{max}$ of cGNR-H$_2$(TPP)-cGNR heterostructure 1 is only slightly shifted (~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 1 can be attributed to the corresponding $S_0 \rightarrow S_1$ transition (Soret band) in the porphyrin core, while the characteristic Q-bands are obscured by the dominant absorption of the cGNR segments. The bathochromic shift (~10 nm) of the Soret band in 1, when compared to the precursor 2 ($\lambda_{max} = 423$ nm), can be attributed to an efficient electronic coupling with the extended $\pi$-system of the adjacent cGNRs. An inherent strength of porphyrins as the central component in functional GNR heterostructures is the ability to reversibly tune the electronic structure of the porphyrin through late-stage metalation. Coordination of Zn$^{2+}$ ions to the
free-base porphyrin in 1 is mirrored in a diagnostic shift (∼10 nm) of the Soret band to longer wavelengths (1•Zn in Figure 2b) (coordination of Ru3+ or Al3+ ions induces a negligible shift, Supporting Information, Figure 2SI). The complexation of Zn2+ is quantitative, reflected in a rigid shift of the Soret band, and is fully reversible. Treatment of 1•Zn with trifluoroacetic acid in CH2Cl2 regenerates the free-base porphyrin 1.

Figure 2a shows a magnification of a region of the spectrum associated with the radial breathing like mode (RBLM) at 194 cm−1. b) UV-Vis spectra of dilute dispersions of cGNRs (black) (normalized to the absorption maximum of the GNR), 1 (red), and metalated 1•Zn (blue) (normalized to the Soret band). EEM fluorescence spectra for c) cGNRs and d) cGNR-H2(TPP)-cGNR heterostructures 1.

Figure 2c,d shows the excitation emission matrix (EEM) fluorescence spectra for cGNRs and cGNR-H2(TPP)-cGNR heterostructure 1, respectively. Excitation of pristine cGNRs at λex = 560 nm leads to a broad fluorescence emission centered around λem = 705 nm (Figure 2c). The emission of the cGNR-H2(TPP)-cGNR heterostructure 1 upon excitation at the same wavelength (λex = 560 nm) decreases significantly (Figure 2d) and no longer represent the emission maximum. If, however, the cGNR-H2(TPP)-cGNR heterostructure 1 is excited at λex = 425 nm, close to the Soret band of the porphyrin core, a very broad emission λem = 650–720 nm featuring emission characteristics of both the porphyrin and cGNR is observed. The energy transfer from the excited state of the porphyrin core (λex = 425) to the cGNR (λem = 705 nm) further support an efficient electronic communication between the central porphyrin and the extended cGNR segments.

Axial coordination of a ligand to the metal in cGNR-Zn(TPP)-cGNR heterostructures can be used as a tool to direct the self-assembly of functional GNRs on patterned substrates. Figure 3a shows an Al2O3 substrate decorated with photolithographically deposited Pt traces (Figure 3a). Self-assembled monolayer (SAM) of either 1-N-(3-(triethoxysilyl)propyl)hexane-1,6-diamine (NH2-SAM), or dodecyltrimethoxysilane (CH2-SAM) were selectively grown on the exposed Al2O3 substrate (NH2-SAM and CH2-SAM do not adhere to Pt traces). While the primary amine in NH2-SAM can reversibly bind to metalated 1, the CH2-SAM serves as a reference to account for dispersion interactions between solubilizing alkyl chains in 1 and an aliphatic SAM. Figure 3b shows a representative Raman map of the G peak intensity attributed to 1•Zn on a patterned substrate functionalized with NH2-SAM. The spatial distribution of the Raman signature of 1•Zn indicates that the interaction between the Zn2+ and the primary amine directs the assembly of 1•Zn exclusively on the NH2-SAM functionalized substrate. The significance of this selective metal ligand coordination is further supported by two control experiments. The spatial distribution of G peak intensity in Raman maps of 1•Zn on CH2-SAM (Figure 3c) or cGNRs on NH2-SAM functionalized substrates (Figure 3d) do not indicate a preference for adhesion to the SAM over the photo lithographically patterned Pt traces.
In summary, we report the deterministic bottom-up synthesis of a GNRL-QD-GNR heterostructure and its electronic characterization by UV-Vis and EEM fluorescence spectroscopy. Our synthetic strategy demonstrates that chains of a heteroditopic monomer can efficiently be fused by a single homoditopic linker. $^{13}$C-NMR labeling experiments, MALDI-TOF MS and Raman spectroscopy confirm that only one linker molecule is incorporated at the center of the heterostructure. UV-Vis and EEM fluorescence spectroscopy reveal a strong electronic coupling between the cGNR segments and the central porphyrin. Besides tuning the electronic structure of the porphyrin core itself, metatlas provides a secondary axial coordination site that can be used to direct the spatial localization of GNRL-QD-GNR heterostructures through the interaction with amine terminated SAMs on photo lithographically patterned substrates.

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The bottom-up solution-based synthesis and selective fractionation of graphene nanoribbon-porphyrin-graphene nanoribbon heterostructures is reported. Absorption and fluorescence spectroscopy reveal a strong coupling between the graphene nanoribbon and the central porphyrin quantum dot.