

Bottom-up Solution Synthesis of Long Graphene Nanoribbons with High Structural Definition

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Graphene nanoribbons (GNRs), namely nano-stripes of graphene, are attracting increasing attention as highly promising candidates for new generation semiconductor materials.¹ Theoretical and experimental studies have revealed that quantum confinement and edge effects impart GNRs with semiconducting properties, i.e. with a finite bandgap. The magnitude of the bandgap depends critically on the width and edge structures. While top-down methods such as lithographical patterning of graphene² and unzipping of carbon nanotubes^{3,4} cannot produce structurally defined GNRs, especially resulting in undefined edge structures, we have developed a bottom-up synthetic approach via intramolecular cyclodehydrogenation, namely “graphitization” and “planarization”, of three-dimensional polyphenylene precursors, which allowed the fabrication of GNRs with a variety of highly defined lateral structures.^{5,6,7} However, it has been challenging to synthesize well-extended (>100 nm) GNRs with high structural definition. In this study we employed Diels-Alder polymerization instead of previously used Suzuki and Yamamoto polymerization for synthesizing the polyphenylene precursors of GNRs, and achieved unprecedentedly high weight-average molecular weight (M_w) of up to 600000 g/mol based on size exclusion chromatography analysis. This M_w value corresponds to the longitudinal length of as long as ca. 600 nm for the resulting GNR **1** with lateral width of ~1 nm (Figure 1). Further, long alkyl chains densely installed on the periphery rendered the GNRs dispersible in standard organic solvents such as tetrahydrofuran and chlorobenzene, allowing characterizations in dispersions as well as solution processing. Characterization by infrared, Raman, and UV–vis absorption spectroscopies as well as investigation of model systems proved the efficiency of the “graphitization” and homogeneity of the GNRs (Figure 2). The optical bandgap of GNR **1** was revealed to be 1.88 eV based on the absorption edge, which was in good agreement with the estimated bandgap of 2.04 eV obtained by density functional theory (DFT) calculations.⁸ Moreover, scanning probe microscope demonstrated the formation of neatly organized self-assembled monolayers on HOPG, indicating high solution processability of GNR **1**. Applying the same synthetic strategy, we have also fabricated laterally extended GNR **2** with the width of ~2 nm (Figure 1). The efficient formation of GNR **2** was corroborated by infrared, Raman, and UV–vis absorption spectroscopies in the same manner as the characterization of GNR **1**. The dodecyl chains at the peripheral positions imparted slight dispersibility to GNR **2**, which allowed spectroscopic analyses in dispersion. Notably, the UV–vis absorption spectrum showed broad absorbance extending to the near infrared region with the optical bandgap of as low as 1.24 eV. This value was consistent with the DFT-calculated bandgap of 1.18 eV,⁸ indicating high structural identity of GNR **2**. These results further demonstrated the controllability of the bandgap of GNRs by changing the lateral width. Such structurally defined and solution processable GNRs with open and controllable bandgap are highly promising candidates for the application in next-generation optoelectronic devices, including field-effect transistors and solar cells.

References

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Figures

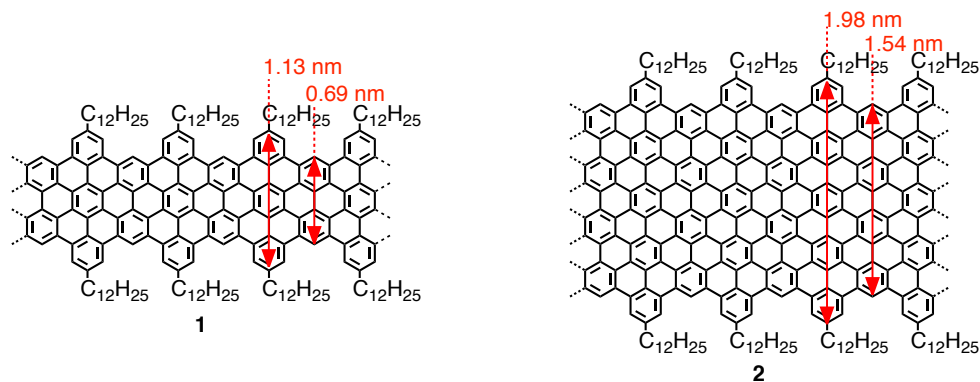


Figure 1. Chemical structures of GNRs 1 and 2.

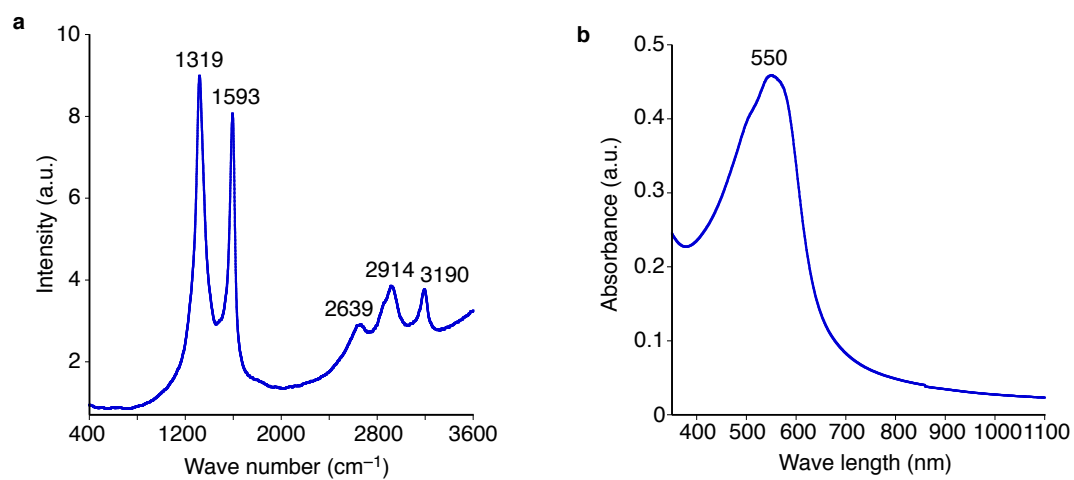


Figure 2. (a) Raman spectrum of GNR 1 measured at 488 nm on a powder sample with laser power below 1 mW. (b) UV-vis absorption spectrum of GNR 1 in NMP.