Supporting Information

**Edge Functionalization of Structurally Defined Graphene Nanoribbons for Modulating the Self-Assembled Structures**

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General Methods

All chemicals were purchased from commercial sources and used without further purification unless otherwise stated. $^1$H NMR spectra were recorded in the listed deuterated solvents on Bruker AVANCE 500 MHz spectrometers. Analytical size exclusion chromatography (SEC) was performed on SDV PSS GPC columns using THF as eluent at a temperature of 303 K. Absorbance was determined on a UV S-3702 detector (SOMA) at a fixed wavelength of 270 nm. The samples were referenced with respect to standard polystyrene (PS) as well as poly(para-phenylene) (PPP) calibration curves. Infrared spectroscopy was measured on a Nicolet 730 FT-IR spectrometer equipped with an attenuated total reflection (ATR) setup. The samples were deposited as pristine material on the diamond crystal and pressed on it with a stamp. Measurements with a scan number of 128 were recorded for each sample and the background was subtracted. The GNRs samples were measured in powder form by using two Raman spectrometers: the XploRA PLUS by Horiba and a Renishaw InVia. Both instruments are equipped with several excitation lines in the visible and near-IR range. A 100X objective and a grating of 2400 grooves/nm was used. The laser power was kept below 0.1 mW to avoid damage and insure reproducible measurements. Matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectra were taken on a Bruker Reflex II mass spectrometer using 7,7,8,8-Tetracyanoanodimethane (TCNQ) as matrix, calibrated against a mixture of $C_{60}/C_{70}$ and poly(ethylene glycol) (3,000 g mol$^{-1}$). X-ray Photoelectron Spectroscopy (XPS) was conducted using a Kratos Axis Ultra$^{DLX}$ spectrometer (Kratos, Manchester, England) using an Al K$\alpha$ excitation source with a photon energy of 1487 eV. The data was acquired in the hybrid mode using a $0^\circ$ take-off angle, defined as the angle between the surface normal and the axis of the analyzer lens. Detailed region XP spectra were collected with setting analyzer pass energy at 80 eV, C 1s and N 1s high-resolution spectra were collected with analyzer pass energy of 20 eV. Neutralizer was always used during spectra collection. Solution UV–vis absorption spectra were recorded at room temperature on a Perkin-Elmer Lambda 900 spectrophotometer. GNR samples were dispersed in N-methyl-pyrrolidone (NMP) or 1,2,4-trichlorobenzene (TCB) by using sonication (30 min) in a Branson-1510 ultrasonicator followed by filtration through polytetrafluoroethylene (PTFE) syringe filters with 5 $\mu$m pores. Atomic force microscopy (AFM) was performed with ScanasystFluid+ probes in peak force nanomechanical mapping mode with Bruker Fastscan instrument. Density functional theory (DFT) calculations were carried out at the B3LYP/6-31G (d) level using Gaussian 09$^1$ and molecular structures were generated using GaussView 5.0.9.$^2$
Materials
Unless otherwise noted, materials were purchased from Aldrich, Acros, TCI, Merck, and other commercial suppliers and used as received. The synthetic details of the bromo-functionalized polyphenylene precursor (PP) and graphene nanoribbon (GNR), PP-Br and GNR-Br, respectively, are described elsewhere. The dodecyl-functionalized GNR-C12 was synthesized by following a reported protocol. The boronic esters of the functional units, namely 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anthracene-9,10-dione (AQ-BPin), N-(2-ethylhexyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalene-1,8-dicarboximide (NMI-BPin), and N-(1-heptyloctyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene-3,4-dicarboximide (PMI-BPin), were prepared following the reported procedures.

Figure S1. Chemical structures of GNR-Br and GNR-C12.
Synthesis of PP-Br (as an isomeric mixture)

Scheme S1. Diels–Alder polymerization of tetraphenylcyclopentadienone precursor CP-Br to bromo-functionalized polyphenylene precursor (PP-Br). Because of the asymmetric structure CP-Br, the resulting PP-Br contains combinations of cis and trans (E and Z) isomers for all the benzene rings formed by the Diels-Alder cycloaddition. Nevertheless, all the isomers lead to the same straight GNR structure upon the oxidative cyclodehydrogenation.

General procedure for synthesis of functionalized polyphenylene polymers (PP-A)
To a solution of PP-Br (100 mg) and corresponding aryl boronic ester (5 equivalents per one bromo group of PP-Br) in toluene (20 mL) was added an aqueous solution of K$_2$CO$_3$ (1 M, 10 mL) and EtOH (2 mL). The reaction mixture was degassed and then the catalyst, tetrakis(triphenylphosphine)palladium (Pd(PPh$_3$)$_4$, 18.5 mg, 10 mol% to one bromo group of PP-Br) along with the ligand, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 13.1 mg, 10 mol% to one bromo group of PP-Br) were added under the argon flow. The reaction mixture was stirred at 100 °C for 48 hours under argon atmosphere. After cooling down to room
temperature methanol was added. The precipitates were collected by filtration with a membrane filter (PTFE, 200-nm pores) to obtain a crude product. The crude material was dissolved in tetrahydrofuran and precipitated with methanol (tetrahydrofuran/methanol = 2:1 in volume ratio), followed by collection with a membrane filter and washing with a mixture of tetrahydrofuran and methanol (2:1 volume ratio). This process was repeated for three times followed by further purification and removal of smaller oligomers with recycling preparative size exclusion chromatography (SEC) to obtain PP-A which is used for the next step. It is noted PP-PMI could not be purified with the recycling preparative SEC due to the low solubility.

Scheme S2. Synthesis of functionalized polyphenyles (PP-A) via Suzuki coupling reaction.

**Synthesis of PP-AQ**

Following the general procedure, Suzuki coupling was carried out between PP-Br (100 mg)
and AQ-BPin (267 mg) to afford 115 mg of dark brown colored PP-AQ (96% yield). $M_w = 76–161$ kg·mol$^{-1}$, $M_n = 34–56$ kg·mol$^{-1}$, PDI = 2.2–2.9, based on SEC analysis with respect to PPP and PS standards. FT-IR (powder): 3074, 3053, 3030, 2958, 2923, 2852, 1674, 1590, 1325, 1288, 1259, 1176, 1089, 1072, 1018, 941, 842, 793, 705, 636 cm$^{-1}$. The solubility of the product was too low to record a reasonable $^1$H NMR spectrum, even in C$_2$D$_2$Cl$_4$ at 120 °C.

**Synthesis of PP-NMI**

Following the general procedure, Suzuki coupling was carried out between PP-Br (100 mg) and NMI-BPin (347 mg) to afford 125 mg of dark brown colored PP-NMI (92% yield). $M_w = 37–99$ kg·mol$^{-1}$, $M_n = 23–49$ kg·mol$^{-1}$, PDI = 2.2–2.9, based on SEC analysis with respect to PPP and PS standards. FT-IR (powder): 3080, 3062, 3052, 3023, 2962, 2923, 2852, 1703, 1660, 1656, 1548, 1535, 1512, 1492, 1462, 1454, 1436, 1353, 1257, 1207, 1152, 1078, 1012, 865, 795, 698, 636, 553 cm$^{-1}$. The solubility of the product was too low to record a reasonable $^1$H NMR spectrum, even in C$_2$D$_2$Cl$_4$ at 120 °C.
Synthesis of PP-PMI

Following the general procedure, Suzuki coupling was carried out between PP-Br (100 mg) and PMI-BPin (524 mg) to yield dark colored crude product. The crude material was redispersed in tetrahydrofuran (10 mL) and then sonicated for 20 min and precipitated with methanol (tetrahydrofuran/methanol = 2:1 in volume ratio), followed by collection with a membrane filter and washing with a mixture of tetrahydrofuran and methanol (2:1 volume ratio). This process was repeated for five times to obtain 160 mg of dark blue colored PP-PMI (93% yield). Further purification with recycling preparative SEC was not performed due to the low solubility. FT-IR (powder) 3080, 3060, 3052, 2923, 2852, 1693, 1656, 1593, 1572, 1434, 1352, 1203, 1149, 1047, 798, 748, 696, 638, 553 cm⁻¹. The solubility of the product was too low for the SEC analysis with hot THF as eluent as well as for recording a reasonable ¹H NMR spectrum in C₂D₂Cl₄ at 120 °C.

General procedure for synthesis of functionalized graphene nanoribbon (GNR-A)

A solution of functionalized polyphenylene PP-A (20.0 mg) in unstabilized dichloromethane (200 mL) was degassed by argon bubbling for 15 min. To the degassed solution was added a suspension of FeCl₃ (7.0 eq. for one hydrogen to be removed) in nitromethane (5 mL). After stirring at room temperature for 48 h under continuous bubbling with argon pre-saturated by dichloromethane, the reaction was quenched by addition of methanol to form black precipitates. The precipitates were collected by filtration with a membrane filter (PTFE, 200 nm pores), and washed with methanol and tetrahydrofuran. This filtrate is then re-dispersed in tetrahydrofuran (10 mL) and then sonicated for 20 min. The precipitates were again collected by filtration with
a membrane filter, washed with tetrahydrofuran to give GNR-A as dark purple powder. Lower yield reported for respective GNR-A’s are due to the repetitive filtrations and loss of product on filter paper.

Scheme S3. Synthesis of functionalized graphene nanoribbons (GNR-A).

Synthesis of GNR-AQ

Purple powder (18 mg, 92% yield): FT-IR (powder): 3074, 3062, 3033, 2948, 2919, 2848, 1672, 1589, 1462, 1437, 1321, 1288, 1203, 1149, 975, 931, 868, 850, 811, 789, 748, 724, 709, 636, 553 cm⁻¹.
Synthesis of GNR-NMI

Purple black powder (17 mg, 86% yield): FT-IR (powder): 3080, 3062, 3020, 2948, 2923, 2852, 1703, 1660, 1589, 1462, 1452, 1435, 1383, 1350, 1294, 1203, 1149, 1064, 1012, 853, 806, 638, 553 cm\(^{-1}\).

Synthesis of GNR-PMI

Black powder (14 mg, 70% yield). FT-IR (powder): 3077, 3058, 3048, 3033, 2920, 2850, 1691, 1653, 1591, 1572, 1462, 1452, 1434, 1348, 1200, 1149, 1114, 1060, 869, 810, 750, 720, 692, 638, 553, 534 cm\(^{-1}\).
Synthesis of GNR-PMI*

To a solution of GNR-Br (50 mg) and PMI-BPin (261 mg, 5 equivalents per one bromo group of GNR-Br) in toluene (15 mL) was added an aqueous solution of K$_2$CO$_3$ (1 M, 6 mL) and EtOH (2 mL). The reaction mixture was degassed and Pd(PPh$_3$)$_4$ (9 mg, 10 mol% to one bromo group of GNR-Br) along with SPhos (7 mg, 10 mol% to one bromo group of GNR-Br) were added under the argon flow. The reaction mixture was stirred at 100 °C for 48 h under argon atmosphere. After cooling down to room temperature methanol was added. The precipitates were collected by filtration with a membrane filter (PTFE, 200 nm pores) to obtain crude product. This filtrate is then re-dispersed in tetrahydrofuran (10 mL) and then sonicated for 20 min. The precipitates were again collected by filtration with a membrane filter, washed with tetrahydrofuran. This process was repeated for three times to obtain GNR-PMI* as black powder (55 mg). The product probably contained free PMIs, as described in the main text, which were most likely encapsulated inside the aggregates and could not be removed by extensive washing. FT-IR (powder): 3081, 3062, 3045, 3025, 2956, 2918, 2848, 1714, 1693, 1654, 1610, 1591, 1564, 1462, 1454, 1436, 1410, 1348, 1257, 1200, 1149, 1072, 1012, 864, 852, 796, 750, 719, 698, 661, 582, 548, 530 cm$^{-1}$. 

Scheme S4. Synthesis of GNR-PMI* from GNR-Br.
SEC analyses of PP-A

Size exclusion chromatography (SEC) analyses of PP-A were carried out in dilute THF solutions. Because of apparently strong aggregations, filtration of solutions of PP-A through syringe filters (PTFE, 200 nm) prior to the SEC analyses has presumably resulted in partial removal of higher-molecular-weight fractions of the polymers, and thus lower molecular weight values of PP-A compared to that of PP-Br (Table S1). Nevertheless, this result could also be partially due to increased rigidity of PP-A, which would lead to smaller molecular weight values based on the SEC analysis. The solubility of PP-PMI was not sufficient even in hot THF to be detected in the SEC analysis. This is assumedly because the PMI units with extended aromatic cores promote the aggregation.

Table S1. Number and weight average molecular weights ($M_n$ and $M_w$, respectively) and polydispersity index (PDI) of PP-A.

| PP-A (standard) | $M_n$ (kg·mol$^{-1}$) | $M_w$ (kg·mol$^{-1}$) | PDI |
|-----------------|-----------------------|-----------------------|-----|
| PP-Br (PPP)     | 58                    | 126                   | 2.2 |
| PP-Br (PS)      | 102                   | 283                   | 2.8 |
| PP-AQ (PPP)     | 34                    | 76                    | 2.2 |
| PPP-AQ (PS)     | 56                    | 161                   | 2.8 |
| PP-NMI (PPP)    | 23                    | 50                    | 2.1 |
| PP-NMI (PS)     | 37                    | 99                    | 2.7 |

MALDI-TOF MS analyses of PP-A

Linear-mode MALDI-TOF MS analyses of low-molecular-weight fractions of PP-Br and PP-A (A = -AQ, -NMI) showed regular mass patterns up to $m/z = 10000$ with intervals in agreement with the molecular weight of one repeating unit, i.e. 627 for PP-Br, 755 for PP-AQ, and 856 for PP-NMI (Figure S2–S4). There is deviation of approximately 20 for PP-AQ, which is most probably due to the addition of sodium ion, as observed in the reflectron-mode analysis (Figure 1). On the other hand, PP-NMI did not show any reasonable signal in reflectron-mode of MALDI-TOF MS analysis, and PP-PMI could not be analyzed by MALDI-TOF MS in both linear and reference modes, even using low-molecular-weight fractions. It should be noted that the highest $m/z$ detected in these measurements do not correspond to the largest polymers in the
samples, considering the limitation of MALDI-TOF MS analysis for high-molecular-weight polymers with a broad molecular weight distribution.  

Figure S2. Linear-mode MALDI-TOF MS spectrum of low-molecular-weight polymer fraction of PP-Br.
Figure S3. Linear-mode MALDI-TOF MS spectrum of low-molecular-weight polymer fraction of PP-AQ.

Figure S4. Linear-mode MALDI-TOF MS spectrum of low-molecular-weight polymer fraction of PP-NMI.
FT-IR spectra

An *opla* band previously assigned to the aromatic C–H at the “cove” position of the GNRs with the same edge structures appeared at around 867 cm$^{-1}$ for GNR-AQ, 853 cm$^{-1}$ for GNR-NMI, 869 cm$^{-1}$ for GNR-PMI, and 852 and 864 cm$^{-1}$ for GNR-Br (Figure S5). These shifts of the *opla* bands are presumably due to the modulation of the vibrational modes of the GNRs by the functional groups, although unambiguous elucidation requires detailed theoretical studies.

![Figure S5. FT-IR spectra of GNR-Br, -AQ, -NMI, and -PMI.](image-url)
**Figure S6.** FT-IR spectra of **PP-AQ** (black line) and **GNR-AQ** (red line).

**Figure S7.** FT-IR spectra of **PP-NMI** (black line) and **GNR-NMI** (red line).
Figure S8. FT-IR spectra of PP-PMI (black line) and GNR-PMI (red line).

Figure S9. FT-IR spectra of GNR-PMI (green line), GNR-Br (black line) and GNR-PMI* (red line).
**Raman spectra**

**Figure S10.** First and second order Raman spectra of GNR-Br, -AQ, -NMI, and -PMI, measured at 2.33 eV with laser power below 0.1 mW.

**Figure S11.** Comparison of Raman spectra in the low-energy region of GNR-PMI (black line) and GNR-PMI* (red line) measured at 2.33 eV with laser power below 0.1 mW.
**XPS analysis**

The C 1s high resolution XP spectra in Figure 2a were self-fitted using individual emission peaks with similar fwhm (full width half maximum), and without additional constraint. For spectra of GNR-NMI and GNR-PMI, the ratios of red to green peaks deviate from 3/2, the value identified from the number of carbon atoms assigned to the respective peaks (see the color code in Scheme 1). This is because the photoelectron of the two sp² carbons marked with red are localized in the conjugated aromatic center, where other sp² carbons close to them can also contribute to the photoemission process. Additionally, the C 1s peak at ~289 eV observed for GNR-AQ (Figure 2a) is possibly caused by shake-up process, which is related to the π-π* transition of C 1s emission. Alternatively, it can also be due to contamination with NMP used as solvent, as the measurement was done on a sample once processed with this solvent.

The elemental composition ratio of C% and N% can be readily derived by evaluating the intensity of core level photoelectron with respect to the manufacturer sensitivity factor:

\[
\frac{\%_C}{\%_N} = \frac{(I_C/1)}{(I_N/1.72)}
\]

Functionalization efficiencies for GNR-NMI and -PMI were calculated to be 90±16 and 91±24%, respectively, based on the N/C atomic composition ratios of 1.5±0.2 and 1.2±0.2% determined by XPS and taking into consideration the fact that 20 and 37 carbon atoms, respectively, are added together with 1 nitrogen atom per repeating unit upon the successful functionalization. Br 3p spectra showed mostly negligible feature from GNR-AQ, -NMI, and -PMI. Although 1 and 2 spots out of 6 showed detectable amounts of C-Br signals for GNR-NMI and -PMI, respectively, it was still at very low levels that did not allow reliable estimation of the atomic composition. On the other hand, the Br/C atomic composition ratio of GNR-Br could be estimated to be 1.9±0.2 %, corresponding to the degree of substitution of 79±9%. Cl 2p spectra of GNR-NMI and -PMI showed signals of aromatic C-Cl species with the atomic composition of approximately 0.3±0.1% and 0.5±0.1%, respectively, suggesting possible partial chlorination during the oxidative cyclodehydrogenation. Nevertheless, Cl 2p spectra of GNR-Br and -AQ did not display such signals, which indicated that the chlorination could be more efficiently suppressed for these two GNRs. Additionally, O 1s spectra could not be reliably measured due to the strong interference with Pd emission, which seemed to have remained inside the polymer samples as neutral metal and/or Pd(II) salt after the Suzuki coupling. Nevertheless, Fe species were not detected in all the GNR samples.
Table S2. XPS derived N/C atomic composition ratio (%) and calculated functionalization efficiency for GNR-NMI and -PMI.

|       | N/C experiment (%) | N/C theory (%) | Functionalization efficiency (%) |
|-------|--------------------|----------------|----------------------------------|
| GNR-NMI | 1.5±0.2            | 1.6            | 90±16                            |
| GNR-PMI | 1.2±0.2            | 1.3            | 91±24                            |

Table S3. XPS derived Br/C atomic composition ratio (%) and calculated degree of substitution for GNR-Br.

|       | Br/C experiment (%) | Br/C theory (%) | Degree of substitution (%) |
|-------|--------------------|-----------------|-----------------------------|
| GNR-Br | 1.9±0.2            | 2.4             | 79±9                         |

Figure S12. Br 3p XPS of the functionalized GNRs.
**UV-vis-NIR absorption spectra**

**GNR-AQ** could be dispersed in NMP at a high concentration of 1 mg/mL with mild sonication, and the dispersion was stable at least for 1 day, without obvious precipitation as showed in Figure S10. **GNR-NMI** and -**PMI** dispersions are only stable up to 30 min in the similar conditions even though these functional units contain branched alkyl chains. Nevertheless, 0.2 mg/mL dispersions of all **GNR-A** in NMP and TCB are stable for a week. The dispersions in NMP and TCB are filtered through syringe filters (PTFE, 5 μm pore), which gives more stable dispersions without visual precipitation for at least three months. These filtrates are used for the analyses by the UV-vis-NIR absorption spectroscopy.

![Figure S13](image1.png)

**Figure S13.** Photographs of **GNR-AQ** dispersions in NMP at different concentrations.

![Figure S14](image2.png)

**Figure S14.** Normalized UV-vis-NIR absorption spectra of **GNR-PMI** and **GNR-PMI** along with **GNR-Br** in NMP.
Computational methods and results

Following our previous studies,\textsuperscript{10-13} all reported electronic properties are given for geometries fully optimized at the hybrid density functional theory using the Heyd-Scuseria-Ernzerhof (HSE) functional,\textsuperscript{14} and a polarized 6-31G(d) basis set.\textsuperscript{15} The electronic properties of the GNRs were calculated for an infinite system by using Periodic Boundary Conditions (PBC). A k-sampling of 24 (47) points uniformly distributed along the Brillouin Zone was used. All calculations were performed by using the Gaussian09 package.\textsuperscript{1}

In order to study the influence of the position of the substituents on the electronic properties of the GNRs, three different unit cells have been studied (Figure S15): One is equivalent to the monomer in a non-functionalized GNR (\textit{n}-unit cell) and another two are equivalent to a dimer, differing by the position of the two substituents, i.e., on the same side of the GNR (\textit{2n}-unit cell) versus on alternating side (\textit{m}-unit cell). Similar band structures were obtained for the three different unit cells as displayed in Figure S16, demonstrating that the electronic properties are not significantly affected by the position of the substituents (\textit{2n}-vs \textit{m}-unit cells) nor by possible intermolecular interactions between the substituents (\textit{n}-vs \textit{2n}-unit cells). In the following sections, we therefore present only the results obtained for the \textit{n}-unit cell (see Table S4).

\textbf{Figure S15.} Chemical structures of the functionalized GNRs used for the theoretical studies. The central red parts highlight the repeat unit; the dashed lines at the edges indicate the direction of elongation of the ribbons.
Figure S16. Band structures (half Brillouin zone) along the longitudinal axis for the studied GNRs (right) together with the corresponding unit cell (left).
Table S4. Band structure parameters of the studied n-GNRs in eV: Highest Occupied Crystalline Orbital (HOCO) and Lowest Unoccupied Crystalline Orbital (LUCO) energies; Valence Band (VB) and Conduction Band (CB) widths; and direct bandgap.

|       | HOCO  | LUCO  | VB width | CB width | Direct gap |
|-------|-------|-------|----------|----------|------------|
| GNR-C12 | -4.64 | -2.59 | 1.2      | 0.91     | 2.05       |
| GNR-Br  | -4.96 | -2.91 | 1.19     | 0.91     | 2.05       |
| GNR-AQ  | -4.84 | -3.15 | 1.19     | 0.19     | 1.69       |
| GNR-NMI | -5.07 | -3.02 | 1.08     | 0.31     | 2.05       |
| GNR-PMI | -5.03 | -3.09 | 0.29     | 0.03     | 1.94       |

The substitution with Br is predicted to induce a rigid shift in energies (–0.32 eV) with respect to the non-functionalized GNR (GNR-C12), without affecting the band or the crystalline orbital (CO) shapes (Figure S17). When introducing the other substituents, the valence band of the GNRs is not strongly affected, except in the case of GNR-PMI, for which there is a decrease in the valence band (VB) width (by 0.91 eV) due to a delocalization of the highest occupied crystalline orbital (HOCOs) over the PMI units. In contrast, the most relevant effects of the substitution are observed in the conduction band (CB), in particular in the cases of GNR-AQ and -PMI, where the lowest unoccupied crystalline orbital (LUCO) gets localized in the functional units, resulting in flat bands (width of 0.19 and 0.03 eV, respectively). As a consequence, there is a bandgap reduction in the presence of these two substituents (by 0.36 and 0.11 eV for GNR-AQ and -PMI, respectively). However, a direct transition between the HOCO and LUCO levels is not expected to give rise to an intense absorption band for GNR-AQ and -PMI, in view of the pronounced charge transfer character associated to the different spatial localization of the two levels; this might actually rationalize the observation a low energy shoulder in the experimental absorption spectra, especially visible in the case of GNR-AQ.
Figure S17. Frontier Crystalline Orbital (CO) shapes for the studied $n$-GNRs in $\Gamma$ point ($k = 0$). The energies of each CO are indicated below. The colors of the units represent whether the COs are localized on the GNR (black), the AQ (red) or the PMI (green) substituent; or delocalized on both GNR and substituent (grey). The isovalue used is ±0.02 a.u.
Simulated optical properties

Time Dependent Density Functional Theory (TD-DFT) calculations were performed to simulate the optical absorption spectra and assess the nature of the relevant electronic excited states, using the same functional and basis set. A finite tetramer was used to perform the TD-DFT calculations on the GNRs. Moreover, the effects of the NMP and TCB solvents were introduced by means of the polarizable continuum model (Figure S18 and Table S5). In line with the experimental findings, these calculations only yield a modest spectral shift of the main optical absorption band in the ribbon upon edge functionalization.

![Absorbance spectra](image)

**Figure S18.** Normalized, simulated UV-vis-NIR absorption spectra of the functionalized GNRs, in NMP as solvent described by the PCM model.

**Table S5.** Simulated lowest-energy absorption maxima of the functionalized GNRs, with the TD-DFT calculations performed in gas phase, and NMP and TCB solvents.

| $\lambda_{abs}$ (nm) | Gas phase | NMP | TCB |
|---------------------|-----------|-----|-----|
| GNR-C$_{12}$        | 498       | 510 | 511 |
| GNR-Br              | 500       | 511 | 513 |
| GNR-AQ              | 505       | 513 | 516 |
| GNR-NMI             | 496       | 501 | 507 |
| GNR-PMI             | 514       | 523 | 523 |
AFM characterization

**GNR-A** (**A** = -**AQ**, -**NMI** and -**PMI**) were dispersed (0.01 mg/mL) in TCB and filtered through syringe filters (PTFE, 0.5 µm pore). These dispersions were drop-caste on freshly peeled graphite crystal and annealed at 100 °C for 30 min. The self-assembled structures of **GNR-A** on these graphite substrates were studied using AFM.

![AFM height (left column) and adhesion (right column) images of functionalized GNRs drop-cast on graphite crystal from dispersions in TCB and annealed at 100 °C.](image)

**Figure S19.** AFM height (left column) and adhesion (right column) images of functionalized GNRs drop-cast on graphite crystal from dispersions in TCB and annealed at 100 °C.
Figure S20. Large area AFM height images (A and B) of GNR-PMI on two different graphite crystals. Isolate individual ribbons can be seen in images and they appear to lay straight.

Geometry optimized structures of GNR-A

Figure S21. Geometry optimized for a dimeric model structure of GNR-NMI.
Figure S22. Geometry optimized for a dimeric model structure of GNR-PMI.

Proposed self-assembled structures of GNR-PMI

Self-assembly 1

Self-assembly 2

Self-assembly 3

Figure S23. The schematic representation of possible self-assembled structures of GNR-PMI at the crossings, leading to rectangular networks. Further theoretical studies are ongoing to elucidate this hypothesis.
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