# Supporting Information for

# On-surface synthesis of singly and doubly porphyrin-capped graphene nanoribbon segments

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**Abbreviations**: CBM = conduction band minimum; DCM = dichloromethane; DCTB = *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile; FT-IR (ATR) = Fourier-transform – infrared (attenuated total reflectance); GNRs = graphene nanoribbons; HRMS = high resolution mass spectrometry; LDOS = local electronic density of states; MALDI-TOF = matrix-assisted laser desorption/ionization-time of flight; m.p. = melting point; MS = mass spectrometry; NMR = nuclear magnetic resonance; nc-AFM = non-contact atomic force microscopy; Por = porphyrin; STM = scanning tunneling microscopy; STS = scanning tunneling spectroscopy; THF= tetrahydrofurane; TLC = thin layer chromatography; VBM = valence band maximum.

#### General and methods

Chemicals and solvents were purchased from commercial suppliers (Aldrich, Fluka, Strem, Acros and Fischer) and used without further purification. All dry solvents were freshly distilled under argon over an appropriate drying agent before use. Column chromatography was carried out on silica gel Merck-60 (230-400 mesh, 60Å). Analytical TLC was performed on aluminium sheets precoated with silica gel 60 F-254 from Merck. Preparative TLC plates ( $20 \times 20$  cm plates) were purchased from Merck (silica gel-60, 0.5 mm).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DPX 400 MHz instrument or a Bruker Bruker DRX 500 MHz instrument. Chemical shifts values ( $\delta$ ) are referred to tetramethylsilane.

UV/vis experiments were carried out by using quartz cells with a 1 cm optical path length in a Varian Cary 50 UV spectrophotometer. IR spectra were recorded on a Bruker ALPHA Platinum-ATR system.

MALDI-TOF MS spectra were obtained in a Bruker ULTRAFLEX III (MALDI-TOF/TOF) spectrometer. GC-MS spectra were obtained from a Waters GCT Agilent Technologies 6890N spectrometer. APCI-MS spectra were obtained from a Bruker MAXIS II spectrometer.

The synthesis and characterization of  $3(H_2)$  has been previously reported.<sup>1</sup>

**STM/STS/nc-AFM**: A commercial low-temperature STM/AFM (Scienta Omicron) system was used for sample preparation and *in situ* characterization under ultra-high vacuum conditions (base pressure ~  $1 \times 10^{-10}$  mbar). The Au(111) single crystal was cleaned by standard argon sputtering and annealing cycles. Deposition of the molecular precursors was performed by thermal evaporation from a 6-fold organic evaporator (Mantis GmbH). STM images were recorded in constant-current mode unless specified otherwise, and the dI/dV spectra were recorded using the lock-in technique (U<sub>RMS</sub> = 20 mV). nc-AFM images were recorded with a CO-functionalized tip<sup>2</sup> attached to a quartz tuning fork sensor<sup>3</sup> (resonance frequency 23.5 kHz, peak-to-peak oscillation amplitude below 100 pm).

**Density functional theory calculations**: DFT calculations for the molecules in gas phase were done with the CP2K code.<sup>4</sup> We used the TZV2P Gaussian basis set<sup>5</sup> for C,

N and H elements, while for Zn we used the DZVP Gaussian basis set. For the plane wave basis set we used a cutoff of 600 Ry. We used norm conserving Goedecker-Teter-Hutter<sup>6</sup> pseudopotentials, the PBE<sup>7</sup> parametrization for the exchange correlation functional and Grimme's DFT-D3 dispersion corrections.<sup>8</sup> All atoms were relaxed until forces were lower than 0.005 eV/Å. Calculations were done within the AiiDA platform.<sup>9</sup>

1. Synthesis and characterization of A<sub>3</sub>B-tris(dimethylphenyl)-di-anthracenyl Zn(II)porphyrin 3(Zn)



 $3(H_2)^1$  (15 mg, 0.0142 mmol, 1 eq) and Zn(OAc)<sub>2</sub> (13 mg, 0.071 mmol, 5 eq) were loaded in a 25 mL round-bottomed flask. Three cycles of vacuum/argon backfilling were applied and THF (10 mL, freshly distilled over metallic sodium) was added under argon. The mixture was heated to 70 °C overnight, then cooled to room temperature and transferred into a separation funnel. Saturated NH<sub>4</sub>Cl (100 mL) was added and the mixture was extracted with dichloromethane (100 mL), washed with water (100 mL) and brine (100 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and dried under reduced pressure. The crude product was then subjected to size exclusion chromatography (BioBeads, CHCl<sub>3</sub>) and the solvent was removed under reduced pressure to a small amount. The crude product was then passed through a short plug of silica gel eluting it with CHCl<sub>3</sub>, and the solvent was removed under reduced pressure. The resulting crude solid was then suspended in MeOH, sonicated, filtered, and the solid washed with MeOH and dried *in vacuo* to yield **3**(Zn) (14 mg, 88%) as a purple solid.

**RF** = 0.49 (1:1 DCM/*n*-hexane); <sup>1</sup>**H** NMR (400 MHz, CDCl<sub>3</sub>) δ = 8.83 (d, J = 8.8 Hz, 2H, H<sub>a</sub>), 8.76 – 8.71 (m, 4H, Hβ<sub>3</sub>+ Hβ<sub>4</sub>), 8.67 (d, J = 4.6 Hz, 2H, Hβ<sub>2</sub>), 8.51 (d, J = 4.5 Hz, 2H, Hβ<sub>1</sub>), 7.71 (dd, J = 8.9, 6.4 Hz, 2H, H<sub>b</sub>), 7.64 – 7.55 (m, 5H H<sub>C'</sub> + H<sub>C</sub> + H<sub>d</sub>), 7.49 (d, J = 7.7 Hz, 2H, H<sub>B'</sub>), 7.43 (dd, J = 11.6, 5.0 Hz, 6H, H<sub>B</sub> + H<sub>c</sub>), 7.34 (d, J = 8.9 Hz, 2H, H<sub>e</sub> or H<sub>h</sub>), 7.28 (d, J = 9.0 Hz, 2H, H<sub>e</sub> or H<sub>h</sub>), 7.15 – 7.08 (m, 2H, H<sub>f</sub> or H<sub>g</sub>), 6.99 – 6.93 (m, 2H, H<sub>f</sub> or H<sub>g</sub>), 1.95 (s, 6H, H<sub>A'</sub>), 1.94 (s, 12H, H<sub>A</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 151.4, 150.0, 149.8, 149.7, 142.1, 142.1, 139.7, 138.3, 135.2, 134.6, 133.6, 132.7, 132.3, 131.4, 131.3, 131.2, 130.9, 130.8, 129.5, 128.4, 128.2, 127.7, 127.5, 127.0, 126.8, 126.6, 125.7, 125.6, 123.9, 119.2, 119.0, 115.4, 29.9, 22.0.; MALDI-TOF MS (DCTB): m/z (% intensity) 1114.2-1123.2 [M]<sup>+</sup> (100%); HRMS

(MALDI, DCTB + PPG1000): calcd for  $C_{72}H_{51}BrN_4Zn$  [M]<sup>+</sup>: 1114.2589; found: 1114.2555; UV/vis (THF):  $\lambda_{max}$  (log  $\epsilon$ ) = 428 (5.64), 558 (4.38), 596 (3.68); FT-IR (ATR)  $\nu$  (cm<sup>-1</sup>) = 2921, 2851, 1461, 1438, 1318, 1202, 1061, 996, 968, 913, 796, 758, 736, 722, 666.



Fig. S1.1. <sup>1</sup>H-NMR spectrum of 3(Zn) in CDCl<sub>3</sub>.



Fig. S1.2. <sup>13</sup>C-NMR spectrum of 3(Zn) in CDCl<sub>3</sub>.



Fig. S1.3. MALDI-TOF (DCTB) spectrum of 3(Zn).



Fig. S1.4. HRMS MALDI-TOF spectrum of 3(Zn). a) isotopic distribution of the MALDI-TOF peaks between 1114.2555 and 1123.2618 m/z; b) calculated isotopic pattern for 3(Zn).



Fig. S1.5. UV/Vis spectrum of 3(Zn) in THF.



Fig. S1.6. FT-IR (ATR) spectrum of 3(Zn).

## 2. Additional scanning probe data analysis and calculations



Fig. S2.0. STM images (top) and differential conductance dI/dV spectra (bottom) of a)  $1(Zn)_0$ , b)  $1(Zn)_1$ , and c)  $1(Zn)_2$ . All the red, green, and blue dI/dV spectra were acquired over the positions indicated by markers with corresponding colors in their respective STM images. The arrows highlight the most prominent peaks. Grey dI/dV spectra are recorded over bare Au(111). Scale bar: 5 Å.

Using 3(Zn) instead of  $3(H_2)$  allowed to fabricate hybrid  $2(Zn)_0$ , an analogous hybrid of the previously reported  $2(H_2)_0$ .<sup>1</sup> The on-surface synthetic route to  $2(Zn)_0$  proceeds analogously to  $2(H_2)_0$ , where a two-step annealing process at 200 and 350 °C is applied to achieve the Ullmann-type coupling and cyclodehydrogenation, respectively (Scheme S2.1).<sup>1</sup>



Scheme S2.1. On-surface synthesis of doubly Por-capped GNR hybrids 2(Zn)<sub>0</sub> from Por 3(Zn).

However, as can be seen from the corresponding overview STM images, the homocoupling "yield" is strikingly lower for the Zn(II)-derivative 3(Zn) than for its free-base analogue  $3(H_2)$  (Fig. S2.1).



Fig. S2.1. Top) molecular structures and bottom) overview STM images of a)  $2(H_2)_0$ (V<sub>s</sub> = -0.5 V, I<sub>t</sub> = 200 pA) and b)  $2(Zn)_0$  (V<sub>s</sub> = 0.45 V, I<sub>t</sub> = 80 pA).

A typical close-up STM image of a sample obtained in this way is shown in Fig. S2.2a,b and the successful fabrication of  $2(Zn)_0$  is further corroborated by high-resolution bondresolved nc-AFM imaging (Fig. S2.2c). Here, a Laplacian filter has been applied to the original nc-AFM image to enhance the image contrast (see the original image in Fig. S2.3). The electronic properties of  $2(Zn)_0$  were explored by dI/dV spectroscopy. Point spectra taken at different positions above  $GNR-Por_2 2(Zn)_0$  show five prominent peaks at 1.65, 0.90, 0.44, -0.84, and -0.92 V (Fig. S2.2d). These spectra of 2(Zn)<sub>0</sub> match very well with those previously reported for GNR-Por<sub>2</sub>  $2(H_2)_0$  in terms of both the peak positions and peak shapes.<sup>1</sup> For an identification of the observed peaks, DFT calculations were performed on GNR-Por<sub>2</sub>  $2(Zn)_0$  and  $2(H_2)_0$  to determine the (gas phase) energy positions of their molecular orbitals. Not unexpectedly, both GNR-Por<sub>2</sub> hybrids exhibit almost identical frontier orbital structure (Fig. S2.4), thus rationalizing the comparable dI/dV spectra of the two hybrids obtained experimentally. Constantcurrent differential conductance (dI/dV) maps were recorded for GNR-Por<sub>2</sub> 2(Zn)<sub>0</sub> at the energies of the most prominent peaks to spatially resolve the corresponding molecular orbitals. In addition, DFT calculations were performed to simulate the molecular orbitals and compare those to the experimental data from dI/dV mapping (Fig. S2.2e). The experimental dI/dV maps show excellent one-by-one matches with the DFT calculated LDOS maps, which allows an unequivocal assignment of the corresponding orbitals. The dI/dV maps measured at 0.44 and 0.90 V are related to the HOMO and LUMO of  $2(Zn)_0$ , respectively. In analogy to the previously reported case of the GNR-Por<sub>2</sub> hybrid  $2(H_2)_0$  on Au(111), the energy level realignment of  $2(Zn)_0$  on Au(111) results in a fully unoccupied gas-phase HOMO. Thus, a HOMO-LUMO gap of ~0.46 eV (where HOMO and LUMO refer to the gas phase frontier states) is determined for  $2(Zn)_0$  adsorbed on Au(111). Comparison of the molecular orbitals of  $2(Zn)_0$ obtained from DFT and the experimental dI/dV maps further suggests that the peak at -0.84 eV (gas phase HOMO-1) derives from hybridization of the Por and GNR segment states (this is the only state that is delocalized over the GNR segment and Por units), whereas the peak at -0.92 eV that is localized to the GNR segment derives from the VBM of the latter. The unoccupied states deriving from the gas phase HOMO and LUMO at 0.44 and 0.90 V, respectively, are both entirely located on the Por part.



Fig. S2.2. a) STM image recorded after sample annealing at 350 °C ( $V_s = 0.45$  V,  $I_t = 360$  pA) showing formation of GNR-Por<sub>2</sub> hybrid 2(Zn)<sub>0</sub> (dashed red circle) and singly Por-capped GNR 1(Zn)<sub>0</sub> (dashed yellow circle). b) Zoom-in STM ( $V_s = 0.44$  V,  $I_t = 400$  pA) and c) Laplace-filtered nc-AFM ( $V_s = -5$  mV, oscillation amplitude: ~80 pm) images of GNR-Por<sub>2</sub> hybrid 2(Zn)<sub>0</sub>. For a better visualization, the chemical structures of 2(Zn)<sub>0</sub> have been superimposed to the STM image in b). d) Red, green, and blue dI/dV spectra of GNR-Por<sub>2</sub> hybrid 2(Zn)<sub>0</sub> taken at the positions indicated by crosses with corresponding colors in b). Grey dI/dV spectrum recorded over Au(111). e) (Top) Constant-current dI/dV maps recorded at the energy positions of the four prominent peaks indicated by arrows in d), and (bottom) corresponding DFT-calculated LDOS maps of 2(Zn)<sub>0</sub>.



**Fig. S2.3.** a) The original nc-AFM image of GNR-Por<sub>2</sub> hybrid  $2(Zn)_0$  (Vs = -5 mV, oscillation amplitude: ~80 pm) and b) its Laplace-filtered counterpart.



**Fig. S2.4.** a) Chemical structure (top) and the calculated energy levels (bottom) of GNR-Por<sub>2</sub> hybrid  $2(H_2)_0$ . b) Chemical structure (top) and the calculated energy levels (bottom) of GNR-Por<sub>2</sub> hybrid  $2(Zn)_0$ . Calculations were done by spin-polarized DFT, and the energy levels are processed by Gaussian smearing to approximate the broadening of the molecular orbitals. H stands for HOMO, L for LUMO. Energies are aligned with respect to the position of the highest occupied molecular orbital (HOMO).



**Fig. S2.5.** a) Chemical structure (left) and STM image (right) of the doubly hydrogenated GNR-Por hybrid  $1(Zn)_0$  showing absence of the finger-like features at the short zigzag end of the GNR segment that are characteristic for the radical state located at the short zigzag end in the case of single hydrogenation. b) dI/dV spectrum taken on the GNR end indicated by the marker in a), showing no state near the Fermi level.



Fig. S2.6. a) STM image and b) the corresponding dI/dV spectra of GNR-Por hybrid  $1(Zn)_0$  taken at the positions indicated by markers with corresponding colors in a). These are the same data than shown in Fig. 1 in the main text. c) Constant-current dI/dV maps recorded at the energy positions indicated by arrows in b) together with the constant-height current map at 0.01 V.



Fig. S2.7. a) STM image and b) the corresponding dI/dV spectra of GNR-Por hybrid  $1(Zn)_1$  taken at the positions indicated by markers with corresponding colors in a). These are the same data than shown in Fig. 1 in the main text. c) Constant-current dI/dV maps recorded at the energy positions indicated by arrows in b) together with the constant-height current map at -0.005 V.



Fig. S2.8. a) STM image and b) corresponding dI/dV spectra of GNR-Por hybrid  $1(Zn)_2$  taken at the positions indicated by markers with corresponding colors in a). These are the same data than shown in Fig. 1 in the main text. c) Constant-current dI/dV maps recorded at the energy positions indicated by arrows in b) together with the constant-height current map at -0.005 V.



**Fig. S2.9.** a) Overview STM image ( $V_s = -1.2$  V,  $I_t = 30$  pA) and b) corresponding close-up STM image ( $V_s = -0.06$  V,  $I_t = 200$  pA) of GNR-Por hybrid  $1(Zn)_9$  on Au(111). b) is repeated from Fig. 2a.



Fig. S2.10. a) Overview STM image ( $V_s = -1 V$ ,  $I_t = 20 pA$ ) of GNR-Por hybrid  $2(H_2)_2$  on Au(111).



Fig. S2.11. Large-scale STM image obtained by co-evaporation of DBBA and 3(Zn)(V<sub>s</sub> = -0.5 V, I<sub>t</sub> = 100 pA).

## **Supporting Information References**

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