Fusing tetrapyrroles to graphene edges by surface-assisted covalent coupling

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Surface-assisted covalent linking of precursor molecules enables the fabrication of low-dimensional nanostructures, including graphene nanoribbons. One approach to building functional multicomponent systems involves the lateral anchoring of organic heteromolecules to graphene. Here, we demonstrate the dehydrogenative coupling of single porphines to graphene edges on the same metal substrate used for graphene synthesis. The covalent linkages are visualized by scanning probe techniques with sub-molecular resolution, directly revealing bonding motifs and electronic features. Distinct configurations are identified that can be steered towards entities predominantly fused to graphene edges through two pyrrole rings by thermal annealing. Furthermore we succeeded in concomitant metallation of the macrocycle with substrate atoms and axial ligation of adducts. Combining such processes with graphene nanostructure synthesis has the potential for creating complex materials systems with tunable functionalities.

Controlled covalent coupling of functional molecular units at interfaces enables new routes for creating hybrid systems where individual components perform specific functions[1-5]. Tetrapyrroles are particularly interesting molecular building blocks because of the important role they play in many biological or artificial systems due to their versatility and robustness. For instance, porphyrins and related species are at the center of crucial processes in nature such as light harvesting in photosynthesis or oxygen and chemical-energy transport. Recently, porphyrins and other tetrapyrroles incorporating different metal centers have been systematically explored at interfaces[6,7] and reveal promise for various technological applications such as molecular electronics[8], gas sensing or catalysis[9, 10], and light harvesting[11, 12]. It is particularly important to combine the functionalities of (metal)-organic molecules with charge transport materials.

The exceptional properties of graphene make it a promising component in such hybrid structures[13, 14]. Indeed, covalent linking of molecules – including porphyrins – to graphene has already been achieved in wet chemical routes using graphene oxide to enable solution processing[15-20]. However, this methodology lacks specificity and thus complex multicomponent architectures may not be realized on its basis. To achieve atomically precise hybrid nanostructures, detailed insight into the anchoring of complementary functional units is mandatory. This may be achieved by surface-assisted covalent coupling of molecular species to graphene edges. In this approach, the role of the surface will be two-fold: to provide a platform for the synthesis of the graphene nanostructures and to mediate the coupling reaction with the molecules. A subsequent transfer of the multifunctional graphene-based nanostructures can be also accomplished for future practical applications[21].

The surface-assisted construction of graphene and other covalent nanostructures by temperature-controlled linking of precursor molecules under well-defined ultra-high vacuum (UHV) conditions provides pathways for synthesizing novel low-dimensional materials with atomic precision[22-29]. Specifically, well-defined and modified graphene edges can play an important role for catalytic conversions[30]. In addition, we recently demonstrated the homo-coupling of porphines, the simplest porphyrin consisting only of a tetrapyrrole macrocycle, on Ag(111) substrates by a surface-assisted dehydrogenation reaction yielding fused derivatives by covalent C-C bond formations[31]. The Ag(111) surface is also a promising substrate for graphene-edge functionalization, because it has been shown that unlike on many other transition-metal supports, the carbon sheets only interact weakly with the noble metal substrate[32,33]. Reduced graphene-edge / substrate interactions will likely reduce barriers for lateral decoration and thus can enable on-surface covalent reactions.

Here, we demonstrate the thermally activated covalent coupling of porphines to graphene edges by high-resolution imaging using advanced scanning probe technology. We notably employed low-temperature non-contact atomic force microscopy (nc-AFM) with carbon monoxide (CO) functionalized probes for atomistic characterization of the porphine / graphene interface, yielding direct structural information on the bond configuration.

Graphene was grown on a Ag(111) surface by deposition of atomic carbon on the substrate kept at 900 K, following the protocol introduced by Kiraly *et al.*[32] (see Supplementary Information). This procedure results in graphene islands as shown in Fig. 1a. Owing to the moderate growth temperature that is dictated by the low melting temperature of silver, the graphene islands exhibit a dendritic shape with a high density of kinks and edge defects, which is quite different from graphene grown on transition metals at optimized conditions[34]. In particular, the graphene edges present transitions between zig-zag and armchair terminations (see Supplementary Fig. 1).

On the partially graphene covered surface, free-base porphines (**2H-P**) are vapor deposited at room temperature. After subsequent cooling to 5.5 K, the STM measurements reveal that the porphines exclusively adsorb as individual units on the bare Ag(111) surface with three different orientations[35], decorating also the graphene edges (Fig. 1c). In order to induce the coupling reaction, the sample is annealed to 620 K. Here, we usually employ an initial porphine coverage in the multilayer regime, to enhance the coupling efficiency, compensating for molecular desorption (*vide infra*). Indeed, some porphines appear now directly attached to graphene edges (Fig. 1e), suggesting a covalent coupling (see the dashed green squares in Fig. 1e highlighting several locations). The covalent interaction between the molecules and the graphene can override site-specific molecule-substrate interactions, partially even inducing deviations from the preferred adsorption orientations of individual porphines on Ag(111). Furthermore, the annealing of porphines on Ag(111) triggers dehydrogenative homocoupling, self-metallation and the desorption of porphine monomers resulting in a reduction of the porphine density on the surface, as previously reported[31].

Several distinct hetero-coupling configurations are observed that are influenced by the local structure of the graphene edge and the ability of porphines to engage in lateral bonding schemes involving different numbers of β- and meso-carbons[31] (cf. Fig 2d). From the orientation and distance of the molecules with respect to the graphene edge four main configurations can be identified. The first row of Fig. 2 shows the corresponding STM images revealing the orientation of the porphines that expose either a single pyrrole ring (Fig. 2a and b) or two pyrrole rings (Fig. 2c and d) towards the graphene edge. In the case of epitaxial graphene, electronic interference effects at the edges complicate the precise determination of the edge position and structure by STM[36-38]. Thus, a conclusive determination of the bonding configuration based solely on STM images is not feasible. To nevertheless corroborate our claim of covalent coupling of porphines to graphene and to determine the detailed bond configuration we performed nc-AFM with CO-functionalized W-tips. Previous achievements with such functionalized tips directly revealed the C-C bonds in various systems, including (nanostructured) graphene and tetrapyrroles[39-43].

In the second and third row of Fig. 2 nc-AFM data are depicted corresponding to the configurations measured by STM (first row). The second row displays the AFM data in the frequency shift channel (Δf). To enhance the contrast and to better visualize the bond characteristics, Laplace-filtering is applied to the AFM images and the results are shown in the third row. In these nc-AFM images the interfacial bond structure between graphene edges and porphines is clearly resolved. Based on the data, we classify the four configurations by the number of C-C bonds formed between the porphine and the graphene. Thus, porphines might form one C-C bond at a β-position (configuration **A**), two C-C bonds at β-positions (configuration **B**), three C-C bonds at β-, meso-, β-positions (configuration **C**) or even four C-C bonds (β-, meso-, β-, β-positions, configuration **D**). AFM images of individual unreacted porphines in close proximity to graphene edges do not show any interfacial bonds whereas the C-C bonds in graphene and the adjacent porphine are clearly resolved (see Supplementary Fig. 5). This corroborates our assignment of the AFM contrast in configuration **A**-**D** to covalent bonds, where distinct coupling motifs are observed. For configuration **A**, Fig 2e shows that one β-carbon from the pyrrole ring is coupled to the graphene edge with a protrusion as link. Even though a precise bond-length determination is hampered by the flexibility of the CO terminating the AFM tip[44, 45], the separation between the graphene edge and porphine's β-carbon clearly exceeds a reasonable C-C distance. Therefore we tentatively assign the protrusion in the junction to a carbon atom protruding from the graphene edge, acting as a connecting bridge. Similar constrictions and carbon atom chains at graphene edges have been previously reported[46, 47]. For configuration **B**, two bonds between the β-carbons of porphine and the graphene edge are clearly resolved in Fig. 2f and j. Fig. 2g and k show an AFM image of configuration **C**. Here, the graphene is terminated by a regular, defect-free zig-zag edge. The porphines on this edge are triply-fused to the graphene edge with one of its side parallel to the edge, i.e., via β-, meso-, β-carbons of the porphine macrocycle. Furthermore, even the formation of four C-C bonds, involving a carbon atom protruding from the graphene edge occurs (configuration **D,** Fig. 2h and l). From the filtered images, schematic models are drawn and presented in the fourth row of Fig. 2. Based on AFM image simulations, the apparent distortions of carbon hexagons at the graphene / porphine interface and at edges (e.g., Fig. 2e-l) are assigned to imaging artifacts induced by the flexibility of the CO terminated tip (see Supplementary Fig. 6).

The nc-AFM images clearly reveal that graphene edges can be functionalized with porphines by an on-surface dehydrogenative coupling reaction. Specifically, the well-defined coupling motifs of configuration **B** and **C** featuring two and three C-C bonds to graphene with arm-chair and zig-zag termination, respectively, appear promising for functionalization of atomically-precise graphene nanostructures, such as nanoribbons or nanographenes[22, 24, 26, 40]. Indeed a comparison of the C-C distances in porphine[48] and graphene for configurations **B** and **C** (Fig. 2n and o) reveals a minor deviation of ≈ 3.6%, indicating a good structural match. The measured bond lengths and the C-C distances calculated by density functional theory (DFT) are provided in the Supplementary Information, including known literature results (Supplementary Fig. 4). Furthermore, configuration **D** - featuring two adjacent sides of one porphine linked to graphene - suggests the possibility to fully embed porphines into graphene. As mentioned above, one of the most appealing features of porpyhrins is their robustness with functionalities bestowed by metal centers hosted in the macrocycle. In a surface science scenario, in-situ metallation was introduced as powerful method to incorporate specific metal centers into tetrapyrroles[49, 50]. Thus, their electronic and magnetic properties as well as their reactivity can be tailored, as exemplified by the reversible ligation of gaseous species[9,51-53]. If intrinsic properties of porphyrin macrocycles, i.e. incorporation of metal centers capable for axial ligation of adducts, were preserved upon the coupling to graphene, further options for the functionalization of graphene nanostructures emerge. Figure 3a sketches the metallation and ligation processes that are manifested in the experimental STM data shown in Fig. 3b. The annealing step and the exposure of the sample to minute amounts of CO at low temperature induces novel characteristics at the graphene edge, highlighted with green and blue squares, respectively. In contrast to the fused free-base porphines, featuring a central depression in the

STM topography, these new species are characterized by a protrusion (Fig. 3b). The entities exhibiting a faint protrusion in the center are assigned to macrocycles self-metallated by silver substrate atoms, similar to **Ag-P** formations in earlier reports[31, 54] (green square, Fig. 3c and Fig. 2d). The species marked by blue squares are characterized by a brighter protrusion (Fig. 3f), which dominates the AFM contrast at large tip-sample distances (Fig. 3g). Only at smaller distances, the graphene lattice is resolved (Fig. 3h). Furthermore, this species can be converted to **Ag-P** upon scanning (see Fig. 3b, porphine marked with red square, where a transition takes place during the data recording). Reversible attachment of CO and other diatomic molecules to surface-anchored metalloporphyrins in STM experiments has been previously reported[9, 55]. Thus, our observations strongly point to a CO molecule adsorbed on **Ag-P** as origin of the pronounced central protrusion. Consequently, we provided a proof-of-principle that the intrinsic properties of porphine as metallation and ligation can be exploited following the covalent coupling to graphene edges.

To investigate the influence of the porphine decoration on the electronic structure of graphene, we recorded the tunneling current simultaneously with the Δf signal in a constant height scan at very low bias voltages. The resulting current images approximate the local density of states near the Fermi level. Applied to graphene nanostructures, this approach proved to yield fingerprints for specific defects[40, 56, 57]. Figure 4 shows current images of an **Ag-P** fused to a zig-zag edge of graphene recorded at ±1 and ±5 mV, respectively. This regular configuration **D** (cf. AFM image and structural model in Fig. 2) was chosen to exclude effects intrinsically related to defects and irregularities of the graphene edge itself. Interestingly, no pronounced modification of the current signal at or near the porphine / graphene interface can be observed. This indicates that the porphine attachment hardly affects the electronic structure of graphene at the Fermi level, in marked contrast to sizeable modifications in graphene nano-ribbon junctions reported recently[40]. Furthermore, d*I*/d*V* spectroscopy in a voltage range of ±1.5 V shows no specific electronic features for the porphines fused to graphene. The pertaining absence of molecular orbital fingerprints around the Fermi level is ascribed to the interaction with the metal substrate (see Supplementary Fig. 2), precluding insights from scanning tunneling spectroscopy (STS)[31]. Indeed, our complementary DFT calculations performed for an isolated model of a porphine-graphene nanoribbon hybrid structure reveals frontier orbitals (highest occupied molecular orbital, HOMO and lowest unoccupied molecular orbital, LUMO) restricted to the nanoribbon, while electronic coupling between the porphine and graphene is visible on the HOMO-2 and LUMO+2 and lower / higher orbitals (see Supplementary Fig. 3).

Finally, we explored the thermal stability of the different porphine / graphene configurations by gradually annealing the sample to 900 K. STM images for increasing annealing temperatures are shown in the Supplementary Information (Supplementary Fig. 7). As reported earlier, annealing to higher temperatures results in a further reduction of the density of porphine monomers on the Ag(111) surface, triggered by concomitant desorption (≈0.03ML/min) and formation of extended, irregular covalently-coupled porphine oligomers[31]. Indeed, such oligomers are frequently coupled to the graphene edges (Supplementary Fig. 7). In particular, we observed a 17% increase of the number of molecules attached to graphene after annealing the sample to 770 K. Importantly, even after annealing to 900 K – the temperature used to grow graphene on Ag(111) – we still observe single porphines coupled to the graphene edges. The prevailing motif (97% of the molecules fused to graphene) corresponds to configurations

C and **D**, with a parallel alignment to the graphene zig-zag edge. The thermal stability of edge-bonded porphines up to the growth temperature of graphene may enable the embedding of such units in the graphene matrix during graphene growth and thus to create not just edge-modified graphene but also intra-sheet functionalization. Interestingly, similar hybrid structures have been predicted to be potential catalysts for CO_2 and CO reduction[58].

In conclusion, we provided a proof of principle for the functionalization of graphene edges with tetrapyrrolic species by a dehydrogenative coupling reaction directly on a metal surface used for graphene synthesis. Initially different bonding mechanisms lead to one, two, three or four C-C linkages between the graphene edge and the employed porphine macrocycle; with increasing annealing temperature the edge-to-edge alignment prevails as most stable configuration and single porphines are still observed. The high thermal and structural stability of this bonding motif up to 900 K opens pathways to incorporate porphines and related species in extended graphene sheets, to apply solution processing or to transfer such hybrid structures to other substrates. We anticipate that a further enhancement of the control on the coupling, necessary to fully exploit the introduced methodology, can be achieved by specifically designed precursor molecules and/or improved synthesis protocols yielding well-defined graphene edges. We demonstrated that intrinsic features of porphines such as metallation and ligation of gases are preserved. Surprisingly, the low-energy electronic structure of graphene is not distorted by the porphine attachment. Thus, the on-surface dehydrogenative coupling protocol introduced here will enable the direct functionalization of graphene nanostructures whose synthesis has already been demonstrated on Ag and similar substrates. Specifically, our findings provide a new tool for the controlled modification of surface-anchored nanographenes and graphene nanoribbons, structures anticipated to play a significant role in diverse application fields as molecular electronics, sensing or optoelectronics and catalysis.

Methods

STM / nc-AFM measurements. All experiments were performed in a custom-designed ultra-high vacuum system (base pressure: 2×10^{-10} mbar). The graphene islands were prepared by depositing atomic carbon on the Ag(111) substrate held at 900 K, followed by post-annealing at the same temperature for several minutes. Free-base porphines (**2H-P**; Frontier Scientific, purity >95%) were deposited using organic molecular beam epitaxy (OMBE) from a quartz container held at 570 K. During deposition the graphene/Ag(111) substrate was kept at room temperature. To trigger the coupling reaction, the sample was subsequently heated to 620 K for 20 minutes. The scanning probe microscopy data were measured in-situ using a CreaTec STM/AFM (createc.de) operating at 5.5K. All STM images were recorded in constant current mode. The AFM images were taken in constant height mode at 0 V bias, using a qPlus sensor (resonance frequency ≈ 22 kHz, oscillation amplitude: 70 pm to 100 pm). For the AFM imaging, the tip was typically approached by a distance Δh of 0.6 or 0.7 Å with respect to the STM set-point on Ag(111) (see figure captions). The tungsten tip was prepared by focused-ion beam processing and in-situ tip forming. For subsequent tip functionalization, carbon monoxide (CO) was dosed on the cold sample and transferred to the tip. The images were processed using the Gwyddion software package[59].

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Author contributions

W.A. and J.V.B. conceived and designed the experiments. Y.H., F.B., J.D. and M.G. performed the experiments. Y.H., F.B., J.D. and M.G. analysed the data. M-L.B. performed the calculations. M.G., W.A., Y.H., M.B. and J.V.B. co-wrote the paper. All authors discussed the results and commented on the manuscript.

Additional information

Details of sample preparation, experimental setup and data acquisition. Characterization of electronic properties by means of STS. DFT calculations of porphine fused to a graphene nanoribbon edge, including molecular orbitals. Additional STM and AFM data of porphine / graphene interfaces with and without covalent bonds and edge structures. AFM image simulations addressing structural distortions. Thermal stability of porphines fused to graphene.

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Figure Captions:

Figure 1. STM images and corresponding models showing the experimental procedure. a *STM image (V = -0.5 V, I = 0.5 nA) of graphene islands grown on Ag(111) using atomic carbon deposition.* ***c*** *After deposition at room temperature, individual* ***2H-P*** *molecules decorate the bare Ag(111) terraces and the graphene edges (V = -0.1 V, I = 50 pA).* ***e*** *STM image recorded after inducing dehydrogenative coupling reactions by annealing the* ***2H-P*** *on graphene/Ag(111) at 620 K (V = 0.2 V, I = 90 pA). Porphines coupled to graphene are marked with green squares.* ***b, d, f*** *Schemes of the experimental situations in (****a, c, e****). The* β*- and meso-carbon positions are labeled in the structural model of* ***2H-P*** *in (****d****).*

Figure 2. STM and AFM data of distinct covalent coupling configurations at the graphene edge. a-d *STM images of configuration* ***A*** *(one C-C bond at a β-position),* ***B*** *(two C-C bonds at β-positions),* ***C*** *(three C-C bonds at β-, meso-, β-positions) and* ***D*** *(four C-C bonds at β-, meso-, β-, β-positions) (I = 50 pA, (a-c): V = 200 mV, (d): V = -200 mV).* ***e-h*** *AFM images representing the frequency shift Δf (Δh = 0.6 to 0.7 Å with respect to the STM setpoint on Ag(111)).* ***i-l*** *Corresponding AFM images after Laplace-filtering. The covalent bonds of the graphene lattice, the porphine and their interface are clearly resolved. The bright protrusion in (****f****) and (****j****) corresponds to a co-adsorbed CO molecule.* ***m-p*** *Schematic models illustrating the coupling configurations. The red lines represent the C-C bonds formed by the dehydrogenative coupling reaction. The characters* ***A-D*** *on top of the figure specify distinct coupling groups based on the number of formed C-C bonds.*

Figure 3. Metallation and ligation of graphene-anchored tetrapyrrole macrocycles. a *Scheme illustrating the metallation of fused* ***2H-P*** *with Ag adatoms to form* ***Ag-P*** *and the reversible binding of a CO molecule to* ***Ag-P****.* ***b*** *STM image revealing the different types of porphine coupled to graphene edges (V = 200 mV, I = 70 pA). Porphines marked with green squares represent* ***Ag-P*** *(faint central protrusion). Porphines marked with blue squares are assigned to CO /* ***Ag-P*** *complexes, featuring a pronounced central protrusion. The porphine marked by a red square lost a CO during scanning. (****c-e****) STM (V = 200 mV, I = 70 pA), AFM (Δh = 0.6 Å) and Laplace-filtered AFM images of an* ***Ag-P*** *fused to the graphene edge.* ***f-h*** *STM (V = 200 mV, I = 50 pA), AFM and Laplace-filtered AFM image of a CO/****Ag-P*** *complex. At close tip-sample distances the graphene lattice is resolved (****h****).*

Figure 4. Low-energy electronic structure of the porphine / graphene interface. a, b *Current images recorded at -1 mV (****a****) and 1 mV (****b****) bias voltage in constant height mode (Δh = 0.6 Å), respectively.* ***c, d*** *Current images recorded at -5 mV (****c****) and 5 mV (****d****) bias voltage. The interfacial structure corresponds to the structural model shown in Fig. 2p representing the AFM data of Fig. 2l. The graphene electronic structure near the Fermi energy at the interface is hardly affected.*