On-Surface Synthesis of a 2D Spin-Bearing Porphyrin–GNR Heterostructure

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On-surface synthesis (OSS) enables the fabrication of atomically precise graphene nanoarchitectures beyond the limits of top-down approaches [1], yet the formation of extended and ordered 2D covalent networks remains challenging. A recently developed templated growth strategy [2] exploits the Au(111) surface reconstruction to guide the parallel alignment of graphene nanoribbons (GNRs) with uniform and tunable inter-ribbon spacing [3]. Such GNR array can act as a 2D template to incorporate additional functional molecular species prior to lateral coupling. In this context, vanadyl tetraphenylporphyrin (VOTPP) hosts a stable out-of-plane S = 1/2 centre with long relaxation and coherence times [4], making it a suitable molecular bridge to investigate the integration and coupling of localized spin centres within π-conjugated graphene architectures.

Here we report the on-surface synthesis of a GNR–VOTPP–GNR framework by depositing VOTPP onto pre-aligned GNR arrays on Au(111) [3] and subsequent annealing. Above ~350°C, the first species covalently bonded to GNR edges and to each other are observed. After annealing at 450°C, extended regions are formed in which individual porphyrins bridge adjacent GNRs, yielding GNR–VOTPP–GNR segments. Scanning tunnelling microscopy (STM) reveals several intramolecular contrasts in topography and conductance, evidencing electronically distinct molecular states arising from different local configurations within the GNR template. These results demonstrate that aligned GNR arrays can serve as versatile 2D scaffolds for the controlled lateral integration of functional molecular building blocks, establishing a viable route toward the design of 2D graphene-based heterostructures with tailored electronic and magnetic properties.

References

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Figures

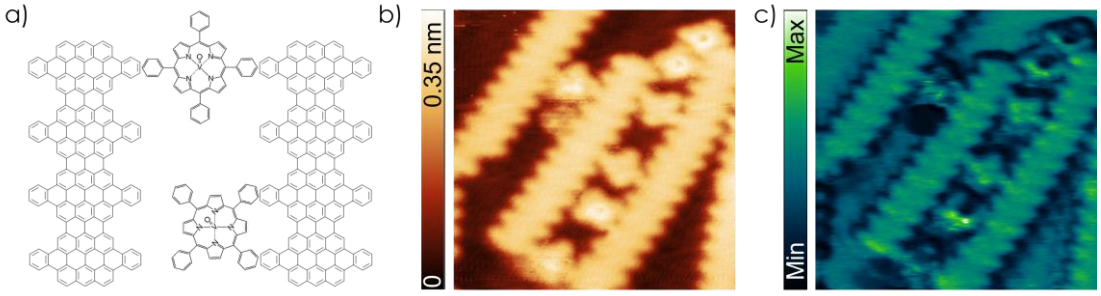

Figure 1: (a) Schematic representation of possible GNR-VOTPP-GNR configurations. (b) STM topography and (c) corresponding conductance map of VOTPP on a pre-aligned GNR array on Au(111) after annealing at 460 °C(images size: 9 x 9 nm^2).

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