Hybrid porphyrin-chiral graphene nanoribbons

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Chiral graphene nanoribbons have a low energy gap which makes them interesting for integration in devices. However, they are reactive due to the presence of unpaired electrons along their zig-zag edges [1]. The functionalization of the edge is a versatile solution that can also add an additional control-knob towards engineering the electronic properties of the system and introduce selective active sites. Here we explore the electronic properties of 3,1,4 chiral graphene nanoribbons (chGNRs) with zinc porphyrins embedded along the edges by means of density functional theory calculations. A metallic band structure is predicted for Zn-Por-chGNRs. Interestingly, substitution of Zn with Fe leads to a magnetic system that shows ferro- or antiferromagnetic order between Fe ions and the ribbons' edge states, depending on the lateral Fe-Por arrangement. Moreover, Zn-Por-chGNRs were successfully synthesized by on-surface synthesis. XPS confirmed the presence of Zn coordinated to the N in the porphyrin. Low temperature STM experiments show the formation of mainly dimers, trimers and tetramers (see figure 1). After O_2 exposure (5000 Langmuir) we observe a shift of the electron density of the low bias feature towards one of the middle porphyrin sites. This result suggests the O_2 interaction with the metal in the porphyrin. This study shows the magnetic interactions in a hybrid system and the interplay between the metal and the edge states of chGNRs where the properties of the active sites could be tuned according to the metal atom of the periodically embedded porphyrins and is promising for its potential in chemical sensing.

References

[1] Li et al., Nature Comm., 65 (2021), 5538

Figures

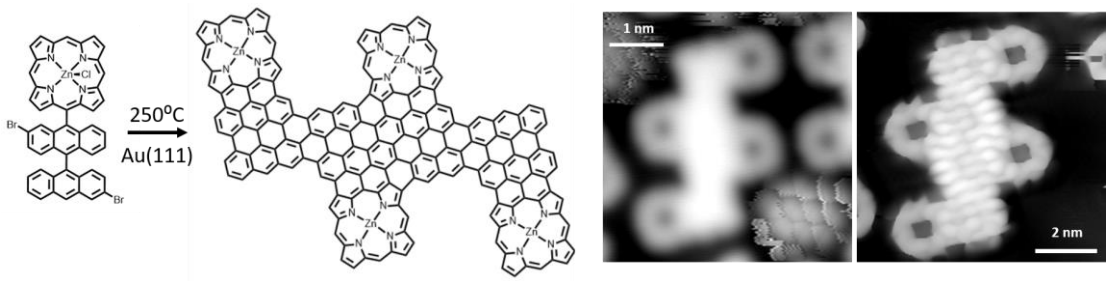

Figure 1: Scheme showing the on-surface synthesis reaction and low temperature STM images taken at constant current (-100 mV, 100 pA) and constant height (-5 mV) with a CO functionalized tip.