Fabrication and Characterization of Self-Assembled Cyano-Functionalized Porphyrin Networks on Graphene

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Supramolecular self-assembly of two-dimensional (2D) architectures has been lauded as a promising route to fabricating novel nanodevices on inorganic substrates. [1] Careful selection and rational design of molecules and their functional endgroups opens up a landscape of potential applications, including organic electronic, optoelectronic and spintronic devices. [2] Realization of these applications is dependent upon understanding the electronic and magnetic coupling between the molecular units of the network. Graphene, which has a low density of states near E_F, is an ideal surface in this respect, acting as a decoupling layer which preserves the inherent electronic structure of the 2D network. [3] In this study, we report on the fabrication of two distinct self-assembled networks of a cyano-functionalized cobalt-porphyrin derivative (Co-TCPP) (see Figure 1a) on graphene/Ir(111), namely: an H-bonded network and a Co-coordinated network. Such networks were previously observed on Au(111). [4] Characterization was done using scanning tunnelling microscopy/spectroscopy (STM/S). Low temperature STS results at 77 K indicate sharp resonances in the differential conductance (dI/dV) spectra (see Figure 1b and c), corresponding to the molecular frontier orbitals (HOMO/LUMO). A reduction in the transport gap of 0.9 eV was observed for the Co-coordinated network with respect to the H-bonded network. Furthermore, a pronounced downshift in energy for the LUMO of about 1 eV was observed on the Co-coordinated network, possibly related to the electron withdrawing character of the cyano-bond. These results indicate the ability to tune the level alignment of the 2D molecular network by changing the bonding motif. Future work will aim to clarify the effect of these Co-TCPP networks on the graphene band structure, and probe their magnetic couplings.

References

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[2] Otero, R. *et al.*, Advanced Materials, 44 (2011) 5148-5176
[3] Pörtner, M. *et al.*, Advanced Materials Interfaces, 15 (2020)
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Figures

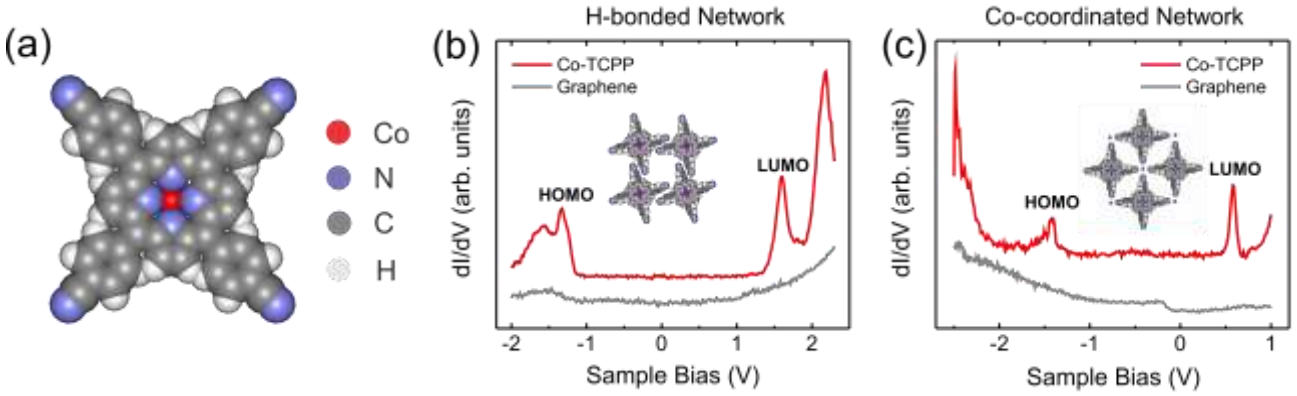

Figure 1: (a) Chemical structure of cobalt(II) 5,10,15,20-(tetra-4-cyanophenyl) porphyrin (Co-TCPP). (b) and (c) STS spectra taken at 77 K, showing peaks corresponding to the HOMO and LUMO. Inset: bonding motif of each network.