# Self-assembly and orbital imaging of metal phthalocyanines on graphene model surface

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Metal phthalocyanines (MPc) consist of a coordinated metal ion surrounded by an organic macrocycle of alternating carbon and nitrogen atoms. As both the central metal ion and the macrocycle can be modified, the electronic properties and self-assembly of these molecules can be tuned over a broad range. The use of arrays of MPcs on graphene has been suggested for tuning the electrical properties of graphene [1]. While the self-assembly of MPcs has been extensively studied on metal substrates, systematic studies of the symmetry of molecular assemblies and energetic position of the molecular orbitals on graphene are lacking.

Here, we study the effect of central ion and macrocycle substitution on the self-assembled MPc structures on epitaxial graphene by low-temperature scanning tunnelling microscopy (STM). We investigate the energetic positions and symmetries of molecular orbitals by scanning tunneling spectroscopy (STS) experiments and density functional theory (DFT) calculations. We focus on cobalt phthalocyanine (CoPc), copper phthalocyanine (CuPc) and fully fluorinated cobalt phthalocyanine ($F_{16}$CoPc) on G/ Ir(111) substrate as model systems. Our results shed light on the molecular ordering and the energies of molecular orbitals with respect to the graphene Dirac point for the different MPcs. This information will be crucial for using molecular overlayers to modify the electronic properties of graphene.

[1] P. Järvinen, S. K. Hämäläinen, K. Banerjee, P. Häkkinen, M. Ijäs, A. Harju and P. Liljeroth, *Nano Letters* **13**, 3199 (2013).