Tailoring interactions in supramolecular networks by fluorination

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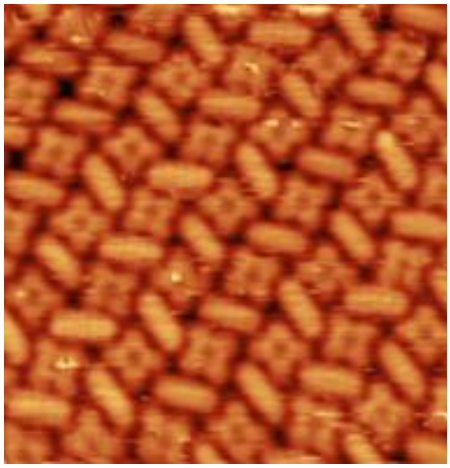
Organic electronics has become an enormously promising field of technology. However, many challenges have still to be overcome to make it mature and commercially competitive, requiring first a thorough understanding of the basic science involved in the operation of organic electronic devices and the physics of organic semiconductors. Of particular interest and relevance for the performance of organic electronics are donor/acceptor/metal interfaces, where crucial processes as e.g. charge injection take place. We investigate the physical-chemical properties of donor-acceptor blends in intimate contact with metal surfaces, using STM and a battery of electron spectroscopies, namely, X-ray photoemission (XPS), angle-resolved ultraviolet photoemission (ARUPS) and near edge X-ray absorption fine structure (NEXAFS), all combined with first principles calculations.

Perfluorination of semiconducting oligomers is an effective route to modify the ionization potential and the electron affinity, favoring *n*-type semiconducting behaviour in molecules that otherwise behave as electron donors [1]. When fluorinated and non-fluorinated molecules are combined, strong intermolecular interactions arise, which steer the spontaneous formation of two-dimensional donor-acceptor assemblies (Fig. 1, [2]). In this work we study the electronic structure changes upon switching the fluorination, i.e., the donor-acceptor character from one molecule species to the other in a binary mixture. In fact, we have tested the electronic structure changes from pure pentacene (PEN) and copper phthalocyanine (CuPc) monolayers, to donor/acceptor blends and reversed fluorination, namely F_{16}CuPc+PEN and PFP+CuPc, using Au(111), Ag(111) and Cu(111) as substrates. We will discuss how, upon mixing, donor/acceptor and molecule/surface interactions change in a complex way that depends on the intimate electronic properties of each system.



STM image of a self-assembled monolayer of PFP (acceptor) and CuPc (donor) on Ag(111) (13.2 nm^2).

[1] Z. Bao, A. J. Lovinger, and J. Brown, *J. Am. Chem. Soc.* **120**, 207 (1998).

[2] D. G. de Oteyza, J. M. García-Lastra, M. Corso, B. P. Doyle, L. Floreano, A. Morgante, Y. Wakayama, A. Rubio, J. E. Ortega, *Adv. Funct. Mater*. **19**, 3567 (2009).

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