

Epitaxial Growth of Organic Nanocrystals on Surfaces

Marta Trelka¹, Anaïs Medina², David Ecija¹, Christian Urban¹, Jose M. Gallego³, Christian G. Claessens², Roberto Otero^{1,4}, Tomás Torres² and Rodolfo Miranda^{1,4}

¹ *Universidad Autónoma de Madrid, Departamento de Física de la Materia Condensada, 28049 Madrid, Spain*

² *Universidad Autónoma de Madrid, Departamento de Química Orgánica, 28049 Madrid, Spain*

³ *Instituto de Ciencia de Materiales de Madrid, CSIC, 28049 Madrid, Spain*

⁴ *Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nano), 28049 Madrid, Spain*

rodolfo.miranda@uam.es; tomas.torres@uam.es

Controlling the formation of nanosized organic particles of well-defined size and shape is one of the challenges facing modern chemistry. The optical properties of such organic nanostructures are extraordinary and very different from the properties found for the same materials in bulk form⁴⁻⁶, similarly to the case for their inorganic counterparts¹⁻³. For example, organic nanoparticles show size-dependent absorption and fluorescence bands^{4,5} or single photon emission⁶. Although these size effects in organic nanoparticles might have been expected on the basis of the optical properties of their inorganic counterparts, the current understanding of these effects is hindered by the difficulty in the synthesis of organic nanocrystals, i.e. organic nanoparticles with an ordered molecular arrangement, as compared to the case of inorganic ones.

A possibility that remains mostly unexplored is the synthesis of such nanocrystals on solid surfaces. In the same way in which crystalline inorganic nanodots can be epitaxially grown on suitable substrates under conditions in which 3D Volmer-Weber growth takes place^{7,8}, an organic system could in principle be devised such that the growth of crystalline 3D islands sets in before the completion of the first monolayer. In practice, however, for organic adsorbates deposited on inorganic substrates intermolecular interactions are much weaker than molecule-substrate interactions⁹, thus promoting a layer-by-layer growth mode, and preventing the fabrication of isolated 3D nanocrystals.

Here we show that, upon deposition of cone-shaped subphthalocyanine¹⁰⁻¹² (SubPc, see Figure 1a) molecules on Cu(111), isolated nanocrystallites up to 3 ML high appear on the surface before the completion of the first monolayer. The structure of such nanocrystals can be explained by the joined effect of electrostatic (dipole-dipole) and dispersive (π - π) interactions. Although 1 ML-thick islands can also be found on the surface, the molecular arrangement in these areas is different from the geometry of the 1st-layer molecules in the crystallites. We suggest that the formation mechanism of the organic nanocrystals is related to the existence of two different adsorption geometries, cone-up and cone-down, each of which sits on different molecular layers placed at different distances from the surface upon crystallite formation.

References:

- [1] Alivisatos, A. P., *Science* **271** (1996) 933.
- [2] Lounis B. & Orrit M., *Rep. Prog. Phys.* **68** (2005) 1129.
- [3] Murray, C. B., Kagan, C. R. & Bawendi, M. G., *Annu. Rev. Mater. Res.* **30** (2000) 545.
- [4] Xiao, D. *et al.*, *J. Am. Chem. Soc.* **125**, (2003) 6740.
- [5] Fu, H.-B. & Yao, J.-N., *J. Am. Chem. Soc.* **123** (2001) 1434.

- [6] Masuo, S. *et al.*, *Jpn. J. Appl. Phys.* **46** (2007) L268.
 [7] Stangl, J., Holý, V. & Bauer, G., *Rev. Mod. Phys.* **76** (2004) 725.
 [8] Otero, R., Vázquez de Parga, A. L. & Miranda, R., *Phys. Rev. B* **66** (2002) 115401.
 [9] Barth, J. V. *Annu. Rev. Phys. Chem.* **58** (2007) 375.
 [10] Kobayashi N. *The Porphyrin Handbook*, vol. 15, pp. 161-262, Kadish, K. M., Smith, K. M. & Guillard, R. (eds.), (Academic Press, San Diego, 2006).
 [11] Claessens, C. G., González-Rodríguez, D. & Torres T., *Chem. Rev.* **102** (2002) 835.
 [12] Torres, T., *Angew. Chem. Int. Ed.* **45** (2006) 2834.

Figures:

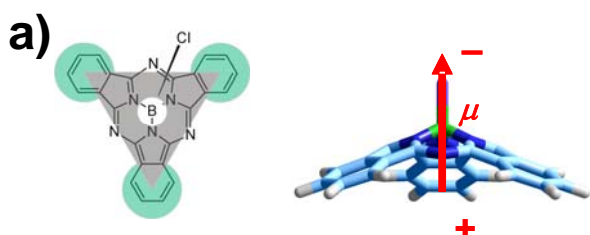


Figure 1. a) Chemical structure of the chlorosubphthalocyanine molecules and side view of its 3D structure showing the dipole moment.

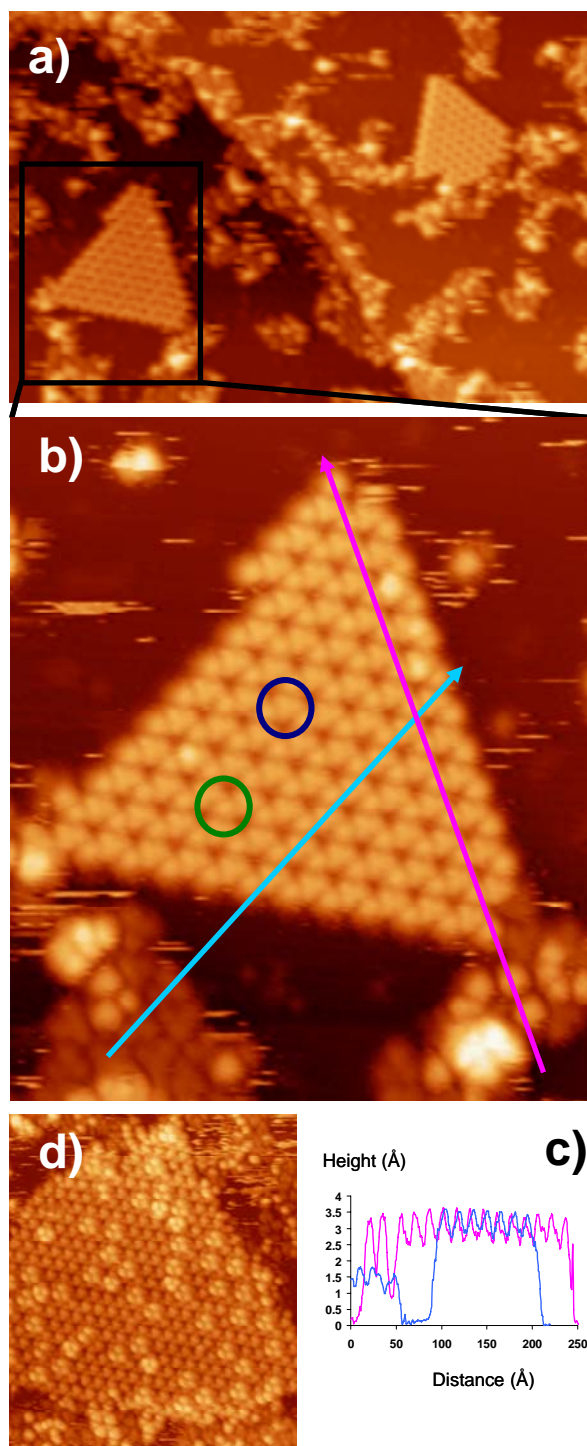


Figure 2. a) $62.4 \times 41.6 \text{ nm}^2$ STM image of 0.4 ML SubPc/Cu(111) ($I = -0,8 \text{ nA}$; $V = -2,9 \text{ V}$). Two triangular islands can be found. As for the 1 ML thick islands, high resolution STM images such as (b, $22.3 \times 26.1 \text{ nm}^2$) show two different molecular features, bright protrusions (green circles) and trefoil shapes (blue circles). The bright protrusions are identical in shape and size to the Cl-up molecules identified in Figure 2, but the trefoil features are 0.2 nm higher (c). Even thicker islands can be found upon further deposition (d, $33.4 \times 39.2 \text{ nm}^2$).