Electronic Supplementary Material (ESI) for ChemComm.

Step by step on-surface synthesis: from manganese phthalocyanines to their polymeric form

M. Koudia and M. Abel*

Aix Marseille Université, CNRS, IM2NP UMR 7334, 13397, Marseille, France

*) Correspondence should be addressed to: mathieu.abel@im2np.fr

Supplementary Information

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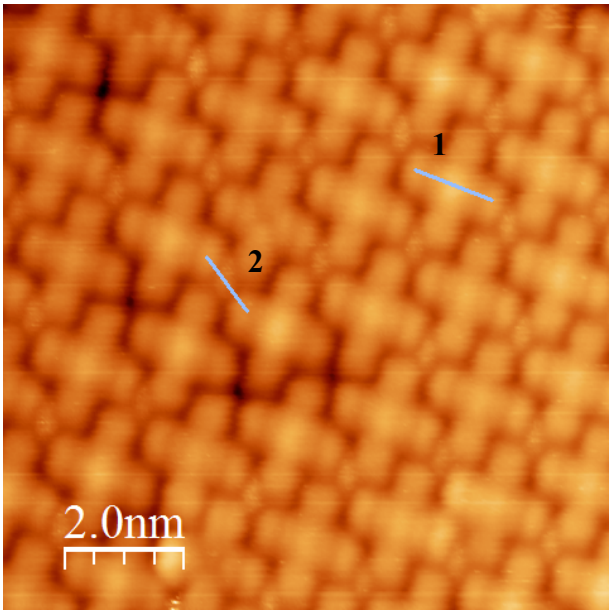
A. DFT Simulations

Electronic structure calculations were performed within the framework of density functional theory using SIESTA Spanish Initiative for Electronic Simulations with Thousands of Atoms [1] and [2]. The exchange-correlation energy is treated within the generalized gradient approximation GGA using a parameterization proposed by Perdew, Burke and Ernzerhof.[3]. The wave function of the valence electrons is expanded in a localized basis set consisting of finite-range pseudoatomic orbitals[4]: a double-zeta plus polarization basis set was used for each atom. The core electrons are treated within the frozen core approximation with norm-conserving Troullier-Martins pseudopotentials [5]. The unit cell used for k-sampling grid is a (4 x 4 x1) unit cell. The molecular networks were relaxed until the forces acting on each atom were smaller than 0.04 $eV.Å^{-1}$ Both pseudopotential and basis set were previously tested by comparing calculated molecular geometry to x-ray geometry characterisation of organometallic compounds such as CuPc.

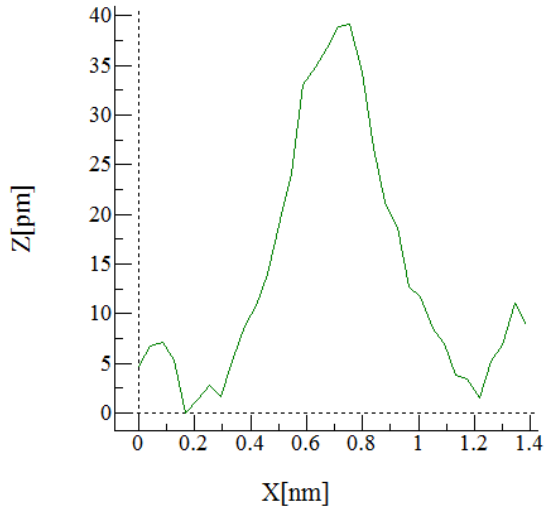
[1] Sánchez-Portal, D., Ordejón, P., Artacho, E., & Soler, J.M. Density-functional method for very large systems with LCAO basis set. *Int. J. Quantum Chem.* **65,** 453-461 (1997).
[2] Soler, J.M., et al. The SIESTA method for *ab initio* order-*N* materials simulation. *J. Phys. Condens. Matter* 14, 2745-2779 (2002).
[3] Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple *Phys. Rev. Lett.* **77,** 3865-3868 (1996).
[4] Junquera J., Paz, O., Sánchez-Portal, D. & Artacho, E. Numerical atomic orbitals for linear-scaling calculations. *Phys. Rev. B* **64,** 235111 (2001).
[5] Troullier, N. & and Martins, J. L. Efficient pseudopotentials for plane-wave calculations. *Phys. Rev. B* **43,** 1993-2006 (1991).

B. Height measurements

a)



b)



c)

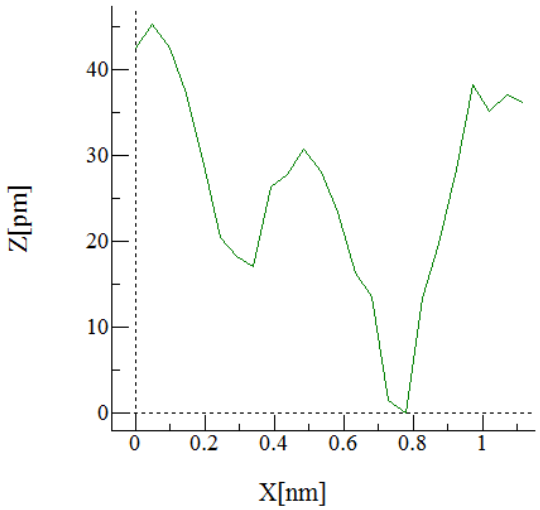


Figure S2: (a) 10 x 10 nm² STM image of MnPc molecules domain metal-organised. (b, c) Line profiles of Mn in MnPc molecule and Mn metal-organised, 1 and 2 respectively.

C. Additional STM images

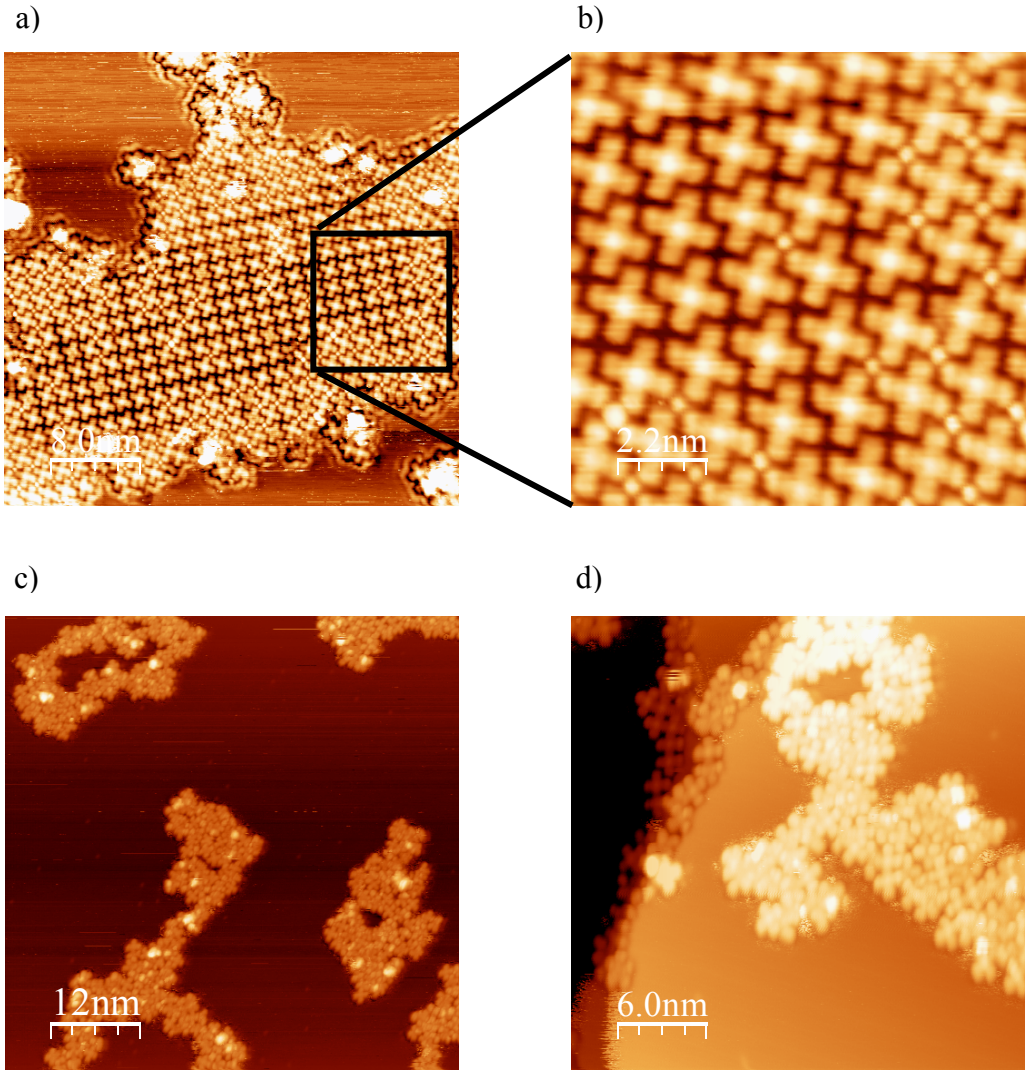


Figure S3: (a, b) STM images of the incorporation of Mn atoms in the $MnPcCN_8$ domain, Left 40 x 40 nm² and right 11 x 11 nm² . (c, d) STM images of the disordered MnPc polymer left 60 x 60 nm² and right 30 x 30 nm².