

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

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

Cite this: DOI: 10.1039/x0xx00000x

M.Koudia and M. Abel

Received 00th January 2012,
8

DOI: 10.1039/x0xx00000x

www.rsc.org/

On-surface synthesis of tetracyanobenzene molecules with Mn atoms is presented. From metal-organic coordination networks at room temperature, Mn-phthalocyanines and finally small domains of polymeric Mn-phthalocyanines are formed upon annealing on the Ag(111) surface. Step-by-step on-surface reaction is studied in situ by scanning tunnelling microscopy under ultra-high vacuum.

Molecular self-assembly has been proven to constitute a powerful tool for the creation of highly ordered self-assembled organic systems¹. The tuning of the subtle balance between intermolecular and molecule-surface interactions thanks to a rational design of the molecular building blocks has led to a whole range of architectures realised on clean surfaces and well-controlled ultra-high vacuum (UHV) conditions²: from unidirectional or two-dimensional structures to more complex architectures such as host-guest and open networks^{3,4,5}. The main driving forces used in these molecular self-assemblies are non-covalent intermolecular interactions such as Van der Waals forces, hydrogen-bonds or metal-organic coordination. With regards to electronic applications, the latter allows the production of regularly and separately distributed transition-metal (TM) atoms that bears significant promise for the creation of unprecedented new materials⁶. Unfortunately, the reversible nature of the interaction poses a further challenge, as they hardly provide sufficient intermolecular electron transport capabilities. In this context, the concept of on-surface synthesis has been recently exploited as a promising strategy to overcome these limitations by covalent bonding of suitable precursors directly on the substrate in UHV. This bottom-up approach should lead to an endless variety of structures with original electronic and magnetic properties⁷. The strategies used so far have mainly involved two kinds of chemical reactions: polycondensation of boronic acid^{8,9} or Ullman reaction with iodine and bromine atoms^{10,11,12}. The on-surface reaction between organic and inorganic species to form organometallic compounds is less documented¹³. Among technologically relevant molecules for

organic electronic devices, metallophthalocyanines (MPc) have been extensively studied for their chemical stability and interesting properties in a wide range of applications such as gas sensors, field effect transistors, organic light-emitting diodes and data storage devices¹⁴. Unfortunately, these potential devices are highly restricted by the grain boundaries deriving from the production of 3D thick films. On the other hand, while the polymeric forms of phthalocyanines have been known for a long time, their synthesis in the single sheet regime is still a delicate matter¹⁵.

In a previous study we introduced the possibility of an organometallic reaction at room temperature between 1,2,4,5-tetracyanobenzene (TCNB) molecules and iron on Au(111)¹⁵. Here we are presenting the same TCNB molecules deposited with Mn atoms on Ag(111), extending this study to a non-reconstructed (111) surface with a rather similar reactivity. In this case, the comparison between metal-organic phases obtained at room temperature and new phases obtained at higher temperature provides evidence of the reaction process. At room temperature, the deposition of TCNB molecules and Mn atoms on Ag(111) leads to the formation of 2D metal-organic structures with 1:2 stoichiometry. Then a first reaction step occurs at 415K with the formation of Mn-2,3,9,10,16,17,23,24-octacyanophthalocyanines (MnPc(CN)₈). The resulting molecules then self-assemble in either hydrogen bonding or metal-ligand supramolecular networks. The second reaction step occurs at 615K and results in the formation of small domains of the 2D phthalocyanine polymeric form with the remaining Mn atoms. Calculations have shown that such material, which presents regularly spaced TM atoms, possesses very interesting magnetic and/or conduction properties⁷.

All experiments were performed in a multicharacterisation chamber under UHV. TCNB were evaporated from a crucible held at 380K. Mn atoms were deposited from a Mn rod (Goodfellow) using an electron-beam evaporator. Different stoichiometries were obtained by modifying the deposition time ratio. The resulting synthetic films were characterised using room-temperature STM (Omicron VT-STM).

Images were plane-corrected and analysed using the WSxM software¹⁶. Gas phase calculations were done in the framework of the density functional theory (DFT) using the SIESTA package¹⁷ (Supplementary S1).

The deposition of TCNB molecules and Mn atoms at room temperature enables the formation of 2D networks of about 10-30 nm, as shown in Figure 1, left. These networks, which are only observed in the presence of Mn atoms, present a square symmetry with a measured unit cell of (12 ± 0.5) Å. This square symmetry is consistent with a tetradentate configuration of Mn atoms linked to four TCNB molecules. DFT simulations of the metal-organic coordination network (MOCN) with a TCNB:Mn stoichiometry of 2:1 (Fig. 1, right) are consistent with the experiments: the calculated lattice parameter is found to be 11.9 Å. This network is also consistent with literature data in the case of tetracyano functionalised molecules such as Fe:TCNB¹⁸ or Mn:tetracyanoquinodimethane¹⁹ (Mn-TCNQ). We therefore conclude that the deposition of Mn with TCNB molecules on Ag(111) leads to the formation of MOCN with Mn atoms in a tetradentate configuration at each corner of the lattice. The depression pointed out by the circle in the inset of Figure 1 corresponds to a missing Mn atom in the 2D metal-organic framework.

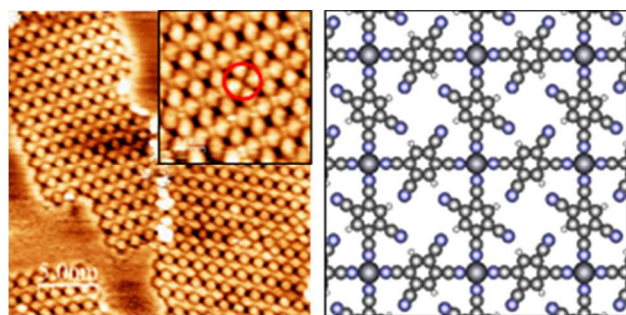


Figure 1: Left ($25 \times 25 \text{ nm}^2$) and inset ($8 \times 8 \text{ nm}^2$): STM images of the 2D metal-organic TCNB framework formed at room temperature on Ag(111) with 2:1 stoichiometry (square unit cell of 12 Å). Right: DFT model (square unit cell of 11.9 Å). H, C and N are represented as white, grey and blue spheres, respectively. Mn atoms are represented as large grey spheres. The circle indicates a missing Mn atom.

Upon annealing at 545K, the MOCN turn into a new structure (Fig. 2, left). Cross-like compounds form on the surface and subsequently self-assemble in a square unit cell of (16 ± 0.5) Å. This network is stable up to 615K.

Contrary to what was observed in the MOCN presented in Figure 1, STM images of the crosses show no more helicity as well as a continuous electron density between the four peripheral arms and the centre. Furthermore the metal centre appears about 0.4 Å higher than the rest of the compound. This behaviour is expected in the case of $\text{MnPc}(\text{CN})_8$ formation whose d_{z^2} orbital, close to the Fermi level, contributes to the tunnelling current (solid line circles in Figure 2). This effect is consistent with STM imaging of MnPc when deposited on Pb surface where Mn is described in Mn(II) state^{20,21}. The modelisation of the $\text{MnPc}(\text{CN})_8$ self-assembly by means of DFT calculations (inset of Fig. 2, left) shows an intermolecular distance of 15.8 Å, which is in line

with the experimental value. In addition, the observed square lattice is consistent with other self-assemblies of functional MPC such as ZnPcCl_8 ²² or ZnPcF_8 ²³ on Ag(111), where the main intermolecular interaction is hydrogen bonding between molecules. Similarly, two of the four arms are aligned with the dense directions of the substrate.

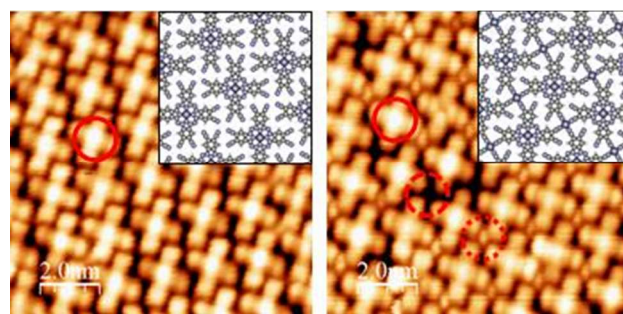


Figure 2: Left ($10 \times 10 \text{ nm}^2$): STM image of the resulting $\text{MnPc}(\text{CN})_8$ molecules on Ag(111) (square unit cell of 16 Å). Inset: DFT model (square unit cell of 15.75 Å). Right ($10 \times 10 \text{ nm}^2$): STM image of the metal-organisation between $\text{MnPc}(\text{CN})_8$ molecules and Mn atoms on Ag(111). Inset: DFT model. The circles indicate: a covalently bonded Mn atom (solid line), Mn-coordinated atom (dotted line) and missing Mn-coordinated atom (dashed line).

Naturally, the covalent reaction between the Mn atom and four TCNB molecules involves only half of the Mn atoms available. This phase coexists with another one, shown to the right of Figure 2, and characterised by a TCNB:Mn ratio of 2:1, as was the case in the previously formed MOCN. This new phase consists again of cross-like compounds, but this time additional Mn atoms are present between the crosses (dotted circle in Fig. 2) involving the other half of the available cyano-groups. Using the same STM tip we can now clearly differentiate between two behaviours of Mn atoms: Mn in the cross-like compounds (solid line circles) appears 0.4 Å above the molecular plane while Mn in between (dotted line circle) appears 0.1 Å lower (See supplementary S2). The main influence of the substrate resides in a vertical deformation of the metal-organic networks as demonstrated in Mn-TCNQ experiments²⁴ whereas MnPc is adsorbed in a rather flat configuration. This should be at the origin of these different heights between the two different Mn atoms. The dashed line circle shows a depression due to a missing Mn atom in this metal-coordinated $\text{MnPc}(\text{CN})_8$ dense phase. The Mn atoms in excess are subsequently incorporated between the resulting $\text{MnPc}(\text{CN})_8$ molecules, binding them with metal-ligand interactions. The incorporation of Mn atoms through the $\text{MnPc}(\text{CN})_8$ dense phase depends on their diffusion through the film upon annealing. Indeed, large domains show a gradient diffusion of these Mn atoms where the periphery of the domains have a higher Mn concentration than in the centre (Supplementary S3). The DFT calculations of this phase (inset of Fig. 2, right) are consistent with this description. They show that four $\text{MnPc}(\text{CN})_8$ are organised around a Mn atom linked by metal-ligand interactions of the same nature as those previously described for the Mn-TCNB network (Fig. 1). Both the thermal stabilities and the STM appearance of the Mn atoms allow us to demonstrate the on-surface synthesis of $\text{MnPc}(\text{CN})_8$. At this stage, it is important to note that even in the presence of a sufficient amount of Mn atoms, no more covalent bonds are created. The temperature needs to be

increased up to 615K for the reaction to continue at the terminating cyano-groups of the $\text{MnPc}(\text{CN})_8$.

Figure 3 is obtained after a 615K annealing of the metal-ligand $\text{MnPc}(\text{CN})_8$ network presented in Figure 2, right. This temperature has no impact on the stability of $\text{MnPc}(\text{CN})_8$ molecules, but it induces the formation of some domains of about 5nm large, compatible with polymeric phthalocyanines formation. This network has a square structure with a measured periodicity of (11 ± 0.5) Å in both directions. Interestingly, while two of the four arms of the MnPc are aligned with the dense direction of the substrate, the 2D polymer is rotated by 15° with respect to the phthalocyanine domains and the polymer lattice vectors are no more aligned with the substrate. The control of the stoichiometry of the precursors is crucial for the reaction to proceed: an excess of molecule can hinder the formation of a well-ordered polymer and result in the formation of disordered undefined phases (Supplementary S3). Noticeably, this reaction produces no by product, so no contamination is created.

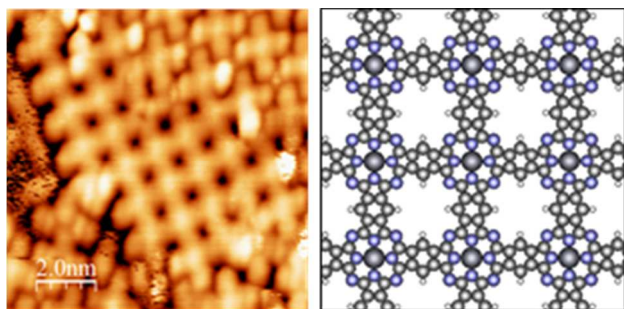


Figure 3: Left ($10 \times 10 \text{ nm}^2$): STM images of the 2D manganese phthalocyanine organometallic polymer (poly-MnPc) formed on Ag(111) surface (square unit cell of 11 Å). Right: DFT model (square unit cell of 10.75 Å).

DFT calculations shows a distance of 10.8 Å for the theoretical 2D lattice (Fig. 3, right), which is in line with the experimental value and previous calculations²⁵. This lattice parameter is smaller than that of the 2D metal-organic framework obtained at room temperature (11.9 Å), revealing the covalent nature of the bonds inside the film. Furthermore, it is interesting to note that the activation energy of the first step of the reaction ($\text{MnPc}(\text{CN})_8$ synthesis) is lower than the activation energy of the polymeric form (615K). This difference in energy is certainly responsible for the small size of the polymerised areas.

In summary, we studied the on-surface reaction between Mn atoms and TCNB molecules, starting with a metal-ligand network at room temperature followed by a $\text{MnPc}(\text{CN})_8$ synthesis at 545K, self-assembled either by hydrogen bonding or by metal-ligand interactions, and ending with the formation of 2D polymeric Mn-phthalocyanine networks at 615K. This π -conjugated system represents a fully delocalised two-dimensional electron system with magnetic metal atoms spread regularly in the polymer lattice. The activation of the reaction at 415K suggests that the previously Fe-TCNB compound was unreacted at room temperature. Changing from Fe to Mn allows to decrease the activation temperature and thus facilitates the reaction. In principle, it should be possible to perform a stepwise growth in order to create networks of alternating metal

centres (e.g., magnetic and non-magnetic) and therefore control the spin density in the film. If necessary, individual spins can be adjusted by functionalization and/or modification of the magnetic centre, thereby allowing the magnetic properties of the molecular network to be adjusted. Molecular precursors of various size, shape and functionality could be used, as well as other metals. Furthermore, the exploration of other kinetic paths could lead to an increase in the size of the 2D polymeric Mn-phthalocyanine. The flexibility of the synthesis method can thus allow for the creation of a wide range of organometallic polymer films of tuneable composition, structure and properties.

The authors wish to thank L. Porte for fruitful discussions.

Notes and references

Aix Marseille Université, CNRS, IM2NP, UMR7334, 13397 Marseille, France. E-mail: mathieu.abel@im2np.fr

- 1 J. M. Lehn, *Science*, 1993, **260**, 1762.
- 2 J. V. Barth, G. Costantini and K. Kern, *Nature*, 2005, **437**, 671.
- 3 J. V. Barth, J. Weckesser, C. Z. Cai, P. Gunter, L. Burgi, O. Jeandupeux and K. Kern, *Angewandte Chemie-International Edition*, 2000, **39**, 1230.
- 4 J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness and P. H. Beton, *Nature*, 2003, **424**, 1029.
- 5 G. Pawin, K. L. Wong, K.-Y. Kwon and L. Bartels, *Science*, 2006, **313**, 961.
- 6 P. Gambardella, S. Stepanow, A. Dmitriev, J. Honolka, F. M. F. de Groot, M. Lingenfelder, S. Sen Gupta, D. D. Sarma, P. Bencok, S. Stanesco, S. Clair, S. Pons, N. Lin, A. P. Seitsonen, H. Brune, J. V. Barth and K. Kern, *Nature Materials*, 2009, **8**, 189.
- 7 J. Zhou and Q. Sun, *Journal of the American Chemical Society*, 2011, **133**, 15113.
- 8 N. A. A. Zwaneveld, R. Pawlak, M. Abel, D. Catalin, D. Gignes, D. Bertin and L. Porte, *Journal of the American Chemical Society*, 2008, **130**, 6678.
- 9 T. Fauray, S. Clair, M. Abel, F. Dumur, D. Gignes and L. Porte, *Journal of Physical Chemistry C*, 2012, **116**, 4819.
- 10 L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters and S. Hecht, *Nature Nanotechnology*, 2007, **2**, 687.
- 11 L. Lafferentz, V. Eberhardt, C. Dri, C. Africh, G. Comelli, F. Esch, S. Hecht and L. Grill, *Nature Chemistry*, 2012, **4**, 215.
- 12 J. Adisojojoso, Y. Li, J. Liu, P. N. Liu and N. Lin, *Journal of the American Chemical Society*, 2012, **134**, 18526.
- 13 T. Bauer, Z. Zheng, A. Renn, R. Enning, A. Stemmer, J. Sakamoto and A. D. Schlüter, *Angewandte Chemie-International Edition*, 2011, **50**, 7879.
- 14 Phthalocyanines: Properties and Applications, C. C. Leznoff and A. B. P. Lever, Eds., VCH Publishers (LSK) Ltd. Cambridge, 1996, Vols. 1-4.
- 15 M. Abel, S. Clair, O. Ourdjini, M. Mossoyan and L. Porte, *Journal of the American Chemical Society*, 2011, **133**, 1203.
- 16 I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.
- 17 D. SanchezPortal, P. Ordejon, E. Artacho and J. M. Soler, *International Journal of Quantum Chemistry*, 1997, **65**, 453.

- 18 S. Kezilebieke, A. Amokrane, M. Boero, S. Clair, M. Abel and J. P. Bucher, *Nanoresearch*, 2014 (Accepted)
- 19 N. Abdurakhmanova, A. Floris, T.-C. Tseng, A. Comisso, S. Stepanow, A. De Vita and K. Kern, *Nature Communications*, 2012, **3**.
- 20 D. Hao, C. L. Song, Y. X. Ning, Y. L. Wang, L. L. Wang, X. C. Ma, X. Chen and Q. K. Xue, *Journal of Chemical Physics*, 2011, **134**.
- 21 Y.-S. Fu, S.-H. Ji, X. Chen, X.-C. Ma, R. Wu, C.-C. Wang, W.-H. Duan, X.-H. Qiu, B. Sun, P. Zhang, J.-F. Jia and Q.-K. Xue, *Physical Review Letters*, 2007, **99**.
- 22 M. Koudia, M. Abel, C. Maurel, A. Blik, D. Catalin, M. Mossoyan, J. C. Mossoyan and L. Porte, *Journal of Physical Chemistry B*, 2006, **110**, 10058.
- 23 V. Oison, M. Koudia, M. Abel and L. Porte, *Physical Review B*, 2007, **75**.
- 24 T.-C. Tseng, C. Lin, X. Shi, S. L. Tait, X. Liu, U. Starke, N. Lin, R. Zhang, C. Minot, M. A. Van Hove, J. I. Cerda and K. Kern, *Physical Review B*, 2009, **80**.
- 25 J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon and D. Sanchez-Portal, *Journal of Physics-Condensed Matter*, 2002, **14**, 2745.