SUPPORTING INFORMATION

Very high temperature porphyrin tiling of rutile TiO_2(110).

Giacomo Lovat,[a,b] Daniel Forrer,[c] Mikel Abadia,[d] Marcos Dominguez,[a,b] Maurizio Casarin,[e] Celia Rogero,[d] Andrea Vittadini*[c] and Luca Floreano*[a]

Supporting Information

Identification of Ti^{5f} and O_{br} rows on (2x1) reconstruction.

On a highly reduced substrate we obtained local coexistence of (1x1) and (2x1) reconstructed domains, as shown in Fig. S1. The Ti^{5f} rows are easily identified on the (1x1) surface since they appear as bright rows extending in the [001] direction at both positive and negative bias. The O_{br} rows are always dark eventually yielding bright atomic spots in correspondence of adsorbed hydrogen (hydroxyl). In the high resolution image of Fig. S1, one can appreciate the (2x1) reconstruction as made of paired bright rows separated by a large dark row. Ti^{5f} rows of the (1x1) surface are seen to correspond alternatively to the middle of the (2x1) dark rows and to the middle of the (2x1) bright paired rows. In the large scale image of Fig. 3b, the paired bright rows are not individually resolved and the (2x1) reconstruction appears as simply made by alternating bright and dark rows, each one corresponding to a Ti^{5f} row of the (1x1) domain (see inset of Fig. 3b).

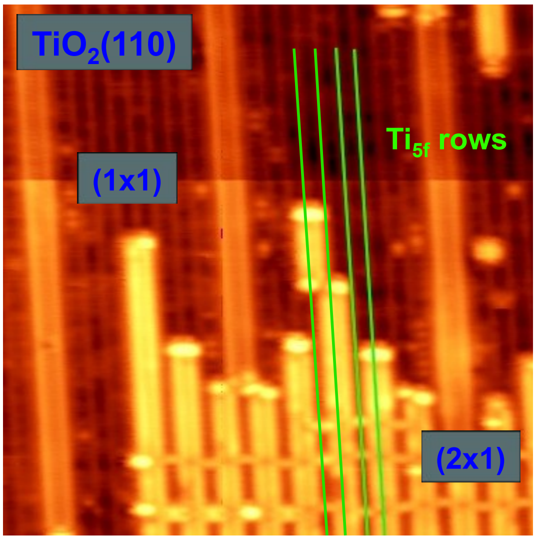

Fig. S1 STM image on a clean TiO_2(110) surface where (1x1) and (2x1) domains coexist on the same terrace. Extrapolation of the Ti^{5f} rows from the (1x1) region to the (2x1) regions is shown, which allows the assignment of the Ti^{5f} rows on the (2x6) superlattice of Fig. 4b.

Comparison of XPS intensities

For a direct comparison of the N and C 1s peak intensity as a function of the annealing temperature, we measured the phtoemission spectra of the relevant core levels at a photon energy of 650 eV. Since the coverage is in the monolayer range, we directly compared the N ad C 1s spectra after simple normalization to the Ti 2p core level, as shown in Fig. S2b. In this case, one can appreciate the almost perfect overlap of the Ti 2p spectra with and without the molecular overlayer, and before and after the different annealing steps. The absence of significant variation of the low energy tail indicates that no change of the amount of Ti^{3+} and Ti^{2+} ions is observed upon self-

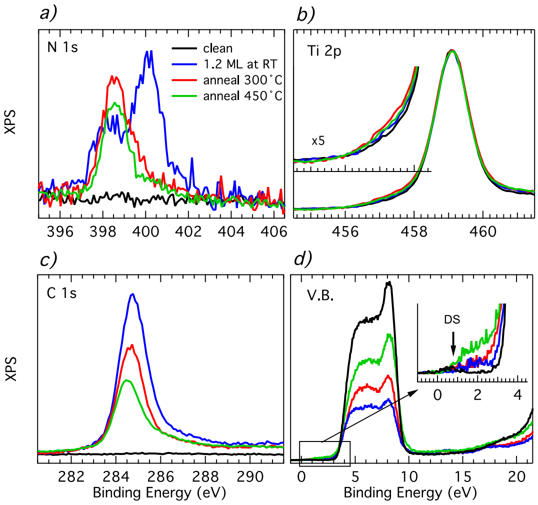

Fig. S2 Photoemission spectra of the N 1s, Ti 2p and C 1s peaks measured with a photon energy of 650 eV and an overall resolution of 250 meV, panels *a), b),* and *c)*. The spectra have been normalized to the Ti 2p peak intensity. The Valence Band spectrum is shown in panel *d)*, as measured with a photon energy of 14o meV and an overall energy resolution of 120 meV. The spectra are to scale after simple normalization to the photon flux. The inset of panel *c)* shows a zoom of the Band Gap putting in evidence the Defect State, DS, of the bare titanium dioxide.

---

[a] *CNR-IOM, Laboratorio Nazionale TASC, I-34149 Trieste, Italy. E-mail: floreano@iom.cnr.it*
[b] *Graduate School of Nanotechnology, University of Trieste, P.za Europa 1, I-34127 Trieste, Italy.*
[c] *CNR-ICMATE and INSTM, via Marzolo 1, I-35131 Padova, Italy. E-mail: andrea.vittadini@unipd.it*
[d] *Materials Physics Center MPC, Centro de Física de Materiales (CSIC-UPV/EHU) and Donostia International Physics Center (DIPC), E-20018 San Sebastian, Spain.*
[e] *Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, I-35131 Padova, Italy.*

metalation and cyclo-dehydrogenation. We can conclude that the Ti atom incorporated in the porphyrin macrocycle must have the same oxidation state of Ti atoms in the substrate. Minor deviations of the Ti 2p tail from the pristine clean surface (as highlighted in the inset of Fig. S2b) are originated by the RHEED irradiation corresponding to the diffraction patterns shown in Fig. 1. These minor changes mostly affect the film after the RT deposition and the intermediate self-metalation reaction (also compare with measurements in Ref. [26]). In fact, electron irradiation is known to reduce the $TiO_2(110)$ surface in vacuum, which may also trigger the formation of residual molecules in different oxidation states. This minority component is however desorbed upon further annealing beyond 350˚C. The corresponding N 1s and C 1s peaks show that the full monolayer of 2H/4HTPP is converted into a metalated TiO_2TPP monolayer. In particular, molecules in excess of 1 ML are simply desorbed after annealing to 300˚C as witnessed by the consistent intensity decrease of the N and C peaks. Further heating beyond 400˚C leads to a decrease of about 20% of the N and C intensity, which is in excellent agreement with the expected decrease of the molecular density across the (2x4)-*obliq* → (2x6) phase transition. Finally, we show in Fig. S2d the Valence Band measured with a photon energy of 140 eV. In this case the spectra are simply normalized to the photon flux, thus one can appreciate the attenuation of the O 2p band (in the 4-9 eV range) after deposition of ~1.2 ML, and the following intensity increase due to desorption of 2nd layer molecules at 300˚C and then to the desorption of excess 1st layer molecules associated with the (2x4)-*obliq* → (2x6) phase transition.