Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

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A $TbPc_2$ sub-monolayer deposit on Titanium Dioxide ultrathin film: a magnetic, morphological, and chemical insight

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XPS characterization

The O*1s* and Ti*2p* spectra were acquired to evaluate the stoichiometry of the TiO_2 film before and after the $TbPc_2$ deposition. The O*1s* region was characterized by three components (see **Figure S1**): the main peak at 530.75 eV was given by the oxygen atoms bonded with Ti^{IV} species, the components at 532.5 eV were attributed to the presence of Ti^{III} sites[1] while the one at 534.0 eV was due to a very small amount of hydroxyl groups[2] or water molecules[3] absorbed on the surface.

The $Ti^{IV}2p_{3/2}$ component was calibrated to 459.3 eV (filled in yellow in **Figure 1a**) and its relative spin-orbit coupling component ($Ti^{IV}2p_{1/2}$) was shifted by 5.7 eV in agreement with the values reported in the literature.[4,5] At 457.5 eV a small component due to the presence of Ti^{III} species [1,4] (filled in green, less than 5% of the total areas) was observed with its relative spin-orbit component shifted by 5.2 eV.[5,6] An additional shake-up component of the main Ti^{IV} component was found at 459.8 eV (filled in dark red in **Figure 1a**) plus the relative spin-orbit coupling contribution at 465.5 eV.[7,8] No change in the signal is observed after the molecular deposition.

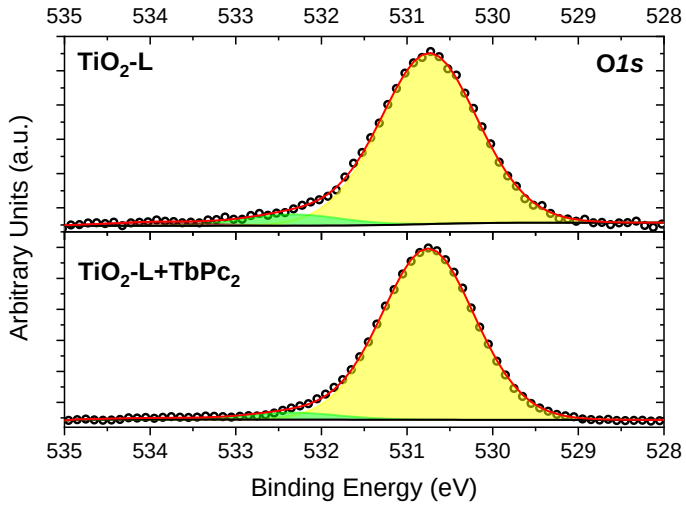

Figure S1. XPS spectra showing the O*1s* regions before and after the $TbPc_2$ deposition on TiO_2–L. Circles are the experimental XPS data, the red line is the XPS fit and filled areas are the fit deconvolution components.

Table S1. Chemical semi-quantitative analysis was obtained by XPS measurements of TiO_2 growth on Ag(100) before and after the $TbPc_2$ deposition.

	Ti	O	Ti/O
Theoretical values	33.3%	66.7%	0.5
TiO_2-L	29.3%	70.7%	0.4
TiO_2-L+ $TbPc_2$	28.8%	71.4%	0.4

LEED and STM characterization

The crystallographic structure of the TiO_2 was investigated by LEED pattern, as a function of the energy, see in **Figure S2a** and **Figure S2c**. The cell parameters obtained from the LEED pattern analysis are *a*=0.362 nm and *b*=0.289 nm, in close agreement with the literature.[9,10] The simulated LEED patterns (**Figure S2b** and **Figure S2d**) of the TiO_2-L structure were obtained by entering the cell parameters extracted from the LEED analysis in the LEEDpat42 software. The simulated images show two rectangular domains (red and blue circles on **Figure S2b** and **Figure S2d**) of the TiO_2-L structure that are fully comparable with the experimental one (**Figure S2a** and **Figure S2c**).

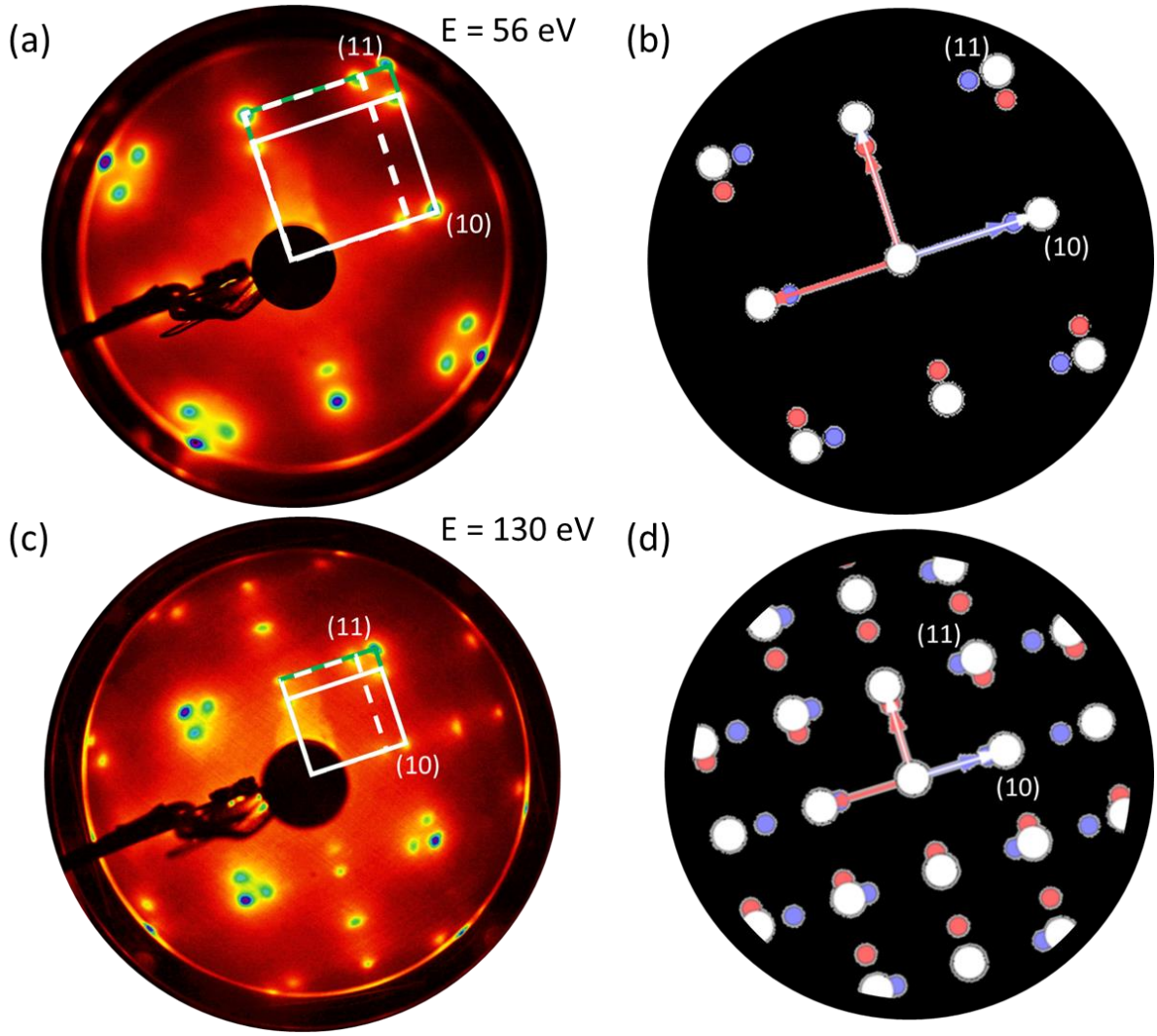

Figure S2. LEED patterns acquired as a function of the energy showing the surface structure of the TiO_2-L single layer growth on Ag(100), (a) 56 eV, and (c) 130 eV. In both LEED images the green square marks the Ag(100) reconstruction. The two rectangular domains related to the TiO_2 lepidocrocite-like phase and rotated by 90° to each other, are marked in white. The simulated patterns of the lepidocrocite-like structure are reported for the two different energies: (b) 56 eV and (d) 130 eV. The red and blue circles identify the two rectangular domains of the TiO_2-L structure, while the white circles correspond to the Ag(100) unit cell.

i. TiO_2-L

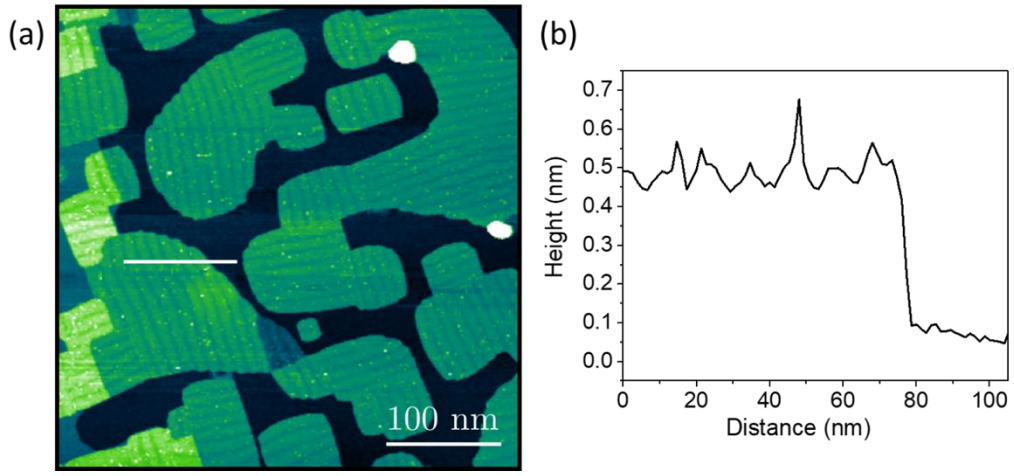

Figure S3. (a) STM image of the TiO_2-L islands. The estimated coverage is about 0.8 ML obtained by STM measure. (b) Line profile of a TiO_2-L island.

ii. $TbPc_2$ on TiO_2-L

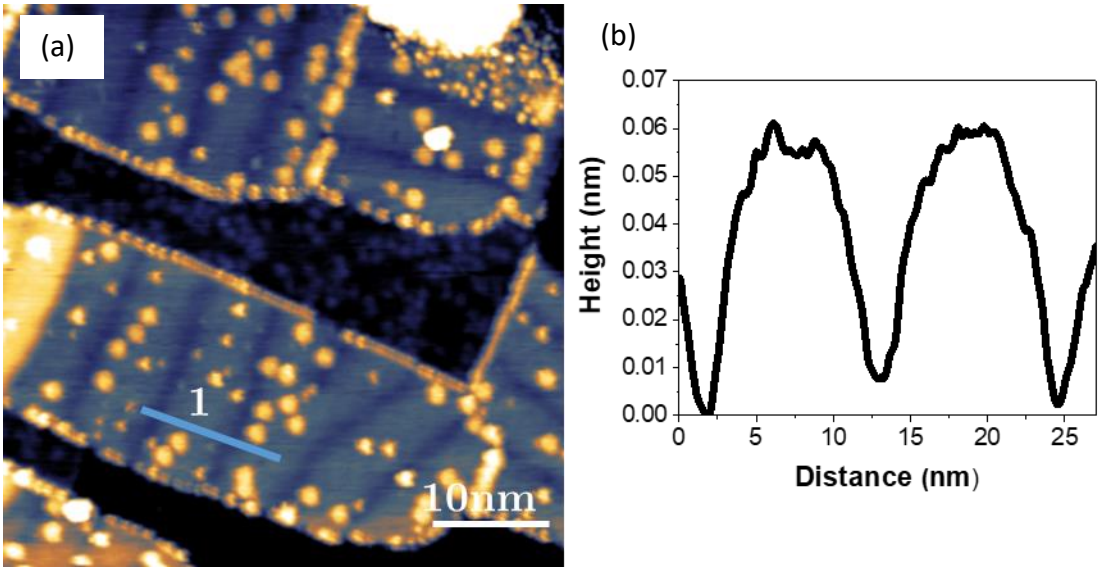

Figure S4. (a) STM image of the $TbPc_2$ molecular deposit on TiO_2-L islands. (b) Line Profile (1) of a TiO_2-L+$TbPc_2$ island.

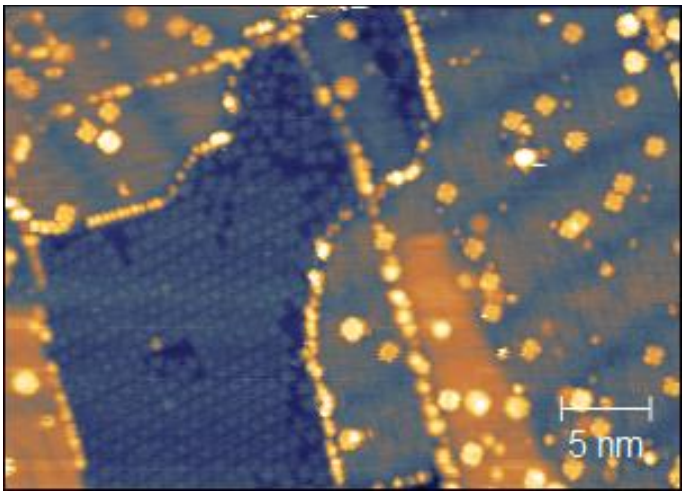

Figure S5. STM Image of TiO_2-L+$TbPc_2$ surface with a magnification on uncovered Ag(100) surface.

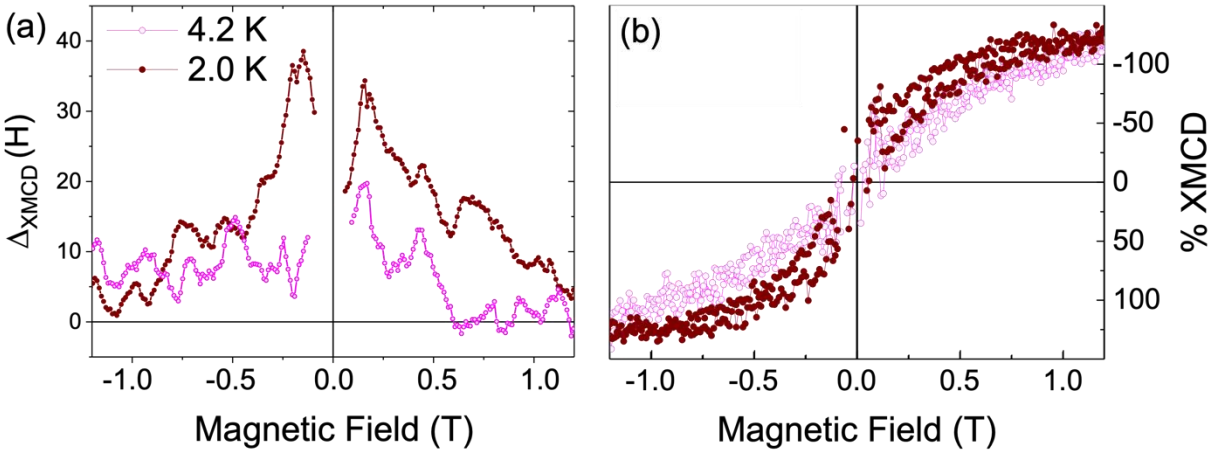

Figure S6. (a) Hysteresis opening estimated as $\Delta_{XMCD}(H)$ by plotting the difference of the maximum of the XMCD signals obtained for the up and down hysteresis branches: $_{\Delta XMCD}(H)=XMCD(H\uparrow)-XMCD(H\downarrow)$. (b) magnetic hysteresis loop recorded at 4.2K and 2.0 K (see main text).

References

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