Electronic Supplementary Information (ESI)

Substrate mediated interaction of Terbium(III) double-deckers with the TiO_2(110) surface.

Giulia Serrano,[*a,b] *Andrea Luigi Sorrentino,*[a,b] *Lorenzo Poggini,*[*a,c] *Brunetto Cortigiani,*[a] *Claudio Goletti,*[d] *Roberta Sessoli,*[a] *Matteo Mannini*[a]

[a.] *Department of Chemistry "U. Schiff" and INSTM Research Unit, University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino (FI), Italy.*

[b.] *Department of Industrial Engineering and INSTM Research Unit, University of Florence, Via Santa Marta 3, 50139 Florence (FI), Italy. E-mail: giulia.serrano@unifi.it*

[c.] *Institute for Chemistry of OrganoMetallic Compounds (ICCOM-CNR), Via Madonna del Piano, 50019 Sesto Fiorentino (FI), Italy. E-mail: lpoggini@iccom.cnr.it*

[d.] *Dipartimento di Fisica, Università degli Studi di Roma "Tor Vergata", Via della Ricerca Scientifica 1, 00133, Rome, Italy.*

Table S1. Semi-quantitative XPS analysis of the samples.[1]

	O/Ti ratio	Ti^{IV} [2] *(%)*	Ti^{III} [2] *(%)*	O bulk *(%)*	O def. (%)	C *1s* *(%)*	N *1s* *(%)*	C/N ratio
Theoretical	2.0	100	0.0	100	0	80	20	4.0
TiO_2-HT	1.7	96.8	3.2	92.8	7.2	/	/	/
TiO_2-HT+$TbPc_2$	1.8	98.3	1.7	95.3	4.7	83.5	16.5	5.0
TiO_2-HT_{Ox}	1.7	99.0	1.00	97.8	2.2	/	/	/
TiO_2-HT_{Ox} +$TbPc_2$	1.7	100	0.0	96.6	3.4	82.2	17.8	4.6
TiO_2-LT	1.5	92.7	7.3	93.0	7.0	/	/	/
TiO_2-LT+$TbPc_2$	1.8	95.0	5.0	94.8	5.2	82.3	17.7	4.6

[1] The experimental error is about the 5% of the reported percental value.
[2] The percentage is calculated considering the total Ti^{III} and Ti^{IV} Ti*2*$p_{3/2}$ components.

Table S2. Used FWHM values for C*1s* and N*1s* XPS analysis of all the molecular deposits of all the samples.

	C *1s*					N *1s*		
	Benzene 284.0eV	**Pyrrole** 285.2eV	**Shakeups** 286.9eV 287.9eV	**Inter. 1** 284.9eV	**Inter. 2** 286.9eV	**Pyrrole** 398.1eV	**Shakeup** 399.4eV	**Inter. 1** 398.5eV
$TbPc_2$ Bulk	1.05 eV	1.05 eV	1.9 eV	//	//	1.2 eV	1.6 eV	//
$TbPc_2$@TiO_2 [1]	1.1 eV	1.1eV	1.95eV	1.36 eV	1.7eV	1.2 eV	1.6eV	1.3 eV

[1] The reported values were fixed for all the molecular deposits.

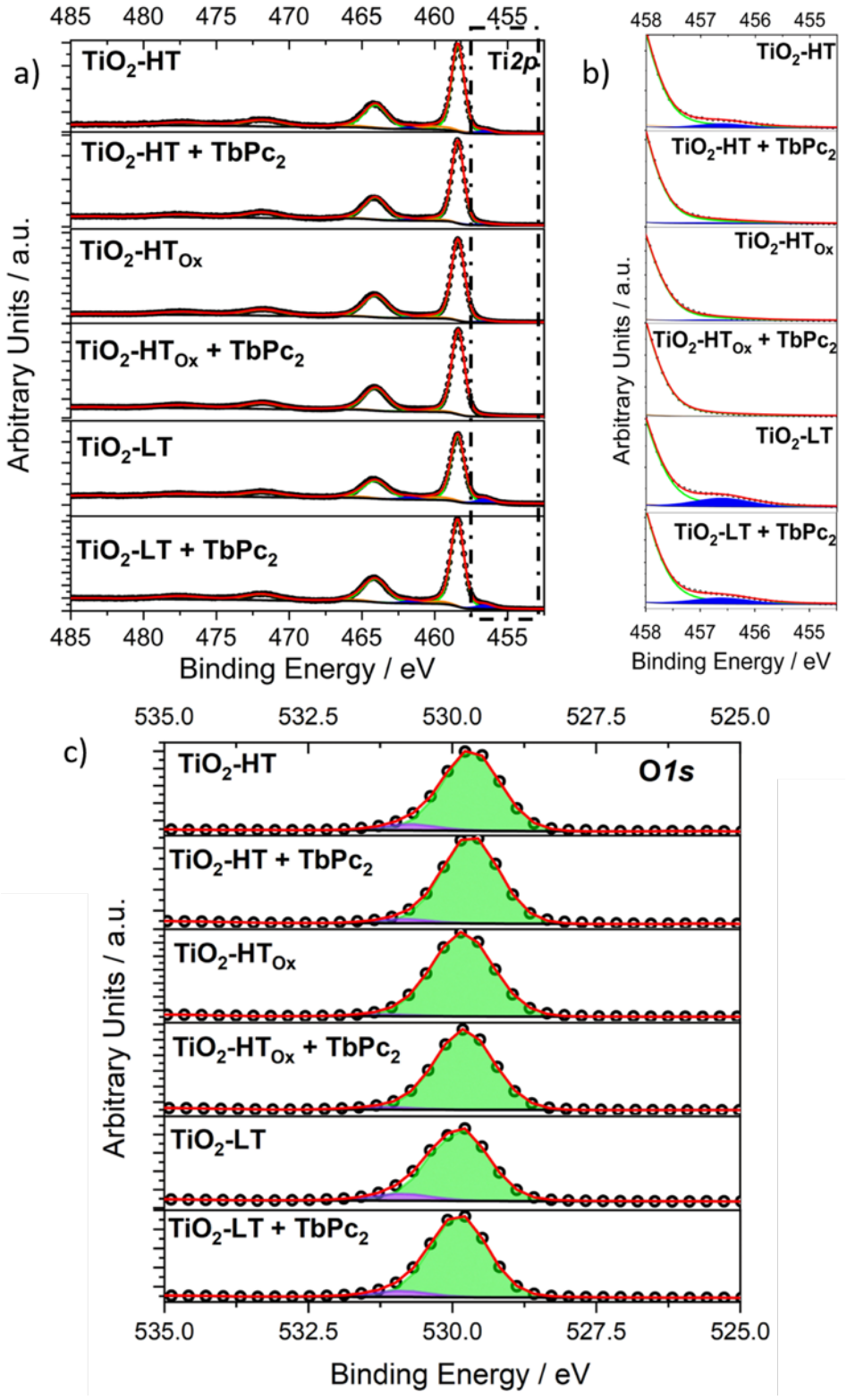

Figure S1. (a) Ti2*p* XPS *s*pectra of the TiO_2(110) surfaces (see main text) before and after $TbPc_2$ depositions, (b) zoom in the rectangular region of panel a to emphasise the Ti$2p_{3/2}$ Ti^{III} component obtained from the fitting procedure and (c) O*1s XPS* spectra of TiO_2 substrates before and after molecular deposition.

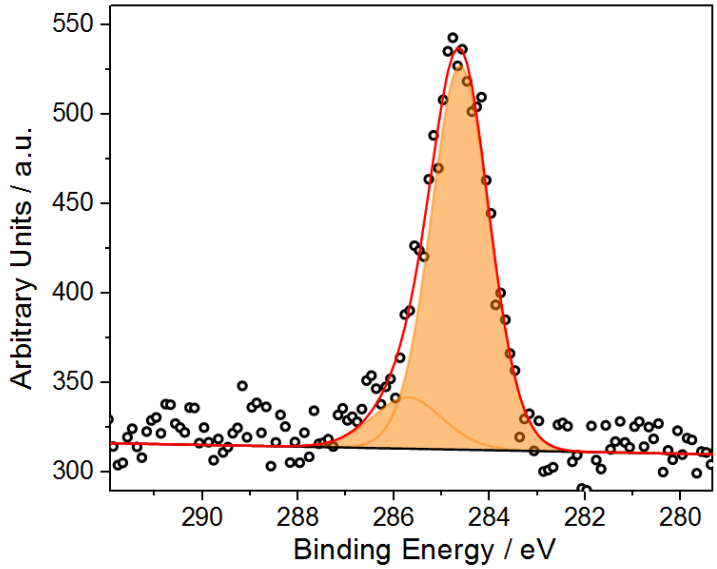

Figure S2. *C1s* XPS spectrum of TiO_2-LT showing residual adventitious carbon after thermal treatment at 570K.

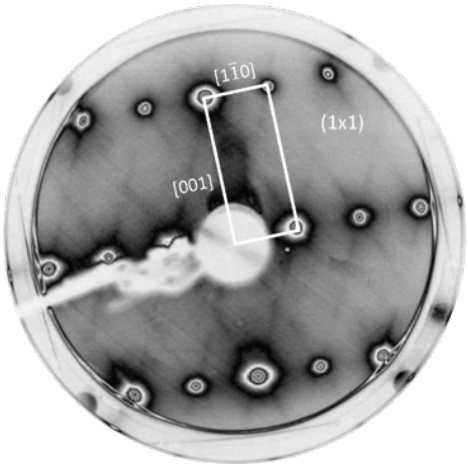

Figure S3. LEED pattern of the TiO_2(110)-HT surface showing the (1x1) reconstruction (E=58eV).

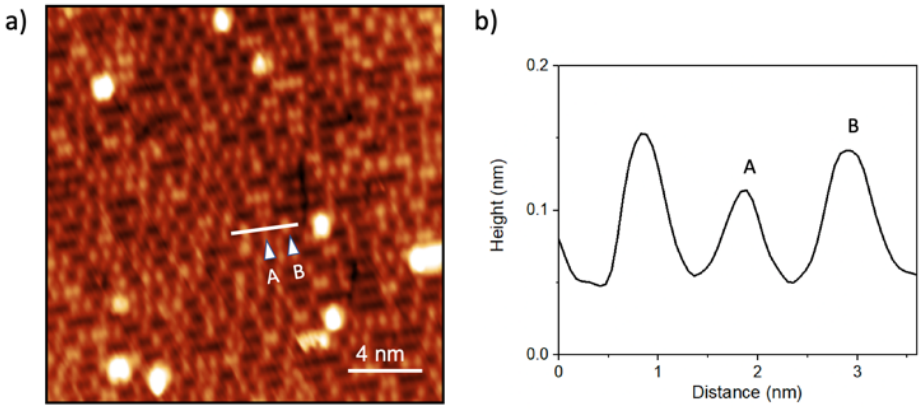

Figure S4. (a) STM image (Figure 3a of the main text) (b) line profile of TiO_2-HT surface defects.

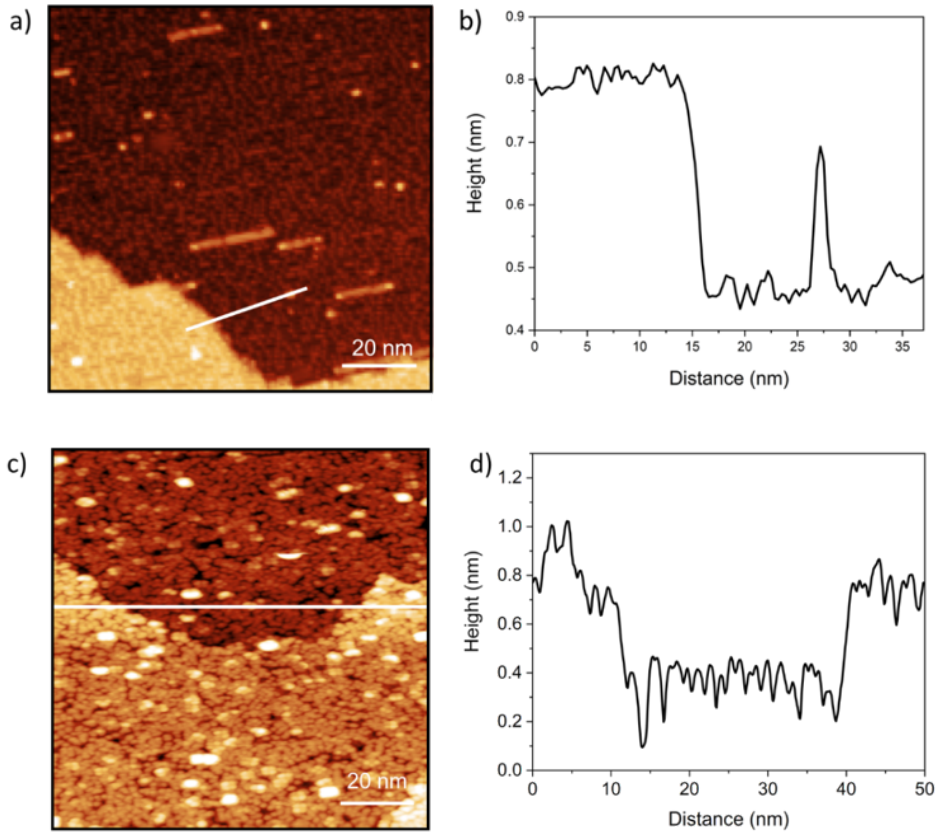

Figure S5. Large scale STM images and line profiles of TiO_2-HT (a-b) before (2V, 200 pA) and (c-d) after $TbPc_2$ deposition (2V, 3pA).

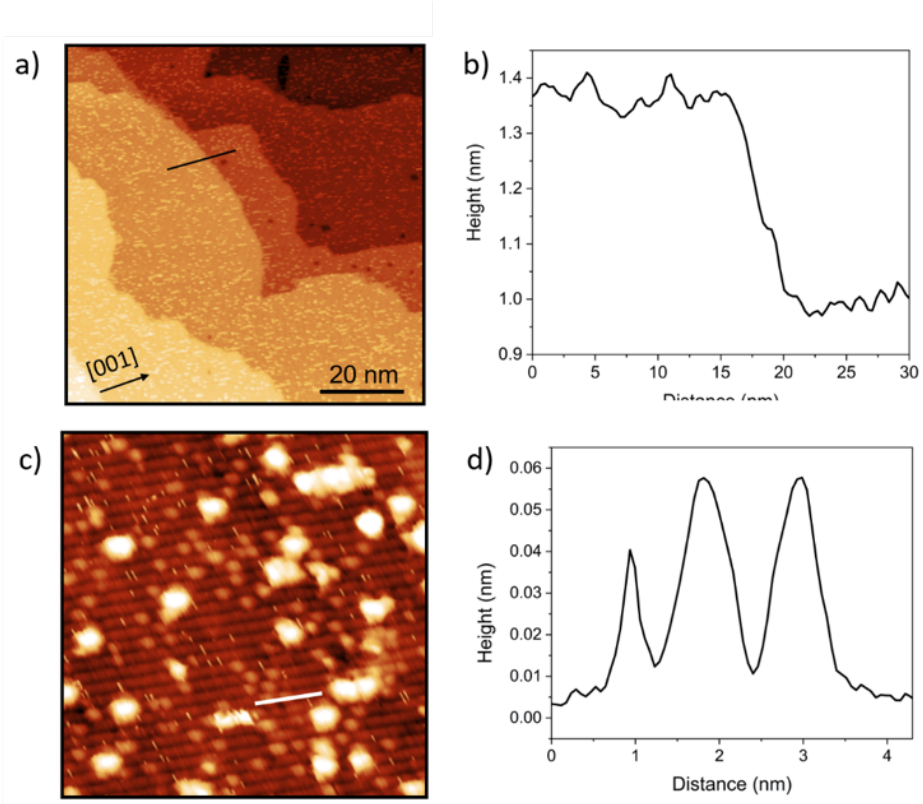

Figure S6. (a) Large scale STM image (2V, 200 pA) and (b) line profile of TiO_2-HT_{Ox} surface; (c) STM image of TiO_2-HT_{Ox} as reported in main text, Figure 3b and (d) line profile.

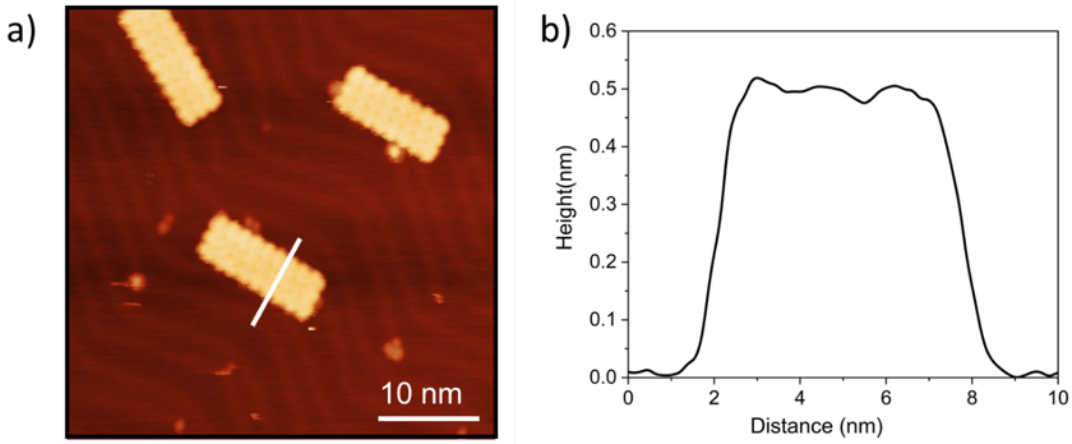

Figure S7. (a) STM image (2V, 10 pA) and (b) line profile of a $TbPc_2$ sub-monolayer on the Au(111) surface. The STM image show the islands of $TbPc_2$ regularly packed on the Au(111) surface, notice that the Au(111) herringbone is visible on the clean surface areas, as expected from the gold surface preparation (see main text).

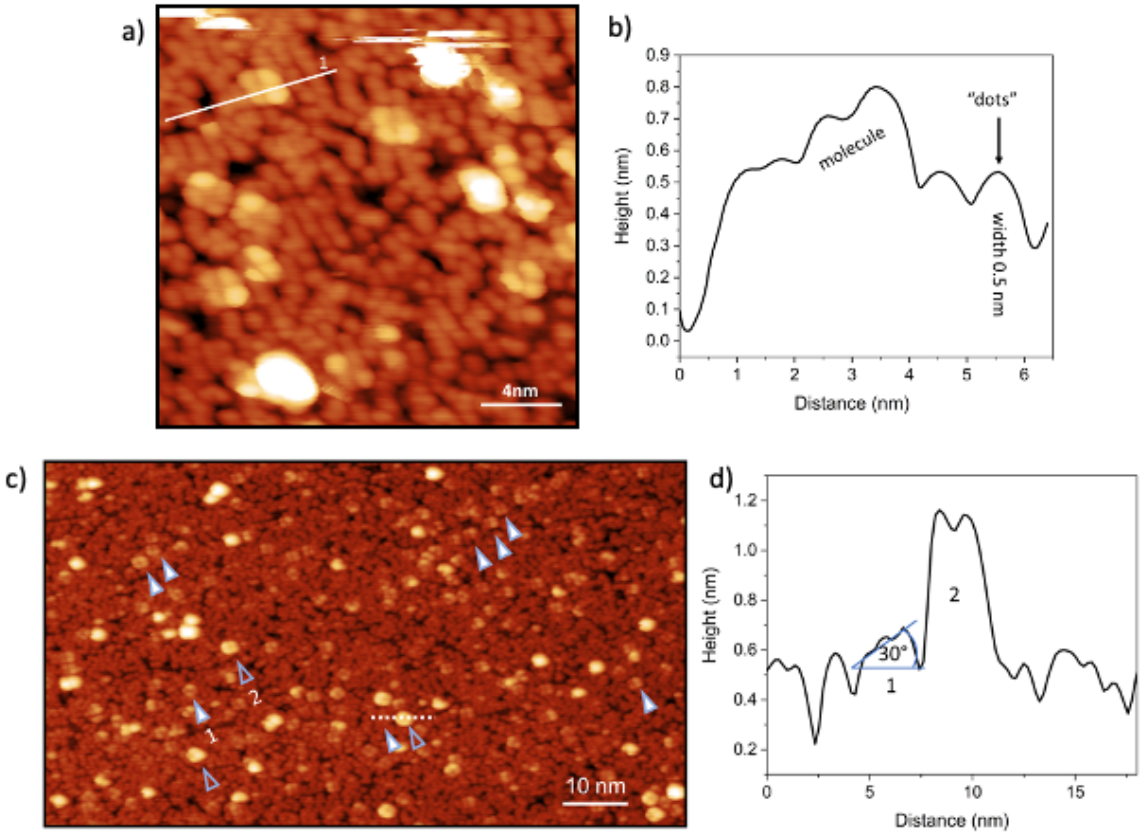

Figure S8. (a,c) STM image showing $TbPc_2$ molecules on the TiO_2(110) surface (3 pA, 2V). (b) Line profile of panel a. (c) Line profile of panel c.

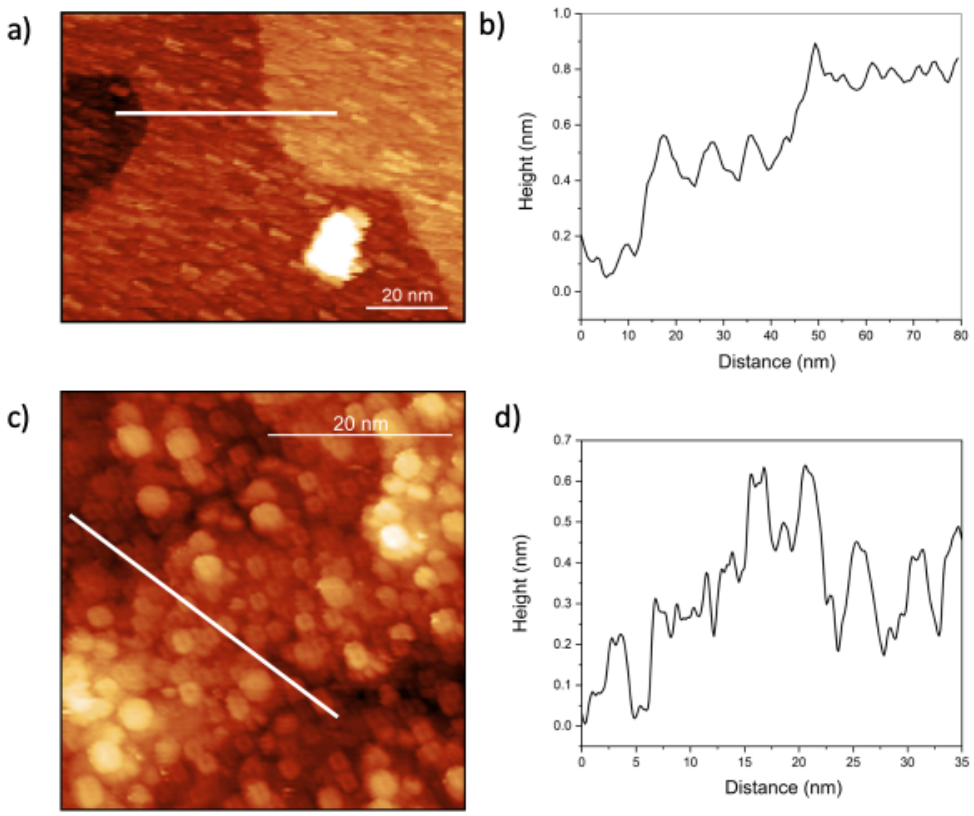

Figure S9. (a) STM image (2V, 200 pA) and (b) line profile of TiO_2- LT surface before; (c) STM image (2V, 3pA) after $TbPc_2$ molecular deposition and (d) line profile of $TbPc_2$ on the TiO_2- LT surface.