Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

The interface between chloroaluminum phthalocyanine and titanium dioxide: The influence of surface defects and substrate termination

Małgorzata Polek,[†] Tamara V. Basova,[‖,⊥] Thomas Chassé,[†,‡] Heiko Peisert[†]*

†Institute of Physical and Theoretical Chemistry, University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

‡ Center for Light-Matter Interaction, Sensors & Analytics (LISA[+]) at the University of Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

‖ Nikolaev Institute of Inorganic Chemistry SB RAS, 3 Lavrentiev Ave., 630090 Novosibirsk, Russia

⊥ Novosibirsk State University, Pirogova Str. 2, 630090 Novosibirsk, Russia

* Corresponding author, heiko.peisert@uni-tuebingen.de, Tel.: (+49) 07071 / 29-76931, Fax: (+49) 07071 / 29-5490

Table S1. *Fitting parameters: Ti 2p peak of TiO_2(100) prepared with oxygen treatment in the last annealing step.*

		AlClPc/TiO_2(100): O_2 treatment					
		Film thickness [nm]					
		0 nm			1.2 nm		
Doublet name		**Ti 4+**	**Sat1**	**Sat2**	**Ti 4+**	**Sat1**	**Sat2**
Position/eV	**P1**	459.5	462.5	472.8	459.5	462.5	472.9
	P2	465.2	468.2	478.5	465.2	468.2	478.6
GP-FWHM/eV	**P1**	0.8	1.7	2.5	0.8	1.6	2.3
	P2	1.5	1.7	2.5	1.5	1.6	2.3
LP-FWHM/eV	**P1**	0.5	0.5	0.5	0,5	0.5	0.5
	P2	0.6	0.5	0.6	0.6	0.5	0.6
Relative Area	**P1+P2**	0.86	0.02	0.12	0.86	0.02	0.12

In the fitting model for the Ti 2p peak of rutile TiO_2(100) surfaces treated with oxygen, the same parameters can be used for both clean substrate and the substrate with AlClPc film. Since the substrate is not reduced, Ti^{3+} contribution is not fitted in the reference spectrum. It does not appear as well in the Ti 2p peak of TiO_2(100) covered with 1.2 nm AlClPc film. The relative area of fitted peaks does not change upon AlClPc adsorption.

Table S2. *Fitting parameters: Ti 2p peak of TiO_2(100) prepared without oxygen treatment in the last annealing step.*

		AlClPc/TiO_2(100): Abesence of O_2							
		Film thickness [nm]							
		0 nm				**1.3 nm**			
Doublet name		**Ti 4+**	**Ti 3+**	**Sat1**	**Sat2**	**Ti 4+**	**Ti 3+**	**Sat1**	**Sat2**
Position/eV	**P1**	459.3	457.4	462.3	472.6	459.4	457.5	462.4	472.7
	P2	465.0	463.1	468.0	478.3	465.1	463.2	468.1	478.4
GP-FWHM/eV	**P1**	1.0	1.1	2.1	3.1	1.0	1.1	2.0	2.7
	P2	1.9	1.4	2.1	3.1	1.8	1.3	2.0	2.7
LP-FWHM/eV	**P1**	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
	P2	0.6	0.5	0.5	0.5	0.6	0.5	0.5	0.5
Relative Area	**P1+**	0.74	0.14	0.02	0.11	0.78	0.10	0.02	0.10

$Ti^{3+}/(Ti^{3+}+Ti^{4+})$		0.16				0.11			

The Ti 2p peak of the defect rich TiO_2(100) surface can be fitted with similar parameters as the oxygen treated surface. However, the Gaussian width of the fitted peaks increased with the introduction of defects through sputtering as shown in literature[1] on anatase TiO_2(101).

Since defects are present in a clean substrate on a reduced rutile TiO_2(100) surface, a Ti^{3+} contribution is included in the fitting model. The relative intensity of the Ti^{3+} contribution (relative to the Ti^{4+} peak area) decreases as the AlClPc film thickness increases.

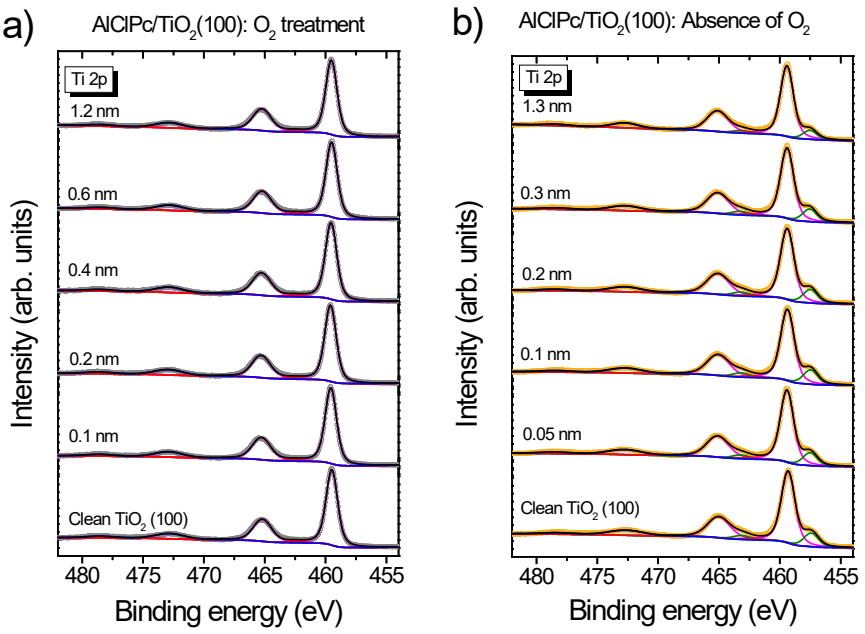

Figure S1. *Ti 2p spectra of (a) AlClPc/TiO₂(100) treated with O₂ and (b) AlClPc/TiO₂(100) prepared in absence of O₂.*

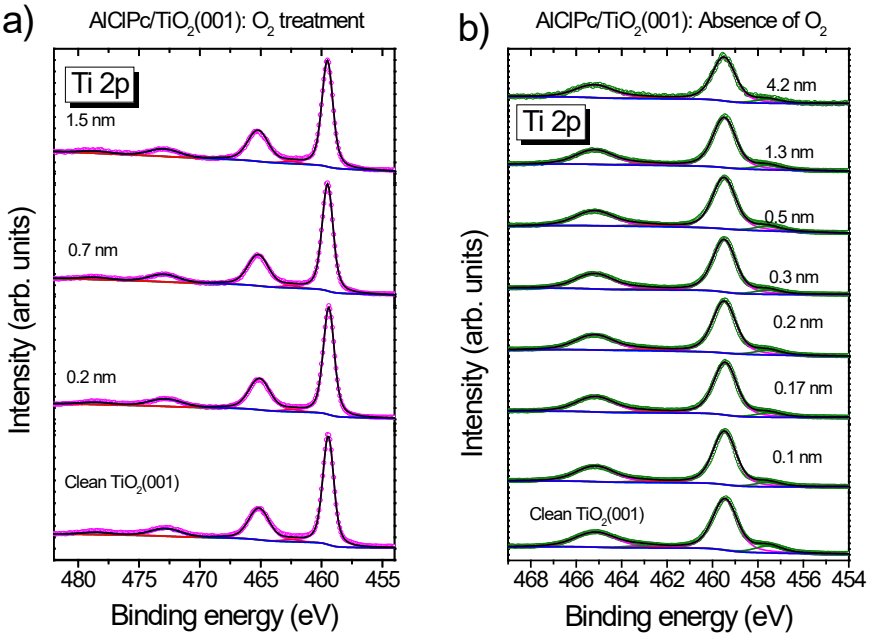

Figure S2. *Ti 2p spectra of (a) AlClPc/TiO₂(001) treated with O₂ and (b) AlClPc/TiO₂(001) prepared in absence of O₂.*

Table S3. *Fitting parameters: O1s peak of TiO_2(100) prepared with and without oxygen treatment during annealing.*

	AlClPc/TiO_2(100): O_2 treatment		AlClPc/TiO_2(100): Absence of O_2	
	Clean Substrate			
Doublet name	**O-1**	**O-2**	**O-1**	**O-2**
Position/eV	530.8	531.9	530.6	531.7
GP-FWHM/eV	1.0	1.1	1.0	1.1
LP-FWHM/eV	0.1	0.1	0.1	0.1
Relative Area	0.97	0.03	0.91	0.09

Table S4. *Fitting parameters: O1s peak of TiO_2(001) prepared with (0% Ti^{3+}) and without (12% Ti^{3+}) oxygen treatment in during annealing.*

	AlClPc/TiO_2(001): O_2 treatment		AlClPc/TiO_2(001): Absence of O_2	
	Clean Substrate			
Doublet name	**O-1**	**O-2**	**O-1**	**O-2**
Position/eV	530.8	531.9	530.6	531.7
GP-FWHM/eV	1.0	1.1	1.0	1.1
LP-FWHM/eV	0.1	0.1	0.1	0.1
Relative Area	0.97	0.03	0.92	0.08

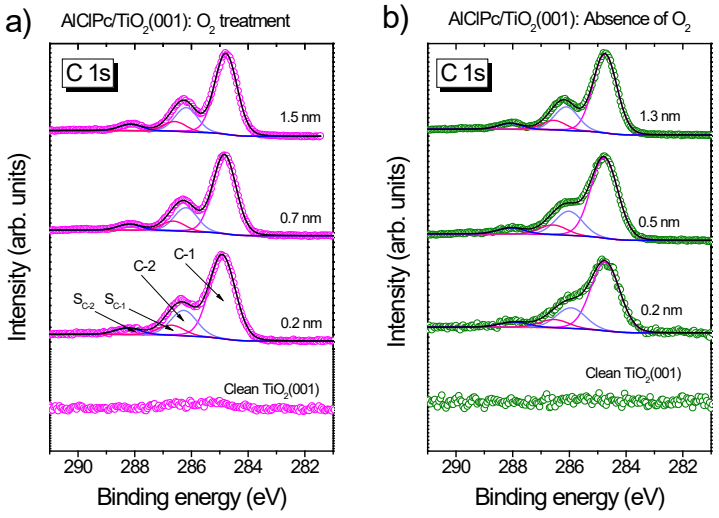

Figure S3. *Thickness dependent C1s core level spectra of AlClPc evaporated on differently prepared TiO_2(001) (a) AlClPc on TiO_2(001) prepared in presence of oxygen, (b) AlClPc on TiO_2(001) prepared in absence of oxygen. All spectra can be described by the same peak shape.*

The C1s spectra of AlClPc on TiO_2(001) both oxygen treated and reduced are shown in **Figure 6a and 6b**. A trend similar to the spectra of AlClPc on TiO_2(100) is seen. The carbon C1s spectra can be fitted with a set of 4 peaks. If the substrate was treated with oxygen, the (C–1) to (C–2) distance is constant at 1.4 eV and independent of film thickness. The difference in Gauss width is even smaller and lies between 1.0 eV and 0.9 eV for 0.2 nm and 1.5 nm film thickness respectively. With the small variation in peak width there is little change in the peak form upon organic film evaporation.

When the (001) surface is reduced (12% Ti 3+), the Gauss width spans between 1.2 and 0.9 eV. The distance between the (C–1) and (C–2) carbons varies between 1.2 eV and 1.4 eV for 0.2 nm and thick film. The peak shape is broadened for the sub-ML films, due to the inhomogeneous adsorption sites as in the case of reduced TiO_2(100) surface, a clear response to the defects present at the surface. The related peak fit tables can be found in Supporting Information (**Table S6**).

***Table S5**. C1s core level spectra fitting parameters of AlClPc films on TiO_2(100) surface.*

	AlClPc/TiO_2(100): O_2 treatment											
	Layer thickness 0.1 nm				**Layer thickness 0.4 nm**				**Layer thickness 1.2 nm**			
Peak name	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**
GP-FWHM/eV	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Position/eV	284.8	286.1	286.6	288.1	284.8	286.1	286.6	288.1	284.8	286.1	286.6	288.1
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
rel. Area	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05
	$(C2+S_{C-2})/(C1+S_{C-1})$			0.33	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34

	AlClPc/TiO_2(100): Absence of O_2											
	Layer thickness 0.1 nm				**Layer thickness 0.3 nm**				**Layer thickness 1.3 nm**			
Peak name	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**
GP-FWHM/eV	1.1	1.1	1.1	1.1	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9
Position/eV	284.6	285.8	286.4	287.8	284.6	285.9	286.4	287.9	284.6	286.0	286.4	288.0
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
rel. Area	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05
	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34

***Table S6**. C1s core level spectra fitting parameters of AlClPc films on TiO_2(001) surface.*

	AlClPc/TiO_2(001): O_2 treatment											
	Layer thickness 0.2 nm				Layer thickness 0.7 nm				Layer thickness 1.5 nm			
Peak name	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**
GP-FWHM/eV	1.0	1.0	1.0	1.0	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Position/eV	284.9	286.3	286.7	288.2	284.8	286.2	286.6	288.2	284.8	286.2	286.6	288.1
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
rel. Area	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05
	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34	$(C2+S_{C-2})/(C1+S_{C-1})$			0.33	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34

	AlClPc/TiO_2(001): Absence of O_2											
	Layer thickness 0.2 nm				Layer thickness 0.5 nm				Layer thickness 1.3 nm			
Peak name	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**	**C - 1**	**C - 2**	**$S_{(C-1)}$**	**$S_{(C-2)}$**
GP-FWHM/eV	1.2	1.2	1.2	1.2	1.1	1.1	1.1	1.1	0.9	0.9	0.9	0.9
Position/eV	284.8	286.0	286.6	288.0	284.8	286.1	286.6	288.1	284.7	286.1	286.5	288.1
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
rel. Area	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05	0.67	0.20	0,08	0.05
	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34	$(C2+S_{C-2})/(C1+S_{C-1})$			0.34	$(C2+S_{C-2})/(C1+S_{C-1})$			0.33

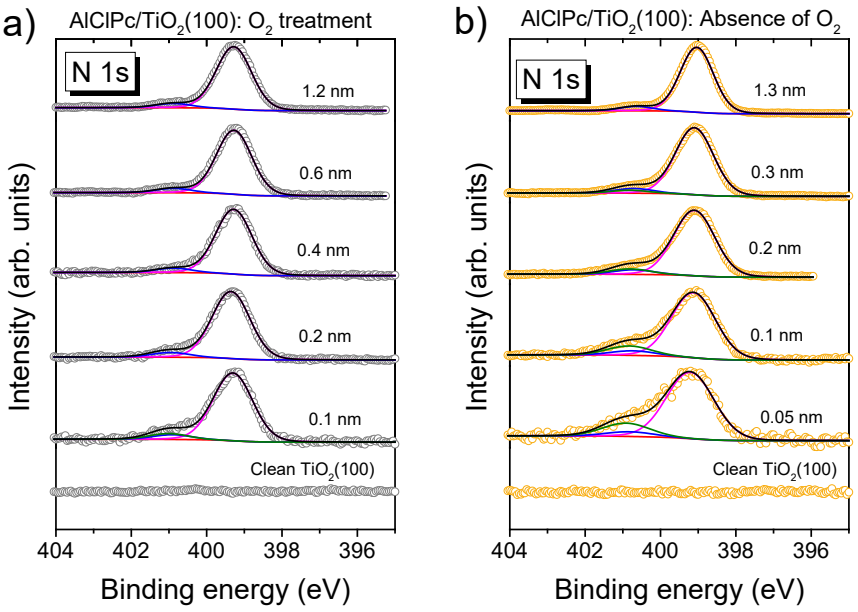

***Figure S4.** All N1s spectra fitted for (a) AlClPc/TiO_2(100) treated with O_2, (b) AlClPc/TiO_2(100) prepared in absence of O_2.*

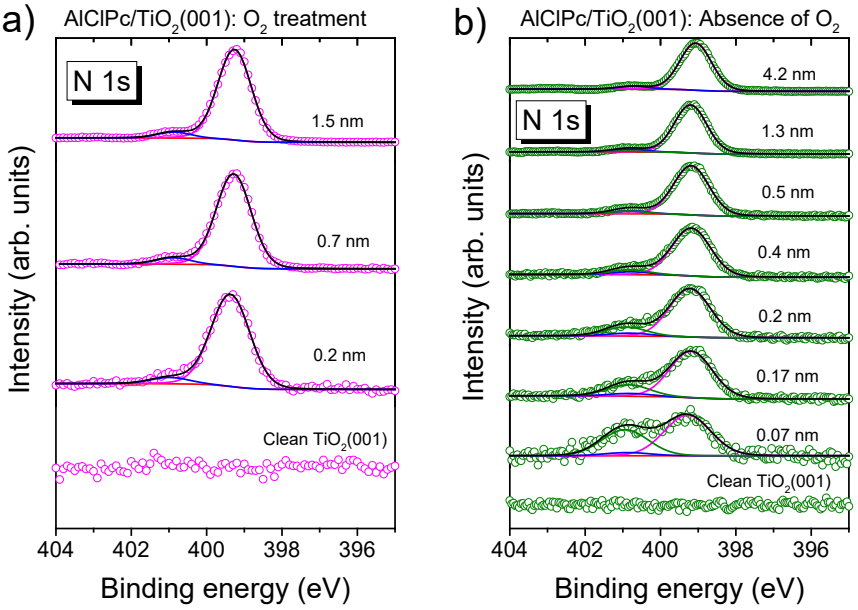

Figure S5. *All N1s spectra fitted for (a) AlClPc/TiO_2(001) treated with O_2, (b) AlClPc/TiO_2(001) prepared in absence of O_2.*

Table S7. *N1s core level spectra fitting parameters of AlClPc films on TiO_2(100) surface.*

	AlClPc/TiO_2(100): O_2 treatment								
	Layer thickness 0.1 nm			**Layer thickness 0.4 nm**			**Layer thickness 1.2 nm**		
Peak name	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**
Position/eV	1.2	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.1
GP-FWHM/eV	399.3	400.9	401.0	399.3	400.9	401.0	399.3	400.9	401.0
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Relative Area	0.87	0.06	0.07	0.94	0.06	0.00	0.94	0.06	0.00

	AlClPc/TiO_2(100): Absence of O_2								
	Layer thickness 0.1 nm			**Layer thickness 0.3 nm**			**Layer thickness 1.3 nm**		
Peak name	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**
Position/eV	1.3	1.3	1.3	1.1	1.1	1.1	1.0	1.0	1.0
GP-FWHM/eV	399.1	400.7	400.8	399.1	400.7	400.8	399.0	400.6	400.7
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Relative Area	0.82	0.06	0.12	0.90	0.06	0.04	0.94	0.06	0.00

Table S8. *N1s core level spectra fitting parameters of AlClPc films on TiO_2(001) surface.*

	AlClPc/TiO_2(001): O_2 treatment								
	Layer thickness 0.2 nm			Layer thickness 0.7 nm			Layer thickness 1.5 nm		
Peak name	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**
Position/eV	1.2	1.2	1.2	1.0	1.0	1.0	1.0	1.0	1.0
GP-FWHM/eV	399.4	401.0	401.1	399.3	400.9	401.0	399.3	400.9	401.0
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Relative Area	0.94	0.06	0.00	0.94	0.06	0.00	0.94	0.06	0.00

	AlClPc/TiO_2(001): Absence of O_2								
	Layer thickness 0.2 nm			Layer thickness 0.5 nm			Layer thickness 1.3 nm		
Peak name	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**	**N-1**	**$S_{(N-1)}$**	**N-3**
Position/eV	1.3	1.3	1.3	1.1	1.1	1.1	1.0	1.0	1.0
GP-FWHM/eV	399.2	400.8	400.9	399.2	400.8	400.9	399.2	400.8	400.9
LP-FWHM/eV	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Relative Area	0.77	0.05	0.19	0.90	0.05	0.05	0.93	0.06	0.02

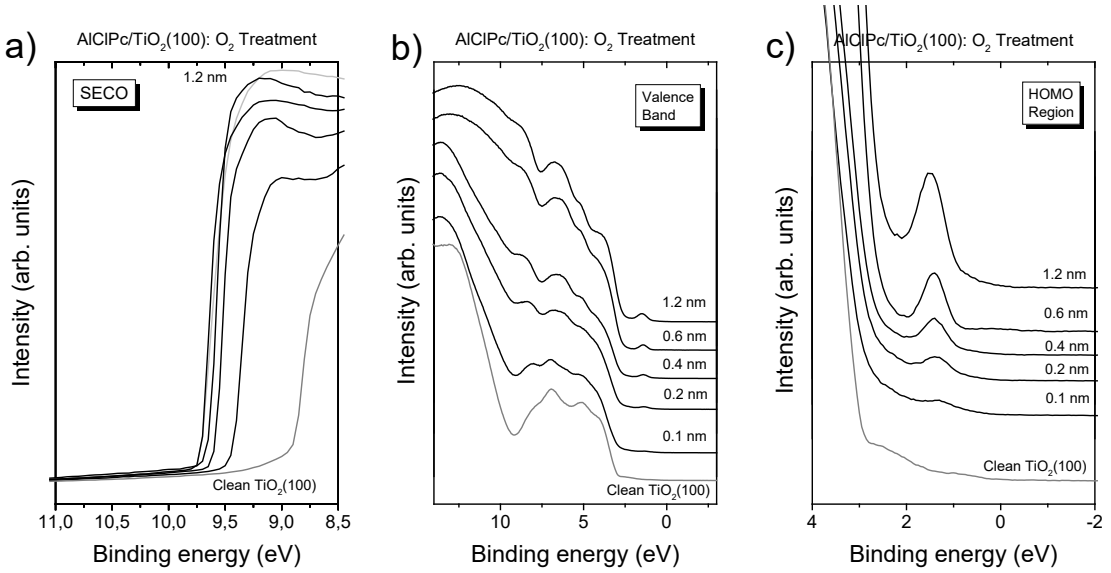

Figure S6. *Thickness dependent UPS results measured for AlClPc films on TiO_2(100) treated with oxygen: (a) secondary electron cut-off, (b) valence band spectra, (c) valence band spectra – HOMO region.*

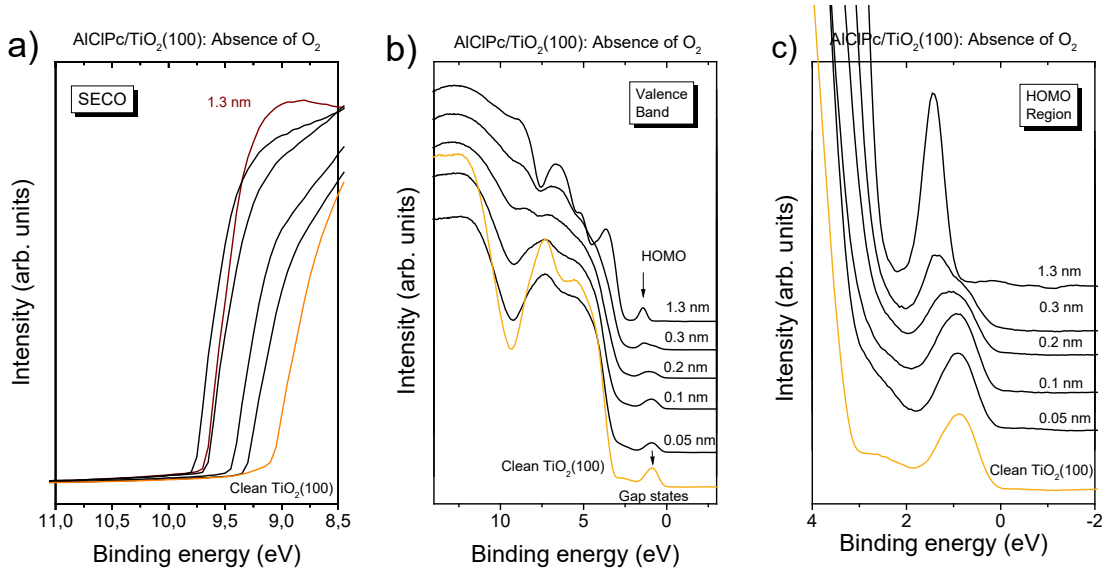

Figure S7. *Thickness dependent UPS results measured for AlClPc films on TiO_2(100) prepared in absence of oxygen: (a) secondary electron cut-off, (b) valence band spectra, (c) valence band spectra – HOMO region.*

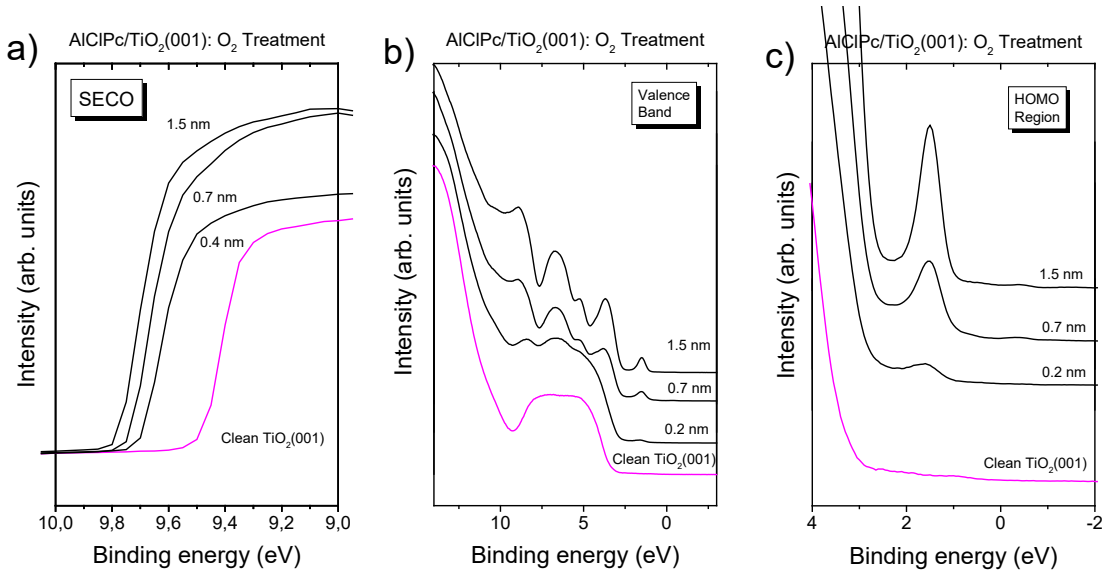

Figure S8. *Thickness dependent UPS results measured for AlClPc films on TiO_2(001) treated with oxygen: (a) secondary electron cut-off, (b) valence band spectra, (c) valence band spectra – HOMO region.*

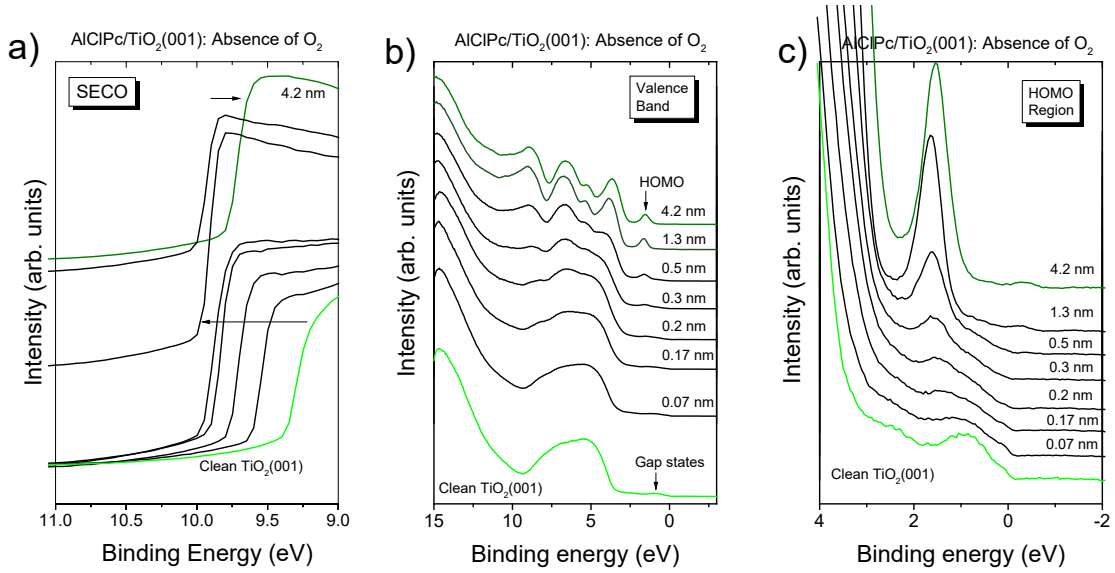

Figure S9. *Thickness dependent UPS results measured for AlClPc films on TiO_2(001) prepared in absence of oxygen: (a) secondary electron cut-off, (b) valence band spectra, (c) valence band spectra – HOMO region.*

An example of valence band spectra with a magnification of HOMO onset is shown in **Figures S9b** and **S9c**. The bottom spectrum of **Figure S9b** and **S9c** is the spectrum of a clean rutile TiO_2(001) with 12% defects. The presence of defects is seen as the increase in intensity (defect/gap states) at 0.8 eV. The band gap of the rutile is expected to be 3 eV, but due to preparation conditions the valence band edge is shifted to 3.4 eV. After evaporation of first layer of AlClPc a small HOMO peak with onset at 0.9 eV arises. As the film thickness increases the HOMO peak shifts to higher binding energies. At 0.5 nm the onset reaches 1.1 eV. For bulk film of 4.2 nm, the HOMO onset moves back to the lower binding energy (1.0 eV). The values of work function, HOMO onset and ionization potential are summarized in **Tables S9** and **S10**.

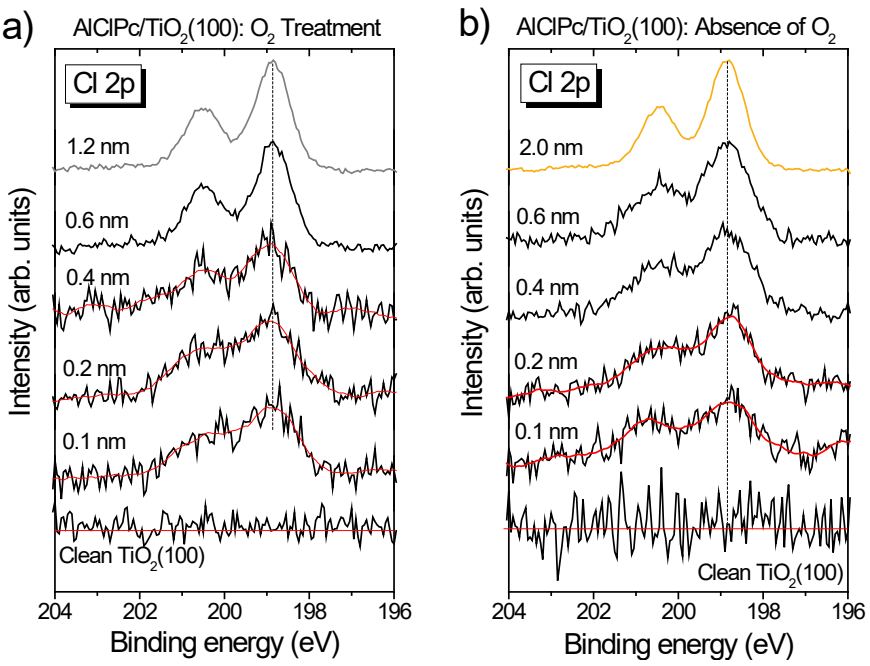

Figure S10. *Thickness dependent Cl 2p spectra of AlClPc evaporated on (a) TiO_2(100) treated with O_2, (b) TiO_2(100) prepared in absence of O_2. The red lines represent the original data after smoothing procedure for the ease of data comparison.*

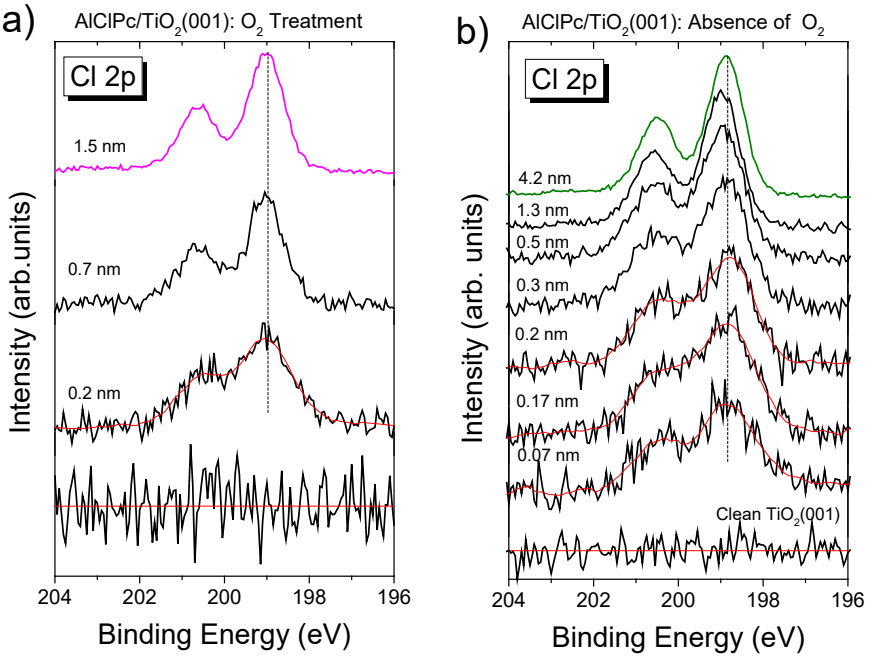

Figure S11. *Thickness dependent Cl 2p spectra of AlClPc evaporated on (a) TiO_2(001) treated with O_2, (b) TiO_2(001) prepared in absence of O_2. The red lines represent the original data after smoothing procedure for the ease of data comparison.*

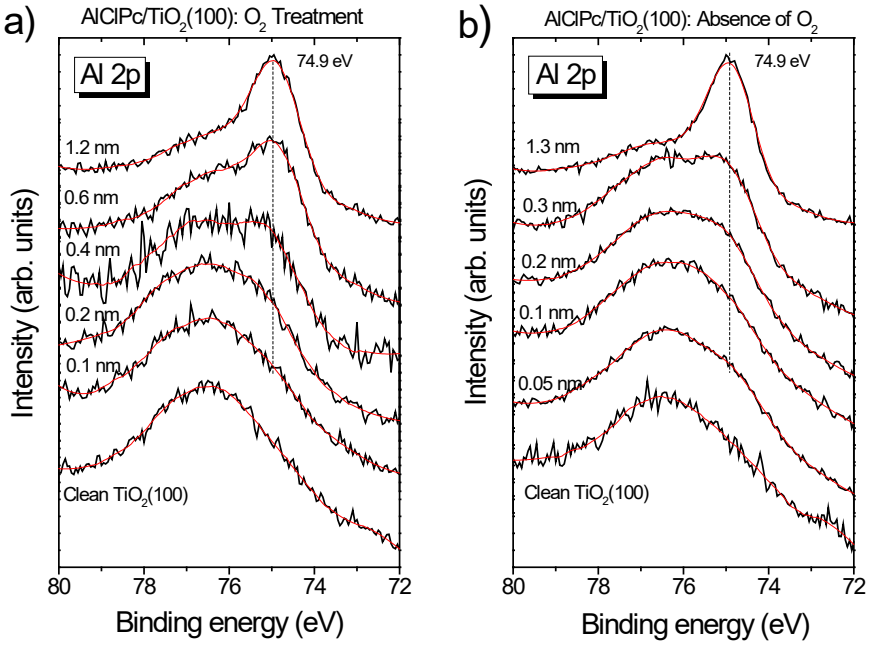

Figure S12. *Al 2p spectra for: (a) AlClPc on TiO_2(100) treated with O_2, (b) AlClPc on TiO_2(100) prepared in absence of O_2. The red lines represent the original data after smoothing procedure for the ease of data comparison.*

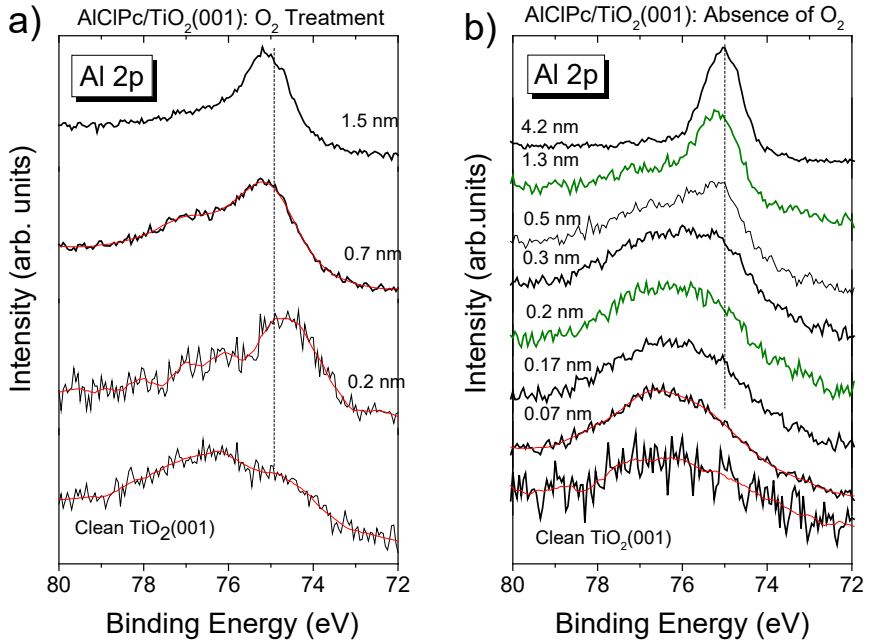

Figure S13. *Al 2p spectra for: (a) AlClPc on TiO_2(001) treated with O_2, (b) AlClPc on TiO_2(001) prepared in absence of O_2. The red lines represent the original data after smoothing procedure for the ease of data comparison.*

Table S9. *UPS parameters: work function, HOMO onset, ionization potential for the following systems: AlClPc/TiO_2(100) treated with oxygen, AlClPc/TiO_2(100) prepared in absence of oxygen.*

AlClPc/ TiO2 (001)	Work function (eV)	Homo Onset (eV)	Ionization Potential (eV)
TiO2	5.3	x	8.3
0.1 nm	4.8	0.8	5.6
0.2 nm	4.6	0.9	5.5
0.4 nm	4.5	0.9	5.4
0.6 nm	4.5	0.9	5.4
1.2 nm	4.5	0.9	5.4

AlClPc/ TiO2 (001)	Work function (eV)	Homo Onset (eV)	Ionization Potential (eV)
TiO2	5.1	x	8.3
0.05 nm	4.9	0.9	5.8
0.1 nm	4.8	0.9	5.7
0.2 nm	4.6	0.9	5.5
0.3 nm	4.4	0.9	5.3
1.3 nm	4.5	0.9	5.4

Table S10. *UPS parameters: work function, HOMO onset, ionization potential for the following systems: AlClPc/TiO_2(001) treated with oxygen and AlClPc/TiO_2(001) prepared in absence of oxygen.*

AlClPc/ TiO2 (001)	Work function (eV)	Homo Onset (eV)	Ionization Potential (eV)
TiO2	4.7	x	8.1
0.2 nm	4.5	1.0	5.5
0.7 nm	4.5	1.0	5.5
1.5 nm	4.4	1.0	5.4

AlClPc/ TiO2 (001)	Work function (eV)	Homo Onset (eV)	Ionization Potential (eV)
TiO2	4.7	x	8.1

0.07 nm	4.6	0.9	5.5
0.17 nm	4.4	1.0	5.4
0.2 nm	4.3	1.0	5.3
0.3 nm	4.2	1.0	5.2
0.5 nm	4.2	1.1	5.3
1.3 nm	4.2	1.1	5.3
4.2 nm	4.4	1.0	5.4

Table S11. *Stoichiometric relations C:N:Cl for AlClPc on (100) and (001) surfaces at different reduction degree.*

Film stoichiometry AlClPc/TiO_2(100) 0% defects						
Thickness	AlClPc molecule	0.1 nm	0.2 nm	0.4 nm	0.6 nm	1.2 nm
C	32.0	32.1	32.0	32.0	32	32
N	8.0	7.7	7.9	8.1	7.7	7.8
Cl	1.0	1.4	1.5	1.2	1.2	1.0
Film stoichiometry AlClPc/TiO_2(100) 16% defects						
Thickness	AlClPc molecule	0.05 nm	0.1 nm	0.2 nm	0.3 nm	1.3 nm
C	32.0	32	32	32	32	32
N	8.0	7.7	7.2	7.5	7.5	7.5
Cl	1.0	1.4	1.0	1.3	0.9	0.7

Film stoichiometry AlClPc/TiO_2(001) 0% defects				
Thickness	AlClPc molecule	0.2 nm	0.7 nm	1.5 nm
C	32.0	32.0	32.0	32.0
N	8.0	8.1	7.6	8.4
Cl	1.0	1.0	1.6	1.5

Film stoichiometry AlClPc/TiO_2(001) 12% defects								
Thickness	AlClPc molecule	0.07 nm	0.17 nm	0.2 nm	0.3 nm	0.5 mn	1.3 nm	4.2 nm
C	32.0	32.0	32.0	32.0	32.0	32.0	32.0	32.0
N	8.0	8.0	7.1	7.9	7.2	7.2	7.8	8.1
Cl	1.0	1.9	1.2	2.0	1.4	1.3	1.4	1.5

The stoichiometric relations presented in Table S11 are compared to stoichiometric relations between atoms in AlClPc molecule presented in Figure 1, where the ratio between C:N:Cl atoms is 32:8:1.

1. Jackman, M. J.; Thomas, A. G.; Muryn, C., Photoelectron Spectroscopy Study of Stoichiometric and Reduced Anatase TiO2(101) Surfaces: The Effect of Subsurface Defects on Water Adsorption at Near-Ambient Pressures. *The Journal of Physical Chemistry C* **2015,** *119* (24), 13682-13690.