Light-Induced Rearrangements of Chemisorbed Dyes on Anatase (101)

Supporting Information

A. Dye-sensitized solar cells

The principle of DSC operation is comparable to that for photosynthesis, where chromophores embedded in proteins transform solar energy into other kind of energy (chemical). In DSC, the cell is constituted of a photosensitized meso-porous electrode, commonly a metal oxide (e.g., TiO₂), a counter-electrode for electrolyte regeneration and an inter-electrode space between them occupied with the redox-couple electrolyte. The excitation and separation of charge at the interface between the dye and the TiO₂ surface is ultra-rapid, in the order of the femto- to picoseconds. A prompt regeneration of the dye is performed by a redox couple, in the order of nanoseconds and facilitates, thereof, a continuous cyclic flow of electrical charge. The charge regeneration of the dye from TiO₂ is much slower, being in the time range of micro to milliseconds, which is comparable with rates in UHV experiments where recovering of the dye is done either from the back electron transfer from TiO₂ or, locally, from the STM tip. Despite the fast kinetics in DSC, a tiny amount of dye (approx. 1 dye per 150 TiO_2) is always present in its oxidation state during normal operation, and this fraction becomes even more substantial in the solid-state DSC, where a deficient filling of the porous film by the regenerative electrolyte, or the hole transport medium has evidently been regarded as a shortcoming for reaching high efficiencyⁱ. Therefore, studies of the light-induced modifications of adsorbed dyes performed in UHV open for new insights, not solely for dye design but also for the scrutiny of plausible effects caused by dye photo-modifications at the interface (e.g., long range interactions) between different organic layers.

It has to be noted that the relatively slow regeneration of the oxidized dye from the single crystal TiO_2 (up to milliseconds) allows the species to undergo, preferentially, non-radiativeⁱⁱ decay transitions. On the other hand, the rate for the dye regeneration in real solar cells is relatively much faster than the rates, in hours, for the changes of N719 observed in the STM experiments.

B. The surface of the single crystal of anatase (101)

The surface structure of anatase TiO_2 (101) has been intensively investigated by other researchers under similar pre-treatment procedures as the employed in the present investigation, i.e., sputtering followed by annealing maintaining the temperature below 600°C.



Fig. S1 At the left, a 150x150 nm² STM image of the bare surface of TiO₂ anatase (101). The arrows indicate the directions of the frequently found monoathomic steps on this surface. The terraces consist of bright rows running along [010] as illustrated by the derivative of the image $\left(\frac{dz}{dx}\right)$ of a 15x15 nm² enlarged part from the area at the left.

The surface structure of TiO_2 (101), shown at the left in Fig. S1 is consistent with the results found in the literature.

As can be seen, the surface is represented by flat terraces with steps running along [010], [11-1] and [-111], giving origin to the triangular (or trapezoidal) patterns on the surface. The angle between the [010] and the other steps is 70° (the change in orientation between patterns I and III that dyes undergo on a flat surface under illumination is also 70°) as shown by the derivative of the STM image of the bare surface (the derivative facilitates edges and contours to be enhanced).

The composition of the steps is discussed in ref. [30]. Accordingly, five-fold and two-fold coordinated titanium and oxygen atoms, respectively, are most probable to be found on [010] and [11-1]. On the other hand, the calculated energies for step [-111] indicate that the most stable surface structure should consist of fourfold coordinated titanium and twofold coordinated oxygen, which imparts the step certain chemical reactivity.

C. The structure of the organic dyes

The three investigated organic dyes contain similar functional units. That is, a triphenylamine acting as donor part, a π -conjugated bridge which effectively separates the charge provided by the donor and a third unit, a cyanoacrylic moiety, acting as charge acceptor and anchoring group. D5 is the stereotype for this kind of donor-bridge-acceptor concept, while D9 and D35 are rather modifications of the previous which for solar cell applications have resulted in better device performance. The higher efficiency of solar cells based on D9 or D35, instead of D5, has been explained by a surface blocking effect of the dye against the redox couple, hindering, thereby, the recombination from TiO₂ to the electrolyte (dark current)ⁱⁱⁱ. On the other hand, our results indicate that photoarrangements may be a more plausible reason for the

recombination since the motion of D5, in comparison to that for D9 or D35, leaves a larger area of bare TiO_2 surface accessible for the electrolyte after isomerization (see below Figs. 5 in the manuscript and S3 below).



Fig. S2 Chemical structure of the organic dyes D5, D9 and D35 used in the STM measurements with respective calculated HOMO and LUMO structures.



D. Simulated Configurational Changes of the Organic Dyes

Fig. S3 DFT calculations of the optimized geometries for the isomers of D5, D9 and D35 fitting the STM measurements (see Fig. 4 in the manuscript).

The STM images support the isomerization of the organic dyes according to the scheme shown in Fig. S3. It can be noted for instance that D5 changes from a completely lying to a standing position. This kind of displacement leaves as mentioned above enough space for smaller species as redox couples to reach the surface and give origin to dark currents. D9 is adsorbed in standing position which is preserved after isomerization. We observe that the isomerization of D35 is less dramatic than in that for D5 and D9. In addition, the isomerization yield for D35 is very low (less than 1 %) and the rearrangement in position is rather modest (25° between *trans* to *cis*-configuration).

Ultra-rapid photoprocesses taking place in dense-packed chromophores are explained as occurring at crossing points between the potential energy planes of the ground and excited states (i.e., conical intersections). Beyond these intersections, the probability and kinetics for crossing the two states decrease with increasing energy gap between states. In dense layers the free volume for nuclear displacement is reduced and the process might occur simply by following different mechanisms. For example, well-known is the conventional one-bond-flip (OBP) mechanism in which one half of the molecule rotates around the double bond and the other half remains immovable. This mechanism demands a certain degree of free volume for rotation of bulky moieties and is, thereby, common for species in solution. Conversely, and particularly for the case of rearrangements of densely packed species, frozen media or the presence of viscous solvents, the so-called Hula-Twist (HT) and the Bicycle Pedal (BP) have been instead suggested. The former is figured out as the simultaneous rotation of adjacent double and single bonds leaving the structure slightly modified. In the latter only the atoms located at the double bond rotate 180° and the molecule remains in principle unchanged. Details about these mechanisms are found elsewhere^{iv}.

E. The thermal treatment



Fig. S4 STM images, $100 \times 100 \text{ nm}^2$, showing the effect on N719 adsorption by the thermal treatment of the sensitized single crystal TiO₂ (101) surface, a) image showing the dye adsorbed by dipping into solution before heating and b) after the thermal treatment. The histograms show the high of the LUMO levels and are measured after flattening and smoothing the images of the areas denoted by the rectangles in a) and b).

Previous to the STM imaging, the sample was slightly heated ($<150^{\circ}$ C) in UHV, in order to remove the residual solvent. The solvent evaporation is easily recorded by a sudden increase in chamber pressure, rapidly decreasing to base pressure. Fig, S4a) shows the TiO₂ surface with dye after solvent evaporation. After subsequent thermal treatment between 220°C -250°C, the TBA⁺ cation is completely removed leading to a stronger coupling to TiO₂, the removal of the big cations are supported by photoelectron measurements reported in a previous work [12], where a single crystal of anatase TiO₂ (100) was used as substrate. Before heating, half of the species in the image in a) have a LUMO merging deeper into TiO_2 while the other species, observed here as bright dots, have a more protruding LUMO, indicating, thereby, a less bound dye. After the thermal treatment the altitudes for most of the species merge deeper into TiO_2 , as can be seen from the image and the histogram in b). It is reasonable to assume that, by decomposition of TBA^+ in the dark, the protons move closer to the surface in order to compensate for the loss of positive charge.

F. Line profiles for N719 on TiO₂ in the dark and upon illumination



Fig. S5 Line profiles (at the bottom) in STM images of $18x18 \text{ nm}^2$ dye/TiO₂ area when scanned in the dark, pattern I (left) and after being exposed 2 hours to illumination, pattern II. Scan parameters: 2.7 V; 0.03 nA. The arrows indicate the positions of the dyes which ascend (\uparrow) or descend (\downarrow).

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G. Relaxation of N719/ TiO $_2$ the interface



Fig. S6 STM image of $9x9 \text{ nm}^2$ of dye/ TiO₂ exposed to dark showing domains of dyes rotating back to pattern I in the dark. Scan parameters: 2.7 V; 0.03 nA. The images were smoothed, filtered and derived in order to enhance contours.



Fig. S7 Relaxation of Dye/TiO2 interface after 1 hour and 7 minutes in the dark. Scan parameters: 2.7 V; 0.03 nA. The distance between the standing species, shown by the white arrows, is approximately 1.1-1.2 nm, which agrees with the size of the dyes and, consequently, the space necessary to acquire a lying position. Observe that from this position the dye can easily acquire the lying position observed in pattern III.



Fig. S8 Pattern II, obtained under relaxation of Dye/TiO2 interface after 1 hour and 40 minutes in the dark. The inset shows a standing dye which has rotated (compared to the standing dyes in Fig. S7). Scan parameters: 2.7 V; 0.03 nA. The dimensions of a dye (projection selected from a 50x50 nm² area and framed by the square) is (1.1-1.2)nm in the elongated direction and (0.6-0.7) nm in the perpendicular direction.

References

[i] Nejati S., Lau K. K. S. Nano Lett. 2011, 11, 419-423.

[ii] Ardo S., Meyer G. J. Chem. Soc. Rev. 2009, 38, 115-164.

[iii] Marinado T., Kazuteru N., Nissfolk J., Karlsson M.K., Hagberg D.P., Sun L., Mori S., Hagfeldt A. *Langmuir* **2009**, 26, 2592–2598.

[iv] Liu R. S. H. Acc. Chem. Res. 2001, 34, 555-562.