Supporting Information

In-situ Investigation of Dye Adsorption on TiO₂ Films Using a Quartz Crystal Microbalance with Dissipation Technique

Hauke A. Harms[†], Nicolas Tétreault[†], Viktoria Gusak[‡], Bengt Kasemo^{*}[‡] and Michael Grätzel^{*}[†]

*Laboratory of Photonics and Interfaces, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland; *Chemical Physics Group, Department of Applied Physics, Chalmers University of Technology, 412 96 Göteborg, Sweden

METHODS

Solvents and Reagents

All solvents and reagents are of *puriss* grade and are used as obtained. The synthesis of the amphiphillic ruthenium complex Z907 (*cis*-RuLL'(SCN)₂ (L = 4,4'-dicarboxylic acid-2,-2'-bipyridine, L' = 4,-4'-dinonyl-2,-2'-bipyridine)) has been detailled elsewhere,¹ as well as the full synthesis procedure of the organic D-pi-A dye Y123 (3-{ $4-[bis(2',4'-dihexyloxybiphenyl-4-yl)amino-]phenyl}-4,4-di-hexyl-cyclopenta-[2,1-b:3,4-b']dithiphene-2-yl}-2-cyanoacrylic acid).²$

Preparation of dye solutions and concentrations

Solutions were prepared by dissolving the Z907 and Y123 pigment in 1:1 mixture of tert-butanol (tBuOH) and acetonitrile (MeCN), the using the plain mixture for reference measurements. For Z907, solutions of concentrations between 30 μ M and 90 μ M were determined using Lambert-Beer ($\epsilon = 12\ 200\ M^{-1}cm^{-1}$)³ from the background-corrected absorbance of solutions in a 10.00 mm quartz cuvette using a Cary-5 UV-Vis-NIR spectrophotometer. Other concentrations were obtained from further dilution by weight.

Flat & mesoporous TiO₂-covered sensor preparation

Standard quartz crystal sensors (QSX-301) from Q-SENSE were cleaned using a mixture of water, ammonia and hydrogen peroxide as well as UV-ozone treatment. Flat TiO_2 -covered sensors were prepared by atomic layer deposition (ALD) using a Cambridge Nanotech Savannah S100 apparatus using a method detailed elsewhere.⁴ The atomic,

layer-by-layer deposition was carried out at 120° C using successive pulses of tetrakis(dimethylamino)titanium (Ti(NMe₂))₄ (75 °C) and deionized water (25°C) using nitrogen as a carrier gas, and films were subsequently annealed for 4 h at 420°C with a ramping in 1 h. The thickness of the flat film was estimated to be 63.0 nm (± 0.96 nm) by ellipsometry and roughness was measured by AFM on a control sample (RMS roughness of 0.27 nm on a 40 nm frame). The XRD scan of the annealed TiO₂ film on the QCM-D sensor is shown in Figure S1 and has anatase peaks at values of 2theta of 25.3°, 48.1° and 54.0°. No rutile peaks have been detected.

For mesoporous TiO₂ films, the anatase titanium oxide colloid is synthesized using the procedure described in the literature.⁵ The average particle and pore sizes are 20 nm and 23 nm respectively with a total porosity of 58%. The cleaned QCM-D sensors were coated with TiO₂ by spray pyrolysis as described elsewhere.⁶ The paste was then screen printed onto the sensors and finally sintered at 420 °C for 1 hours with 1 hour ramp time. Film thickness was measured on a control sample using a KLA Tencor alpha-step 500 surface profiler within the experimental error of ± 0.2 µm.



Figure S1: XRD scan of a QCM-D sensor with an annealed TiO_2 film (red) and a blank QCM-D sensor (blue). The arrows indicate three TiO_2 anatase peaks at values of 2theta of 25.3°, 48.1°, 54.0°, see jcpds card 00-021-1272. The blank QCM-D sensor consists of an alpha-quartz disk, coated with a chromium adhesion layer and a 100 nm thick sputtered gold electrode. Quartz accounts for the large peaks at 26.6° and 54.9°, meanwhile the large peaks at 38.2°, 44.5° and 64.9° are related to the gold and chromium electrode.

Cleaning procedure

The sensors were repeatedly used so they were thoroughly cleaned to remove adsorbates and obtain the same surface termination for each experiment. To do so the sensor is placed in 0.1 M tetrabutylammonium hydroxide (TBAOH) in dimethylformamide (DMF) for 10 min at room temperature. Thereafter, the sensor is rinsed successively in deionized water and ethanol while ultrasonicating at 80°C for 15 min each. For porous sensors, the duration was approximately doubled. After drying, the sensor is sintered at 420°C for 30 min and cooled to 80°C to be transferred to the QCM-D instrument for the measurement.

After each measurement, the QCM-D modules were rinsed using the sequence MeCN, water, 2% Hellmanex in water, water, MeCN, tBuOH:MeCN (1:1), MeCN at 45°C through the instrument over 3 hours. Between different sets of measurements, the modules were

disassembled and cleaned using sodium dodecyl sulfate in a standard cleaning procedure.

QCM-D measurements

In QCM-D measurements, the QCM resonance frequency is measured as well as the dissipation (or damping) of its oscillation. The observed frequency shift depends on adsorbed mass, as well as the viscoelastic properties of the adsorbed layer and of the overlying bulk liquid. The dissipation depends only on the viscoelastic properties of the adsorbed layer and of the overlying bulk liquid. If a small mass is rigidly adsorbed to the sensor, dissipation will not change, but the frequency will change according to the Sauerbrey relation.

QCM-D measurements were carried out using an E4 instrument from Q-SENSE with resistive gaskets based on KALREZ. The temperature of the chamber platform was set to approx. 25°C and held constant with fluctuations smaller 0.03°C. The pump speed was constant at approx. 100 μ l/min and the chamber volume above the sensor is approx. 40 μ l. The reference liquid was pumped for approximately 1 hour in order to obtain a stable baseline. When switching between different solutions, the pump is stopped for about 1 min.

Shifts of frequency and dissipation are scaled according to their overtone number. Here, only the scaled shifts of the 7th overtone (35 MHz) are shown being representative of the other overtones while being less sensitive to noise than low frequency overtones. The data was smoothened with a 50 pts FTT filter. The baseline was set to zero for all measurements, and exposure onsets were shifted to compare different measurements. To illustrate the choice of the 7th overtone and the validity of the Sauerbrey equation,



Figure S2: Shift of dissipation and frequency of different overtones during a double exposure to 45 μ M Z907 in MeCN:tBuOH mix against a plain MeCN reference. The spreading *during* dye exposure is due to the different viscosity of the overlying bulk liquid. Upon rinsing, dissipation shift goes back to zero, and all frequency shifts converge to the same final value. The 7th overtone (35 MHz) is representative for the behavior of the other overtones.

figure S2 shows a typical QCM-D measurement displaying scaled shifts of frequency and dissipation for the 5th to 13th overtone (25 MHz to 65 MHz). The experiment is a double exposure to 45 μ M Z907 dye in MeCN:tBuOH mixture against a plain MeCN reference that is used for rinsing. First, we note that the dissipation goes back to zero upon rinsing. This shows that the adsorbed dye forms a thin, rigid film and that the Sauerbrey equation can be used to calculate its area mass. The general spreading of different overtones *during* the two exposures is due to the different viscosity of the overlying bulk liquid. Considering the frequency shifts, almost all of them converge to the same final value upon rinsing. Deviations of this behavior can be due to imperfections of the acoustic properties of the TiO₂ film or of the sensor itself, which is the case with the 9th overtone in this example. Lower overtones (1st, 3rd and 5th) are more sensitive to external noise. The oscillations on the 5th overtone in this measurement were caused by an air bubble inside the chamber during the first exposure.

Desorption of dye and subsequent quantification by fluorescence measurements

In order to quantify the amount of Z907 dye on the sensor after the QCM-D measurement, a complementary optical fluorescence technique was used by first rinsing the stained sensor in MeCN before drying and desorbing the dye by immersing it in a known quantity of 0.1 M TBAOH in DMF for 15 min. Fluorescence emission was measured with a HORIBA JOBIN YVON FLUOROLOG-3 using an excitation wavelength of 515 nm and subtracting a blank. Special care was taken to carry the measurements quickly after the stating in the QCM-D while exposing the sample to minimal ambient light.

Quantitative concentrations were obtained through a comparison to a set of reference solutions of Z907 in 0.1 M TBAOH in DMF. These were prepared by diluting by weight a solution of approx. 30 μ M determined precisely by absorbance (assuming ϵ = 12200 M⁻¹cm⁻¹). The intensity of the fluorescence emission was found to scale linearly with concentration between 0.05 μ M and 0.3 μ M wherein lies the concentration of interest.

For Y123, a concentration of 0.01 M TBAOH in DMF was used for desorption. In this case, the fluorescence signals after the pure Y123 exposure and the one after exposure to Y123+cheno were compared directly to each other; the blank was negligible against the measured emission intensities, see figure 3 of the manuscript.

Sources of error

Small contaminations can cause major frequency drifts or block binding sites to the dye. Drift of the frequency shift may be caused by ambient temperature fluctuations whereas both the frequency shift and dissipation can drift due to viscosity change due to evaporation from the solvent mixture or water contamination from ambient air. Thus, special care was taken to properly seal the experiments and conduct the measurements expeditiously.

TiO₂ thickness on flat sensors was found to be unaffected by repeated use and cleaning of the sensors over five times, although surface roughness would start to increase after about 10-15 successive uses. In some cases up to 10% increase of dye uptake has been observed after 10-15 successive uses. Thus, an error of up to 10% should be attributed to all measurements on Y123 and of varying tBuOH:MeCN ratio in the Z907 dye solution (Figure S1) which are likely to overestimate dye uptake. In contrast, the concentration-dependent measurements on Z907 shown in figure 1 and 2 should not suffer from this error since they were carried out using fresh sensors.

Considering the behavior of different overtones and different measurements, we attribute an error of 0.3 Hz to all measured frequency shifts. This leads to the errors given on Δf_{max} and $K_{\text{eq},2907}^A$ in the article.

The fluorescence measurements on desorbed Z907 have a low signal intensity and high detector noise in the region of interest.

COMPLEMENTARY DATA

The complementary data shown here has been referenced to in the paper. Please consider the detailed captions for explanation.



Figure S3. FTIR measurements on 9 μ m thick porous TiO₂ film showing the methyl peaks of the absorbance signal of tBuOH. The blank is a porous TiO2 film previously soaked in MeCN and dried prior to measuring. An additional background subtraction is performed. The different lines correspond to different soaking times in the mix MeCN:tBuOH (1:1), and subsequent rinsing times in MeCN as denoted in the legend. The film was always soaked in MeCN for at least 4 min (and dried) to remove liquid solvent from the pores which is not adsorbed onto the surface. The fact that there is tBuOH in all cases, and that the peak intensity above the background seems to be almost independent of the MeCN washing time after soaking in the mixture, indicates that adsorbed tBuOH is only very slowly replaced by MeCN. The same should hold on a flat film.



Figure S4. (a) QCM-D measurements on approximately 50 μ M Z907 against a MeCN baseline with varying ratios of tBuOH: MeCN *in the dye solution* from 4:96 to 70:30. The observed frequency shifts during exposure are mainly due to the varying viscosity. (b) Close-up of the different final frequency shifts upon rinsing.

In general, there is competitive adsorption between the solvent molecules MeCN, tBuOH and the Z907 dye molecules with different adsorption rate constants ($k_{ad,MeCN} << k_{ad,tBuOH}$ <<< $k_{ad,Z907}$). Here, starting from an MeCN reference, pre-adsorbed MeCN is replaced by tBuOH or Z907. Adsorption of tBuOH will not change the area weight itself, see figure 1(b) of the article. However, low tBuOH fraction in the dye solution itself will lower the solubility of the dye and thereby enhance adsorption and slow down desorption. Figure S2(a) shows exposures to dye solutions containing different ratios of tBuOH:MeCN against a plain MeCN baseline. The frequency shift *during* exposure is mainly due to viscosity effects. The data in supplementary figure S4(b) shows the frequency shift after rinsing which corresponds to mass change and not to viscosity effects. It indicates an increase of dye uptake with decreasing tBuOH fraction. Since the trend is not fully

consistent, we refrain from further analysis for the moment. The inconsistency can be attributed to the possible roughness of the sensors that have been used more than ten times. In addition, there were irregularities in the tBuOH:MeCN (70:30) measurement (light blue line).



Figure S5. QCM-D data on Y123 and cheno. Scaled shifts of dissipation and frequency.

Figure S5 shows Y123 dye loading and the influence of cheno against a MeCN reference solution. The green solid line corresponds to a 0.1 mM Y123 solution in tBuOH:MeCN (1:1) against plain MeCN, the dashed line is the blank. For Y123 a fast adsorption onto the surface followed by a quasi-linear frequency shift with a slope of approximately -3 Hz/h during exposure is obtained. Upon rinsing, we observe a slight desorption and measure a final frequency shift of approximately -12.7 Hz after the second exposure and

final rinsing. The solid orange line shows the coadsorption of 0.1 mM Y123 and 5 mM cheno in tBuOH:MeCN (1:1), with the dashed orange line representing the corresponding 5 mM cheno in tBuOH:MeCN (1:1) against a MeCN reference. During exposure to Y123+cheno (solid orange line), we observe a shift with a steep linear slope of approximately -12 Hz/h. Upon rinsing with the reference solution, considerable desorption from the film can be observed. The second exposure shows a similar trend with a measured absolute frequency shift of -15.0 Hz after rinsing for 80 min. In the case of the cheno solution alone (dashed orange line), a moderate linear frequency shift of -3.5 Hz after rinsing.

Interestingly, the negative linear slopes observed during exposure are mirrored by linear increases in dissipation (figure S5, upper part) indicating the build-up of a viscous multilayer. However, mass loss during rinsing is found to be of the same magnitude as the linear mass uptake during exposure. This desorption is accompanied by an analogous decrease of dissipation reaching it initial zero-value after 80 min of rinsing ($D = 0.4 \times 10^{-6}$ for Y123 and $D = 0.7 \times 10^{-6}$ for Y123+cheno). Thus, we can confidently assume that we have a thin rigid film and use the Sauerbrey equation to quantify the mass uptake.

The exposure to cheno alone yields a final frequency shift of -3.5 Hz. Using an effective molecular weight of MW_{CDA} – MW_{MeCN} = 352 g/mol we obtain a coverage of 1.74 x 10⁻¹⁰ mol/cm².



Figure S6. QCM-D measurement on 2 µm thick porous films, blank measurement exposing to tBuOH:MeCN (1:1) mixture against a MeCN reference, different overtones.

REFERENCES

- (1) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Nazeeruddin, M. K.; Sekiguchi, T.; Grätzel, M. *Nat Mater* **2003**, *2*, 402–407.
- (2) Tsao, H. N.; Yi, C.; Moehl, T.; Yum, J.-H.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M. *ChemSusChem* **2011**, *4*, 4.
- (3) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 808–809.
- (4) Tétreault, N.; Heiniger, L.-P.; Stefik, M.; Labouchère, P. L.; Arsenault, É.; Nazeeruddin, N. K.; Ozin, G. A.; Grätzel, M. *ECS Transactions* **2011**.
- (5) Ito, S.; Murakami, T.; Comte, P.; Liska, P.; Gratzel, C. Thin solid films 2008.
- (6) Bach, U.; Lupo, D.; Comte, P.; Moser, J. E.; Weissörtel, F. *Nature* **1998**, *395*, 583–585.