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Energy Alignment and Surface Dipoles of Rylene Dyes Adsorbed to TiO₂ Nanoparticles

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Abstract

The energy loss in dye-sensitized solar cells calculated from the energy difference between the lowest electronic transition of the dye and the obtained open-circuit voltage is often 1 eV or even more. To minimize this loss, it is important to accurately determine the energy alignment at the TiO₂/dye/redox-mediator interface. In this study, we compared the results from electrochemistry and photoelectron spectroscopy for determining the energy alignment of three rylene dyes, two of which absorb relatively far in the red. The trends observed with the methods were different, as in the former, the energy alignment is measured relative to an external reference and includes contributions from solvent reorganization energies, while in the latter, it is measured relative to the energetics of the TiO₂ and is lacking such contributions. The influence of the dyes' dipole moments on the energetics of the TiO₂ was also measured and explained some of the differences in trends. Finally, we compared the injection efficiencies of the two red-absorbing dyes and found that the differences in injection efficiencies can be better explained using the energy alignment determined from photoelectron spectroscopy. This shows that the method for measuring the energetics of a DSC should be chosen according to what process one intends to study.

1 Introduction

Dye-sensitized solar cells (DSCs) are a promising technology for converting solar energy to electricity at a low cost¹ and the topic of an active research field.^{2,3} They are based on a mesoporous titanium dioxide network with a monolayer of dye molecules adsorbed on the surface. The dye (sensitizer) molecules absorb visible photons and inject electrons into the titanium dioxide. They are then regenerated by a redox couple, usually iodide/tri-iodide, in an organic solvent. Power conversion efficiencies of up to 12 % have been obtained when using ruthenium complexes as sensitizers.^{4,5} Many organic dyes have been tested as sensitizers for DSCs,^{6,7} and some of those now reach efficiencies of 10 %.⁸

Accurate determinations of the energy levels of these dyes are important for predicting the electron transfer kinetics in dye-sensitized solar cells, which to a large extent determine the conversion efficiency. Furthermore, it is important to understand where the energy losses in the system are to tune the energy levels of dyes and minimize these losses. The most common method for determining the energy alignment of dyes involves measuring the redox potential for oxidation either of the sensitizer in solution or of the sensitizer adsorbed to a TiO₂ electrode. Excited state potentials are then estimated by subtracting the zeroth-zeroth energy (E_{0-0}) of the sensitizer from the redox potential. E_{0-0} is usually determined from the cross-section of absorption and fluorescence or from an absorption onset. With this method, one therefore determines redox potentials relative to an external reference electrode. However, the exact position of potentials relative

to the titanium dioxide conduction band is often not known as the position of the conduction band is influenced by the nature of ions or dipoles adsorbed to its surface. Organic dyes used in DSCs can have strong dipole moments and can therefore shift the position of the conduction band to different potentials.⁹ This is not accounted for in electrochemical investigations and a value of -0.5 V vs. NHE is often used as an estimate of the conduction band position. This value was determined for the flat band potential of TiO₂ particles in aqueous solutions at pH 7,^{10,11} and is therefore not necessarily a good estimation of the conduction band position in a DSC where organic solvents are used. Furthermore, the reorganization energy due to solvent molecules is included in potentials determined in electrochemical measurements and therefore these potentials do not correspond to actual energy levels. Depending on the mechanism and time scale of a charge transfer reaction, it might be the latter values which are important for the reaction.

A method, which can be used to determine energy levels of dye molecules, is photoelectron spectroscopy (PES).^{12,13} We have recently used this method to determine the highest occupied molecular orbital (HOMO) position of a perylene sensitizer relative to the TiO₂ conduction band.¹⁴ This sensitizer (ID176) showed unusual behaviour as it did not work well in liquid electrolyte DSCs but showed promising performances in solid state DSCs,¹⁵ which used 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD) as the hole conductor.^{16,17} One of the reasons for this behaviour was that the dye only injected well into titanium dioxide when lithium ions were

Figure 1: Chemical structures of the dye molecules used in this study.

present on the surface in absence of an organic solvent.

We compare the energy alignments determined by electrochemistry and PES of this sensitizer, a structurally similar perylene (ID28)^{18,19} and a terrylene sensitizer called ID1 (or TMIMA).²⁰ ID28 has a different anchoring group than ID176 and performed very well in liquid electrolyte DSCs. The injection efficiency of ID1 was shown to be dependent on the size of the cations present in a supporting electrolyte: ID1 was able to inject well into the TiO_2 in presence of lithium ions but injection efficiencies were low in presence of tetrabutylammonium (TBA) ions.²⁰ The chemical structures of these dye molecules are shown in Figure 1. ID176 and ID1 both absorb further in the red than many other organic dyes used in DSCs and estimations by electrochemistry placed their excited states at approximately the same potential (-0.65 V vs. NHE). However, two times higher IPCE values were obtained with ID1 than with ID176 in liquid electrolyte DSCs using a LiI electrolyte.^{15,20} In this study, we show that also in absence of solvent and ions, ID1 shows good injection while ID176 shows poor injection.

Furthermore, high kinetic energy photoelectron spectroscopy (HIKE)²¹ may be used to investigate the effect of ground-state dipole moment of molecules on the energy level alignment at an interface.²² In this report, we used HIKE to study the ground-state dipole moments of the dye molecules and analyzed the relation to the energy level alignment at the interface between the dye molecules and the TiO_2 . Stark shifts in the ground-state absorption spectra of dye molecules have recently been shown to be induced by electrons injected in the TiO_2 and to influence the results of transient absorption spectroscopy and of photo-induced absorption spectroscopy (PIA).^{23,24} We induced Stark shifts by electrochemically charging the TiO_2 and determined the directions of the change in dipole moment between the ground- and the excited state of the different dyes this way.

2 Results and Discussions

2.1 Adsorption behaviour of the dyes on TiO_2 surfaces

ID28 and ID1 both have an anhydride anchoring group and are expected to adsorb to the titanium dioxide surface with the two carboxylate groups which are formed by ring-opening of the anhydride group.^{18,25} Adsorption to the TiO_2 surface therefore results in a significant structural change of the dye molecules. For ID28, this change causes a more than 100 nm blue-shifted absorption maximum, when the dye adsorbs to TiO_2 . ID176 on the other hand has only one carboxylic acid anchoring group. The difference in anchoring group and size of the dye molecules may result in different amounts of dyes being bound to the titanium dioxide surface. We compared the amount of dye on the surface by dividing the intensities of the C1s peaks from PES by the number of carbon atoms in the dye molecules (Table 1). For ID176, this ratio is highest

Table 1: Intensities of C1s peaks relative to Ti2p intensities from PES measured with a photon energy of 758 eV and relative intensities divided by number of carbon atoms.

Dye	Peak	Rel. Intensity	$\frac{\text{Rel. Intensity}}{\text{No. C atoms}}$
ID28	Ti2p	1	
ID28	C1s	2.9	0.06
ID176	Ti2p	1	
ID176	C1s	4.8	0.09
ID1	Ti2p	1	
ID1	C1s	2.1	0.02

and therefore ID176 has the highest dye loading out of the three dyes. The ratio and the dye loading decreased by a third for ID28, and they decreased to less than a quarter for ID1.

In recent experiments, maleic anhydride was deposited

on anatase TiO_2 single crystal surfaces and investigated by PES.²⁵ It was suggested that the molecule bound to specific sites of the anatase 101 surface by ring-opening of an anhydride group. The number of bound ID28 and ID1, which have a similar binding group, might therefore be limited due to geometry constraints to attach to these specific sites. In comparison, there might be more binding sites available for ID176, which binds only through one carboxylic acid group. The different number of available binding sites is one likely reason for the lower surface coverage of ID28 and ID1 compared to ID176. Additionally, ID1 is a much bulkier molecule than ID28 or ID176 further limiting the amount of ID1, which can adsorb to the TiO_2 surface.

Figure 2 shows the visible absorption spectra of the three dyes after they had been adsorbed to mesoporous TiO_2 films of approximately $1\ \mu\text{m}$ thickness. The films were immersed in $0.1\ \text{M}\ \text{TBAClO}_4$ electrolyte in 3-methoxypropionitrile (MPN) for this measurement. ID28 absorbs at higher energies than the two other dyes. Superimposed Gaussian functions were used to fit the spectra and to determine the inflection points. These fitted spectra are used in further analysis and plotting.

Figure 2: Ground-state absorption spectra of ID28, ID176 and ID1 adsorbed to approximately $1\ \mu\text{m}$ thick TiO_2 films and surrounded by $0.1\ \text{M}\ \text{TBAClO}_4$ in MPN on an energy scale (dotted lines). Gaussian fits to the absorption spectra are indicated by solid lines. Crosses indicate the position of the maximum gradient of the absorption spectra.

2.2 Energy alignment

Oxidation potentials of ID28, ID176 and ID1 were determined using differential pulse voltammetry (DPV) of the dyes adsorbed to mesoporous TiO_2 electrodes in $0.1\ \text{M}\ \text{TBAClO}_4$ in MPN as supporting electrolyte (Figure 3). The currents measured with ID1 were approximately a factor of five lower than for the other two dyes and cyclic voltammetry of ID1 was not reversible (data not shown). When adsorbed to mesoporous TiO_2 , dye molecules are oxidized by a hole hopping mechanism through the dye layer²⁶ as the TiO_2 is inert

at the potentials which are used. In case of ID1, this hole hopping mechanism might be less efficient than for the other dyes due to the lower surface coverage. The determined potential is therefore not as accurate as for the other two dyes.

The oxidation potentials vs. NHE ($U_{\text{ox}}^{0'}$) were calculated from the peak potentials (U_p) using the following equation:²⁷

$$U_{\text{ox}}^{0'} = U_p + \frac{\Delta V}{2} + 0.63\ \text{V} \quad (1)$$

where ΔV was the voltage step in DPV ($0.05\ \text{V}$). The results are summarized in Table 2 and in Figure 4a. The fits to

Table 2: Electrochemical potentials of the rylene dyes adsorbed to TiO_2 surfaces.

Dye	U_p / V vs. Fc/Fc^+	$U_{\text{ox}}^{0'}$ / V vs. NHE
ID28	0.41	1.07
ID176	0.56	1.22
ID1	0.5	1.16

Figure 3: Differential pulse voltammograms obtained with a pulse amplitude of $50\ \text{mV}$ of ID28, ID176 and ID1 adsorbed on mesoporous TiO_2 in $0.1\ \text{M}\ \text{TBAClO}_4$ in MPN as supporting electrolyte.

the absorption spectra from Figure 2 are included in Figure 4a. Their energies were subtracted from the redox potentials of the dyes. Included in dashed lines are the oxidation potentials, E_{0-0} energies and excited state potentials reported in literature. For ID28, the oxidation potential was measured by electrochemistry in solution and was slightly higher than the potential determined here. E_{0-0} was determined from the 10 % absorption onset.¹⁸ The oxidation potential of ID176 was previously determined by cyclic voltammetry of ID176 adsorbed to TiO_2 and E_{0-0} was determined to be $1.85\ \text{V}$ from the absorption and emission cross section of the dye in solution as well as adsorbed to titanium dioxide.^{14,15} The oxidation potential of ID1 was previously determined by cyclic voltammetry of the dye adsorbed to an FTO electrode and is more negative than the potential determined here. More positive redox potentials on TiO_2 than on SnO_2

Figure 4: a) Potentials of ID28, ID176 and ID1 determined by electrochemistry. Literature values^{18,20} are indicated by dashed lines. Absorption spectra were subtracted from the oxidation potentials determined in this study. The conduction band of TiO₂ is indicated at -0.5 V vs. NHE. b) Energy levels of ID28, ID176 and ID1 determined by PES. The results were calibrated to the Fermi level of an undyed TiO₂ film placed at 0 eV binding energy. Absorption spectra were subtracted from the HOMO energy and dashed lines indicate the 10 % onset of the absorption spectra.

were also observed for indolene dyes, and the difference was explained by the much more electropositive nature of Ti(IV) compared to Sn(IV).²⁸ The E_{0-0} transition of ID1 was determined from the absorption and emission cross-section of the ring-opened sensitizer in solution.²⁰ For all three dyes, the excited state potentials were previously estimated by subtracting E_{0-0} from the redox potentials, and these excited states lie in the same potential regions as the absorption onsets (Figure 4a). One obtains an ordering of the redox potentials: ID28 < ID1 < ID176 and an ordering of excited state: ID28 << ID176 = ID1.

The HOMO levels of the dyes relative to the TiO₂ energies were determined by PES in a similar way as described previously.¹⁴ The cut-off positioning of band gap states of a blank TiO₂ substrate was measured, set to 0 eV binding energy and defined as the Fermi level. Valence spectra of the dye-sensitized samples were energy calibrated relative to the Ti3p peak of this blank TiO₂ substrate. These energy calibrated spectra are shown in Figure 5. Approximate HOMO positions were determined based on the assumption that both ID176 and ID28 have two levels contributing to the measured peaks and ID1 has only one. The estimated positions are 2.4 eV for ID28, 2.3 eV for ID176 and 2.1 eV for ID1 and should be seen as representing a relative trend rather than exact positions of the HOMOs. The ordering of the levels in binding energy relative to the energetics of the titanium dioxide surface is ID1 << ID176 < ID28. This ordering is very different to the ordering of redox potentials. Subtracting the absorption energies (Figure 2) from the HOMO levels, one obtains a very different picture of the dye energetics relative to the TiO₂ (Figure 4b). The conduction band position is indicated at the Fermi level of the blank titanium dioxide surface here, as this level can be seen as an upper binding energy limit for the conduction band position.²⁹ Indicating the relaxed excited state at the position of the 10 % absorption onset one

Figure 5: Valence spectra from PES measured with an excitation energy of 150 eV. HOMO peak positions of the dyes are indicated.

notices that it is located below the TiO₂ conduction band for all dyes. We observed this previously for ID176 and suggested that band gap states might be relevant for electron injection.¹⁴ The ordering of the excited states in binding energy is ID28 < ID1 << ID176. From this result, the question

arises what these different trends are due to and which of the measurements holds information relevant for the interface processes of dye-sensitized solar cell.

2.3 Effects of surface dipoles

The dipole moment of the dye molecules (μ) may also be of importance for the energy level alignment at the interface. A common model to describe the energy levels at the interface between materials is to assume that the vacuum levels of the materials align at the interface. This model for two materials and the effect of a dipole between them is shown in Figure 6. In the model we have included the valence band (VB), the conduction band (CB) and a higher binding energy core level (i.e. Ti2p) of TiO₂. A thiophene polymer (P3HT) is in this case in contact with the TiO₂. This polymer was chosen as it contains sulphur, which is not present in the other components of the system. The HOMO, the lowest unoccupied molecular orbital (LUMO) levels and a core level (i.e. S2p) of the polymer are included in the model.

In the left-hand panel in Figure 6, the interface between TiO₂ and the polymer is shown. In the middle of Figure 6, a dipole is inserted in between the TiO₂ and the polymer. The dipole has the positive charge directed towards the polymer and the negative charge towards the TiO₂ (it points towards the polymer). In the model, the dipole gives a change in the energy level alignment between the TiO₂ and the polymer, and we see that the TiO₂ levels are lifted upward with the respect to the polymer levels in comparison to the interface without the dipole molecule. In the right-hand panel in Figure 6 the dipole is pointing in the other direction, with the negative charge towards the polymer and the positive charge towards the TiO₂. In this case, the TiO₂ energy levels are lowered versus the polymer, compared to without the dipole molecule.

Figure 6: Schematic model of the energy levels for the TiO₂/P3HT interface with no molecule in between (left), a dipole with the positive charge close to P3HT and the negative charge close to TiO₂ (middle), and a dipole with the positive charge close to TiO₂ and the negative charge close to P3HT (right).

The changes in the energy level alignment are apparent not only in the valence electronic levels, but also in the core electronic levels (i.e. Ti2p and S2p), which are element specific and well defined. In summary, we can distinguish the energy levels from TiO₂ and the energy levels from P3HT

and therefore follow the changes in energy level alignment by following the changes in the core energy levels.

The energy levels of TiO₂ and P3HT can be measured using PES. PES is usually a very surface sensitive technique where only the outermost molecular layers can be measured. However, using higher energy X-rays (HIKE or HAXPES) the technique is more bulk sensitive and effects from buried interfaces may also be measured. We have previously measured the energy level alignment in the fully assembled three material (TiO₂/molecule/polymer) systems using HIKE.²² Using a dipole molecule between the TiO₂ and the polymer, such as benzoic acid and 4-nitrobenzoic acid, we could change the energy level alignment between the TiO₂ and the polymer, and the change was dependent on the dipole moment and dipole direction at the interface.

In this work, we used mesoporous TiO₂ films sensitized with the different dye molecules and with the polymer P3HT spin-coated on these samples. Figure 7 shows the Ti2p_{3/2} and the S2p spectra for the different TiO₂/dye/polymer interfaces. The S2p spectra contain two peaks, S2p_{3/2} and S2p_{1/2}, due to the spin-orbit splitting and the splitting between them is about 1.2 eV and the intensity relation is 2 to 1. The x-axis in Figure 7 shows the binding energy and on the y-axis the intensity of the normalized spectra is shown.

Figure 7: The Ti2p_{3/2} and the S2p HIKE spectra of TiO₂ and P3HT with different dye molecules at the interface showing that ID1 has a different magnitude in dipole moment resulting in downward shift in energy (upward shift in binding energy) of the TiO₂ energies relative to the P3HT.

Comparing the spectra, we observe that the S2p feature from the sample with ID1 differs from the other spectra. It has a larger energy difference of approximately 0.2 eV in relation to the Ti2p. This means that the energy levels of the polymer is shifted toward lower binding energies in relation to the TiO₂, in comparison to the other dye molecules. This situation is explained by the energy level diagram in the right-hand panel of Figure 6. ID1 therefore changes the energy level alignment in the solar cell. The results also show that the dipole moment of ID1 is different in comparison to the other dye molecules. This observation seems to agree with

calculations in previous studies which suggested that ID28 and ID176 have large ground-state dipole moments, which point away from the titanium dioxide surface.^{15,18} For ID1, such a dipole moment was not predicted by calculations.²⁰

The dipole moments discussed above can explain why the HOMO of ID1 was observed at a lower binding energy than the HOMO of ID28 or ID176, while such a difference was not seen in the redox potentials. However, the different trends for ID28 and ID176 cannot be explained as the molecules seem to have the same magnitude of dipole moment. The difference in HOMO levels and redox potentials might come from a difference in the magnitude of the solvent reorganization energy, which is included in electrochemical measurements.

We recently showed that the absorption spectra of organic dyes adsorbed to TiO_2 surfaces can be Stark shifted by electrons injected into the TiO_2 .²⁴ This effect was shown to depend on the magnitude and direction of the change in dipole moment between the ground and excited state of the dye molecules normal to the TiO_2 surface ($\Delta\mu_z$). Figure 8 shows a representation of the changes in transition energy and in absorbance when $\Delta\mu_z$ is pointing away from and towards the TiO_2 surface. The change in absorbance can be described by

Figure 8: Representation of the first order Stark shift when the change in dipole moment, $\Delta\mu_z$, points away from (top) and towards (bottom) the TiO_2 surface.

the following equation:^{24,30}

$$\Delta A = -\frac{dA}{dE}\Delta\mu_z F_z \quad (2)$$

where $\frac{dA}{dE}$ is the derivative of the absorption spectrum with respect to energy and F_z is the electric field normal to the TiO_2 surface induced by the injected electrons.

In this study, we measured the Stark shifts of the dye molecules in spectroelectrochemical experiments with a TBAClO_4 supporting electrolyte. A negative potential was applied to dyed mesoporous TiO_2 electrodes, which led to the injection of electrons into the TiO_2 but not to a reduction of the dye molecules. The change in absorbance of the dye molecules was measured and it was found to vary linearly with the amount of injected charge.

We therefore rewrite Equation 2 as:

$$\Delta A = -\frac{dA}{dE}\Delta\mu_z \frac{Q}{C_H l} \quad (3)$$

where Q is the charge in the TiO_2 , C_H is the Helmholtz capacity and l is the average distance between an electron in the TiO_2 and the counter charge in the electrolyte. This treatment assumes that the dye molecules are completely located within the Helmholtz layer. This assumption might be true for the TBAClO_4 electrolyte used here but is less to be true for electrolytes containing smaller cations.³¹

To compare the Stark shifts of the three dye molecules, we divided the change in absorbance by the magnitude of the accumulated charge determined from voltammograms and the maximum derivative with respect to energy ($(\frac{dA}{dE})_{\max}$), as determined from the ground-state absorption spectra in Figure 2. The resulting spectra (Figure 9) show that the ground-

Figure 9: Change in absorbance when applying negative potentials to mesoporous TiO_2 films dyed in ID28, ID176 or ID1 normalized to the amount of charge in the films and to the maximum of the derivative with respect to energy of the films prior to applying a potential.

state absorption spectra of ID28 and ID176 were blue-shifted by the presence of the electric field while the absorption spectrum of ID1 was red-shifted. By comparing the spectra to the diagrams in Figure 8, we could determine the directions of $\Delta\mu_z$ relative to the TiO_2 surfaces. For ID28 and ID176, $\Delta\mu_z$ points away from the TiO_2 surface (the negative part of the dipole is at the surface), while $\Delta\mu_z$ points towards the TiO_2 surface for ID1.

If l and C_H are determined by properties of the electrolyte and do not depend on the dye molecules, the spectra in Figure 9 will also show the relative magnitudes of $\Delta\mu_z$. However, considering the different surface coverages of the dye molecules and the larger size of ID1, both quantities might be dye dependent, and also the assumption that the dye molecules are contained within the Helmholtz layer might not hold true. We therefore only determine the relative directions of the changes in dipole moment from Figure 9.

Considering these results, we propose that the dipole moments of the excited states point in the same direction as the dipole moments of the ground-states but have a larger magnitude. ID28 and ID176 behave similarly to organic donor-acceptor dyes which are typically used in DSCs and show

internal charge transfer towards the TiO_2 surface upon excitation. This is thought to be beneficial for photo-induced electron injection into the titanium dioxide. ID1 has at least to some extent internal charge transfer in the opposite direction, i. e. away from the TiO_2 surface.

2.4 Photo-induced electron injection

Finally, we also compared the electron injection abilities of ID176 and ID1 in absence of surrounding electrolyte or ions following excitation at 640 nm (1.94 eV). This particular comparison is interesting as electrochemistry predicts a similar driving force for electron injection for both dyes, while PES predicts a larger driving force for ID1. Measurements of the Stark shift show that ID176 has beneficial intramolecular charge transfer towards the TiO_2 surface while ID1 lacks this. ID28 was not included in this comparison, as it does not absorb at 640 nm and has already been shown to inject well in previous studies.^{18,19}

Photo-induced absorption spectra for both dyes are shown in Figure 10. For ID1, a large signal is observed while for

Figure 10: PIA spectra of ID176 and ID1 adsorbed to mesoporous TiO_2 at air.

ID176 signals are nearly absent. The peak at 760 nm for ID1 was previously assigned to the oxidized ID1,²⁰ and we confirmed this by measuring the absorption spectrum of electrochemically oxidized ID1 (data not shown). ID1 therefore injects electrons into the TiO_2 creating oxidized ID1 and electrons in the TiO_2 . This strongly suggests that ID1 is able to more efficiently inject electrons into the TiO_2 than ID176, even accounting for higher light harvesting efficiencies of ID1 at 640 nm and higher extinction coefficients of the oxidized dye. Electron injection efficiencies can be limited by a short excited state lifetime. However, we have previously shown that this is not the case for ID176.¹⁴ The improved injection efficiency of ID1 compared to ID176 can therefore be explained by the larger driving force for electron injection seen in the PES measurement. This therefore suggests that PES is a good method for determining energy levels relevant for electron injection in absence of solvent and ions. When using

electrochemistry to determine energy diagrams care has to be taken to consider the influence the dye molecules themselves may have on the energetics of the titanium dioxide.

3 Conclusions

In this study, we compared electrochemistry and photoelectron spectroscopy as methods for determining the energy alignment of dye molecules adsorbed to TiO_2 surfaces. The methods showed different trends when comparing the dye/ TiO_2 interfaces containing three rylene dyes. In the photoelectron spectroscopy measurements the energy of the HOMO level of ID1 was observed at a lower binding energy relative to the energy levels of the TiO_2 than the HOMO levels of ID28 and ID176. Such an ordering was not observed in the redox potentials, which were measured relative to an external reference redoxpotential. This difference could partly be explained by the influence of the molecular dipole organisation on the TiO_2 energetics: The ground-state dipole of ID1 pointed towards the TiO_2 and caused a downward shift in the TiO_2 energies compared to ID28 and ID176, thus leading to the observation of the HOMO peak at a lower binding energy.

Electron injection in absence of solvents could be better predicted by the energy levels derived from PES, as they were referenced to the titanium dioxide. This result demonstrate that a method for following the energy alignment should be chosen according to what process one intends to study. Electrochemistry of dyes adsorbed to TiO_2 surfaces may be used to determine how to minimize the energy loss of the regeneration process in a liquid electrolyte DSC, while PES might be more relevant for determining the energetics of a solid state device. In future, it will be interesting to measure the energy alignment by PES on functional dye-sensitized systems, which include hole conductors or even solvents.

Experimental Details

Sample preparation

Mesoporous TiO_2 films were prepared on FTO substrates by doctor blading of a colloidal TiO_2 paste (Dyesol, DSL 18NR-T) diluted with terpineol. The films were sintered at 450 °C for 30 minutes. Resulting film thicknesses were approximately 1 μm . Where applicable the films were immersed into dye solution when they had cooled down to approximately 80 °C after sintering and dyed over night. Dichloromethane was used as the solvent for all three dyes. For ID28 and ID176 dye solutions had a concentration of 0.5 mM and for ID1 the concentration was 0.2 mM. The films were washed in ethanol after the dyeing step. For the samples used in HIKE experiments, P3HT was applied to the samples by spincoating from a 10 mg P3HT per ml of chlorobenzene solution.

Spectroelectrochemistry

Electrochemical experiments were carried out on a CH Instruments 660 potentiostat with a 3-electrode set-up. Dyed mesoporous TiO_2 electrodes on FTO substrates were used as working

electrodes. The supporting electrolyte was 0.1 M TBAClO₄ in MPN. An Ag/Ag⁺ wire in the same electrolyte was used as reference electrode and a platinum wire was used as counter electrode. The system was internally calibrated by measuring cyclic voltammetry of the ferrocene/ferrocenium redox couple at a platinum working electrode. The oxidation potentials of the dyes were determined from differential pulse voltammograms with a pulse amplitude of 0.05 V, a pulse width of 0.06 s and a pulse period of 0.2 s. For measurements of the Stark shift, oxygen was removed from the electrolyte solutions by bubbling with Argon gas. Cyclic voltammetry scanning towards negative potential with a scan rate of 0.05 V s⁻¹ was then carried out while simultaneously recording absorption spectra of the working electrode with a HR-2000 Ocean Optics fiber optics spectrophotometer using a halogen lamp as light source. Data analysis was carried out in MATLAB®.

Photoelectron spectroscopy

The soft X-ray photoelectron spectroscopy (PES) measurements were performed at the Swedish National Synchrotron facility MAX-lab at beam-line BLI411.³² The electron take off angle was 70° and the electron take off direction was collinear with the e-vector of the incident photon beam. The kinetic energy of the photoelectrons was measured using a Scienta R4000WAL-analyzer. The PES spectra were energy calibrated by setting the Fermi-level of the TiO₂ sample to binding energy 0 eV and aligning the Ti 3p level of the dye-sensitized samples to the Ti3p signal of the TiO₂ sample without dye. The photoelectron spectroscopy measurements at high kinetic energy were performed using hard X-ray synchrotron light at the HIKE end station on the beamline KMC-1 at BESSY in Berlin.²¹ The HIKE spectra were measured using the photon energy 2010 eV and the spectra were calibrated by alignment of the Ti2p_{3/2} set to 458.56 eV.¹²

Photo-induced absorption spectroscopy

Photo-induced absorption spectroscopy was carried out on a similar set-up as described previously.^{14,33} A white probe light provided by a 20 W tungsten-halogen lamp was superimposed at the sample with a red diode laser (640 nm). The laser was used for excitation and was square wave modulated (on/off) using a function generator (HP 33120A). The probe light was focused onto a monochromator (Acton Research Corporation SP-150) and detected by a UV enhanced silicon photodiode connected to a current amplifier and lock-in amplifier (Stanford Research Systems models SR570 and SR830, respectively). A modulation frequency of 9.33 Hz was used. ΔA was calculated from the in-phase and out-of-phase parts of the change in transmission.

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