

# Electronic and molecular structures of organic dye/TiO<sub>2</sub> interfaces for solar cell applications: a core level photoelectron spectroscopy study

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The electronic and molecular properties of three organic dye molecules with the general structure donor–linker–anchor have been investigated using core level photoelectron spectroscopy (PES). The molecules contain a diphenylamine donor unit, a thiophene linker unit, and cyanoacrylic acid or rhodanine-3-acetic acid anchor units. They have been investigated both in the form of a multilayer and adsorbed onto nanoporous TiO<sub>2</sub> and the experimental results were also compared with DFT calculations. The changes at the dye-sensitized TiO<sub>2</sub> surface due to the modification of either the donor unit or the anchor unit was investigated and the results showed important differences in coverage as well as in electronic and molecular surface properties. By measuring the core level binding energies, the sub-molecular properties were characterized and the result showed that the adsorption to the TiO<sub>2</sub> influences the energy levels of the sub-molecular units differently.

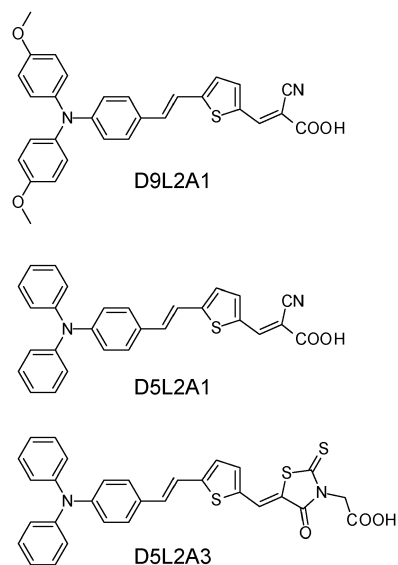
## 1. Introduction

Dye-sensitized solar cells (DSC) have received widespread interest as a new promising alternative to conventional solar cells.<sup>1</sup> A typical DSC is constructed from three main components: a nanoporous network of electron conducting material, a monolayer of light absorbing dye molecules adsorbed to the surface of the electron conducting material, and a hole conducting material in contact with the dye molecules. The efficiency of the solar cell is largely dependent on the molecular properties of the interfacial region between the materials. Therefore, information about the interfaces is of great importance in understanding and optimizing the photo conversion function.

In the most efficient DSCs, reaching over 11% efficiency, metal complexes, such as ruthenium polypyridines, are adsorbed on a nanostructured TiO<sub>2</sub> network and used as a light harvesting material. In such devices, the dye-sensitized nanostructured TiO<sub>2</sub> surface is in contact with a liquid based electrolyte containing the redox couple I<sup>-</sup>/I<sub>3</sub><sup>-</sup>.<sup>2</sup> In recent years, however, there has been an increasing interest in organic dyes as light harvesting materials.<sup>3–7</sup> Specifically, the organic sensitizers compete with the more traditional inorganic dyes in the solid-state dye-sensitized solar cell configuration. This is because these systems currently benefit from high extinction coefficients of the dyes for efficient light harvesting, which is an advantage in solid-state devices due to limitations in charge transport.<sup>8</sup>

In the present study, three organic dyes, **D5L2A3**, **D5L2A1**, and **D9L2A1**, are investigated. The molecules are each built up

by three parts, an electron donor unit, a linker unit, and an anchor unit, see Fig. 1, and they have been used as dye molecules in DSC. Upon absorption of a photon in such solar cell configurations, an electron is excited from the HOMO to the LUMO, which in turn injects an electron into the TiO<sub>2</sub> network. In a general donor–bridge–acceptor model used for similar compounds, the HOMO is located on the donor part of the molecule and the LUMO is located on the acceptor part of the molecule. In the donor–linker–anchor formalism used for the molecules in this investigation, calculations indicate that the HOMO is located mostly around the donor part with only



**Fig. 1** Molecular structure of (going from top down) **D9L2A1**, **D5L2A1** and **D5L2A3**. The molecules are built up by three units, the donor unit (diphenylamine moiety), the linker unit (thiophene moiety) and the anchor unit (cyanoacetic moiety for **D5L2A1** and **D9L2A1** and rhodanine moiety for **D5L2A3**).

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a small contribution at the linker and anchor groups, while the LUMO is located largely around the anchor part with important contributions from the linker unit and only minor contributions from the donor part.<sup>9,10</sup> These molecules have previously been investigated using a range of techniques.<sup>3,4,9–12</sup>

Photoelectron spectroscopy (PES) is a technique that can be used to gain atom specific information on the electronic structure and molecular surface structure.<sup>4,13,14</sup> The probing depth in a PES experiment is only a few nm into the material, and thus this technique is very sensitive to the interfacial region between the materials used, which is important when investigating a monolayer of dye on a surface. The focus of this investigation is to use core level photoelectron spectroscopy (PES) in combination with theoretical calculations to study the effect in the dye sensitized surface composition of these interfaces as the donor/anchor units are exchanged (**D5L2A1** to **D9L2A1** or **D5L2A1** to **D5L2A3**). The investigation also focuses on studying the effect of the adsorption to the TiO<sub>2</sub> surface on the energetic core levels of the dye molecules using core level PES.

## 2. Experimental

### 2.1 Sample preparation

The synthesis procedures of the 3-{5-[4-(diphenylamino)styryl]thiophen-2-yl}-2-cyanoacrylic acid (**D5L2A1**), 3-{5-bis[4-(methoxyphenylamino)styryl]thiophen-2-yl}-2-cyanoacrylic acid (**D9L2A1**), and 3-{5-[4-(diphenylamino)styryl]thiophen-2-yl}-2-rhodanine-3-acetic acid (**D5L2A3**) dyes, as well as the preparation of the TiO<sub>2</sub> colloidal solution are described elsewhere.<sup>3,9,12</sup> Preparations of the nanostructured dye-sensitized electrodes were done according to the following procedure. The colloidal TiO<sub>2</sub> solution was firstly diluted with ethanol (1 : 1) in order to produce a thin nanostructured TiO<sub>2</sub> film. The TiO<sub>2</sub> solution was thereafter spread out onto conducting F:SnO<sub>2</sub> glass pieces. The electrodes were heated to 450 °C for 30 min. This produced a 1–2 μm thick nanoporous TiO<sub>2</sub> film. The electrodes were thereafter immersed into the dye solutions optimized for solar cell performance (1 mM **D5L2A1** dissolved in acetonitrile, 1 mM **D9L2A1** dissolved in acetonitrile and 0.5 mM **D5L2A3** dissolved in acetonitrile) for 12 h. Finally, the samples were rinsed with acetonitrile before being dried in air and put in the PES analyzing chamber at the synchrotron radiation laboratory within ten minutes.

The in-house PES measurements using Al K $\alpha$  radiation were performed on the same samples prepared for the synchrotron radiation based PES measurements in MAX-lab, Lund. The samples were stored in a dark environment in air during the transport between the measurement stations.

The formation of a complete and conducting multilayer (ML) of dye molecules is complex. We successfully prepared a **D5L2A1** multilayered sample by dropping the 1 mM **D5L2A1** solution onto a silicon wafer and thereafter letting the solvent evaporate. A **D9L2A1** multilayered sample was prepared by dropping the 1 mM **D9L2A1** solution onto a F:SnO<sub>2</sub> substrate and letting the solvent evaporate. So far, we have not been able to produce a multilayer of the **D5L2A3** molecule from solution. Instead, a **D5L2A3** multilayer sample was

prepared by smearing out the dye powder onto a SnO<sub>2</sub>:F surface. The thickness of a powder layer is such that the conductivity in the sample is reduced and thus the peak resolution in these samples benefit from measurement using lower photon flux, as produced in the in-house ESCA 300 spectrometer. In Table 3, all multilayer samples were prepared by smearing out the dye powders. The formation of a complete multilayer, with negligible spectroscopic contribution from the substrate, was determined by following characteristic substrate elements (*i.e.* Si and Sn).

### 2.2 Measurements

The photoelectron spectroscopy (PES) measurements were performed using synchrotron radiation at BL I411 at the Swedish national laboratory MAX-lab in Lund. 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 energies of the photoelectrons were measured using a Scienta R4000 WAL analyzer. The PES spectra of the dye-sensitized samples were energy calibrated by setting the Ti2p substrate signal to 458.56 eV.<sup>14</sup> The multilayered spectra were energy calibrated by aligning the S2p<sub>L</sub> peak, *i.e.* the sulfur peak originating from the thiophene linker unit, of the multilayered spectra against the S2p<sub>L</sub> peak from the dye sensitized samples, respectively. Therefore, when comparing the binding energies of the dye-sensitized sample to the multilayer, only differences in binding energies can be discussed.

Charging and radiation effects during measurements were monitored continuously and are negligible for all spectra reported in the present investigation.

In a PES experiment, the mean free path of the electrons depend on their kinetic energy. Thus, when working at a synchrotron radiation facility, the surface sensitivity in a measurement can be controlled by variation of the photon energy. Measurements (of a specific peak) using lower photon energies are more surface-sensitive than those performed using higher photon energies.

Quantitative characterization comparing amounts of the different elements at the surface were performed with an in-house ESCA 300 spectrometer, using monochromated Al K $\alpha$  radiation (1486.7 eV). The instrument is calibrated for cross section and analyzer transmission. The electron take off angle was 90°.

## 3. Theory

Electronic structure calculations on the single free molecules were used to model the experimental spectra for multilayer and monolayer adsorption of **D5L2A1**, **D9L2A1**, and **D5L2A3** on the TiO<sub>2</sub> surface. There is at present too little information on the structures in adsorption to use extended models, but in future work we aim at using constraints from a combination of different experimental probes to evaluate adsorption models and the effect on the electronic structure. Density functional calculations including geometry optimizations and core-level photo emission spectrum simulations were performed using the StoBe-deMon code<sup>15</sup> on the level of gradient-corrected exchange and correlation functionals.<sup>16</sup> All atoms were described with double-zeta valence basis sets including polarization

functions,<sup>17</sup> except for the calculation of the core-level binding energy for N1s, O1s and S2p. The core-level binding energies were determined from explicit  $\Delta$ Kohn–Sham calculations of the initial (ground state) and final (core-ionized) electronic states in the photoemission process. A converged value of the electronic relaxation in the presence of the core-hole was obtained by using a flexible IGLO basis set<sup>18</sup> on the core-ionized atom. In order to localize the core-hole to individual atoms, other atoms of the same element were described by effective core potentials.<sup>19</sup> Hence, after optimizing each molecule, separate calculations to determine the core-level binding energy were performed for every nitrogen, oxygen and sulfur atom in the system.

The calculated core-level binding energies are used in the assignment of the experimental core-level PES spectra. Since only the isolated molecules are used to model the adsorbents, the comparison of the absolute energies is not meaningful. Moreover, the core-level binding energies derived from  $\Delta$ Kohn–Sham calculations are strongly dependent on the choice of density functional.<sup>20</sup> However, the relative energies are representative of the isolated molecule and can be employed to analyze the chemical shift in the adsorbent structures. When comparing the relative binding energies (Table 4), the theoretical values are energy calibrated in the same way as the multi-layered core level binding energies, *i.e.* against the S2p<sub>L</sub> level.

## 4. Results and discussion

Sub-molecular experimental information about electronic and molecular structures at molecular interfaces can be obtained from core-level measurements since these levels are not directly involved in chemical bonding and thus are atom specific. Each element has its own characteristic core-level pattern, but the detailed energy positions depend on charge redistributions linked to the chemical environment of the specific atom, so called chemical shifts.

The assignment of the observed peaks is generally done by the comparison with model compounds or from quantum chemical calculations. The dye molecules investigated here are built up according to the donor–linker–anchor scheme, where the diphenylaniline moiety is referred to as the donor unit, the thiophene unit is referred to as the linker unit and the cyanoacrylic acid and the rhodanine-3-acetic acid units are referred to as the anchor units. Each unit contains atoms in

specific chemical states that can be resolved in the core level spectra, acting as indicators for charge redistribution in that unit, see Fig. 1. Specifically, in the donor unit, there is a nitrogen level, N1s<sub>D</sub>, in the linker unit there is a sulfur level, S2p<sub>L</sub>, and in the anchor unit, there is a nitrogen level, N1s<sub>An</sub>. The different anchor unit of **D5L2A3** also contains a characteristic sulfur level, S2p<sub>An</sub>. The general peak assignments will be discussed in the initial part of the discussion below.

The peak intensities depend on the density of the element in the specific state and are often used to estimate concentrations. However, in an organized molecular layer, differences in attenuation over the molecular layer due to scattering is also important. Variation in intensity can therefore be used to probe the surface molecular structure and this is the focus of the second part of the discussion.

Finally, the changes in core-level binding energies of the atoms in the different units (donor, linker, and anchor) when comparing different molecules and different molecular layers, as well as theoretical and experimental calculations, will allow us to follow electronic changes linked to that sub-molecular unit. This is the aim in the last part of the discussion.

### 4.1 Peak assignments

In Table 1, the calculated energies of the N1s, O1s, and S2p core-levels in **D5L2A1**, **D9L2A1**, and **D5L2A3** are presented. In **D5L2A1** and **D9L2A1**, the two N1s core levels are well separated, located approximately 1.8 eV apart with the N1s<sub>D</sub> level at higher binding energies compared to the N1s<sub>An</sub> core level. In **D5L2A3**, the two nitrogen peaks are closer together compared to the other two molecules. For **D5L2A1** the N1s peaks are located 0.65 eV apart and here with the N1s<sub>An</sub> at higher binding energies compared to the N1s<sub>D</sub> core level. The calculated S2p<sub>L</sub> core level is located around a binding energy of 169 eV for all molecules. For **D5L2A3**, the single bonded S2p<sub>An</sub> is also located around a binding energy of 169 eV, only 0.1 eV apart from the S2p<sub>L</sub> energy level, whereas the double bonded S2p<sub>An</sub> core level is well separated from the other two S2p levels by approximately 2 eV. The O1s<sub>OH</sub> and the O1s<sub>C=O</sub> core levels are located approximately 2.6 eV apart with the O1s<sub>OH</sub> core level at higher binding energies. For **D9L2A1**, the O1s<sub>D</sub> energy level is located at approximately the same binding energy as the O1s<sub>OH</sub> core level, and for the **D5L2A3**, the O1s<sub>An</sub> is located at a binding energy of approximately 1.3 eV lower than the O1s<sub>C=O</sub> core level.

**Table 1** Single molecule calculated core level binding energies with respect to the vacuum level. The calculated  $\Delta E_B$  is the binding energy difference between a specific core level binding energy of the **D9L2A1** and **D5L2A3**, respectively, relative the same core level binding energy in **D5L2A1**

Core level	<b>D5L2A3</b> /eV	<b>D5L2A1</b> /eV	<b>D9L2A1</b> /eV	$\Delta E_B^{\text{D5L2A3}}$ /eV	$\Delta E_B^{\text{D9L2A1}}$ /eV
N1s <sub>An</sub>	405.27	402.85	402.67	—	−0.18
N1s <sub>D</sub>	404.62	404.69	404.47	−0.07	−0.22
S2p <sub>L</sub>	169.17	169.06	168.87	0.11	−0.19
S2p <sub>An</sub> (single)	169.07	—	—	—	—
S2p <sub>An</sub> (double)	166.97	—	—	—	—
O1s <sub>C=O</sub> (COOH)	536.68	535.57	535.41	1.11	−0.16
O1s <sub>OH</sub>	539.17	538.19	538.04	0.98	−0.15
O1s <sub>D</sub>	—	—	537.97 <sup>a</sup>	—	—
O1s <sub>An</sub>	535.39	—	—	—	—

<sup>a</sup> There is a small difference in binding energy for the two methoxy oxygens.

The experimentally measured N1s, O1s, and S2p spectra of **D5L2A3**, **D9L2A1**, and **D5L2A1** adsorbed on TiO<sub>2</sub> are displayed in Fig. 2–4 together with the multilayer spectra. For the **D5L2A1** and **D9L2A1** spectra in Fig. 2, the peak at the higher binding energy is assigned to the nitrogen atom in the donor unit and the peak at the lower binding energy is assigned to the nitrogen atom in the anchor unit, which are in accordance with previous assignments<sup>4</sup> and are also in reasonable agreement with the calculation, see Table 1. These two nitrogen peaks are hereafter referred to as N1s<sub>D</sub> and N1s<sub>An</sub>, respectively. For the **D5L2A3** spectra, the peak at higher binding energy is assigned to the nitrogen atom in the anchor unit and the peak at lower binding energy is assigned to the nitrogen atom in the donor unit, where the position of the N1s<sub>D</sub> of **D5L2A3** is rather close to that of **D5L2A1**. The two nitrogen peaks for **D5L2A3** are hereafter referred to as N1s<sub>An</sub> and N1s<sub>D</sub>, respectively. The assignment of peaks in the **D5L2A3** nitrogen spectrum is also in reasonable agreement with the theoretical calculation, see Table 2.

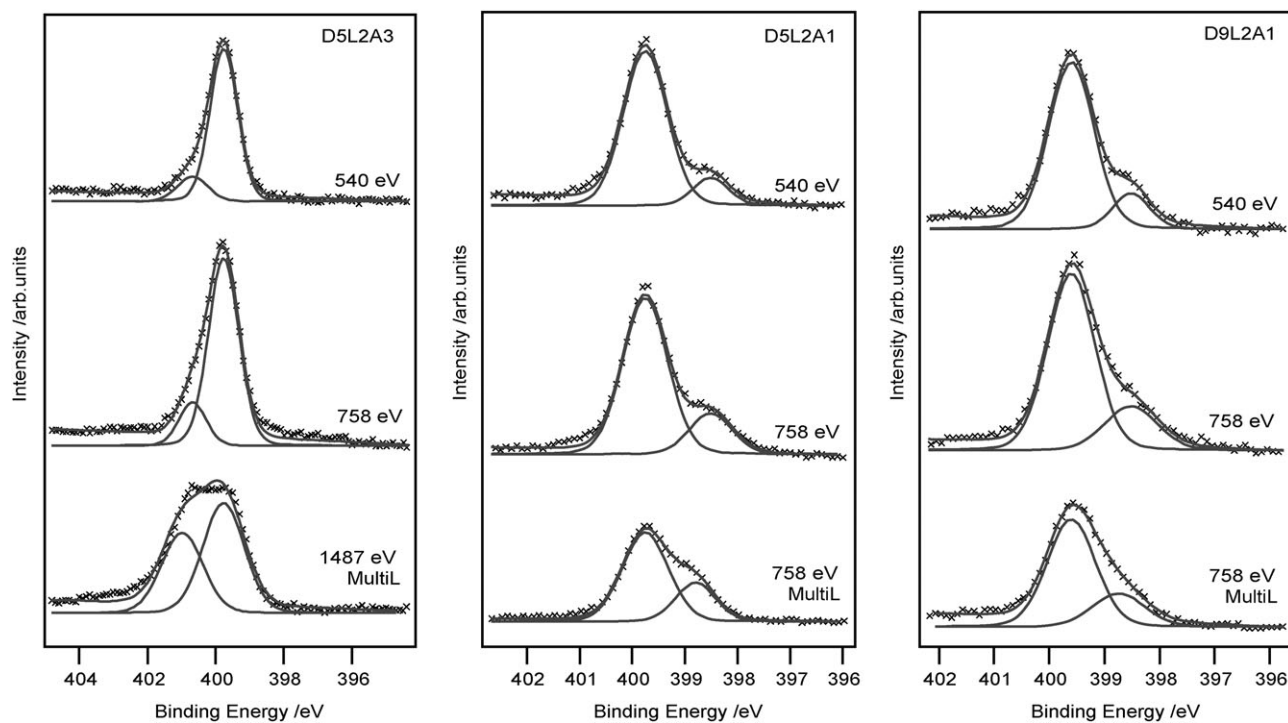
The O1s spectra are displayed in Fig. 3. In the dye-sensitized spectra, the substrate oxygen peak is observed at a lower binding energy. The peaks in the O1s spectra located at higher binding energies originate from surface adsorbed species, such as the two oxygen atoms in the carboxylic moiety. Detailed analysis of the O1s spectra originating from the carboxylic groups is difficult since the *ex situ* preparations also implies contributions from a small amount of contaminations such as water and organic molecules. However, a peak at high binding energy, which originates from the oxygen atoms in the methoxy groups, is clearly distinguishable in **D9L2A1** when

compared to the **D5L2A1** and **D5L2A3** samples. This peak is hereafter referred to as O1s<sub>D</sub>.

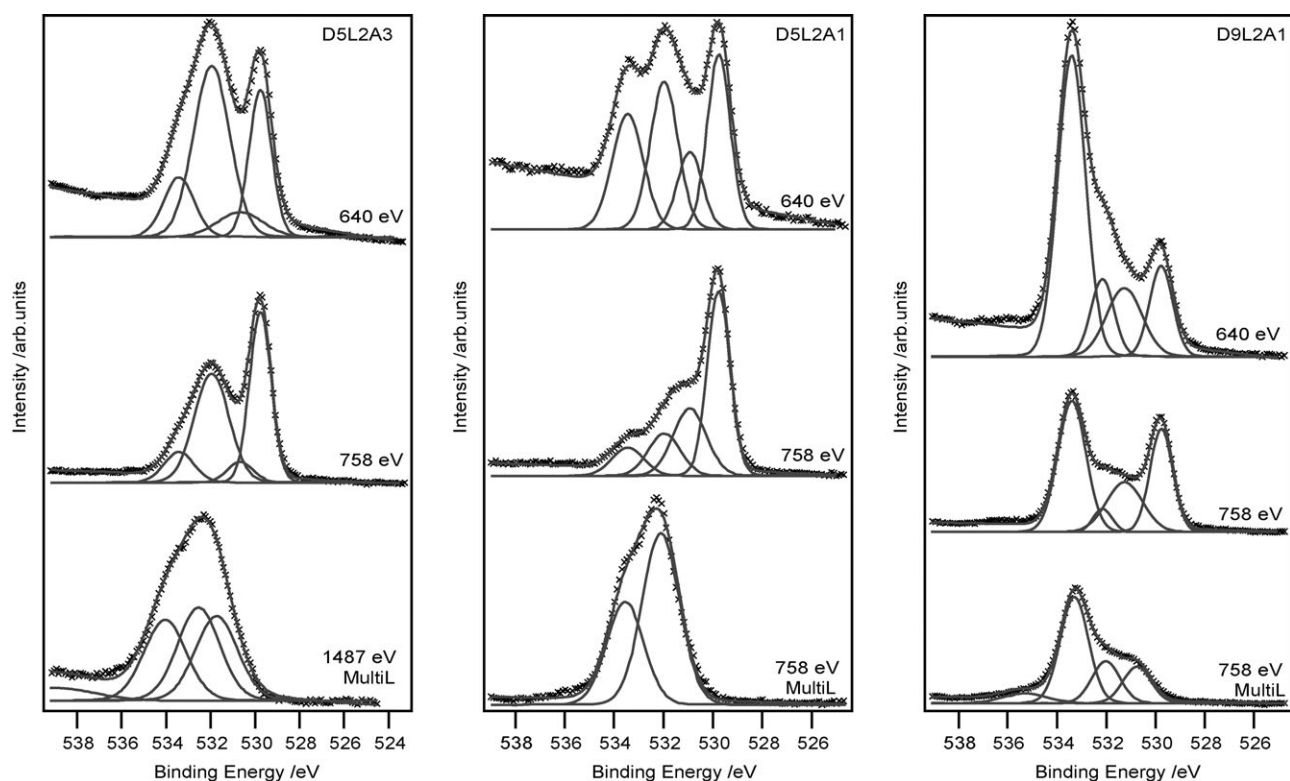
The S2p spectra of **D5L2A3**, **D5L2A1**, and **D9L2A1** are shown in Fig. 4. A S2p spectrum can be de-convoluted with a spin-orbit split doublet for each chemical state, *i.e.* one doublet, S2p<sub>3/2</sub> and S2p<sub>1/2</sub>, with intensity ratio 1:2 and peak split of 1.18 eV. In the S2p spectra of the multilayered sample, only one doublet is present for **D5L2A1** and **D9L2A1**, and this doublet is assigned to the sulfur atom in the linker unit, and is hereafter referred to as S2p<sub>L</sub>. For the dye sensitized **D5L2A1** and **D9L2A1** cases, two doublets are needed to de-convolute the sulfur spectrum. These are both assigned to the sulfur in the linker unit and the largest doublet is referred to as S2p<sub>L</sub> and the smaller doublet is referred to as the extra S2p, the origin of which will be discussed below. The **D5L2A3** molecule contains three chemically inequivalent sulfur atoms, and thus the S2p spectrum of **D5L2A3** is expected to be more complex. Here, two different doublets can be resolved. The largest doublet is assigned to the linker unit as well as the ring sulfur in the anchor unit. The small energy difference makes a de-convolution between these sulfur atoms difficult. The smaller doublet is assigned to the double bonded sulfur in the anchor unit. This peak is hereafter referred to as S2p<sub>An</sub>. Details of all spectra will be discussed further below.

## 4.2 Peak intensities: surface molecular structure

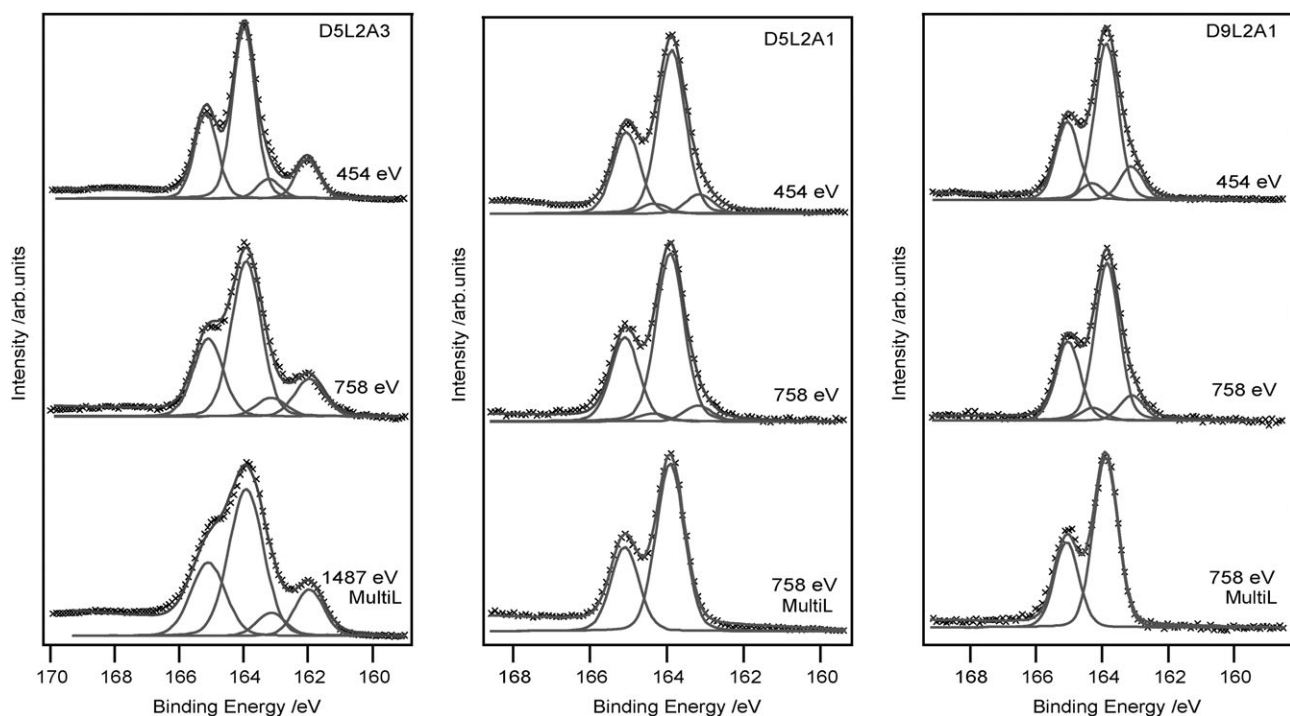
**4.2.1 Surface coverage.** Basic information on the dye coverage is obtained by comparing a nanostructured surface modified with **D5L2A1** and an unmodified nanostructured TiO<sub>2</sub> substrate. The unmodified TiO<sub>2</sub> mainly shows strong



**Fig. 2** The N1s spectrum of the **D5L2A3**, **D5L2A1** and **D9L2A1** sensitized TiO<sub>2</sub> electrodes, measured using photon energy 540 eV and 758 eV, along with N1s spectra of multilayers of **D9L2A1** and **D5L2A1**, measured with photon energy 758 eV, and multilayer of **D5L2A3**, measured using photon energy 1487 eV.



**Fig. 3** The O1s spectra of **D5L2A3**, **D5L2A1** and **D9L2A1**, measured using photon energy 640 eV and 758 eV, along with the O1s spectra of multilayer **D5L2A1** and **D9L2A1**, measured with photon energy 758 eV, and multilayer of **D5L2A3** measured with photon energy 1487 eV.



**Fig. 4** The S2p spectra for the **D5L2A3**, **D5L2A1** and **D9L2A1** dye sensitized TiO<sub>2</sub> electrode, measured using photon energy 454 eV and 758 eV, along with the S2p spectra of a multilayered sample of **D5L2A1** and **D9L2A1** measured using photon energy 454 eV, and the S2p spectrum of the **D5L2A3** sample measured using photon energy 1487 eV.

Ti2p and O1s substrate signals. It also contains small amounts of surface adsorbed oxygen and carbon containing contaminants

as expected for a sample not cleaned by *in situ* methods. However, for the sample surface modified with **D5L2A1**, the

**Table 2** The relative atomic percentage of Ti, S, N, O and C in the dye sensitized **D5L2A3**, **D9L2A1** and **D5L2A1** samples. The numbers are based upon a uniform distribution of elements

Element	<b>D5L2A1</b> (%)	<b>D9L2A1</b> (%)	<b>D5L2A3</b> (%)
Ti	10.8	10.2	10.1
S	1.8	1.3	3.9
N	2.5	1.9	2.3
O	28.5	33.3	28
C	56.4	53.2	55

**Table 3** The relative atomic percentage of S, N, O and C in multilayer samples of **D5L2A3**, **D9L2A1** and **D5L2A1**. The results are with respect to a uniform distribution of elements

Element	<b>D5L2A1</b> (%)	<b>D9L2A1</b> (%)	<b>D5L2A3</b> (%)
S	3.6	3.3	7.3
N	4.5	4.7	4.0
O	7.6	11.4	7.6
C	84.3	80.7	81.2

C1s and O1s molecular signals are substantially higher and the substrate signal is damped. According to the molecular structure, the relative number of S *versus* C is 1:28 and the experimentally observed value of 1:31, see Table 2, therefore shows that the amount of contaminants on the TiO<sub>2</sub> surface is small relative to the amount of dye molecules. The damping in the substrate signal (Ti2p) can be used to estimate the thickness of the dye molecular layer assuming that the modified and the unmodified samples contain only small amounts of contaminants. Based on the observed damping of 40%, together with a mean free path of 20 Å for electrons with a kinetic energy of 1000 eV,<sup>21</sup> and using the take off angle 90°, the mean thickness of the **D5L2A1** molecular layer was estimated to be 11 Å. Since the length of the molecule is about 18 Å, the experimental results are in agreement with a rather close packed molecular layer pointing out from the surface.

Differences in the amount of surface adsorbed **D5L2A1**, **D9L2A1**, and **D5L2A3** molecules can be determined rather accurately by measuring the photoemission intensity from a spectroscopically well-defined core level, such as S2p or N1s, in the two molecules, relative to a substrate signal. This procedure is most accurate for samples measured with high photon energy and for which the binding distance of the atoms in the molecule with respect to the substrate is short compared to the electron mean free path and when the molecular structure is similar. The obtained surface percentage (often referred to as atom percentages) of Ti, S, N, O and C are shown in Table 2 and can be used to make such comparisons. The intensity of the total N1s signal *versus* the Ti2p substrate signal is 20% lower for **D9L2A1** compared to **D5L2A1**, while for **D5L2A3** compared to **D5L2A1**, it is 2% lower. Using the intensity of the S2p<sub>L</sub> peak *versus* the Ti2p peak, the ratio is 24% lower for **D9L2A1** compared to **D5L2A1** and 10% lower for **D5L2A3** compared to **D5L2A1**. These ratios show that the surface coverage of **D5L2A1** is higher than the surface coverage of **D9L2A1** and also that the surface coverage of **D5L2A1** is more similar to the surface coverage of **D5L2A3**.

A different probe of the coverage can be obtained from the intensity of a spectroscopically well-defined atom for the two

molecules acquired under the same experimental conditions, that is, with the same time for acquisition, X-ray intensity and sample configuration. Following this procedure for the nitrogen in the donor unit, a spectroscopic signal is expected to show small and similar attenuation effects for the different molecules. We determine the intensity of N1s<sub>D</sub> for **D9L2A1** and **D5L2A3** to be 79% and 93% in comparison with the **D5L2A1** sensitized film.

In summary, the methods used to determine the amount of dye adsorbed indicate that the intensity of the **D5L2A1** and **D5L2A3** molecular signals are close to values expected from a molecular layer with an estimated thickness slightly lower than that expected from a stretched out molecule. However, the **D9L2A1** molecule forms a somewhat less dense molecular layer at the TiO<sub>2</sub> surface. The effect of the addition of the more bulky methoxy groups is therefore to lower dye coverage by approximately 20%, while changing the anchor unit from cyanoacrylic acid to rhodanine-3-acetic acid has only a small effect on the dye coverage. Turning to the functional properties in working solar cell devices, **D9L2A1** and the **D5L2A1** show rather similar current conversion efficiencies. Therefore together these results indicate that the differences in coverage observed here have a minor effect on the contribution to charge generation from the individual molecule.<sup>9</sup> On the contrary, the current conversion efficiency of solar cells based on **D5L2A3** are lower, although the coverages found here are similar. Again, this indicates that differences in dye load cannot explain the observed lowering in efficiency.<sup>12</sup>

**4.2.2 General surface molecular structure.** Further information on the surface molecular structure can be obtained by comparing the intensities of different atoms in the molecular layer. Such comparisons are given in Table 2 for sensitized surfaces and Table 3 for multilayer measurements performed at 1487 eV photon energy. In this table, the intensities have been corrected for differences in cross-section and spectrometer transmission. Often, such values are referred to as atomic percentages. However, for organized surface layers, differences in position of the atom in the molecular layer affect the attenuation, due to scattering and thereby the measured intensity. Below, we focus on describing the intensity changes for the different core levels and leave the detailed discussion of the peak position to the section on electronic structure.

Firstly, we note that when comparing the relative intensities for the different atoms in the N1s spectra of the surface adsorbed molecules at photon energies of 540 eV and 758 eV, the most striking observation is the minor contribution from the N1s<sub>An</sub> intensity compared to the N1s<sub>D</sub> intensity, see Fig. 2. This effect is attributed to a relative increase in scattering and, as reported previously for **D5L2A1**,<sup>4</sup> the results therefore support a molecular surface configuration in which the dye molecules are bonded to the surface with the anchoring unit close to the TiO<sub>2</sub> substrate and the donor unit pointing out from the surface. In general, all three molecules show the same effect, although the magnitudes differ.

It is further interesting to note that a significant deviation from the stoichiometric ratio between the nitrogen signals also prevails for the multilayer spectra. This indicates that a similar

preferential molecular orientation is also present for the surfaces of the multilayer samples.

A more detailed picture of the molecular surface structure can be obtained by analyzing relative peak intensities at different photon energies and thus different surface sensitivities.<sup>4,6</sup> A comparison between the two N1s peaks reveals that the intensity of the N1s<sub>An</sub> peak compared to the total N1s intensity is about 15% for **D5L2A1**, when measuring with photon energy 540 eV and about 20% when measuring with photon energy 758 eV. Assuming a mean free path of the electrons in the molecular layer of 6 Å at 540 eV and 8 Å at 758 eV, this difference is expected from a simple molecular layer model at a flat surface, in which the difference in distance from the surface for the two nitrogen atoms is on average about 9 Å.<sup>21</sup> The increase of this ratio in the **D9L2A1** molecule is from about 18% to 20% when changing the photon energies from 540 eV to 758 eV, which is consistent with a distance of about 9 Å between the nitrogen atoms, indicating that the **D9L2A1** molecule has a similar angle towards the TiO<sub>2</sub> surface as the **D5L2A1**. The increase in this ratio for the **D5L2A3** molecule is from about 14% to 19%, which is consistent with a difference in distance between the nitrogen atoms of approximately 11 Å. The narrow binding energy distance between the nitrogen peaks in the spectrum of the **D5L2A3** makes it difficult to de-convolute, and therefore the uncertainty is greater in the case of **D5L2A3** than in the case of **D5L2A1**. Also, remembering that the distance between the nitrogen atoms in the **D5L2A3** is greater than in the case of **D5L2A1**, we draw the conclusion that the orientation of the **D5L2A3** molecule on the TiO<sub>2</sub> surface is rather similar to that of **D5L2A1**. Although a quantitative analysis as discussed above contains errors due to *e.g.* the surface morphology, it clearly suggests an organized molecular geometry on the surface, with the donor unit pointing out from the TiO<sub>2</sub> surface. At this point, it is important to note that these dyes were designed for the DSC system with the intention of positioning the molecule with a HOMO level away from the TiO<sub>2</sub> surface, in order to reduce recombination in the DSC, and with the LUMO positioned close to the TiO<sub>2</sub> surface, in order to favour electron injection. The general dye orientation found from the analysis above support such an orientation allowing for high conversion efficiencies.

The O1s spectra of **D5L2A1**, **D9L2A1**, and **D5L2A3** on TiO<sub>2</sub> are displayed in Fig. 3. The substrate oxygen peak can be observed at the lowest binding energy, and at higher binding energies, the surface adsorbed species are identified. The main observation is the substantial intensity of the O1s<sub>D</sub> peak (at the highest binding energy in the O1s spectrum) of the dye-sensitized **D9L2A1** sample. This peak becomes larger in a surface sensitive mode compared to the intensity of the other oxygen peaks related to the molecule. The increase of the O1s<sub>D</sub> peak, relative to other surface oxygen peaks, implies that this atom is further out towards the vacuum interface, thus supporting the results of the N1s spectra discussed above, where the binding configuration of the **D9L2A1** molecule was found to have the donor unit furthest from the TiO<sub>2</sub> surface.

In the oxygen spectra for the dye-sensitized **D5L2A1** and **D5L2A3** samples, we also observe contributions from the molecules. Although such features for an *ex situ* prepared

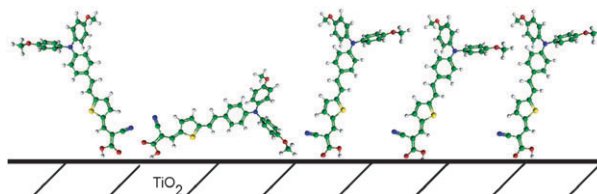
sample is more difficult to interpret, we note the presence of a feature at 533.45 eV, which indicates a substantial amount of OH groups.

**4.2.3 Mixed adsorption configuration.** The S2p spectra of **D9L2A1** and **D5L2A1** are shown in Fig. 4. In the multilayer films, the peak can be de-convoluted into one spin-orbit split doublet corresponding to sulfur atoms in the same chemical environment, which is expected from the molecular formula. However, in the measurements of the surface adsorbed molecules, two spin-orbit split doublet are needed to account for the spectra, see Fig. 4. The intensity of the smaller doublet peak is approximately 11% of the total S2p signal in the case of **D5L2A1**, and 18% in the case of **D9L2A1**, both measured using photon energy 454 eV. The binding energy difference between the main S2p<sub>L</sub> peak and this extra S2p peak is approximately 0.7 eV for both **D5L2A1** and **D9L2A1**, which indicates that the sulfur atoms responsible for the extra S2p peak is clearly in a different chemical environment. The origin of this extra S2p peak is unclear but, as observed for the metalorganic dyes,<sup>14</sup> this indicates a small mixing in adsorption configuration. It is interesting to note that in the multilayer samples for both **D5L2A1** and **D9L2A1**, only one spin-orbit split doublet is needed to account for the spectrum. This clearly suggests that the formation of the extra state in the dye-sensitized samples is induced by the surface adsorption.

From the above observation, a different adsorption configuration in addition to the main binding configuration may be inferred where some (~11% and ~18% for **D5L2A1** and **D9L2A1**, respectively) molecules lie almost flat at the TiO<sub>2</sub> surface planes or adsorb at lattice edges in order to allow for the sulfur atom to interact directly with the surface to produce such a large chemical shift, see Fig. 5.

The **D5L2A3** molecule contains three sulfur atoms and a similar analysis is therefore more complex. The double bonded sulfur atom in the anchoring unit is clearly separated from the other two sulfur atoms, while the sulfur states originating from the linker unit and the anchor unit are very similar in binding energy and cannot be de-convoluted in the experimental spectra. The spectrum of the surface adsorbed **D5L2A3** can be satisfactory modelled using only two spin-orbit split doublets. However, a similar S2p mixture, as found in the S2p spectra of the dye sensitized **D5L2A1** and **D9L2A1** samples, cannot be excluded for the **D5L2A3** sample.

In a molecular device, the effect from a mixed configuration, as schematically displayed in Fig. 5, may have consequences



**Fig. 5** Schematic picture of a simple model of the **D9L2A3** molecular layer at the TiO<sub>2</sub> surface. Two different S2p states (visible in Fig. 3) imply the possibility of a second adsorption configuration at the TiO<sub>2</sub> surface. Excluding the signal from the molecules with the minority binding configuration results in only minor changes in the previously calculated distances between the nitrogen atoms.

on the molecular function. Specifically, the charge transfer dynamics will be affected and mixing may explain the observation of multi-exponential charge injection as well as allow specific charge recombination mechanisms.

### 4.3 Core-level binding energies: sub-molecular electronic changes and energy matching

**4.3.1 Comparing theoretical calculations and dye multilayer.** The theoretical PES core level values are based on single molecule calculations and should ideally be compared to PES measurements of molecules in the gas phase. So far, our attempts to evaporate the **D5L2A1** molecule have unfortunately resulted in the decomposition of the molecule, leaving this option not possible. Instead, the relative theoretical core level energies values are compared here to the values of the multilayer sample in order to observe some specific intermolecular interactions.

Comparing the theoretical core level binding energy values between the different molecules first, information on how the substitutions of either the donor or the anchor unit affects the electronic structure of the dyes is gained. The theoretically calculated core level values are presented in Table 1. Comparing the calculated binding energy difference ( $\Delta E_B$ ) between the core levels in **D9L2A1** and **D5L2A1**, we find that these are generally lower for all levels of **D9L2A1**. This indicates that for the obtained configurations, all the orbitals of the molecule are affected by the exchange of the donor unit, although the magnitude differs.

The calculated binding energy shifts between the core levels in **D5L2A3** and **D5L2A1** show only small differences in the donor,  $-0.07$  eV ( $\Delta E_B(N1s_{TPA})$ ), and linker units,  $0.11$  eV ( $\Delta E_B(S2p)$ ), while the changes in the carboxylic acid group is larger,  $1.11$  eV ( $\Delta E_B(O1s_{CO})$ ) and  $0.98$  eV ( $\Delta E_B(O1s_{OH})$ ). Thus the theoretical results indicate that the incorporation of the rhodanine unit mainly affects the orbitals of the carboxylic unit. The calculated difference in the carboxyl unit as the anchor unit is exchanged may have an effect on the coupling between **D5L2A3** and the  $TiO_2$ .

In Table 4, the relative binding energies of the donor units, represented by the  $N1s_D$  peaks, for the experimental multilayered samples and the theoretical calculations are found to be very similar for all three dyes, with the largest difference being below  $0.1$  eV. This shows that the theoretical calculations model the difference in binding energy between the donor unit and linker unit, *i.e.* the binding energy difference between the  $N1s_D$  and the  $S2p_L$  core levels, in the multilayer very well. Importantly, this also indicates that for a multilayer, the structures of the donor and linker unit resemble that of a non-interacting dye molecule, *i.e.* with little or no specific interaction with the surroundings.

On the other hand, the binding energies of the anchor units, the  $N1s_{An}$  peaks, for the multilayered samples are very different to the theoretical values for all three dyes, see Table 4, with the largest difference being almost  $1$  eV. The good agreement for the  $N1s_D$  and the  $S2p_L$  between the experimental and theoretical binding energies in contrast to the large difference found for the  $N1s_{An}$  core levels suggest a specific interaction, such as hydrogen bonding, between the anchor units of the dyes in the

multilayer, as previously discussed by Kitamura *et al.*<sup>5</sup> A less pronounced effect of the binding energy difference between the theoretical and experimental values for the anchor unit in the **D5L2A3** molecule indicates that the effect of such specific intermolecular interactions is smaller than for **D5L2A1** and **D9L2A1**.

Next, we compare the core levels of the **D9L2A1** and the **D5L2A3** molecules to that of the **D5L2A1** molecule to follow electronic effects from substitutions in the donor and anchor units, respectively. In the multilayered sample, a minor increase of about  $0.06$  eV of the binding energy difference between the  $N1s_D$  and  $S2p_L$  energy levels is observed when the donor unit is modified (comparing **D5L2A1** to **D9L2A1**). As discussed previously, the theoretical calculations show a negligible change in relative binding energy ( $-0.03$  eV). The minor difference observed between the  $N1s_D$  and the  $S2p_L$  core levels indicates that the electronic changes induced by the donor modification also couple with the linker unit due to electronic conjugation. In the experiments on the multilayered sample, as well as in the theoretical calculation, a minor decrease of about  $0.1$  eV of the binding energy difference between the  $N1s_D$  and  $S2p_L$  energy levels is observed when the anchor unit is exchanged.

**4.3.2 Comparing the dye sensitized surfaces.** In Table 4, the binding energies for the dye-sensitized surfaces are also presented, and we now analyze the effect that the substitution has on the energy levels of the molecules adsorbed on  $TiO_2$ . It may be noted that the  $S2p_L$  binding energy is very similar for all three dyes, differing at most by only  $0.07$  eV relative to  $Ti2p$ . This indicates that the energy levels of the linker unit of the adsorbed molecule are very similar relative the  $Ti2p$  energy level in the substrate for all three dyes. Also, the binding energies of  $N1s_{An}$  for the **D5L2A1** and **D9L2A1** sensitized surfaces are very similar. The same position of the  $N1s_{An}$  and the  $S2p_L$  energy levels of **D5L2A1** and **D9L2A1** indicate that the addition of the methoxy groups does not influence the energy levels in the linker and anchor units of the dye molecules when adsorbed at the  $TiO_2$  surface. Interestingly, the similar binding energy also obtained for the  $S2p_L$  energy level in the **D5L2A3** and **D5L2A1** molecules indicates that the substitution at the anchor unit between the thiophene and the carboxylic acid group has a minor effect on the energy levels of the thiophene linker unit with respect to the substrate.

Turning to the binding energies of the donor units when adsorbed at the  $TiO_2$  surface the changes are more pronounced. In Table 4, it can be seen that the binding energies of the donor unit, represented by the  $N1s_D$  core level, are very similar for the **D5L2A3** and **D5L2A1** dyes relative the  $Ti2p$  energy level. This may be expected since the donor molecular structures are the same. However, the energy level of the donor unit in the **D9L2A1** molecule differs by approximately  $0.15$  eV toward lower binding energies relative to **D5L2A1**.

In summary, the effect of the addition of the methoxy units is thus only a shift of the energy level related to the donor unit towards lower binding energies relative to the  $TiO_2$  substrate. The similar binding energies experimentally observed for the  $N1s_D$  relative to  $Ti2p$  of the **D5L2A1** and the **D5L2A3** sensitized samples imply that the substitution of the anchor

**Table 4** Experimental PES core level binding energies for the **D5L2A3**, **D9L2A1** and the **D5L2A1** molecules. The theoretically calculated PES binding energies are energy calibrated by setting the S2p<sub>L</sub> to the same binding energy as for the dye-sensitized samples

Unit	Core level	D5L2A3/eV			D5L2A1/eV			D9L2A1/eV		
		DS	ML	Theo	DS	ML	Theo	DS	ML	Theo
Donor	O1s <sub>D</sub>	—	—	—	—	—	—	533.40	533.14	532.95 <sup>a</sup>
	N1s <sub>D</sub>	399.77	399.36	399.37	399.75	399.45	399.54	399.60	399.45	399.45
Linker	S2p <sub>L</sub>	163.92	163.92	163.92	163.91	163.91	163.91	163.85	163.85	163.85
Anchor	S2p <sub>An</sub>	161.96	161.96	161.72	—	—	—	—	—	—
	N1s <sub>An</sub>	400.68	400.57	400.02	398.51	398.50	397.70	398.51	398.59	397.65

<sup>a</sup> There is a small difference in binding energy for the two methoxy oxygens.

unit does not have any influence on the donor unit of the **D5L2A3**. With respect to the visible light absorbing properties for these dyes, shifts in the donor unit towards lower binding energies is expected to induce a red shift of the adsorption spectrum. Indeed, such a red shift of the absorption maximum was found when comparing **D9L2A1** and **D5L2A1** dissolved in ethanol solution.<sup>9</sup>

**4.3.3 Adsorption induced energetic changes.** It was noted above that the binding energy difference between the donor, N1s<sub>D</sub>, and linker, S2p<sub>L</sub>, units for the multilayer was in accordance with the theoretical calculations and thus indicate that there is no specific intermolecular interaction in this part of the molecule. The adsorption of the dyes to the TiO<sub>2</sub> surface involves strong chemical bonding between the dye molecule and the surface, and such adsorption may influence the internal energetic properties of the dye molecules itself. We will now focus on the effect of the adsorption by comparing the relative binding energies of the dye donor and linker unit in the sensitized sample with respect to the dye multilayer sample.

A comparison of the trends in the binding energy differences is shown in Table 5. (Since the calibration of the multilayered sample was made through the S2p<sub>L</sub> unit, this value becomes 0 eV.) Firstly, it may be noticed that there are large differences between energy levels of the dye molecules in the sensitized sample compared to the multilayered sample. The differences between the linker and donor units show that the adsorption to the TiO<sub>2</sub> surface affects the electronic structure of large parts of the dye molecules, not only the anchor group.

Further, when comparing the different dye molecules, the trends given in Table 5 show that the surface always induces similar specific electronic changes, both with respect to magnitude and direction of the core level shifts. For the **D5L2A1** molecules, the difference is about 0.3 eV at the donor unit, and the **D9L2A1** and **D5L2A3** molecules have similar overall differences, although the values for **D9L2A1** are somewhat lower and for **D5L2A3**, somewhat higher. The observed changes imply that the ground state energy level matching of the dye molecules are changed upon adsorption to the surface.

The differences between the dye molecules in the dye-sensitized sample compared to in the multilayered sample originate from the surface adsorption and the electronic changes can be interpreted as a sign of strong interaction and large electronic coupling to the surface. However, the effects may also be a consequence of the fact that the molecules have all lined up relative the TiO<sub>2</sub> surface. The specific

**Table 5** The core level binding energy difference between the same experimentally measured dye-sensitized (D-S) and multilayer sample peaks

$E_B^{D-S} - E_B^{MultiL}$	D5L2A3/eV	D5L2A1/eV	D9L2A1/eV
O1s	—	—	0.26
N1s <sub>D</sub>	0.41	0.3	0.15
S2p <sub>L</sub>	0	0	0
S2p <sub>An</sub> , N1s <sub>An</sub>	0	0.1	-0.08

molecular ordering of the dye-sensitized surface implies that the strong dipole moments of these molecules, 10.88 D, 12.22 D, and 13.46 D for **D5L2A3**, **D5L2A1**, and **D9L2A1**, respectively (all pointing from the anchor unit to the donor unit), are lined up relative to the TiO<sub>2</sub> surface. This organization results in the formation of a dipole layer and the electric field over this layer would affect the energy of photoelectrons transferred over the interface. While such effects may also be of importance for the molecular functions in a DSC, the dipole moments may be efficiently screened by an electrolyte surrounding the molecules. However, in the solid state DSC, this screening may not be as efficient as in the liquid DSC and may therefore play a more important role. Most likely, the differences found between the binding energies of the monolayer and multilayer is a combination of surface interaction and intermolecular interaction, such as the formation of a dipole layer.

## 5. Summary

The surface electronic and molecular structures of three related organic dyes, **D5L2A1**, **D9L2A1**, and **D5L2A3**, for use in molecular solar cell devices and with the structure donor-linker-anchor have been investigated using photoelectron spectroscopy. It is found that all molecules form a rather close packed molecular layer on the TiO<sub>2</sub> surface. Comparing the molecules, **D9L2A1** has shown the highest conversion efficiencies.<sup>9</sup> Still, however, it was found that the more bulky donor unit in **D9L2A1**, containing methoxy groups, reduced the coverage by approximately 20% in comparison with **D5L2A1** and **D5L2A3**.

The trends observed in peak intensities support a molecular surface configuration for all dyes, in which the dye molecules are bonded to the surface with the anchoring unit close to the TiO<sub>2</sub> substrate and the donor unit pointing out from the surface. The general design of the investigated molecules, with the HOMO mainly centered on the donor unit and the LUMO mainly centered at the linker and anchor units, favors efficient

light induced charge injection for such a surface configuration. However, a detailed investigation of the S2p spectrum indicates that a fraction of the molecules (about 10–20%) adsorb in a different configuration. With respect to the function in a solar cell configuration, this allows for a mixture of charge transfer kinetics over the interface.

The energy matching between the different constituents of the interfacial region is important for the light induced charge transfer reactions. The element specificity of PES, as well as theoretical calculations, were used to investigate electronic effects from changes in donor and linker structure, as well as from surface adsorption. Specifically, it was found that the theoretical calculations model the relative core level binding energies of the donor and linker units in the multilayered sample and that the donor modification only gives rise to small relative variations.

The element specificity of PES was also used to investigate the effect of the adsorption to the TiO<sub>2</sub> surface on the energetic properties of the dye molecules on a sub-molecular level. The investigation show large differences between energy levels of the dye molecules in the sensitized sample compared to the multilayered sample for all three dyes, indicating that the adsorption to the TiO<sub>2</sub> surface affects the electronic structure in large parts of the dye molecules. In particular, for the adsorbed molecules, donor modification increases the energy level in the donor unit relative the TiO<sub>2</sub> substrate, but leaves the levels in the linker and anchor units unchanged. This interesting finding indicates that the red shift of the absorption spectrum partly arises from a shift of the donor-related energy levels as a consequence of the surface molecular configuration. The anchor substitution, on the other hand, has only a minor influence on the energy levels of the donor and linker units. With respect to charge transfer reactions in a device, this result shows the importance not only of controlling the levels of the molecule by proper molecular modification but also controlling molecular surface structures resulting from the dye sensitization procedure.

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