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Electronic structure modulation in ruthenium (II) polypyridine complexes adsorbed on rutile $TiO_2(110)$ surfaces



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A R T I C L E I N F O Keywords: Ru complex TiO ₂ XPS Work function UPS	Ruthenium polypyridine complexes anchored to TiO ₂ surfaces are promising anodes for dye sensitized photo- voltaic and photoelectrochemical solar cells. In this work, we synthesized a series of ruthenium polypyridine complexes, $[Ru^{II}(tpy)(dcb)L]^{n+}$ (tpy = 2,2',2' -terpyridine, dcb = 4,4'-dicarboxy-2,2'-bipyridine and L = Cl ⁻ (Ru- Cl), CN ⁻ (Ru-CN) and CH ₃ CN (Ru-ACN), and employed them to functionalize rutile TiO ₂ (110)–(1 × 1) single crystal surfaces. Photoelectron spectroscopy measurements show that deposition of the Ru complexes from so- lution results in surface coverages close to a monolayer, with the Ru complexes maintaining their coordination sphere intact. Furthermore, all the complexes bind to the substrate through the deprotonated carboxylic acids in a bidentate manner leading to a decrease in the substrate work function. Additionally, the energy of the HOMO electronic state shifted toward the valence band of the semiconductor as the electron-donating capacity of the ligand decreased from Ru-Cl to Ru-CN to Ru-ACN . DFT calculations of the three systems are in good agreement with the experimental results showing how the chemical nature of the substituted ligand governs the energy of the HOMO state whereas the position of the LUMO state remains practically unchanged. The findings presented here contribute to a deeper understanding of the factors that control the electronic structure of Ru polypyridine complexes on semiconductor surfaces.				

1. Introduction

Ruthenium polypyridine complexes have attracted significant attention since the discovery of dye-sensitized solar cells, representing promising devices for generating clean and renewable energy [1–3]. Since then, a wide variety of applications based on ruthenium complexes adsorbed on semiconductor surfaces have arisen. These applications span water oxidation catalysts [4,5], photoelectrochemical cells [6], photonic and optoelectronic devices [7,8], photochemical drug delivery [9,10] and photoswitches [11]. The versatility of Ru polypyridine complexes in this broad set of applications is attributed to their strong absorption in the visible region, the photostability and energy-donating ability of their excited states coupled with their synthetic flexibility that allows tuning of their electronic properties.

Ruthenium complexes must be anchored to a suitable electrode, typically a metal oxide semiconductor [2,3], to function as

photosensitizers in solar cells. Carboxylic acids are commonly employed as anchoring groups as they can form covalent bonds with oxide surfaces [12]. Upon excitation of the molecule with a photon from a visible light source an electron is injected to the conduction band and the Ru complex is subsequently regenerated by an electron donor. Conversion efficiencies rely mostly upon energy matching of the HOMO and LUMO electronic states with the bands of the semiconductor and the electron donor [13,14]. Therefore, comprehending the factors that control the electronic structure of the Ru complex-functionalized surfaces is essential for designing complexes with enhanced photoenergy conversion efficiency.

The literature offers numerous examples of ruthenium polypyridine complexes acting as photosensitizers adsorbed on different surfaces. Most studies have focused on n-type semiconductors, particularly nanostructured and mesoporous TiO₂ (anatase and rutile) films due to their high surface areas [8,13,15–26]. Furthermore, anatase TiO₂ (101)

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and rutile TiO_2 (110) well-defined single crystal surfaces have been employed to achieve a better understanding of the molecular and electronic structure of the adsorbed Ru complexes [27–30]. Some investigations have also explored using ZnO surfaces, although they showed smaller conversion efficiencies [31]. There are also studies on the adsorption of Ru complexes on p-type semiconductors such as CuI, CuSCN, NiO and CuO [14,32]. In these cases, the photosensitization process involves hole transfer from the complex to the electrode [15] and achieving energy matching between the HOMO state and the valence band is important for efficient energy conversion. These studies underscore the significance of comprehending the factors governing the energy levels of the HOMO and LUMO electronic states relative to the valence and conduction bands of the semiconductor.

Density functional theory (DFT) calculations play an important role investigating the structure, electronic properties and electron transfer mechanisms of Ru-complexes adsorbed on TiO₂ [33–38]. Researchers have employed both clusters and, more recently, periodic slabs to model the semiconductor surface. DFT studies indicate that carboxylic acid containing dyes bind to the surface through carboxylate groups in a bidentate geometry [34,37,39]. In the absence of protons, a bidentate bridging binding mode is observed, while in the presence of protons, a mixed bidentate/monodentate binding mode is favored [35]. Calculations also showed the dye HOMO located in the band gap of the semiconductor substrate [33]. Furthermore, interfacial electron transfer from the excited dye to the semiconductor is facilitated when the dye LUMO overlaps with the semiconductor conduction band [38].

In this study we designed, synthesized and characterized, a series of ruthenium polypyridine complexes containing carboxylic acids as anchoring groups and ligands with different electronic donor properties: $[Ru^{II}(tpy)(dcb)L]^{n+}$ (tpy = 2,2',2''-terpyridine, dcb = 4,4'-dicarboxy-2,2'-bipyridine and $L = Cl^-$ (Ru-Cl), CN^- (Ru-CN) and CH_3CN (Ru-ACN)) (see Fig. 1). These Ru^{+2} complexes were deposited from solution onto rutile TiO₂ (110)–(1 \times 1) single crystal surfaces. We characterized the molecular and electronic structure of the absorbed complexes using X-ray and UV photoelectron spectroscopy (XPS and UPS) in conjunction with density functional theory (DFT) calculations. Experimental measurements indicate that changes in the electronic structure of the complexes caused by substituting a ligand influence the electronic structure of the adsorbed complex. Furthermore, DFT calculations effectively reproduce these findings, offering a comprehensive understanding of the electronic structure of the system, surface bonding, and geometric arrangement.



1.1. Experimental methods

We synthesized and characterized the Ru complexes as detailed in the supporting information. Rutile $TiO_2(110)$ single crystals were obtained from CrysTec GmbH. Solvents used for spectral, electrochemical, and photoelectronic measurements were purified following established procedures [40,41]. All other synthesis materials were of reagent grade and obtained commercially without further purification. Before characterization, all complexes underwent a minimum of 24 h of vacuum desiccation.

Absorption spectra in the UV-vis region were recorded with a Hewlett-Packard 8453 diode array spectrometer (range 190-1100 nm). IR spectra of the samples in KBr pellets were obtained with a Nicolet iS10 FT-IR spectrometer (range 11,000–400 cm⁻¹). ¹H NMR spectral data were acquired with a Bruker ARX500 spectrometer, using deuterated solvents from Aldrich. Electrochemical measurements were performed with millimolar solutions of the compounds, using a TEQ V3 potentiostat and a standard three-electrode arrangement consisting of a glassy carbon disc (area = 9.4 mm^2) as the working electrode, a platinum wire as the counter electrode and a silver wire as the reference electrode plus an internal ferrocene (Fc) standard. The supporting electrolyte was tetra-n-butylammonium hexafluorophosphate (TBA)PF₆ 0.1 M. A scan rate of 100 mV s⁻¹ was employed in all cases. All potentials reported here were referenced to the standard Ag/AgCl saturated KCl electrode (0.197 V vs. NHE), with the conversions being performed with literature values for the Fc⁺/Fc couple [42]. UV-vis and electrochemical measurements were also performed on Ru complexes adsorbed on highly porous and ordered mesoporous TiO₂ thin films deposited on transparent and conductive substrates. Films were grown on a fluorine-doped tin oxide (FTO) covered glass by using stablished procedures [43] and complexes were deposited by dipping the substrate in a 5.10^{-4} M methanolic solution overnight. The film was subsequently removed from the solution, immersed in methanol overnight, and then washed with acetone before being left to dry in air.

XPS measurements were conducted in an ultrahigh vacuum (UHV) chamber with a base pressure below 5×10^{-10} mbar using a SPECS spectrometer system equipped with a 150 mm mean radius hemispherical electron energy analyzer and a nine channeltron detector. XPS spectra were obtained on grounded conducting substrates at a constant pass energy of 20 eV using a monochromatic Al Ka (1486.6 eV) X-ray source operated at 15 kV and 20 mA at a detection angle of 20° with respect to the sample normal. Binding energies of the Ti 2p and O 1s regions were aligned to the substrate Ti $2p_{3/2}$ signal at 459 eV [44], while the C 1s-Ru 3d, N 1s and Cl 2p regions were referenced with respect to the aliphatic C 1s signal at 285 eV [45]. Prior to each experiment, the rutile TiO₂ (110) single crystal was cleaned by several cycles of Ar⁺ sputtering and annealing until no impurities were detected by XPS. UPS measurements were conducted in the same UHV chamber using a He I radiation source (21.2 eV) operated at 100 mA with normal detection and a constant pass energy of 2 eV.

Deposition of the Ru complexes on the TiO₂ (110) surface was carried out in an argon-filled liquid cell attached to the UHV chamber. The clean TiO₂ (110) crystal was dipped in a 10^{-4} M methanolic solution of the ruthenium polypyridine complexes at room temperature for 1 h without exposure to the laboratory atmosphere. Afterwards, the crystal was removed from the solution, rinsed with methanol (3 × 10 mL) and dried with Ar. The sample was then transferred from the argon atmosphere to the UHV chamber for measurements.

DFT calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) which employs a plane-wave basis set and a periodic supercell method [46–48]. Potentials within the projector augmented wave (PAW) method [49] and gradient-corrected functionals in the form of the generalized-gradient approximation (GGA) with Perdew Burke Ernzerhof (PBE) functional [50] were used. Van der Waals interaction between pairs was included by means of Grimme DFT-D2 method [51]. A kinetic energy cutoff of 400 eV was employed for all the calculations. The strong electron correlation effects of the Ti 3d electrons were described by a Hubbard-type on-site Coulomb repulsion using the DFT + U Duradev's approach with an effective U value of 10 eV [52,53]. The rutile TiO₂ (110)–(1 \times 1) surface was modeled with a slab containing three Ti layers and 3×5 surface unit cells, resulting in a $1.97 \times 1.47 \times 0.78$ nm supercell (see Fig. 2), large enough to avoid the interaction between adsorbed molecules. Lattice parameters obtained from bulk optimization were used to build the slab. The first Ti layer including all its neighboring O ions was allowed to fully relax, while the bottom layers of the slab were fixed to their bulk positions. A vacuum gap of approximately 3.2 nm was employed to avoid interactions with neighboring slabs. In order to determine the most stable adsorption sites, in all cases, the ruthenium complex adsorbate was fully relaxed as well as the first Ti layer, including all its neighboring O ions. For all calculations, a cut condition of 10-3 eV for the total energy between two ionic relaxation steps was considered. The electronic relaxation convergence criterion was set to 10–4 eV and a set of 5 \times 5 \times 1 Monkhorst-Pack *k*-points was used [54]. Total density of states (TDOS) and projected density of states (PDOS) curves were used to analyze the electronic structure. In this case a $7 \times 7 \times 1$ *k*-points grid was employed. Finally, the work function (Φ) was calculated as the difference between the potential in the middle of the vacuum layer and the Fermi energy [55].

2. Results and discussion

The influence of ligands in the electronic properties of Ru polypyridine complexes is well-understood [56,57] and the properties of the three complexes reported here illustrate this point. The left panel in Fig. 3 shows the UV-vis absorption spectra of the three complexes in methanol with their signal positions listed in Table I. This family of compounds exhibits strong low energy metal-to-ligand charge-transfer (MLCT) bands in the visible region corresponding to the overlap of electronic transitions from $d\pi(Ru)$ orbitals to $\pi^*(tpy)$ and $\pi^*(dcb)$ orbitals [58,59]. These bands are centered at 2.71 eV (457 nm), 2.59 eV (478 nm) and 2.46 eV (504 nm) for Ru-ACN, Ru-CN and Ru-Cl respectively. The energy of these transitions depend on the energy of the 4d Ru donor orbitals and the acceptor orbitals located on the polypyridine ligands. The chloride ligand acts as an electron density donor via π interactions and destabilizes the 4d Ru orbitals upon bonding [60, 61]. The cyanide ligand also exhibits π interactions, but it is a weaker π donor. The acetonitrile ligand serves as a weak base and a π acceptor. Since the ligands have minimal impact on the acceptor orbitals of the polypyridines, the destabilization of the 4d Ru orbitals, due to the increasing electron donor capacity of the substituted ligand, results in a redshift of the MLCT bands in the series from Ru-ACN, to Ru-CN, to



Fig. 2. DFT-optimized geometry of the supercell employed in the calculations. The slabs contain three Ti layers and 3×5 surface unit cells. Red spheres represent O atoms and blue spheres Ti atoms.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Ru-Cl.

The observed electrochemical properties of this series also reflect the impact of the ligand's electron-donor ability on destabilizing the Ru 4d orbitals [57]. Fig. 3 shows cyclic voltammograms of the complexes in solution. In all cases a single peak attributed to the oxidation of the metallic ion is observed consistent with the behavior of other ruthenium (II) polypyridine compounds [58,62]. For the complexes **Ru-ACN**, **Ru-CN** and **Ru-Cl** the π electron-donor capacity of the substituted ligand increases causing a shift to lower potentials. Specifically, it shifts from 1.52 V vs. Ag/AgCl for **Ru-ACN** to 1.24 and 0.99 V, for **Ru-CN** and **Ru-Cl** respectively.

Visible spectroscopy, in principle, can also be used to monitor changes in Ru polypyridines attached to the surface of transparent semiconductors. Unfortunately, the molar absorptivity of these complexes, while relatively high, is not sufficient to detect a monolayer of complexes on flat substrates; instead, thick films with high surface area are required. Fig. 4 shows UV-vis absorption spectra and cyclic voltammograms of the Ru complexes adsorbed on mesoporous TiO₂ thin films deposited on transparent and conductive substrates. Overall, we observe the same trends as those seen for the Ru complexes in solution (see Fig. 3), where MLCT transitions are red-shifted and oxidation peaks shift to lower potentials as the electron-donor capacity increases from Ru-ACN, to Ru-CN to Ru-Cl. Furthermore, we note a significant broadening and change in shape of the peaks, indicating Ru complexes in different local environments within these films. Note that in the case of Ru-ACN the peak at around 400 nm is the second MLCT band of Ru-ACN (also visible in the solution spectra of this complex) enhanced by the light dispersion of the substrate film. It is important to take into consideration that the spectra of Fig. 4 were acquired using different films and that the light dispersion properties of these films may vary preventing from removing the contribution of the film from the spectra. The same second MLCT band is also apparent as shoulders in the spectra of complexes Ru-Cl and Ru-CN as these films showed less light dispersion.

Fig. 5 shows the Ti 2p_{3/2} and O 1s XPS regions of the three complexes deposited on TiO₂ (110) surfaces: the initially clean TiO₂ (110) surface (black curves) and after functionalization with Ru-ACN, Ru-CN and Ru-Cl (blue, red and pink curves, respectively). Note that the intensity of the spectra corresponding to the initial TiO_2 (110) surface was multiplied by a factor of 0.2 for the sake of clarity. Ru complex adsorption results in the expected attenuation of the substrate Ti 2p_{3/2} and O 1s XPS signals as some substrate photoelectrons lose energy as they travel though the topmost Ru complex molecular layers. Indeed, the Ru complex coverage can be estimated from the attenuation of the Ti 2p3/2 XPS peak. Using the inelastic mean free path measured for carboxylic acid functionalized porphyrin molecules deposited on TiO_2 (110) [12] a coverage close to a monolayer was estimated for Ru-Cl (1.1 ML) and Ru-CN (1.0 ML). However, in the case of Ru-ACN a coverage of 0.6 ML was estimated. These findings show that, under the same deposition conditions, the acetonitrile complex results in half the coverage compared to the other systems. The reason for this may be found in the charge of each complex, as larger charge would imply larger lateral repulsion interactions and hence lower coverage (Ru-Cl and Ru-CN are 1+ cations whereas Ru-ACN is a 2+ cation). Given that XPS indicates no adsorption of the hexafluorophosphate counter anion, overall charge neutrality of the surface might be obtained by deprotonation of the carboxylic acid functional groups and by the rapid proton exchange taking place at the solution/TiO₂ interface resulting in the formation of Ti-OH groups at the surface [63].

The O 1s XPS spectra is dominated by the TiO₂ signal at around 530.5 eV [12]. Adsorption of the Ru complexes results in the appearance of a broad shoulder centered at approximately 532.4 eV with contributions from -C=0, -C-0—Ti and Ti—OH [64]. Furthermore, the O 1s XPS spectra shows no evidence of a peak at 534 eV which would correspond to -C—OH [12], this suggests that all Ru complexes bind to the substrate through the deprotonated carboxylic acids. This finding is in



Fig. 3. Left panel: UV–vis spectra of 10⁻⁵ M methanolic solutions of **Ru-Cl** (blue line), **Ru-CN** (red line) and **Ru-ACN** (pink line). Right panel: cyclic voltammograms of **Ru-Cl** (blue line) and **Ru-CN** (red line) in dimethylformamide and of **Ru-ACN** (pink line) in acetonitrile.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table I

Surface coverage (ML), complex stoichiometry, work function change (eV) and HOMO state energy position with respect to the Fermi level (eV) calculated from the XPS and UPS data. Standard potential (V) versus Ag/AgCl and position of the MLCT band maximum (eV).

	Coverage (ML)	Ru:N:Cl	ΔΦ (eV)	HOMO (eV)	E (V)	MLCT (eV)
Ru-Cl	1.1	1:5.1:1.1	-1.18	2.15	0.99	2.46
Ru-CN	1.0	1:6:0	-1.17	2.3	1.24	2.59
Ru- ACN	0.6	1:6.2:0	-1.18	2.5	1.52	2.71

complete agreement with experimental and theoretical calculations showing that 4,4'-dicarboxy-2,2'-bipyridine (dcb) adsorbs on TiO₂ (110) surfaces in a bidentate mode after the deprotonation of both carboxylic acid functional groups [65,66]. Furthermore, it is also in agreement with the DFT calculation discussed below.

The C 1s, Ru 3d, N 1s and Cl 2p XPS spectra measured for the clean and Ru complex functionalized surfaces are shown in Fig. 6. Note that the initial TiO_2 (110) substrate surface does not show any XPS detectable C, Ru, N or Cl, which confirms that it was atomically clean prior to the deposition of the Ru complexes. Formation of the complex layers results in the appearance of carbon, ruthenium, nitrogen and chlorine signals

(chlorine only in the case of Ru-Cl) as expected. The C 1s region of all adsorbed complexes show a broad signal centered at 285 eV due to the aryl carbons in the polypyridine backbone which overlaps with the Ru $3d_{3/2}$ signal (see below) [67]. The shoulder present at 286.2 eV is due to the C—N groups in the polypyridine ligands [67]. The shoulder present at 288.2 eV corresponds to the O-C-O moiety [68] overlapping with the shake-up satellite present in extended conjugated π systems [68]. The Ru $3d_{5/2}$ XPS peak is observed at ~ 281 eV confirming an oxidation state of +2 [69]. Also, the Ru $3d_{3/2}$ signal is buried underneath the broad 285 eV C 1s signal with a 4.2 eV spin-orbit-coupling binding energy difference to the Ru 3d_{5/2} signal. In addition, the slight high binding energy shift observed in the Ru 3d_{5/2} XPS peak when going from Ru-Cl to Ru-ACN is consistent with the stabilization of the Ru 3d orbitals as the electron donor capacity of the ligand decreases from chloride to cyanide to acetonitrile, in agreement with the shifts observed in the UV-vis spectra and cyclic voltammograms discussed above. The N 1s XPS spectra of all complexes is dominated by a peak centered at ~400.2 eV due to the polypyridine ligands. In the case of Ru-CN, a new peak is observed at \sim 398 eV. This peak is due to the cyanide ligand [70] and it has the expected 1:5 area ratio to the main peak at 400.2 eV. Whereas in Ru-ACN, a low binding energy shoulder at ~399 eV is observed. This shoulder can be fitted with a 1:5 ratio to the polypyridine peak and is due to the acetonitrile ligand. The Cl 2p XPS region shows the expected 2p_{3/2} and 2p_{1/2} spin orbit coupling doublet present only in the case of



Fig. 4. UV–vis spectra (left panel) and cyclic voltammograms (right panel) of **Ru-Cl** (blue line), **Ru-CN** (red line) and **Ru-ACN** (pink line) adsorbed on mesoporous TiO₂ films deposited over transparent and conductive substrates. All UV–vis spectra were obtained in acetonitrile. Cyclic voltammograms of **Ru-Cl** and **Ru-CN** were measured in dimethylformamide and that of **Ru-ACN** was collected in acetonitrile. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Ti 2p and O 1s XPS spectra regions of the clean substrate (black lines) and the functionalized surfaces with **Ru-Cl** (blue lines), **Ru-CN** (red lines) and **Ru-ACN** (pink lines).(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Ru-Cl and indicating a single chloride chemical environment.

The Ru:N:Cl ratios calculated from the integrated XPS signals and the corresponding atomic sensitivity factors yield 1:5.1:1.1 (**Ru-Cl**), 1:6.0 (**Ru-CN**) and 1:6.2 (**Ru-ACN**) which are in excellent agreement with the nominal ratios. This gives a strong indication that the molecular structures of the Ru complexes are preserved upon adsorption on the TiO₂ (110) surfaces. We note that all surfaces present a higher-than-expected carbon amount due to the inevitable co-deposition of unwanted carbonaceous species present in traces in the deposition solutions. However, these are minority species which are treated as innocent spectator species. Table I shows the main parameters obtained from the XPS and UPS measurements.

Fig. 7 shows the UPS spectra of the initial TiO_2 (110) substrate and after deposition of the Ru complexes. The left panel shows the highbinding energy region focusing on the secondary electron cut-off, while the right panel highlights the low binding energy region focusing on changes in the electronic states present just below the Fermi level. The initial surface (black curve) does not show any significant signal in the band gap below the Fermi level except for a barely visible electronic state at 0.9 eV due to oxygen defects and Ti interstitials [69, 71]. This spectrum also indicates that the O 2p valence band commences at approximately 2.8 eV below the Fermi level. Upon deposition of Ru complexes a new electronic state emerges in the band gap. The position of this electronic state is 2.15 eV for **Ru-Cl**, 2.30 eV for **Ru-CN** and 2.50 eV for **Ru-ACN** and is assigned to the HOMO Ru 4d orbitals (see DFT calculations below). In accordance with the aforementioned results, the energy of the HOMO state shifts towards higher binding energies as the electron donor capacity of the ligand decreases from **Ru-Cl** to **Ru-ACN**. Note that in the case of the acetonitrile ligand the HOMO state begins to overlap with the semiconductor valence band. Changes in the HOMO electronic state intensities could be attributed to changes in the not-measured intensity of the UV photon source as well as changes in the surface coverage (relevant in the case of **Ru-ACN**) [72].

Deposition of the Ru complexes also affects the substrate work function which can be calculated from the width of the UPS spectra. In all cases the secondary electron cut-off shifts approximately 1.18 eV towards higher binding energies, indicating a uniform decrease in the work function. This change is consistent with the formation of a surface dipole layer featuring negative charges at the surface/molecule interface and positive charges at the molecule/vacuum interface [45]. Given that the observed work function decrease is similar for all Ru complexes and considering that the coverage of **Ru-ACN** is approximately half that of **Ru-Cl** and **Ru-CN** (see XPS results above), it can be inferred that the magnitude of the molecular dipole is stronger in **Ru-ACN**, aligning with its larger nominal charge. Once again, these observations are in line with the DFT calculations discussed below.

DFT calculations have proven to be extremely useful for understanding the electronic structure of Ru polypyridines. Here we carry out DFT calculations of the adsorbed complexes to determine the geometric and electronic structure. Several geometrical configurations (see supporting information) were modeled to determine the most energetically favorable adsorption sites for the complexes on TiO₂(110). Geometry optimizations were carried out on the TiO2 (110) supercell surface described above employing different bonding modes. The results show a molecular surface density of 2.93 nm⁻². Note that this surface coverage could be in the order of the experimental monolayer. Fig. 8 displays the optimized structures obtained. In all cases the deprotonated bidentate configuration proves to be the most stable. This finding is consistent with previous DFT calculations of similar complexes adsorbed on TiO₂(110) showing similar bonding geometries with the oxygen atoms in the carboxylic acid groups deprotonated and attached to titanium atoms [39].

Density of state curves were calculated to analyze the electronic structure of the Ru-complex adsorbed on TiO_2 (110). Curves for the total density of states (TDOS) and partial density of states (PDOS) on the ruthenium complexes Ru 4d and C 2p atomic orbital are shown in Fig. 9. TDOS for the clean TiO_2 is also included as a reference.



Fig. 9(a) corresponds to Ru-Cl adsorbed on the TiO₂ (110) surface.

Fig. 6. C 1s-Ru 3d, N 1s and Cl 2p XPS spectra regions of the clean substrate (black lines) and the functionalized surfaces with Ru-Cl (blue lines), Ru-CN (red lines) and Ru-ACN (pink lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 7. Cutoff and bandgap UPS spectral regions of the clean substrate (black lines) and the functionalized surfaces with **Ru-Cl** (blue lines), **Ru-CN** (red lines) and **Ru-ACN** (pink lines). The inset in the right panel shows the normalized signals from the bandgap region after background subtraction. Simplified energy level diagram showing valence band (VB), conduction band (CB), Fermi level (E_F) and HOMO state. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. DFT-optimized geometry for **Ru-Cl** (a), **Ru-CN** (b) and **Ru-ACN** (c) adsorbed on TiO_2 (110) surfaces. The coloring scheme for the molecule is: O = red, Cl = dark blue, Ru = green, N = light blue, C = grey and H = pink.(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Total DOS (blue line) shows a small shoulder, indicated by an arrow, above the valence band. Comparison with the TDOS of the clean surface (Fig. 9(d)) indicates that this shoulder is located inside the TiO_2 band gap region and that it corresponds to a molecular state. PDOS on the adsorbed complex (red line) and on Ru 4d states (green line) indicate that these states are mainly composed of Ru 4d atomic orbitals and correspond to the HOMO level of the system.

A similar situation occurs when **Ru-CN** is adsorbed on the surface (Fig. 9(b)). In this case, these molecular states composed mainly by Ru 4d orbitals are also in the band gap of the semiconductor but they are shifted towards lower energy values. Finally, **Ru-ACN** (Fig. 9(c)) also shows the HOMO state at the band gap but shifted towards even lower energies. These results are in full agreement with the observed electronic state assigned to Ru 4d orbitals in the UPS spectra. Furthermore, the same shift towards higher binding energies is observed in the series going from **Ru-Cl** to **Ru-CN** to **Ru-ACN**. Additionally, Fig. 9 shows that the LUMO state, composed mainly by the C 2p orbitals of the ligands, overlaps with the semiconductor conduction band and that it remains with essentially the same energy as the ligand is modified. The spatial distribution of the HOMO and LUMO states is exhibited in Fig. 10. The HOMO state presents a great contribution from the Ru 4d orbitals whilst the LUMO is delocalized over the π^* orbitals of the tpy ligand.

DFT calculations also show that the work function of the system decreases after the adsorption of the different ruthenium complexes. Indeed, the difference between the work function of the functionalized and clean surfaces yields $\Delta \Phi \sim -0.90$ eV for **Ru-Cl** and **Ru-CN** and $\Delta \Phi \sim -1.95$ eV for **Ru-ACN**. Note that the larger work function decrease obtained for the acetonitrile complex can be explained by the larger charge of the complex that should result in a larger molecular dipole. These results are in excellent agreement with the UPS results discussed above noting that in the UPS measurements Ru-ACN was present with a lower surface coverage compared to the other molecules. Therefore, Ru-ACN presents a larger molecular dipole as the same work function change was measured in the three cases.

3. Conclusions

Photoelectron spectroscopy measurements and DFT calculations demonstrate that ruthenium polypyridine complexes, modified with carboxylic acid functional groups, effectively bind to well-defined rutile $TiO_2(110)$ single crystal surfaces, forming covalent bonds in a bidentate configuration following deprotonation of the anchoring groups. These molecules maintain their coordination sphere upon adsorption, resulting in the formation of a surface dipole layer characterized by negative charges at the surface/molecule interface and positive charges at the molecule/vacuum interface leading to a decrease in the work function of the system. The electronic state of the Ru 4d HOMO is found to reside within the semiconductor band gap. Importantly, our investigation reveals that modifying the electron-donor capacity of the monodentate ligand in the Ru complex modulates the position of the Ru 4d HOMO



Fig. 9. DOS curves for **Ru-Cl** (a), **Ru-CN** (b) and **Ru-ACN** (c) adsorbed on TiO₂ (110) surfaces. For each system TDOS (blue lines), PDOS on the adsorbed ruthenium complex (red lines), PDOS on Ru 4d atomic orbitals (green lines) and PDOS on C 2p atomic orbitals of the complex (light blue lines) are included (PDOS are multiplied by a factor 10). (d) shows TDOS (black line) for the clean TiO₂ (110) surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

state within the band gap. Notably, the chemical nature of the monodentate ligand in the Ru complex does not influence the energy of the polypyridine-centered LUMO state, which consistently overlaps with the semiconductor conduction band. Our findings provide valuable insight into the role of ligands in modulating the electronic structure of Ru polypyridine complexes adsorbed on TiO₂ surfaces.

Author statement

We confirm that this manuscript contains original research that has not been published previously and that is being submitted exclusively to surface science. Furthermore, the manuscript is not under consideration for publication elsewhere and its publication is approved by all authors.

Synthesis and characterization of the Ru polypyridil complexes and geometrical configurations evaluated in the DFT calculations are available in the Supporting Information.

CRediT authorship contribution statement

Luciano Sanchez Merlinsky: Investigation, Formal analysis. Carolina Pistonesi: Writing – review & editing, Investigation, Formal analysis. M. Estela Pronsato: Writing – review & editing, Investigation, Formal analysis. Luis Baraldo: Writing – review & editing, Investigation. Federico J. Williams: Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Federico Williams is a member of the Surface Science advisory editorial board. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 10. HOMO and LUMO of Ru-Cl, Ru-CN and Ru-ACN adsorbed on TiO₂ (110) surfaces.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.susc.2024.122452.

References

- B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dyesensitized colloidal TiO₂ films, Nature 353 (1991) 737–740, https://doi.org/ 10.1038/353737a0.
- [2] M. Grätzel, Dye-sensitized solar cells, J. Photochem. Photobiol. C 4 (2003) 145–153, https://doi.org/10.1016/S1389-5567(03)00026-1.
- [3] A. Reynal, E. Palomares, Ruthenium polypyridyl sensitisers in dye solar cells based on mesoporous TiO₂, Eur. J. Inorg. Chem. (2011) 4509–4526, https://doi.org/ 10.1002/ejic.201100516.
- [4] D. Wang, Z. Xu, M.V. Sheridan, J.J. Concepcion, F. Li, T. Lian, T.J. Meyer, Photodriven water oxidation initiated by a surface bound chromophore-donorcatalyst assembly, Chem. Sci. 12 (2021) 14441–14450, https://doi.org/10.1039/ d1sc03896f.

- [5] A. Kobayashi, S. ya Takizawa, M. Hirahara, Photofunctional molecular assembly for artificial photosynthesis: beyond a simple dye sensitization strategy, Coord. Chem. Rev. 467 (2022), https://doi.org/10.1016/j.ccr.2022.214624.
- [6] M.K. Brennaman, R.J. Dillon, L. Alibabaei, M.K. Gish, C.J. Dares, D.L. Ashford, R. L. House, G.J. Meyer, J.M. Papanikolas, T.J. Meyer, Finding the way to solar fuels with dye-sensitized photoelectrosynthesis cells, J. Am. Chem. Soc. 138 (2016) 13085–13102, https://doi.org/10.1021/JACS.6B06466/ASSET/IMAGES/ MEDIUM/JA-2016-064666,0020.GIF.
- [7] K. Kalyabasundaram, M. Gratzel, Applications of functionalized transition metal complexes in photonic and optoelectronic devices, Coord. Chem. Rev. 77 (1998) 347–414, https://doi.org/10.1007/978-3-642-00205-2_12.
- [8] M.F. Oszajca, K.L. McCall, N. Robertson, K. Szaciłowski, Photocurrent switching effects in TiO₂ modified with ruthenium polypyridine complexes, J. Phys. Chem. C 115 (2011) 12187–12195, https://doi.org/10.1021/jp201805t.
- [9] P.C. Ford, From curiosity to applications. A personal perspective on inorganic photochemistry, Chem. Sci. 7 (2016) 2964–2986, https://doi.org/10.1039/ c6sc00188b.
- [10] A.C. Benniston, L. Zeng, Recent advances in photorelease complexes for therapeutic applications, Dalt. Trans. 51 (2022) 4202–4212, https://doi.org/ 10.1039/d2dt00254j.
- [11] A. Cotic, S. Cerfontaine, L.D. Slep, B. Elias, L. Troian-Gautier, A. Cadranel, A photoinduced mixed valence photoswitch, Phys. Chem. Chem. Phys. 24 (2022) 15121–15128, https://doi.org/10.1039/d2cp01791a.
- [12] D. Wechsler, C.C. Fernández, H.P. Steinrück, O. Lytken, F.J. Williams, Covalent anchoring and interfacial reactions of adsorbed porphyrins on rutile TiO₂(110), J. Phys. Chem. C 122 (2018) 4480–4487, https://doi.org/10.1021/acs. jocc.7b12717.
- [13] G. Liu, A. Klein, A. Thissen, W. Jaegermann, Electronic properties and interface characterization of phthalocyanine and Ru-polypyridine dyes on TiO₂ surface, Surf. Sci. 539 (2003) 37–48, https://doi.org/10.1016/S0039-6028(03)00721-0.
- [14] M. Buchalska, J. Kuncewicz, E. Świetek, P. Łabuz, T. Baran, G. Stochel, W. Macyk, Photoinduced hole injection in semiconductor-coordination compound systems, Coord. Chem. Rev. 257 (2013) 767–775, https://doi.org/10.1016/j. ccr.2012.09.017.
- [15] M. Grätzel, Photoelectrochemical cells, Nature 414 (2001) 338–344, https://doi. org/10.1007/978-3-030-43346-8_4.
- [16] K. Murakoshi, G. Kano, Y. Wada, S. Yanagida, H. Miyazaki, M. Matsumoto, S. Murasawa, Importance of binding states between photosensitizing molecules

and the TiO₂ surface for efficiency in a dye-sensitized solar cell, J. Electroanal. Chem. 396 (1995) 27–34, https://doi.org/10.1016/0022-0728(95)04185-Q.

- [17] Z. Xiao, M. Li, M. Xu, Z. Lu, The influence of new binding state of dye-molecules to TiO₂ electrode surface on IPCE performance, J. Phys. Chem. Solids 59 (1998) 911–914, https://doi.org/10.1016/S0022-3697(98)00025-0.
- [18] H. Rensmo, K. Westermark, S. Södergren, O. Kohle, P. Persson, S. Lunell, H. Siegbahn, XPS studies of Ru-polypyridine complexes for solar cell applications, J. Chem. Phys. 111 (1999) 2744–2750, https://doi.org/10.1063/1.479551.
- [19] C.R. Rice, M.D. Ward, M.K. Nazeeruddin, M. Grätzel, Catechol as an efficient anchoring group for attachment of ruthenium–polypyridine photosensitisers to solar cells based on nanocrystalline TiO₂ films, New J. Chem. 24 (2000) 651–652, https://doi.org/10.1039/b003823g.
- [20] K. Westermark, H. Rensmo, J. Schnadt, P. Persson, S. Södergren, P.A. Brühwiler, S. Lunell, H. Siegbahn, Electron dynamics within Ru-2,2'-bipyridine complexes—An N1s core level excitation study, Chem. Phys. 285 (2002) 167–176, https://doi.org/10.1016/S0301-0104(02)00700-0.
- [21] Y.v. Zubavichus, Y.L. Slovokhotov, M.K. Nazeeruddin, S.M. Zakeeruddin, M. Grätzel, V. Shklover, Structural characterization of solar cell prototypes based on nanocrystalline TiO₂ anatase sensitized with Ru complexes. X-ray diffraction, XPS, and XAFS spectroscopy study, Chem. Mater. 14 (2002) 3556–3563, https:// doi.org/10.1021/cm020123d.
- [22] K. Westermark, A. Henningsson, H. Rensmo, S. Södergren, H. Siegbahn, A. Hagfeldt, Determination of the electronic density of states at a nanostructured TiO₂/Ru-dye/electrolyte interface by means of photoelectron spectroscopy, Chem. Phys. 285 (2002) 157–165, https://doi.org/10.1016/S0301-0104(02)00699-7.
- [23] T. Stergiopoulos, M.C. Bernard, A. Hugot-Le Goff, P. Falaras, Resonance micro-Raman spectrophotoelectrochemistry on nanocrystalline TiO₂ thin film electrodes sensitized by Ru(II) complexes, Coord. Chem. Rev. 248 (2004) 1407–1420, https:// doi.org/10.1016/j.ccr.2004.03.023.
- [24] E.M.J. Johansson, M. Hedlund, H. Siegbahn, H. Rensmo, Electronic and molecular surface structure of Ru(tcterpy)(NCS)₃ and Ru(dcbpy)₂(NCS)₂ adsorbed from solution onto nanostructured TiO₂: a photoelectron spectroscopy study, J. Phys. Chem. B 109 (2005) 22256–22263, https://doi.org/10.1021/jp0525282.
- [25] S. Rühle, M. Greenshtein, S.G. Chen, A. Merson, H. Pizem, C.S. Sukenik, D. Cahen, A. Zaban, Molecular adjustment of the electronic properties of nanoporous electrodes in dye-sensitized solar cells, J. Phys. Chem. B 109 (2005) 18907–18913, https://doi.org/10.1021/jp0514123.
- [26] W.B. Heuer, H.L. Xia, W. Ward, Z. Zhou, W.H. Pearson, M.A. Siegler, A.A. Narducci Sarjeant, M. Abrahamsson, G.J. Meyer, New dicarboxylic acid bipyridine ligand for ruthenium polypyridyl sensitization of TiO₂, Inorg. Chem. 51 (2012) 3981–3988, https://doi.org/10.1021/ic201395q.
- [27] L.C. Mayor, J. ben Taylor, G. Magnano, A. Rienzo, C.J. Satterley, J.N. O'Shea, J. Schnadt, Photoemission, resonant photoemission, and X-ray absorption of a Ru (II) complex adsorbed on rutile TiO₂(110) prepared by in situ electrospray deposition, J. Chem. Phys. 129 (2008), https://doi.org/10.1063/1.2975339.
- [28] E. Jakubikova, R.C. Snoeberger, V.S. Batista, R.L. Martin, E.R. Batista, Interfacial electron transfer in TiO₂ surfaces sensitized with Ru(II)-polypyridine complexes, J. Phys. Chem. A 113 (2009) 12532–12540, https://doi.org/10.1021/jp903966n.
- [29] E.S. Skibinski, W.J.I. Debenedetti, M.A. Hines, Solution Deposition of phenylphosphinic acid leads to highly ordered, covalently bound monolayers on TiO₂ (110) without annealing, J. Phys. Chem. C (2017) 14213–14221, https://doi. org/10.1021/acs.jpcc.7b04167.
- [30] M. Ikeda, N. Koide, L. Han, A. Sasahara, H. Onishi, Work function of dye-adsorbed TiO₂ surfaces measured by using a Kelvin probe force microscope, J. Phys. Chem. C 112 (2008) 6961–6967, https://doi.org/10.1021/jp077065.
- [31] K. Westermark, H. Rensmo, H. Siegbahn, K. Keis, A. Hagfeldt, L. Ojamäe, P. Persson, PES studies of Ru(dcbpyH₂)₂(NCS)₂ adsorption on nanostructured ZnO for solar cell applications, J. Phys. Chem. B 106 (2002) 10102–10107, https://doi. org/10.1021/jp0142177.
- [32] B. Mahrov, G. Boschloo, A. Hagfeldt, H. Siegbahn, Photoelectron spectroscopy studies of Ru(dcbpyH₂)₂(NCS)₂/CuI and Ru(dcbpyH₂)₂(NCS)₂/CuSCN interfaces for solar cell applications, J. Phys. Chem. B 108 (2004) 11604–11610.
- [33] P. Persson, M.J. Lundqvist, Calculated structural and electronic interactions of the ruthenium dye N3 with a titanium dioxide nanocrystal, J. Phys. Chem. B 109 (2005) 11918–11924, https://doi.org/10.1021/jp050513y.
- [34] F. De Angelis, S. Fantacci, A. Selloni, M.K. Nazeeruddin, M. Grätzel, Timedependent density functional theory investigations on the excited states of Ru(II)dye-sensitized TiO₂ nanoparticles: the role of sensitizer protonation, J. Am. Chem. Soc. 129 (2007) 14156–14157, https://doi.org/10.1021/ja076293e.
- [35] F. Schiffmann, J. Vandevondele, J. Hutter, R. Wirz, A. Urakawa, A. Baiker, Protonation-dependent binding of ruthenium bipyridyl complexes to the anatase (101) surface, J. Phys. Chem. C 114 (2010) 8398–8404, https://doi.org/10.1021/ jp100268r.
- [36] F. De Angelis, S. Fantacci, A. Selloni, M.K. Nazeeruddin, M. Grätzel, First-principles modeling of the adsorption geometry and electronic structure of Ru(II) dyes on extended TiO₂ substrates for dye-sensitized solar cell applications, J. Phys. Chem. C 114 (2010) 6054–6061, https://doi.org/10.1021/jp911663k.
- [37] S.H. Liu, H. Fu, Y.M. Cheng, K.L. Wu, S. Te Ho, Y. Chi, P.T. Chou, Theoretical study of N749 dyes anchoring on the (TiO₂)₂₈ surface in DSSCs and their electronic absorption properties, J. Phys. Chem. C 116 (2012) 16338–16345, https://doi.org/ 10.1021/jp3006074.
- [38] F. Labat, I. Ciofini, H.P. Hratchian, M.J. Frisch, K. Raghavachari, C. Adamo, Insights into working principles of ruthenium polypyridyl dye-sensitized solar cells from first principles modeling, J. Phys. Chem. C 115 (2011) 4297–4306, https:// doi.org/10.1021/jp108917c.

- [39] M. Weston, T.J. Reade, K. Handrup, N.R. Champness, J.N. OShea, Adsorption of dipyrrin-based dye complexes on a rutile TiO₂(110) surface, J. Phys. Chem. C 116 (2012) 18184–18192, https://doi.org/10.1021/jp3025864.
- [40] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, fourth ed., Butterworth-Heinemann, 1996.
- [41] D.B.G. Williams, M. Lawton, Drying of organic solvents: quantitative evaluation of the efficiency of several desiccants, J. Organ. Chem. 75 (2010) 8351–8354, https:// doi.org/10.1021/jo101589h.
- [42] L. Méndez De Leo, E. de la Llave, D. Scherlis, F.J. Williams, Molecular and electronic structure of electroactive self- assembled monolayers, J. Chem. Phys. (2013) 114707, https://doi.org/10.1063/1.4795575.
- [43] I.L. Violi, M.D. Perez, M.C. Fuertes, G.J.A.A. Soler-Illia, Highly ordered, accessible and nanocrystalline mesoporous TiO₂ thin films on transparent conductive substrates, ACS Appl. Mater. Interfaces 4 (2012) 4320–4330, https://doi.org/ 10.1021/am300990p.
- [44] C.C. Fernández, D. Wechsler, O. Lytken, H.P. Steinrück, F.J. Williams, Selfmetalation of monophosphonic acid tetraphenylporphyrin on TiO₂(110)-(1 × 1), Surf. Sci. 717 (2022) 122005, https://doi.org/10.1016/J.SUSC.2021.122005.
- [45] E. de la Llave, R. Clarenc, D.J. Schiffrin, F.J. Williams, Organization of alkane amines on a gold surface: structure, surface dipole, and electron transfer, J. Phys. Chem. C 118 (2013) 468–475, https://doi.org/10.1021/jp410086b.
- [46] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Phys. Rev. B 47 (1993) 558, https://doi.org/10.1103/PhysRevB.47.558.
- [47] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1996) 15–50, https://doi.org/10.1016/0927-0256(96)00008-0.
- [48] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169, https:// doi.org/10.1103/PhysRevB.54.11169.
- [49] P.E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953, https://doi.org/10.1103/PhysRevB.50.17953.
- [50] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865, https://doi.org/10.1103/ PhysRevLett.77.3865.
- [51] S. Grimme, Semiempirical GGA-type density functional constructed with a longrange dispersion correction, J. Comput. Chem. 27 (2006) 1787–1799, https://doi. org/10.1002/JCC.20495.
- [52] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Electronenergy-loss spectra and the structural stability of nickel oxide: an LSDA + U study, Phys. Rev. B 57 (1998) 1505, https://doi.org/10.1103/PhysRevB.57.1505.
- [53] E. German, R. Faccio, A.W. Mombrú, Comparison of standard DFT and Hubbard-DFT methods in structural and electronic properties of TiO₂ polymorphs and Htitanate ultrathin sheets for DSSC application, Appl. Surf. Sci. 428 (2018) 118–123, https://doi.org/10.1016/J.APSUSC.2017.09.141.
- [54] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188, https://doi.org/10.1103/PhysRevB.13.5188.
- [55] N.D. Lang, W. Kohn, Theory of metal surfaces: work Function, Phys. Rev. B 3 (1971) 1215, https://doi.org/10.1103/PhysRevB.3.1215.
- [56] S.I. Gorelsky, E.S. Dodsworth, A.B.P. Lever, A.A. Vlcek, Trends in metal-ligand orbital mixing in generic series of ruthenium N-donor ligand complexes—Effect on electronic spectra and redox properties, Coord. Chem. Rev. 174 (1998) 469–494, https://doi.org/10.1016/S0010-8545(98)00144-1.
- [57] A.B.P. Lever, Electrochemical parametrization of metal complex redox potentials, using the Ruthenium(III)/Ruthenium(II) couple to generate a ligand electrochemical series, Inorg. Chem. 29 (1990) 1271–1285, https://doi.org/ 10.1021/ic00331a030.
- [58] E. Sondaz, A. Gourdon, J.P. Launay, J. Bonvoisin, (Bipyridine)(terpyridine)(4iodophenylcyanamide)ruthenium(II) complex: crystallography, electronic absorption spectroscopy, cyclic voltammetry and EPR measurements, Inorg. Chim. Acta 316 (2001) 79–88, https://doi.org/10.1016/S0020-1693(01)00382-6.
- [59] M. Maestri, N. Armaroli, V. Balzani, E.C. Constable, A.M.W.C. Thompson, Complexes of the Ruthenium(II)-2,2':6',2" -terpyridine family. Effect of electronaccepting and -donating substituents on the photophysical and electrochemical properties, Inorg. Chem. 34 (1995) 2759–2767, https://doi.org/10.1021/ ic00114a039.
- [60] P.S. Oviedo, G.E. Pieslinger, A. Cadranel, L.M. Baraldo, Exploring the localized to delocalized transition in non-symmetric bimetallic ruthenium polypyridines, Dalt. Trans. 46 (2017) 15757–15768, https://doi.org/10.1039/c7dt02422c.
- [61] S.E. Domínguez, M.V. Juarez, G.E. Pieslinger, L.M. Baraldo, A strongly coupled biruthenium complex as catalyst for the water oxidation reaction, Eur. J. Inorg. Chem. 2022 (2022) 1–9, https://doi.org/10.1002/ejic.202100843.
- [62] M.A. Bork, H.B. Vibbert, D.J. Stewart, P.E. Fanwick, D.R. McMillin, Varying substituents and solvents to maximize the luminescence from [Ru(trpy)(bpy)CN]+ derivatives, Inorg. Chem. 52 (2013) 12553–12560, https://doi.org/10.1021/ ic4016367.
- [63] J. Balajka, M.A. Hines, W.J.I. DeBenedetti, M. Komora, J. Pavelec, M. Schmid, U. Diebold, High-affinity adsorption leads to molecularly ordered interfaces on TiO₂ in air and solution, Science 361 (2018) 786–789, https://doi.org/10.1126/ science.aat6752 (1979).
- [64] M. Wagstaffe, A.G. Thomas, M.J. Jackman, M. Torres-Molina, K.L. Syres, K. Handrup, An experimental investigation of the adsorption of a phosphonic acid on the anatase TiO₂(101) surface, J. Phys. Chem. C 120 (2016) 1693–1700, https://doi.org/10.1021/acs.jpcc.5b11258.
- [65] L. Patthey, H. Rensmo, P. Persson, K. Westermark, L. Vayssieres, A. Stashans, Å. Petersson, P.A. Brühwiler, H. Siegbahn, S. Lunell, N. Martenson, Adsorption of

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bi-isonicotinic acid on rutile TiO₂ (110), J. Chem. Phys. 110 (1999) 5913–5918, https://doi.org/10.1063/1.478491.

- [66] F. Persson, A. Stashans, R. Bergström, S. Lunell, Periodic INDO calculations of organic adsorbates on a TiO₂ surface, Int. J. Quantum Chem. 70 (1998) 1037–1043, https://doi.org/10.1002/(SICI)1097-461X(1998)70:4/5%3C1055:: AID-QUA53%3E3.0.CO;2-0.
- [67] H. Rensmo, K. Westermark, S. Södergren, O. Kohle, P. Persson, S. Lunell, H. Siegbahn, XPS studies of Ru-polypyridine complexes for solar cell applications, J. Chem. Phys. 111 (1999) 2744–2750, https://doi.org/10.1063/1.479551.
- [68] E.M.J. Johansson, M. Hedlund, H. Siegbahn, H. Rensmo, Electronic and molecular surface structure of Ru(tcterpy)(NCS)₃ and Ru(dcbpy)₂(NCS)₂ adsorbed from solution onto nanostructured TiO₂: a photoelectron spectroscopy study, J. Phys. Chem. B 109 (2005) 22256–22263, https://doi.org/10.1021/JP0525282.
- [69] R.E. Shepherd, A. Proctor, W.W. Henderson, T.K. Myser, Assessment of the .pi.acceptor capability of selected ligands based on the photoelectron spectra of ruthenium ammine complexes, Inorg. Chem. 26 (2002) 2440–2444, https://doi. org/10.1021/IC00262A021.
- [70] A. Cano, Y. Avila, M. Avila, E. Reguera, Structural information contained in the XPS spectra of nd10 metal cyanides, J. Solid State Chem. 276 (2019) 339–344, https://doi.org/10.1016/j.jssc.2019.05.021.
- [71] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z. Li, J. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, F. Besenbacher, The role of interstitial sites in the Ti3d defect state in the band gap of titania, Science 320 (2008) 1755–1759, https://doi.org/10.1126/science.1159846 (1979).
- [72] J.E. Whitten, Ultraviolet photoelectron spectroscopy: practical aspects and best practices, Appl. Surf. Sci. Adv. 13 (2023) 100384, https://doi.org/10.1016/j. apsadv.2023.100384.