Adsorption of Sensitizer into Surface of TiO₂ from the Form of Carboxylic Ester Group Anchor

ZABRI Hervé
Laboratoire de Chimie BioOrganique et de Substances Naturelles, UFR-SFA
Université d’Abobo-Adjamé, 02 BP 801 Abidjan 02, Côte d’Ivoire

Abstract: Transition metal complexes composed of a central ruthenium cation liganded by one thiocyanato, one 4,4'-((diethoxycarbonyl)-2,2'-bipyridine or 4,4'-((diacidecarboxylic)-2,2'-bipyridine and one 4'-toly1-2,2'-6',2''-terpyridine are synthesized with good yield. The aim is to realise adsorption of dye from ester form of anchorage group into TiO₂ surface. IR steady of nanocristalline TiO₂ sensitized and UV-visible absorption spectroscopy of dyes ester and acid showed that it is possible to obtain chemical reaction between ester group of ruthenium complex and TiO₂ like acid group of complex with TiO₂. We chemisorbed the sensitizer ester directly after cooling dye on dioxane solution with TiO₂ at 80 °C during 4 hours. The chemical link is considered to be bidentate anchorage like chelating or ponting.

Key words: photovoltaic, complex, sensitizer, acid, ester, adsorption, TiO₂

INTRODUCTION

The development of molecular systems capable of converting solar energy into electricity and achieve energy storage attracting increasing groups of researchers (Wasielewski and Chem, 1992; Grust et al., 2001; Kurreek et al., 1995; Balzani et al., 2001; Durr et al., 2001; Bard et al., 1995). Photovoltaic cells DSSC type in English Dye Sensitizer Solar Cells, represent a promising opportunity for an alternative photovoltaic and hence for the fight against pollution is to the quality of the environment due to its simplicity of approach. This device called (Hagfeldt et al., 2000; Gratzel and Nature, 2001) Grätzel cell consists of a semiconductor broadband prohibited, usually titanium dioxide, TiO₂ white origin. TiO₂ is coated with a dye whose role is to collect the maximum wavelength of white light. The dye, sensitizer, is central performance of the cell injection of electrons into the conduction band of TiO₂. In general, the attachment of sensitisers on TiO₂ is from the acid form of the anchor. For reasons of solubility in organic solvents, the method is to prepare the first ester form more soluble in common solvents and hydrolyze the esters by strong acids. The structure of target molecules, the complex thiocyanate 4'-toly1-2, 2'; 6'; 2''-terpyridine (4,4'-dicarboxylate diethyl-2, 2'-bipyridine) ruthenium complex 28 and thiocyanate 4'-toly1-2, 2'; 6'; 2''-terpyridine (4,4'-dicarboxylic acid-2, 2'-bipyridine) ruthenium 30, consists of one share of a 2,2' bipyridine-based carrier of carboxylic ester (28) or carboxylic acid functions (30), in position 4 and 4', and partly of a molecule of 4'-toly1-2, 2'; 6', 2 terpiridine'. These two systems and a pyridine molecule thiocyanate focus on one atom of ruthenium (Figure 1).

Fig. 1: Structure of ruthenium complex 28 and 30 surveyed
The synthesis of target compounds 28 and 30 is described in literature (Fabrice). The originality of the strategy is to achieve a method of binding sensitizers directly from the ester form, which seems to have never been described. Yet it would be advantageous for at least three reasons. First, this strategy a step would reduce the synthesis of dyes, since the hydrolysis reaction is no longer necessary. Secondly, the risk of deterioration of sensitizer by heating under acidic or basic would be avoided. Moreover, it would overcome the purification of sensitizer form carboxylic acid, often painful because of the polarity and low solubility of the compound.

An article published in 2001 Viox et al., (2001). Shows that it is possible to chimisorber phenyl phosphonate ester on TiO₂ particles heated by reflux of these compounds in toluene. Knowing that the phosphonic ester is much more resistant to hydrolysis than the carboxylic acid ester, it seems that this objective could be achieved under mild conditions. As a measure of IR spectroscopy sensitizers of only 28 or 30 or chimisorbés on TiO₂, it is possible to compare the forms of liaison anchor. A study of absorption spectroscopy performed on the dye adsorbed on TiO₂ would conclude on our method of adsorption from the ester form.

Experimental:

2.1. uv-visible Spectrometry:
Solvants were carefully distilled just before the UV-visible. These solvents are kept by standard methods. Measurements were made with a UV-2401PC Shindzu and Perkin-Elmer Lamba 40 spectrophotometer.

Photoanodes Preparation of Titanium Dioxide:
Solutions of colloidal TiO₂ are prepared by hydrolysis of isopropoxyde titanium, Ti (OCH₂(CH₃)₂)₄ (fulka). 50 mL of this solution are added, drop by drop, to 300 mL of distilled water acidified with 2.1 mL HNO₃ to 65% under vigorous stirring. The mixture is kept under agitation for 8 hours at 80 ° C. During the reaction, the volume of the mixture is reduced to 120 mL, corresponding to a concentration of TiO₂ 170 g / L. 50 mL of this solution is heated to 220 ° C in an autoclave for 12 hours. After cooling particles at room temperature, 3 g Carbowax 2000 (Aldrich) are added to the resulting gel, and then the mixture is shaken at room temperature for 8 hours.

The driver is a glass covered, on one side, an adhesive. The TiO₂ film is applied to the face in order to maintain fixed glass driver. The electrode is left some time in the air to dry and then heated to 450 ° C for 30 minutes in the presence of air.

Chemisorption Complexes on TiO₂ from the Carboxylic Acid:
The sensitizer is solubilised in a mixture dichloromethane / methanol (8 / 2) and TiO₂ electrode was immersed for one night. The electrode is then rinsed by DMF, a mixture dichloromethane / methanol (8 / 2), and finally dichloromethane.

Chemisorption Complexes on TiO₂ from the Carboxylic Ester:
The sensitizer is solubilised in 5 mL dioxane in a 20 mL flask and TiO₂ electrode is immersed and then heated to 80 ° C in the home to light for 4 hours. The electrode is then rinsed by DMF, a mixture dichloromethane / methanol (8 / 2) and finally dichloromethane pure.

IR Spectroscopy:
For infrared studies, 20 mg TiO₂ (Degussa P25) are added to 3 mL of a solution sensitiser (approximately 10-3 M). The mixture is heated to 80 ° C for 4 hours and then filtered. TiO₂ powder color is washed with DMF, ethanol, dichloromethane and finally diethyl ether. The precipitate is dried under vacuum ramp for 4 hours.

RESULTS AND DISCUSSION

Synthèse:
The preparation of 2,2 'bipyridine functionalized in position 4 and 4' by groups or carboxylic acid éthylcarbonyl have not been described in the procedure by which the laboratory synthesis possessed a large quantity. The synthetic route used is described by the littérature (Breault et al., 1998; Hammarstrom et al., 1997). It involves reducing the dimerization of picoline by the nickel Ramey (Sasse and Org, 1996). There are few examples in literature describing the preparation of ruthenium complex ligands by one bipyridine. Articles describing such molecule corresponds to the work on the synthesis of complex hétéroleptiques of ruthénium (Freedmann et al., 2001; Zakeeruddin et al., 1998; Hesek et al., 2000; Treadway et al., 1999). Various strategies have been developed for this purpose, apart from the soft Grätzel et al., (2003) presented the conditions were not suitable for the training of our complex ruthenium (II). The (2,2 'bipyridine) -4,4'-
dicarboxylate Diethyl) dichloro bis (dimethylsulfoxide) ruthenium (II) 24 that we have prepared is an important because of the presence of hydrolysable esters. We are based on the method of preparation of complex ruthenium (II) bis (dimethylsulfoxide) Dichloro (4,4’-dimethyl-2, 2’-bipyridine) through the strategy Zakeeruddin 18. NMR compound 24 gives two cis and trans. In the trans configuration, the two pyridines of bipyridines are magnetically equivalent, while in the cis, one of pyridines is close to a chlorine and the other east of DMSO (see Figure 2).

This mixture of isomers is not an embarrassment in view of their future use. The complex 28, carboxylic ester with thiocyanate ligand was prepared from his chlorinated, with a good yield of 75%. The complex 30 with a carboxylic acid thiocyanate was obtained using a quantitative as sensitiser acid is insoluble in water and sparingly soluble in common solvents except DMF and DMSO.

The IR Spectra after Adsorption of Sensitisers on TiO₂:
The complex features 30 with carboxylic acids, was chimisorbé on TiO₂ electrode by soaking overnight at room temperature (method). The electrode is initially transparent color of an intense purple color. The particle filter and a series of rinsing abundant by various solvents used to remove particles that have been physisorbés. The complex includes 28 functions esters carboxylates, unlike compound 30, was adsorbed hot in different solvents (dioxane, dichloromethane, DME and THF). The electrodes were obtained colored also rinsed thoroughly in different solvents.

The IR spectra of TiO₂ particles sensitized by the complex 28 or 30 or 30 single complex, are represented in Figure 3.
IR spectroscopy has been used to study the adsorption of molecules on surfaces of TiO\textsubscript{2}. In particular, there are several detailed articles relating to the study of IR sensibilisateur N3 19-23 or ruthenium complex panchromique 24 after adsorption of them on TiO\textsubscript{2}. The registration of the IR spectrum was made on the spectral range 400 - 4000 cm\textsuperscript{-1}. The IR spectrum of complex 30 contains a number of characteristic bands between 2200 - 1200 cm\textsuperscript{-1} (see diagram). A frequency of 2103 cm\textsuperscript{-1}, an intense band is attributed to the vibration of thiocyanate. A frequency of 1724 cm\textsuperscript{-1}, another intense band is the carboxyl group. The region 1200 - 1600 cm\textsuperscript{-1} is dominated by gangs elongation of pseudo-double bonds cycle Pyridine (including 1606, 1469, 1428, 1320 cm\textsuperscript{-1}). Pursuant to what is described in the literature (Sayana \textit{et al.}, 1998; Yanagida \textit{et al.}, 2003; Falaras \textit{et al.}, 1998; Hugot-Le Goff \textit{et al.}, 1999; Bauer \textit{et al.}, 2002; Persson \textit{et al.}, 2000), after chemisorption of TiO\textsubscript{2} awareness, we can see a change in the IR spectrum in three bands.

First, the carbonyl band at 1720 cm\textsuperscript{-1} has almost disappeared, indicating that no or very little light carboxylic acid ester or free. This band is intense absorbance at this frequency would be significant if the complex had just physisorbeh on the surface of TiO\textsubscript{2} by hydrogen bonds or electrostatic. We can therefore conclude that there are chemisorption TiO\textsubscript{2} after contact with a solution of 30 sensitiser at room temperature or with a solution of 28 sensitiser in dioxane heated to 80 °C for 4 hours. The disappearance of the carbonyl band varies depending on the solvent used. The best results are obtained with dioxane while with dry solvents such as dichloromethane, THF or DME, we can see the persistence of the band at 1720 cm\textsuperscript{-1}. With these, the adsorption of the complex 28, is not complete and / or mode of engagement is different from that obtained from the acid form. As against, with dioxane adsorption is conclusive.

Secondly, after adsorbing sensitiser, it appears around 1600 cm\textsuperscript{-1} band corresponding to intense vibration asymmetrical group OC = O (vs (OC = O)). We can see a significant increase in absorbance around 1610 cm\textsuperscript{-1} after the dye adsorption on TiO\textsubscript{2} (cf. Figure 3). The complex has a free low absorbance at this frequency and even more significant if one compares the intensity of this band to that of thiocyanate vibrator.

Third, previous studies conducted on the N3 sensitizer adsorption on TiO\textsubscript{2}, show the emergence of a large and intense band around 1380 cm\textsuperscript{-1}, which corresponds to the symmetrical vibration OC = O (vs (OC = O)). We can see that, whatever the technique of adsorption (acid form at room temperature or hot ester form), the IR spectrum of TiO\textsubscript{2} exhibits the same characteristics which are: the disappearance of carbonyl vibrator, the emergence of two new bands intense 1610 cm\textsuperscript{-1} and 1385 cm\textsuperscript{-1}, corresponding to symmetric and asymmetric vibration of the OC = O. The IR spectrum can be regarded as an indelible borrows the state obtained. The same position the last two bands are independent of the method of adsorption, it allows us to conclude that the state of chemisorption of sensitisers on TiO\textsubscript{2} must be similar in both methods. By way of comparison, the IR spectrum of compound N3 adsorbed on TiO\textsubscript{2}, and recently published by Arakawa \textit{et al.} (2003). We can see the similarity of these spectra with those registered with the complex 28 and 30. In our case we see a band protruding additional to 1650 cm\textsuperscript{-1} which is attributed to the vibration of hydroxyl TiO\textsubscript{2}, because our samples were probably hydrated. This band is actually in the IR spectrum of TiO\textsubscript{2} free. The spectrum of semiconductor colored N3 this band and 1722 cm\textsuperscript{-1}, indicating the presence of carboxylic acid functions libres (Falaras \textit{et al.}, 1998) because, given the geometry of these four functions, it is impossible that they are all engaged in an affair with TiO\textsubscript{2}. In the case of compounds 28 and 30, the bipyridine probably bind simultaneously by the two carboxylic functions.

It is recognized that there are three modes anchor possible sensitiser (Sayana \textit{et al.}, 1998; Yanagida \textit{et al.}, 2003; Falaras \textit{et al.}, 1998; Hugot-Le Goff \textit{et al.}, 1999; Bauer \textit{et al.}, 2002; Persson \textit{et al.}, 2000) on TiO\textsubscript{2}: the mode Monodentate type ester method bidentate bridging and chelating bitantate (see Figure 4).

The difference in frequency $\Delta$vas-s between the frequency of vibration of asymmetric OC = O group and symmetrical vibration frequency was used to distinguish these three modes of anchoring 19. It was shown 19 \textit{IN} $\Delta$vas-s (Monodentate ester)$\Delta$vas-s (bridging bidentate)$\Delta$vas-s (chelating bidentate). The IR measurements with the N3 sensitizer adsorbed on TiO\textsubscript{2} form acid leads to a value-s $\Delta$vas between 220 - 250 cm\textsuperscript{-1} (Sayana \textit{et al.}, 1998; Yanagida \textit{et al.}, 2003; Falaras \textit{et al.}, 1998). Based on this value, the authors conclude that an anchor-type chelating bidentate or bridging. For complex 28 and 30, the IR can calculate a value-$\Delta$vas $s = 225$ cm\textsuperscript{-1}, leading us to the same mode of coordination of the carboxylic group that obtained with the N3 sensitizer.

\textbf{Uv-visible Spectrometry of TiO\textsubscript{2} Electrode Sensitized by the Complex 28 and 30:}

The registration of the absorption spectrum of UV-visible electrode sensitized TiO\textsubscript{2} colors 28 and 30 reinforces our observations. We can see that the electronic absorption spectra of TiO\textsubscript{2} electrodes are substantially identical regardless of the method of adsorption (see Figure 5). The position of maximum absorption of the MLCT band (in English Metal to Ligand Charge Transfer) is little affected by the method of deposit, indicating that the final adsorbing sensitiser is almost identical by both methods.
Fig. 4: Illustration of three modes liaison with carboxylic group TiO$_2$: a = Monodentate ester type b = bidentate bridging type c = type chelating bidentate

Fig. 5: Absorption spectrum of complex 28 and 30 on TiO$_2$. Continuous line: adsorption from the acid form (30). Dotted: adsorption from the ester form (28) by heating for 4 hours in dioxane.

The maximum absorption of the MLCT band is located at 511 nm after adsorption complex TiO$_2$, whereas in the DMF solution in this transition appears at 503 nm and 522 nm respectively in the acid form (30) and the ester form (28) (Cf. Figure 6).

The absorption spectrum of focus on p - p ruthenium complex is dominated by three main bands. Transitions terpyridine ligand in the UV region and two MLCT bands between 350 and 550 nm. These gangs are moving to replace the blue when the ligand chlorine by thiocyanate ligand, as can be seen by comparing the spectra of the complexes 27 donor and p and s and 28 and then 29 and 30, because the chlorine ligand is more than thiocyanate 25. Hydrolysis of esters function also causes a shift hypsochrome because of the electroattracteur lowest CO$_2$H group compared the CO$_2$Et group.

This suggests that the state's electronic sensitizer after latching on TiO$_2$ is different from the complex 28 and complex 30 in solution. It can be seen as an intermediary between these two molecules.

Conclusion:
Adsortion on TiO$_2$ awareness holders functions carboxylic esters can be obtained simply by heating to 80 °C for 4 hours in dioxane. The mode of connection between the ruthenium complex ester and TiO$_2$ is identical to that obtained by adsorption from the classical form acid. It can be described as a chelating bidentate or bridging. This result is quite exciting because it allows you to work directly from the ester form much more soluble in common solvents therefore more easily manipulated. In addition, it avoids the hydrolysis sensitizers which remains a painful step inducing loss products. One can even imagine the replacement of the ethyl ester of the carboxylic group by the tert-butyl, this should help to lower the temperature adsorption because it is more easily hydrolyzable.
Fig. 6: Superposition of the absorption spectra measured in solution of the complex. Composition 27 (complex carrying a chlorine ester, black curve), comprising 28 (complex ester holder a thiocyanate, blue curve), comprising 29 (acid complex carrying chlorine, green curve) and made 30 (acid complex bearer thiocyanate, red curve)

ACKNOWLEDGMENT

The Laboratory of Organic Synthesis of the University of Nantes to have achieved the work that led to my PHD.

REFERENCES

Fabrice ODOBEL and Hervé ZABRI