Chemically Modified Electrodes: Tin(IV) Oxide Electrodes Surface Modified with Immobilized Bis(2,2′-bipyridine)-(2,2′-bipyridine-4,4′-dicarboxylato)ruthenium(II). Part 1. Synthesis and Characterization *

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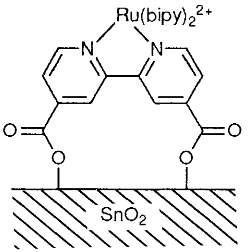
Four different synthetic routes (based upon esterification) result in the immobilization of [Ru(bipy)$_2$(bpdc)] (bipy = 2,2′-bipyridine, H$_2$bpdc = 2,2′-bipyridine-4,4′-dicarboxylic acid) upon the surface of polycrystalline tin(IV) oxide electrodes. These processes have been compared for efficacy with each other, and with a related silylation modification method. Multilayer, monolayer and submonolayer coverages can be achieved by appropriate selection of experimental conditions. The chemically modified electrodes were characterized by X-ray photoelectron spectroscopy and scanning electron microscopy, and their chemical stability investigated under a wide variety of conditions.

During the past ten years, a large number of immobilization procedures and characterization techniques have been developed for chemically modified electrodes,[1–4] and the inclusion of ruthenium-based electrocatalysts into polymeric films is being actively pursued.[5–7] We describe here the preparation, characterization and stability of chemically modified tin(IV) oxide electrodes, **1**, bearing a 2,2′-bipyridine complex of ruthenium which has been immobilized by an esterification technique. Electrodes of this type have possible applications in both the areas of photoelectrolysis and electrocatalysis.



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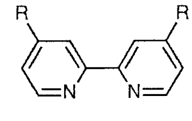

R	
H	bipy
CO$_2$H	H$_2$bpdc
COCl	bpcc

We have previously demonstrated[8,9] that [Ru(bipy)$_2$(bpdc)] (bipy = 2,2′-bipyridine, H$_2$bpdc = 2,2′-bipyridine-4,4′-dicarboxylic acid) acts as a sensitizer for the photoelectrolysis of water, when immobilized at a titanium(IV) oxide electrode by esterification. Here, the type of electrode used in this work is fully characterized for the first time.

A number of 2,2′-bipyridine complexes of ruthenium have been shown to act as electrocatalytic oxidants. Thus [Ru(bipy)$_2$(NO$_2$)Cl] and [Ru(bipy)$_2$(NO$_2$)(py)]$^+$ (py = pyridine) will electrocatalytically oxidize triphenylphosphine to triphenylphosphine oxide[10] and [Ru(bipy)(terpy)O]$^{2+}$ (terpy = 2,2′:6′,2″-terpyridine) will electrocatalytically oxidize a number of organic substrates.[11] Since many chemical and electrochemical reactions can be reproduced at chemically modified surfaces,[7,12–14] we have here the possibility of preparing useful electrocatalytic electrodes by immobilization of analogues of the above complexes.[9,15] Thus it is important to investigate fully any method that could be used to immobilize these, or related, types of complexes. Esterification techniques similar to those employed in this work have been previously found to be inferior to the more popular silylation technique[2] for the immobilization of aromatic organic compounds.[16] Here we show that esterification is of at least comparable efficacy to silylation for the immobilization of [Ru(bipy)$_2$(bpdc)]. This paper is the first of three concerned with the preparation and properties of electrodes modified as in **1**: the subsequent papers concern the electrochemical[17] and photophysical[18] properties of these electrodes.

Experimental

General Procedures.—The electrochemical techniques and equipment used will be described in a subsequent paper.[17] Scanning electron microscopy was performed using a JEOL 100C microscope; an electron-beam energy of 100 keV was used. X-Ray photoelectron spectroscopic measurements were performed using a Vacuum Generators ESCALAB 5 instrument; Mg-Kα radiation was used, generated at 15 kV by a current of 10 mA.

Gold Label (*ex* Aldrich) nitromethane and ethanenitrile and reagent grade trichloromethane and dichloromethane were distilled from P$_2$O$_5$ immediately prior to use. Aristar grade sulphuric acid was used to prepare aqueous electrolytes for electrochemical experiments. All other solvents and chemicals were of at least reagent grade and used as received. The compounds [Ru(bipy)$_2$Cl$_2$],[19] H$_2$bpdc[20] and [Ru(bipy)$_2$(bpdc)][20] were prepared as described elsewhere.

Electrode Preparation.—The tin(IV) oxide electrodes used in this work were prepared by a method similar to that described by Kim and Laitinen.[21] They consisted of a glass disc coated

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* *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

with a thin film (*ca.* 500 nm) of polycrystalline SnO_2 doped with approximately 6 mol % antimony(III), to give optimum *n*-type conductivity.[22] Such electrodes have been well characterized by Kuwana and co-workers.[23]

Three different types of glass disc were used. Pyrex discs (*ex* Wingents; diameter 5 mm, 0.5 mm thick) were used for the bulk of the electrochemical studies,[17] optical silica discs (*ex* Thermal Syndicate; diameter 20 mm, 1.5 mm thick) for the photochemical studies,[18] and glass discs (cut from microscope slides; diameter 13 mm, 1 mm thick) for the X-ray photoelectron spectroscopy (XPS) experiments.

The glass discs were soaked in a hot water–detergent mixture for several minutes to remove surface grease, rinsed well with distilled water, and air dried. They were then heated to approximately 500 °C (determined with a thermocouple) on a hot-plate and sprayed with an aqueous tin(IV) chloride solution containing antimony(III) chloride. This solution was 2.7 mol dm^{-3} in $SnCl_4$, 0.08 mol dm^{-3} in $SbCl_3$ and 0.8 mol dm^{-3} in hydrochloric acid [typically, $SnCl_4$ (8.85 cm^3), $SbCl_3$ (0.53 g) and hydrochloric acid (20 cm^3, 1.2 mol dm^{-3})].* The sprayer was a conventional all-glass atomizer, and compressed air was used to provide the spray pressure. A distance of >20 cm was maintained between the sprayer and the disc to prevent the gas stream from disturbing the substrate; this procedure was especially important for the optical silica discs, since for these only one side of the electrode was coated. Each spraying period (*ca.* 5 s) was followed by a few minutes waiting period, in order to prevent excessive cooling of the hot substrate; after each spraying period, the substrate was rotated clockwise through 90° to obtain a uniform thickness over the entire surface. The deposited film had an apparent colour, caused by an interference pattern from the reflected room light, and the spraying procedure was continued until the third red interference colour began to appear: this indicated that a film of thickness *ca.* 400 nm had been formed.

The temperature of the substrate was critically important to the nature of the electrode formed. If the temperature was too low (*i.e.* <500 °C) at the start of the spraying procedure then the film formed did not adhere strongly to the glass, and could be easily wiped off. If it was too high (*i.e.* >500 °C) during the spraying procedure a poorly conducting film was produced. Mechanically resistant, highly conducting electrodes were produced by heating the substrate to above 500 °C for the first few sprays, and then allowing the substrate to cool to *ca.* 400 °C for the remainder of the coating procedure.

Before being used, the cooled electrodes were pretreated by boiling in hexane for several minutes (to remove any grease), boiling in concentrated hydrochloric acid (10 min), washing with water, and drying at 80 °C for 2 h. Boiling the electrodes in acid served to remove any loose material from the surface, and to protonate surface hydroxylic sites (to produce as reproducible a surface as possible). This pretreatment procedure was also used to recycle used electrodes: it removed surface-immobilized complexes and ligands, and reactivated the surface for modification. No electrochemical or photochemical differences between freshly prepared and recycled electrodes were ever observed.

Electrode Modification.—Five different methods were used to attach ruthenium complexes to the surface of the tin(IV) oxide electrodes. In all cases the electrodes were pretreated as described above.

Method 1.[9] 2,2′-Bipyridine-4,4′-di(carbonyl chloride) was prepared *in situ*. Thus, 2,2′-bipyridine-4,4′-dicarboxylic acid (0.25 g, 1.0 mmol) was heated to reflux in sulphinyl chloride ($SOCl_2$, 25 cm^3) for 1.5 h. The sulphinyl chloride was then removed by distillation *in vacuo*. Trichloromethane (25 cm^3) was distilled from P_2O_5 and condensed onto the 2,2′-bipyridine-4,4′-di(carbonyl chloride) *in vacuo*. The SnO_2 electrode was then added to the solution, and the mixture heated under reflux for 1.5 h under dinitrogen. The electrode was then washed with trichloromethane and air dried.

The electrode was added to a solution of $[Ru(bipy)_2Cl_2]$ (0.1 g, 0.2 mmol) in, for example, aqueous ethanol (1:1 v/v). This was then heated under reflux for 2 h. The electrode was then removed, washed with ethanol and water, and air dried.

Method 2.[9] The compound $[Ru(bipy)_2(bpdc)]$ (0.15 g, 0.2 mmol) was suspended in dry nitromethane (25 cm^3) and dicyclohexylcarbodiimide (3 g) was added. The electrode was added, and the mixture was heated under reflux for 6 h. The electrode was removed from the solution, washed with nitromethane and trichloromethane and air dried.

Method 3. The compound $[Ru(bipy)_2(bpdc)]$ (0.15 g, 0.2 mmol) and the electrode were heated at reflux in sulphinyl chloride (25 cm^3) for 1.5 h. The electrode was removed from the solution, washed with dry nitromethane, methanol and water, and then air dried. In a variation upon this method, $[Ru(bipy)_2(H_2bpdc)][PF_6]_2$ was used instead of $[Ru(bipy)_2(bpdc)]$.

Method 4. The compound $[Ru(bipy)_2(bpcc)]Cl_2 \cdot 2SOCl_2$ was prepared by heating $[Ru(bipy)_2(bpdc)]$ (0.1 g, 0.15 mmol) in sulphinyl chloride (25 cm^3) under reflux for 1.5 h. The excess of $SOCl_2$ was removed by distillation *in vacuo* and the product used immediately (Found: C, 37.2; H, 2.5; Cl, 26.7; N, 7.9. Calc. for $C_{32}H_{22}Cl_8N_6O_4RuS_2$: C, 37.30; H, 2.20; Cl, 28.25; N, 8.4%).

Nitromethane (25 cm^3) was distilled from phosphorus(V) oxide and condensed onto the $[Ru(bipy)_2(bpcc)]Cl_2 \cdot 2SOCl_2$ *in vacuo*. The electrode was added to the solution, and it was then heated at reflux for 1.5 h. The electrode was then removed from the solution, washed with dry nitromethane, methanol and water, and finally air dried.

Method 5 (*silylation*).[15] The dried electrodes were placed in a serum-capped flask, which had been flushed with dry dinitrogen. They were washed with dry toluene and then treated under a positive dinitrogen pressure with a solution of [3-(2′-aminoethylamino)propyl]trimethoxysilane (1.6 cm^3) in dry toluene (20 cm^3) for 5 min. The electrodes were then washed six times with dry toluene, twice with dry ethanenitrile, and then air dried.

The electrodes were added to a solution of $[Ru(bipy)_2(H_2bpdc)][PF_6]_2$ (0.1 g, 0.1 mmol) and dicyclohexylcarbodiimide (1 g) in dry ethanenitrile (5 cm^3) and were allowed to react with this solution for 24 h at room temperature. They were then washed well with ethanenitrile, propanone, dichloromethane, methanol and finally water, and then air dried. As a variation upon this procedure, $[Ru(bipy)_2(bpdc)]$ was used in place of $[Ru(bipy)_2(H_2bpdc)][PF_6]_2$.

Results and Discussion

Methods of Electrode Modification.—One of the main aims of this work was to compare the chemical modification of metal oxide electrodes by esterification techniques with the more commonly used silylation methods, and to establish their chemical, physical, electrochemical and photophysical properties. The complex selected for immobilization was $[Ru(bipy)_2(bpdc)]$: as well as its desired structural relationship to molecules of interest for the photochemical oxidation of water,[8,9,24] the molecule is reasonably chemically inert, is stable under a wide range of conditions, gives rise to reversible electrochemical characteristics, and has an intense and characteristic electronic absorption spectrum. Tin(IV) oxide was chosen as the substrate because it can be doped to a highly conducting state, and also because it is optically transparent across the visible region of the electromagnetic spectrum.

Five methods for the attachment of $[Ru(bipy)_2(bpdc)]$ to

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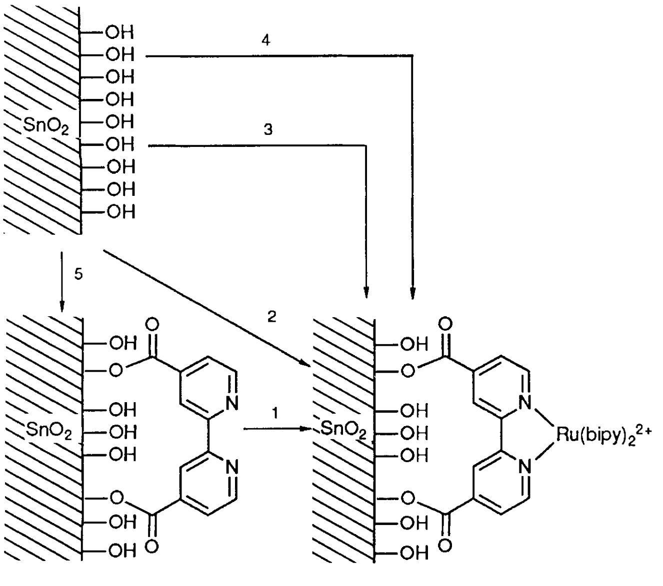
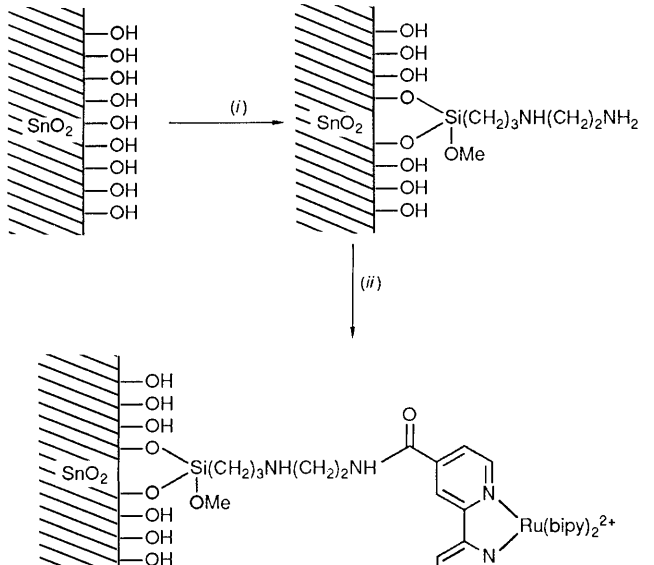
* It is important to note that a 3 mol % $SbCl_3$ solution is required in the spray mixture to produce a 6 mol % antimony doping level in the SnO_2 film.[22]



2 **1**

Scheme 1 Four different esterification methods (1–4) for the synthesis of chemically modified tin(IV) oxide electrodes, as in **1**. 1 [Ru(bipy)$_2$Cl$_2$]; 2 [Ru(bipy)$_2$(bpdc)], dcc; 3 (Ru(bipy)$_2$(bpdc)], SOCl$_2$; 4 [Ru(bipy)$_2$(bpcc)]$^{2+}$; 5 bpcc



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Scheme 2 A silylation method[15] (5) for the synthesis of chemically modified tin(IV) oxide electrodes, as in **3**; R represents O$^-$, OH or a second immobilized amine functionality. (i) (MeO)$_3$Si(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$; (ii) [Ru(bipy)$_2$(H$_2$bpdc)]$^{2+}$

SnO$_2$ electrodes were employed. Four different esterification methods (see Scheme 1) were used in order to achieve the same target result, **1**, and a literature[15] silylation method (see Scheme 2) was used to produce a close analogue, **3**, for comparison. These methods, and their success in achieving their aims, are now discussed in more detail.

Assessment of the Five Different Modification Methods.—Each method was assessed in terms of the surface coverage that it produced. This was determined (using the method to be described in a subsequent paper[17]) from the area under the oxidation wave in the cyclic voltammogram of the immobilized complex (measured in 0.1 mol dm^{-3} H$_2$SO$_4$). The meaning of a monolayer with respect to this system will be discussed in ref. 17.

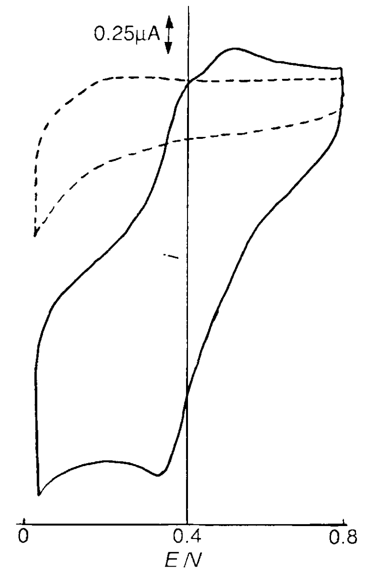


Fig. 1 D.c. cyclic voltammograms (v = 50 mV s^{-1}, ambient temperature) of an unmodified SnO$_2$ electrode (– – – –) and a SnO$_2$ electrode modified as in **2** (——) in aqueous potassium chloride solution (0.1 mol dm^{-3}), after exposure to aqueous silver(I) nitrate solution (0.1 mol dm^{-3}) for 5 min

(i) *Method* 1. This procedure consists of two steps. The first step involves treatment of the SnO$_2$ electrode with 2,2′-bipyridine-4,4′-di(carbonyl chloride) (bpcc) to form a modified electrode as illustrated in Scheme 1. This reaction is formally analogous to an organic esterification, the acid chloride bpcc reacting with a 'polyhydric alcohol' (the hydroxylic sites on the electrode surface). The second step involves treatment of this modified electrode (**2**, the surface of which may be considered as a polydentate ligand) with [Ru(bipy)$_2$Cl$_2$] to give an electrode modified as in **1**, in a reaction analogous to those used to produce mixed-ligand tris(diimine)ruthenium(II) complexes (*e.g.* refs. 20 and 25): [Ru(bipy)$_2$Cl$_2$] + L–L $\longrightarrow$ [Ru(bipy)$_2$(L–L)]Cl$_2$.

The highest surface coverage obtained by this method was only 0.2 × 10^{-10} mol cm^{-2} (*ca.* one seventh of a monolayer) and could be obtained by using either water or propanone as the solvent for the second step. Using nitromethane, trichloromethane, ethanenitrile or aqueous ethanol (1:1 v/v) as the solvent for the second step resulted in much lower surface coverage. In order to discover which of the two steps was primarily responsible for the low surface coverages, an electrode was treated with bpcc, according to the first step of this procedure, and then treated with an aqueous solution of silver(I) nitrate. It was washed well with water and its cyclic voltammogram (in 0.2 mol dm^{-3} aqueous KCl) was obtained. The result is shown in Fig. 1, together with the result of a control experiment with an unmodified SnO$_2$ electrode. A wave corresponding to bound silver(I),[26] which was absent in the control voltammogram, was detected at about 0.4 V. The area under the cathodic wave corresponds to *ca.* 3 × 10^{-10} mol cm^{-2} of bound silver(I), indicating that a high surface coverage of bpdc had been obtained in the first modification step.

Thus, it appears that the problem with method 1 lies in the second step. As [Ru(bipy)$_2$Cl$_2$] reacts with H$_2$bpdc under relatively mild conditions,[20] but sterically hindered ligands [such as 2-(2′-pyridyl)quinoline and 2,2′-biquinoline] require much higher temperatures to induce reaction,[27] it is perhaps not too surprising that the reaction of [Ru(bipy)$_2$Cl$_2$] with **2** is disfavoured under mild conditions. However, raising the temperature for this latter reaction in the presence of alcoholic solvents would increase the rate of solvolysis of the ester linkage, and be of little advantage.

(*ii*) *Method* 2. This procedure involves a one-step reaction in which the acid groups of $[Ru(bipy)_2(H_2bpdc)]^{2+}$ or the carboxylate groups of $[Ru(bipy)_2(bpdc)]$ are condensed with the surface hydroxyl groups of SnO_2, in the presence of dicyclohexylcarbodiimide (dcc).

The highest surface coverage obtained by this method was only 0.14×10^{-10} mol cm^{-2} (*ca.* one tenth of a monolayer). Similar or lower surface coverages were obtained under a variety of conditions (at room temperature or under reflux, in ethanenitrile or nitromethane) using either $[Ru(bipy)_2(H_2bpdc)]^{2+}$ or $[Ru(bipy)_2(bpdc)]$: the former complex was a more effective reagent than the latter. The low coverage obtained indicates that the surface coverage is limited by the mechanism of the action of dicyclohexylcarbodiimide. The mechanism of the action of dcc in promoting the reaction between carboxylic acids and alcohols is well known,[28] and the bulk of the *O*-acylurea intermediate formed between dcc and $[Ru(bipy)_2(H_2bpdc)]^{2+}$ must create a very sterically crowded transition state for the subsequent coupling reaction with the hydroxyl groups upon the electrode surface. In consequence, coupling will only be able to occur at the more exposed sites of the electrode surface.

(*iii*) *Method* 3. This procedure is also a one-step reaction, in which the salt bis(2,2′-bipyridine)[2,2′-bipyridine-4,4′-di(carbonyl chloride)]ruthenium(II) chloride, $[Ru(bipy)_2(bpcc)]Cl_2$, is formed *in situ* and condenses with the surface hydroxyl groups of the electrode. The solvent for the modification procedure is $SOCl_2$.

A single modification by this method consistently produces a surface coverage of about 0.2×10^{-10} mol cm^{-2} (*ca.* one seventh of a monolayer). The use of $[Ru(bipy)_2(H_2bpdc)][PF_6]_2$ in place of $[Ru(bipy)_2(bpdc)]$ produces inferior (*ca.* 0.1×10^{-10} mol cm^{-2}) surface coverage, presumably due to its lower solubility in sulphinyl chloride. Higher surface coverage (*ca.* 0.6×10^{-10} mol cm^{-2}) can be obtained by exposing the modified electrode to 0.1 mol dm^{-3} sulphuric acid and then repeating the modification procedure. These results are consistent with a deactivation (by dehydration) of the tin(IV) oxide surface by sulphinyl chloride during the modification reaction.

(*iv*) *Method* 4. This procedure is another one-step reaction in which the isolated salt bis(2,2′-bipyridine)[2,2′-bipyridine-4,4′-di(carbonyl chloride)]ruthenium(II) chloride is condensed with the surface hydroxyl groups upon the electrode surface, in a solvent other than $SOCl_2$.

Using very dry nitromethane as a solvent for this reaction produces consistently high surface coverage of up to one monolayer. For ten samples modified in this way, surface coverages of between 0.6×10^{-10} and 1.4×10^{-10} mol cm^{-2} (average 0.8×10^{-10} mol cm^{-2}) were obtained. The use of $CHCl_3$, CH_2Cl_2 or CH_3CN as the solvent for the modification procedure gave greatly inferior surface coverage.

Repeated modifications of the same electrode, using the same batch of complex (after removal of solvent, drying and reactivation with $SOCl_2$), increased the surface coverage obtained up to a monolayer level (*ca.* 1.7×10^{-10} mol cm^{-2}, depending upon the degree of surface roughness). However, if the solvent was slightly wet [*i.e.* using dried nitromethane with 1 mol of water deliberately added per mol of ruthenium complex (0.008% w/w water) or using undried Gold Label (*ex.* Aldrich) nitromethane (<0.03% w/w water)], repeated modifications of the same electrode produced multilayers of immobilized ruthenium complex of up to thirty monolayers. Significantly higher levels of water added to the solvent produce no modification. Although the mechanism for multilayer formation has not been determined, a clear possibility is *via* the formation of an anhydride-based polymer [*i.e.* $RC(O)Cl + RC(O)OH \longrightarrow RC(O)OC(O)R + HCl$].

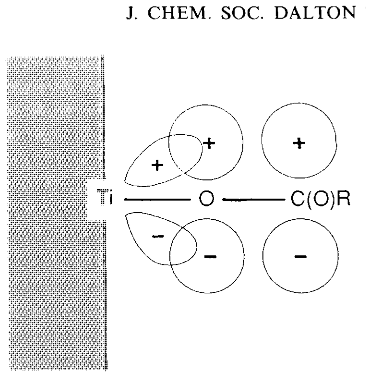


Fig. 2 A schematic representation of the π bonding between modified TiO_2 and the ester linkage

(*v*) *Method* 5. This procedure is summarized in Scheme 2: it was found to proceed as described by Murray and co-workers.[15] A surface coverage of 0.9×10^{-10} mol cm^{-2} was obtained. The compound $[Ru(bipy)_2(bpdc)]$ was found to be ineffective as a modifying reagent; the protonated form $[Ru(bipy)_2(H_2bpdc)][PF_6]_2$ was required to produce a significant surface coverage.

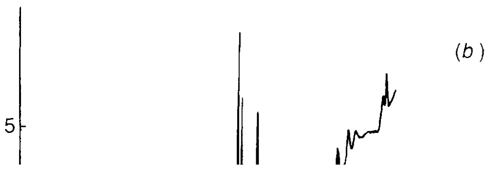
Comparative Discussion of Modification Procedures.—All five of the methods discussed above can be used to immobilize $[Ru(bipy)_2(bpdc)]$ on tin(IV) oxide. A complete monolayer coverage can only be obtained by methods 4 and 5. Method 5 has been discussed in detail elsewhere,[15] and is included here for comparison.

The failure to produce complete monolayer coverages by methods 1–3 is due to different causes for each method. Method 1 has been shown to give low surface coverages becuse of problems with the reaction of immobilized bpdc with $[Ru(bipy)_2Cl_2]$. Moreover, it has been found that solvents which promote this reaction (water and alcohols) also cause the removal of the $[Ru(bipy)_2(bpdc)]$, once formed, from the electrode surface. However, in contrast, this method has been used successfully to modify the surface of a single crystal of titanium(IV) oxide.[8,9] Approximately monolayer coverage of $[Ru(bipy)_2(bpdc)]$ on TiO_2 (as determined by both α-back-scattering spectrometry[29] and an analysis of the transients observed in its photocurrent *vs.* time response[8]) has been achieved using this method with ethanol–water (1:1 v/v) as the solvent for the second step.[29] Presumably the ester linkage to TiO_2 is more stable towards hydrolysis than that to SnO_2, due to a d_π–p_π contribution to the bonding in the former case (see Fig. 2).

Method 2 was found to be less effective than 1, as was also found for TiO_2 and SnO_2 powders.[27] The use of a bulky coupling agent (dicyclohexylcarbodiimide) for the surface esterification reaction means that only a fraction of the surface hydroxyl sites are available for modification in this way. It is interesting, however, that dcc is effective in method 5 for the coupling of $[Ru(bipy)_2(H_2bpdc)]^{2+}$ with the amine groups of an immobilized silane (see Scheme 2). Here the coupling reaction takes place well removed from the surface, thus removing the above steric restrictions.

It is clear that the problem with method 3 is the use of sulphinyl chloride as a solvent, since the desired reaction proceeds smoothly in nitromethane (method 4). The observation that two 1.5 h modifications (with interposed reactivation by exposure to aqueous sulphuric acid) produce a much higher surface coverage than a single 5-h modification indicates that the electrode surface becomes passive owing to dehydration by the sulphinyl chloride. In contrast, method 4 works well and gives high surface coverages and reproducible results. Its main disadvantage is that it requires the complex to be immobilized with $SOCl_2$, which means that complexes with labile ligands cannot be immobilized in this way.

The first four methods should all give modified electrodes that are indistinguishable from one another chemically, electrochemically and photophysically, as they should all result in the formation of a surface modified as in **1**. Indeed, the fact that we have been unable to distinguish between electrodes modified by each of these procedures strongly substantiates the proposed reactions (Scheme 1). The cyclic voltammograms



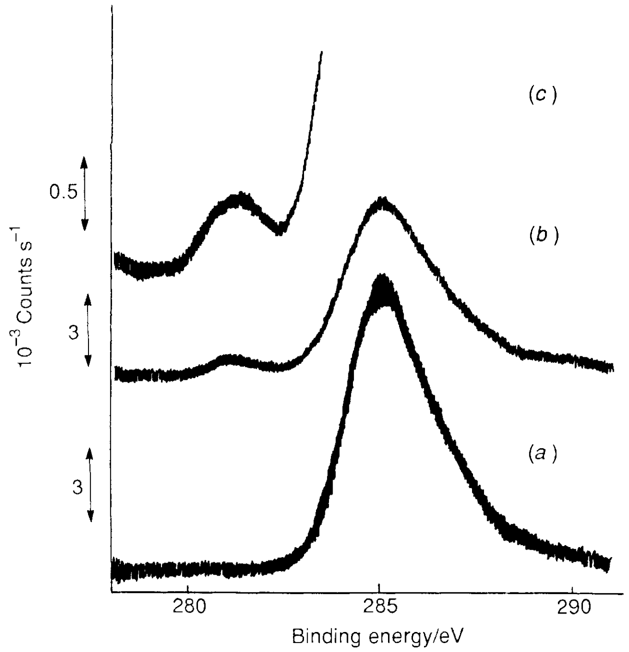


Fig. 4 X-Ray photoelectron spectra in the C 1s region for (*a*) an unmodified SnO_2 electrode, (*b*) a SnO_2 electrode modified as in **1** by method 4, and (*c*) a six-fold expansion of (*b*)

Table 1 Chemical stability of chemically modified electrodes prepared by method 4

	Chemical treatment			$10^{10}\ \Gamma_T{}^a$/mol cm^{-2}	
Sample	Solvent	*T*/°C	*t*/h	Before treatment	After treatment
1[b]	H_2SO_4[c]	22	5.0	0.43	0.38
2[b]	H_2SO_4[c]	22	12.5	3.00	1.23
	H_2SO_4[c]	22	6.5	1.23	0.78
	H_2SO_4[c]	22	2.5	0.78	0.65
	H_2SO_4[c]	22	17.0	0.65	0.48
3[b]	MeCN	Reflux	1.0	1.83	1.61
	Water	Reflux	0.08	1.61	0.27
	Water	Reflux	0.25	0.27	0.15
	Water	Reflux	1.0	0.15	0.05
4[b]	MeOH	Reflux	1.0	1.75	0.29
	MeOH	Reflux	1.0	0.29	0.15
5[d]	MeCN	*e*	8.0	9.7	2.9
	MeCN	*e*	8.0	2.9	2.7
6[d]	H_2SO_4[c]	22	2.0	3.6	1.7

[a] The surface coverage, measured electrochemically.[17] [b] Modified under anhydrous conditions. [c] Aqueous sulphuric acid (0.1 mol dm^{-3}). [d] Modified in the presence of small amounts of water. [e] Soxhlet extraction.

respectively. The polycrystalline nature of the surface can be observed and the real surface area is obviously much greater than the geometric surface area. Comparison of a number of samples showed that their surface roughness was very variable, thus making a definition of a surface-roughness factor for a generalized SnO_2 electrode difficult. Fig. 5(*c*) (× 20 000) and (*d*) (× 50 000) illustrate an electrode modified by method 2; the electrochemically measured surface coverage was 0.5 × 10^{-11} mol cm^{-2}. The structure of the electrode surface has clearly undergone significant change during the modification procedure, having become more angular and rougher. A consideration of sixteen similar pictures leads to an acceptable range for the roughness factor of 1.4–3.0.

In order to obtain a better comparison between a modified surface and an unmodified surface, an electrode was modified by method 4. The electrochemically measured surface coverage was 2.0 × 10^{-10} mol cm^{-2}. The ruthenium complex was then electrochemically removed from half of the electrode by the following procedure. Half of the electrode was covered with high-vacuum silicone grease (*ex.* Dow Corning), causing the area under the voltammogram to decrease. The electrode was then maintained at a potential of − 1.0 V in aqueous sulphuric acid (0.1 mol dm^{-3}) for 1 min, which induced an electrochemical dissolution of the SnO_2 and cleaned the surface of any immobilized molecules {as evidenced by the disappearance of the $[Ru(bipy)_2(bpdc)]$ wave}. The grease was then removed from the electrode [by washing with light petroleum (b.p. 60–80 °C)] in order to expose the still modifield half of the electrode. The presence of $[Ru(bipy)_2(bpdc)]$ on the protected half of the electrode was then confirmed by cyclic voltammetry. Thus, the electrode possessed a modified portion and an unmodified portion. Fig. 5(*e*) (× 100 000) illustrates the unmodified portion of the electrode, (*f*) (× 100 000) the modified section. It can be seen that reduction at − 1.0 V has brought about considerable damage to the surface and significantly changed its topology [Fig. 5(*a*) and (*b*)]. The poor resolution of Fig. 5(*f*) is not due to the resolution of the microscope since the conditions were exactly the same as those used for (*e*): rather it must be ascribed to the monolayer of ruthenium complex on the surface. Similar poor-resolution photographs were obtained for an untreated modified electrode, indicating that the effect is not due to residual grease in the above case.

Chemical Stability of Electrodes modified by Esterification.— Generally, the chemical stability of these electrodes is variable, especially for multicoated electrodes. Presumably this is affected by how close-packed the surface layer is and by the degree of access the solvent molecules have to the reactive ester and anhydride bonds. The results of a variety of chemical stability tests are summarized in Table 1.

Samples 1, 2 and 6 show that modified electrodes with less than a monolayer coverage are reasonably stable at room temperature in dilute sulphuric acid. The slow loss of $[Ru(bipy)_2(bpdc)]$ from the surface is probably due to hydrolysis of the surface ester bonds. For the multicoated electrodes, the loss of $[Ru(bipy)_2(bpdc)]$ was much more rapid, presumably because of the higher reactivity, towards hydrolysis, of the anhydride bonds. That $[Ru(bipy)_2(bpdc)]$ is being removed from the surface by a hydrolysis mechanism in the above cases is supported by the results obtained with samples 3 and 5. With sample 5 there was a large initial loss of surface $[Ru(bipy)_2(bpdc)]$ during the first extraction with ethanenitrile. This can be attributed to the removal of adsorbed material that was not removed during the washing procedure. The second extraction with ethanenitrile results in a negligible loss of $[Ru(bipy)_2(bpdc)]$, despite the fact that the electrode is still multicoated. Sample 3 lost very little $[Ru(bipy)_2(bpdc)]$ upon heating at reflux in ethanenitrile. Thus it appears that both the ester and anhydride bonds are stable, under these conditions, as would be expected. When sample 3 was then heated at reflux in water the majority of the $[Ru(bipy)_2(bpdc)]$ was lost during the first 5 min, but some still remained after over 1 h. It is possible that some bound $[Ru(bipy)_2(bpdc)]$ is in holes and crevasses in the surface of the SnO_2 and so protected from hydrolysis, because water molecules cannot access the labile ester bonds. Sample 4 indicates that both ester and anhydride bonds are solvolysed by hot methanol, although more slowly than by water. Again some bound $[Ru(bipy)_2(bpdc)]$, at the submonolayer level, appears to be particularly resistant.

Thus, it appears that the chemical stability of these electrodes can be explained in terms of the stability towards solvolysis of the linking ester and anhydride bonds. The results are encouraging in that at room temperature, even in aqueous acid, the electrodes are sufficiently stable to be useful as electrocatalytic electrodes. In solvents such as enthanenitrile the stability is even greater.

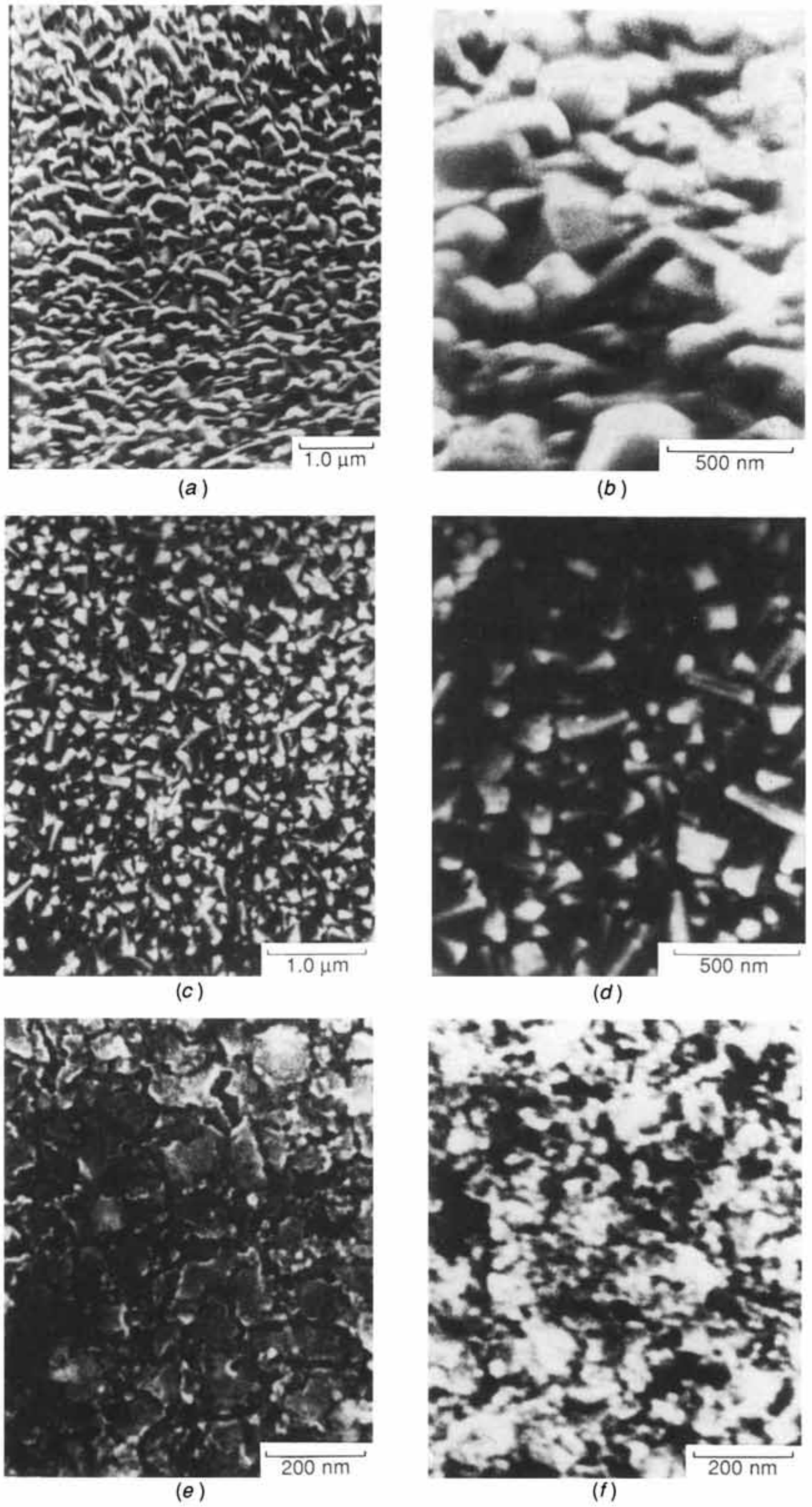


Fig. 5 Scanning electron micrographs of (*a*) an unmodified tin(IV) oxide electrode (magnified × 15 000), (*b*) as in (*a*) but magnified × 50 000, (*c*) a tin(IV) oxide electrode, modified by method 2 (magnified × 20 000), (*d*) as in (*c*) but magnified × 50 000, (*e*) a tin(IV) oxide electrode, modified by method 4 and then electrochemically stripped (magnified × 100 000), and (*f*) a tin(IV) oxide electrode, modified by method 4 (magnified × 100 000)

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