



# Organometallic chemistry at the interface with materials science

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Received 4 October 1999; accepted 29 November 1999

## Abstract

Surface hydroxyl groups of indium tin oxide (ITO) react with zirconium or tin alkoxides to give surface metal alkoxide complexes, which can be converted to surface metallic complexes of carboxylates or phenoxides. These latter surface complexes can be used to modify electrode properties of the ITO. ©2000 Elsevier Science Ltd All rights reserved.

**Keywords:** Indium tin oxide; Surface modification; Alkoxides; Interfaces

Organometallic materials play an important role as essential components of modern optoelectronic devices, for example of organic light emitting diodes (OLEDs). In one OLED process, ‘holes’ are injected from an inorganic anode into an organic ‘hole transport layer (HTL)’ material; typically, the anode is a mixed oxide of indium and tin (ITO), and the HTL is an aromatic hydrocarbon derivative (Fig. 1) [1–3]. ‘Hole injection’ into (oxidation of) the HTL is often inefficient, perhaps owing to poor molecular contact at the interface between the hydrophilic ITO and the hydrophobic HTL; this inefficiency results in device failure after only short utilization times [1,4,5]. Until the surface chemistry of ITO is better understood, it is unlikely that precisely designed interfaces can be developed for applications in microelectronic devices. Fortunately, surface hydroxyl groups can provide a chemical ‘handle’ with which to accomplish ITO surface modification in a well controlled, systematic way, and because they react with surface OH groups, organometallic species seem perfectly set up to enhance, on the molecular level, the interface between an oxide-based inorganic electrode and an organic overlayer.

Metal alkoxides react with OH groups of metal oxides to give surface organometallic complexes by protolytic loss of one or more alkoxide ligands [6–10]. Alkoxide ligands remaining in the coordination sphere of the metal following ‘chemisorption’ can react by ligand metathesis to give families of new surface-bound complexes from a common precursor [11–16]. Tetra(*tert*-butoxy)zirconium (**1**) is a

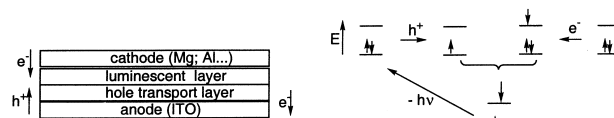
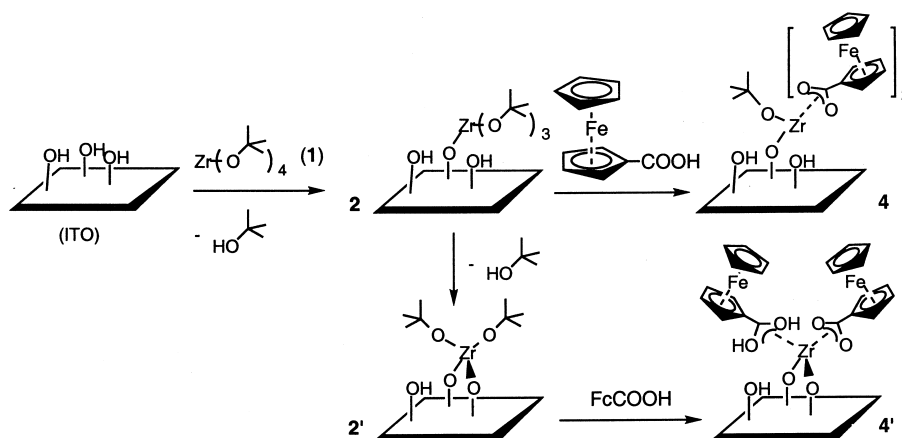


Fig. 1. Schematic diagram of a simple OLED.

particularly useful ‘linker’ to interface metal oxide surfaces with organic materials. Reaction of **1** with ITO/glass was accomplished both in ultrahigh vacuum (UHV) and under ‘normal’ laboratory conditions ( $10^{-2}$ – $10^{-4}$  Torr). Products were determined in UHV using reflectance–absorbance IR spectroscopy (FT-RAIRS), X-ray photoelectron spectroscopy (XPS), and thermally programmed desorption mass spectrometry (TDS), all of which indicated the presence of *tert*-butoxy ligation. Chemisorption involves protolytic loss primarily of one *tert*-butoxide ligand to give **2**; a small amount of **2'**, formed by a second protonolysis step, may also be present at room temperature. A similar deposition stoichiometry is to be expected for reaction of **1** with ITO/glass under ‘normal’ laboratory conditions (Scheme 1).

Ligand metathesis of **2/2'** with simple carboxylic acids [16] was modeled in UHV using Al-bound Zr alkoxide complexes [11]. Carboxylate-for-alkoxide exchange was accomplished by repetitive dosing of the substrate with butanoic acid at 170 K, followed by heating to 300 K. FT-RAIRS analysis after one cycle of treatment of **1** with  $0.6 \times 10^{-6}$  Torr-sec. of butanoic acid showed both alkoxide and carboxylate ligands. Even after eleven further ‘dose–desorb’ cycles, FT-RAIRS showed only two *tert*-butoxy ligands had been exchanged for butanoate ligands, to give butanoate com-

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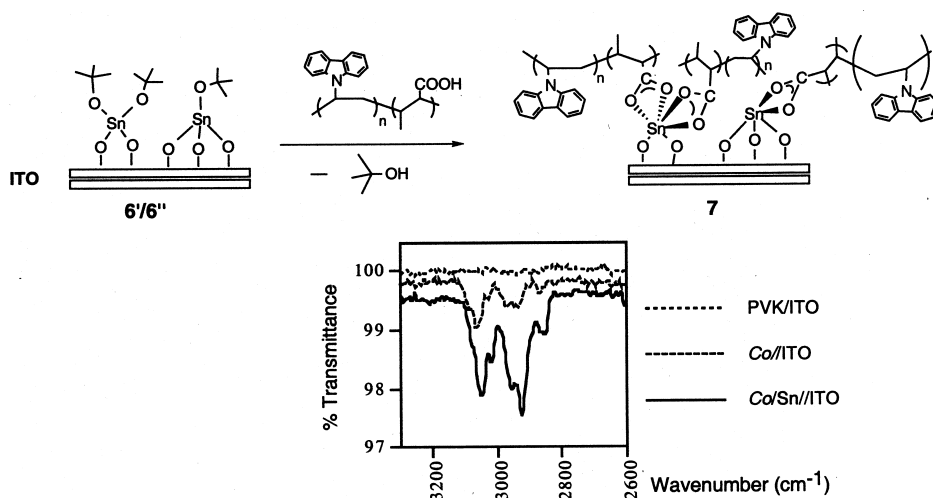


Scheme 1. Synthesis of surface organometallic complexes on ITO.

plexes **3/3'**. Reaction of **3'** with a third equivalent of carboxylic acid may be sterically unfavorable.

Surface hydroxylated ITO/glass was treated with vapor of **1** to give **2/2'**; slides were then sprayed with an aerosol of a 1 mM solution of ferrocenecarboxylic acid (FcCOOH) in ether, dried, washed, and dried again, to give **4** and **4'** [15]. ITO/glass electrodes coated with **4/4'** were rinsed thoroughly and subjected to electrochemical analysis. The cyclic voltammogram of the **4/4'**-modified ITO electrode showed a redox peak at  $E_{1/2} = 0.55$  V versus SCE, which is reasonable for a surface bound carboxyferrocene derivative [17,18]. The loading density of surface-bound ferrocene carboxylate ligands of **4/4'** on the surface per nominal unit area is ca.  $5 \times 10^{-11}$  mol cm $^{-2}$ , comparable to the amount reported by 'self-assembly' of elaborated ferrocenyl derivatives on ITO [18,20–22]. Importantly, our studies show that the redox properties of the FcCOOH-derived reagent have not been changed significantly by its incorporation into a surface organometallic complex: The surface complex does not constitute an insulating barrier.

Tin interfaces are attractive for ITO surface modification, in that their use does not entail introduction of a new metallic species, such as Zr. UHV stoichiometric determination for reaction products of ITO/glass and tetra(*tert*-butoxy) tin (**5**) indicated a mixture of tin analogs of **2/2'** (**6/6'/6''**), similar to that found for deposition of **5** onto hydroxylated Ti [10]. It is interesting that both on ITO and on oxidized metals, Sn alkoxides are more reactive toward multiple chemisorption than are Zr analogs [7]. Polyvinylcarbazole (PVK) is an HTL material of significance for polymer-based OLEDs [23], but PVK does not adhere well to untreated ITO. We prepared a co-polymer of polyvinylcarbazole and crotonic acid, which incorporates a low level of the acidic component, by polymerizing a large excess of vinylcarbazole (relative to crotonic acid) using AIBN initiation [24]. The co-polymer adhered [14] better to ITO than did PVK, but it adhered even better in the presence of **6'/6''**, which gives **7** (see Scheme 2). Using typical spin-coating techniques, we were able to prepare a simple OLED with **7**. Analysis of current versus voltage for this simple device indicated much higher carrier mobility compared with a device prepared simply by spin-coating a solution of PVK onto untreated ITO.



Scheme 2. Preparation of PVK co-polymer/ITO via an Sn interface.

An interesting model to facilitate ‘hole injection’ from ITO into an HTL material involves the organization of a dipole at the surface of the ITO [3,25]. Phenols are acidic compared to *tert*-butanol, and we find that **2/2'** react with phenols from the gas phase to give products of ligand metathesis in which *tert*-butoxy ligands are replaced by phenoxides [13]. A series of substituted phenolic compounds was reacted with **2/2'** to give a family of similar phenoxyzirconium complex surface materials. An analogous series was made using **6'/6''**. Surface phenoxides were structurally elucidated through a combination of FT-RAIRS, XPS and TPD measurements. Functional studies of Zr and Sn phenoxides on ITO are now underway.

In conclusion, we have shown that covalently binding a metallic complex interface to the surface of ITO can enhance interactions between generally hydrophobic organic materials and the hydrophilic oxide substrate surface. In conventional cases, the interaction between such organic materials and the oxide surface would depend on either hydrogen bonding effects or Lewis acid/Lewis base interactions. However, for an oxide such as ITO which is not heavily hydroxylated, and for tertiary amines such as are present in PVK, hydrogen bonding and Lewis acid/Lewis base interactions will likely be weak. In marked contrast, using the metallic interface, strong covalent bonding can be effected irreversibly between the substrate and the organic material.

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