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Growth of Lamellar Hofmann Clathrate Films by Sequential Ligand Exchange Reactions: Assembling a Coordination Solid One Layer at a Time

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Over the past decade, significant progress has been made in the preparation and characterization of molecular thin films on surfaces.[1] The applications of self-assembled monolayer films have ranged from model systems for the study of electron transfer reactions[2] and molecular rectifiers[3] to photoresists[4] and gas-phase chemical sensors.[5] One particularly interesting synthetic development in this field has been the growth of self-assembling multilayers, in which covalent or noncovalent links are formed between layers. The resulting surface assembly can be used in applications where thicker-than-monolayer films are needed, for example as dielectric spacers[6] or non-linear optical materials.[7]

Strategies for forming interlayer linkages in organic thin films have included covalent,[8,9] ionic,[10,11] and hydrogen bonding.[12] Coordinate covalent bonding represents an attractive means of joining molecular building blocks into extended assemblies and has been used effectively in the preparation of one-, two-, and three-dimensional supramolecular arrays.[13] Nevertheless, the growth of surface thin films through coordination reactions has met with limited success.[14] We describe here a new approach, in which kinetic control of ligand exchange reactions allows one to prepare multilayer surface films based on the lamellar Hofmann clathrate structures.

The lamellar Hofmann clathrates (Figure 1) contain planar metal–cyanide–metal sheets.[15] Within these sheets, every other metal ion (the one coordinated to the nitrogen atom of the CN group) has two additional ligands at axial coordination sites. Nitrogen-containing bridging ligands, such as 4,4′-bipyridine and 1,12-diaminododecane, can be used to join the layers.[16] These solids also contain void spaces that can include small molecules such as benzene, toluene, or aniline. The multilayer films described in this paper are analogs of the bulk $Ni(bpy)Pt(CN)_4$ Hofmann clathrate. The layer growth scheme (Figure 2) involves the sequential adsorption of the three components of the solid from ethanol (or ethanol–water in the case of the $Pt(CN)_4^{2-}$ ion) solutions. The film is anchored to the gold surface by means of an asymmetric ethyl 4-pyridyl disulfide; the ethyl "diluent" in the pyridine monolayer is included in order to achieve a surface density of pyridine groups roughly comparable to the density of Ni^{2+} in the Hofmann clathrate layers.

There are several factors, such as the solubility of molecular precursors and of the resulting structure, that contribute to the success of a multilayer adsorption technique. One factor that is crucial in the present case is the kinetics of ligand exchange. For example, in adsorption step 2 (Figure 2), if the Ni^{2+} salt is dissolved in water and the adsorption performed at room temperature, any Ni^{2+} that binds to the surface pyridyl groups is easily washed away with water. The fast ligand exchange rate of Ni^{2+} ($k_{exch}(H_2O) \approx 10^4\ s^{-1}$) does not allow adequate time for removing excess salt without undoing the coordination reaction. This complication was eliminated by performing the adsorption and washing steps at low temperature (–60 to –75 °C). From the activation energy of the water exchange reaction,[17] lowering of temperature is estimated to reduce the desorption rate by a factor of ca. 2500, leaving ample time for the rinsing step. The desorption rate is probably further reduced by the weaker coordinating ability of ethanol relative to water. In addition, because the displacement of solvent by nitrogen-containing ligands (bipyridine or cyanide) is exothermic, the ligand exchange equilibrium shifts in favor of the complexed form at low temperature.[18] Earlier attempts[19] at solving this kinetic problem by substituting Ru^{2+} ($k_{exch}(H_2O) = 10^{-2}$) and other slowly exchanging ions for Ni^{2+} were moderately successful but were complicated by other factors, and the extreme

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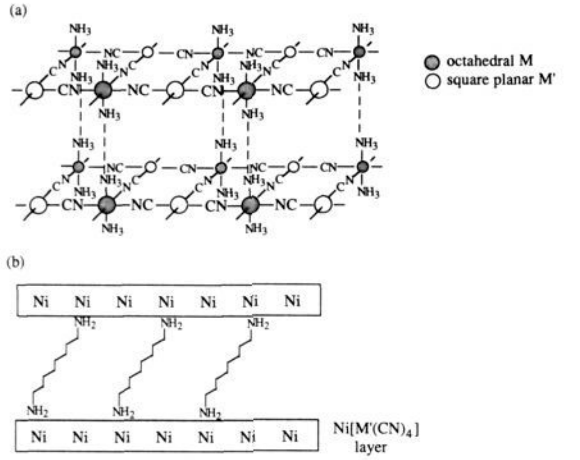

Figure 1. (a) Schematic structural drawing of a Hofmann-type clathrate compound. For clarity, the guest molecules are not shown.[15b,c] (b) Lamellar Hofmann-like structure containing bridging bipyridine or diamine ligands.[16]

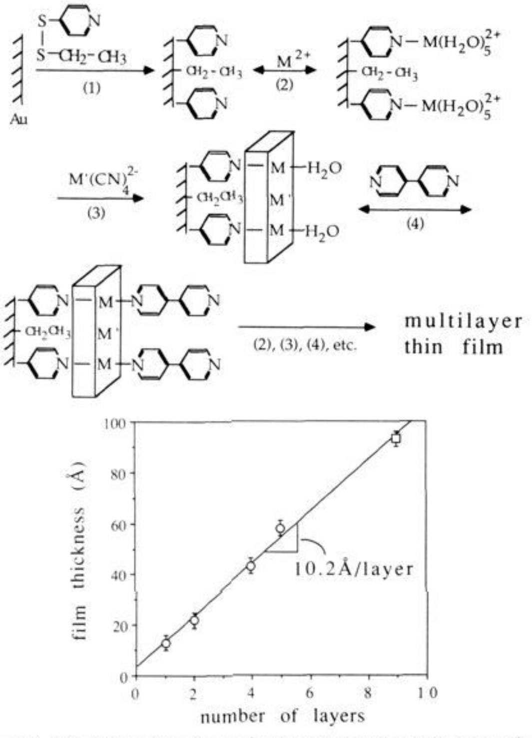

Figure 2. (Top) Growth scheme for deposition of multilayer Hofmann clathrate films (M = Ni, M' = Pt). (Bottom) Ellipsometric measurements of thickness versus number of layers for Ni(bpy)Pt(CN)$_4$ films. Circles and square indicate two different batches of samples. The reference sample is bare gold, and the thickness of "zero" layers corresponds to the adsorbed disulfide anchoring agent. One layer refers to the sequence of adsorption steps 2–3–4.

oxygen sensitivity of Ru(H$_2$O)$_6^{2+}$ made the manipulations involved in film growth very difficult.

Figure 2 shows a plot of film thickness derived from ellipsometric measurements for stepwise layer growth[20] of Ni(bpy)Pt(CN)$_4$. The average layer spacing of 10.2 ± 1 Å is in close agreement with the layer spacing (10.3 ± 0.3 Å) found for the bulk compound.[21] The uncertainty in film thickness measurements derives from the nonuniqueness of the ellipsometric fit and consequent uncertainty in the film refractive index used in the calculation.

Reflectance IR spectroscopy, together with the transmission spectrum of the bulk solid, confirmed the identity of the self-assembled films. Peaks at 2172 (bulk solid) and 2177 cm^{-1} (film) correspond to the bridging cyanide group. The position of this peak is sensitive to cyanide coordination,[19] and provides good evidence that the connectivity in the film is Ni–NC–Pt. Absorption bands between 1610 and 1400 cm^{-1} are assigned to the C–C and C–N ring stretching vibrations of the bridging bipyridine ligand. The intensity of these peaks grows linearly as more layers are added. In the bulk solid, it is difficult to resolve the C–H stretch of the bipyridine from the large broad peak that results from clathrated water. In the film spectra, these C–H stretches are not observed, most probably because this mode has a dipole change approximately parallel to the gold surface, making the absorbance weak in reflectance FTIR. The presence in the film spectrum of a rather strong C≡N peak, which should be similarly absent if the plane of the Pt(CN)$_4^{2-}$ group were rigorously parallel to the surface, suggests that there may be incomplete substitution of bipyridyl for Pt(CN)$_4^{2-}$ at the axial site in adsorption step 4 (Figure 2). Some of the axial sites may indeed still contain Pt(CN)$_4^{2-}$, although the strength and steady growth of the C–C and C–N ring stretches imply that the majority of the film structure reflects that of the bulk, with bipyridine linking the sheets of metal cyanide. An alternative explanation for the strength of the C≡N stretch is that the metal cyanide sheets may be puckered or disordered at grain boundaries and defects.

Preliminary XPS data confirm the presence of all elements (Ni, Pt, N, C) expected in the film. The observed Pt:Ni intensity ratio (1.6:1, corrected for atomic sensitivity factors) is consistent with the proposed structure, considering that the photoelectron mean free path for Pt photoelectrons in dense matter (17.1 Å) is nearly twice that for Ni photoelectrons (9.9 Å), and the film is capped with a bipyridine layer of ca. 9 Å thickness. The exact stoichiometry cannot be determined without knowledge of the photoelectron mean free paths in the Ni(bpy)Pt(CN)$_4$ films. A more detailed XPS analysis of these materials is currently in progress.[22]

We have shown that self-assembled multilayer films, in which molecular building blocks are held together solely by coordinate covalent bonds, can be prepared by sequential adsorption reactions. Kinetic control of ligand exchange is essential to the success of this method. With the wealth of experience available in the field of coordination chemistry, it is possible to envision many other systems that could lend themselves similarly to adaptation as thin films.

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(20) Films were grown on gold surfaces as follows. Freshly sputtered gold samples (2000 Å Au/150 Å Cr on polished Si (100) substrates) were incubated in 1 mM ethanolic ethyl 4-pyridyl disulfide overnight and rinsed with ethanol. Solutions of Ni(NO$_3$)$_2$·6H$_2$O, K$_2$Pt(CN)$_4$, and 4,4'-bipyridine were 5 mM in ethanol, 90:10 ethanol:water, and ethanol, respectively. These solutions were cooled in dry ice/acetone baths, and samples were immersed in them sequentially for 6–8 h. Between adsorption steps, the samples were rinsed by immersion in three consecutive clean, cold ethanol baths, for a total time of ca. 10 s. Ellipsometric, XPS, and infrared measurements followed the bipyridine adsorption and rinsing steps. Samples were dried with nitrogen and stored in a desiccator prior to analysis.

(21) Elemental analysis (CHN) of the pale blue bulk compound (crystallized from aqueous solution) indicates clathrated water and a formula Ni(bpy)Pt(CN)$_4$·2.5H$_2$O. The X-ray powder pattern of this material was indexed to a pseudotetragonal (monoclinic) unit cell with a layer spacing of 10.3 ± 0.3 Å and in-plane lattice constants (7.44, 7.23 Å) similar to that of tetragonal Ni^{II}–Pt^{II} Hofmann clathrates (7.26 Å, ref 15).

(22) XPS spectra were collected with an Mg Kα source at a take-off angle of 20°. The experimental procedure has been described previously (ref 9e).