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# Langmuir–Blodgett (LB) Films of Tris(2-phenylpyridine)iridium(III)

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Monolayer and multilayer Langmuir–Blodgett (LB) films of the neutral hydrophobic Ir(ppy)$_3$ (**1**) (ppy = 2-phenylpyridine) have been produced on the water surface when mixed with a fatty acid (stearic acid). The molecular area of the complex in the close-packed film is 55 Å$^2$. The homogeneity of the films was verified by measuring the absorbance vs the number of layers on a substrate (quartz) and also by comparing the relative emission intensity of multilayer mixed LB films of different molar ratios. The films are stable and capable of being transferred from the water surface onto a substrate with a transfer ratio very close to unity. A blue shift in the maxima of the emission, as the complex concentration is decreased, occurs for both room-temperature fluid solution and a rigid matrix at 77 K. In-trough cyclic voltammetry (horizontal touch) of the mixed film is also reported and compared to the cyclic voltammetry of a film transferred to an indium–tin oxide plate (vertical dip).

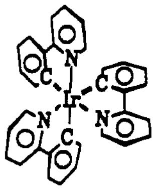
## Introduction

The Langmuir–Blodgett (LB) technique has received significant attention in the last decade, since it offers a simple and precise method for constructing ultrathin monolayer and multilayer films whose thickness and orientation can be controlled. The potential of thin molecular films in telecommunication transmission, sensor devices, and charge storage motivated new interest in the LB technique.[1] However, the stability of the monolayer remains a significant problem in the architecture of the ultrathin films. Typically, attaching a long amphiphilic alkyl chain to the molecules can produce an LB film.[2–4] But, the hydrocarbon chain substituent can hinder vertical (perpendicular to the substrate) charge transfer in the multilayer LB films and occasionally results in a thermal process involving the alkyl chain.

The mixed fatty acid–metal complex LB films described by Kuhn and Mobius[5] represented an alternative approach for preparing films. Using this general approach, several recent results have been published describing the production of mixed LB films. Of particular interest are those films containing luminescent transition metal complexes such as [Ru(dpphen)$_3$][ClO$_4$]$_2$[6] and [Ru(tmebpy)$_3$][ClO$_4$]$_2$[7] (where dpphen is 4,7-diphenyl-1-10-phenanthroline and tmebpy is 4,4′,5,5′-tetramethyl-2,2′-bipyridine). We have reported the production and characterization of mixed square planar platinum(II) complexes/stearic acid LB films containing inorganic complex molecules.[8,9] In the current paper, we report the preparation of mixed LB films containing neutral hydrophobic iridium(III) complexes and the spectroscopic properties of these films.

## Experimental Section

**Materials.** *fac*-Tris(2-phenylpyridine)iridium(III), Ir(ppy)$_3$ (**1**), was prepared as previously described.[10] Benzene, chloroform, dimethylformamide, acetonitrile, methanol, and ethanol were of high-purity HPLC grade and were Aldrich products. The benzene was freshly distilled before use, while the other solvents were used as received without further purification. The quartz and the indium–tin oxide (ITO) coated plates used were obtained from Delta Technologies, Ltd., and they were of dimensions 2.5 × 7.5 cm. The subphase water was purified using deionization, charcoal filtering, and reverse osmosis.



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**Instrumentation.** The films were prepared using an NIMA alternate layer trough of 1000-cm$^2$ area. The film emission and lifetime measurements were performed with an LS-100 luminescence system (PTI). The UV–vis absorption spectra were measured on a Cary 14 spectrophotometer with an updated operating and data acquisition system. For cyclic voltammetry (CV) measurements, a BAS 100A electrochemical potentiostat (Bioanalytical Systems) was employed with a Pt auxiliary electrode and a AgCl/Ag reference electrode. A glassy carbon working electrode was used in 1 mM Na$_2$SO$_4$ with water as solvent for in-trough LB film studies.

**Methods.** The surface of the water subphase on the trough was cleaned by spreading a monolayer film of stearic acid on the water surface and then vacuuming the film under pressure control. Stock solutions of 3.36 × 10$^{-4}$ M concentration for the Ir(ppy)$_3$ and the stearic acid were prepared separately in freshly distilled benzene. Solution mixtures of 1:1, 1:2, 1:5, 1:10, 1:20, 1:30, and 1:50 **1**:stearic acid ratios were prepared from stock solutions by mixing the calculated volumes to produce the desired molar ratios shortly before use. The pressure–area ($\pi$–$A$) isotherms were obtained by compressing at a barrier speed of 50 cm$^2$/min a spread monolayer of the mixture solutions on a subphase of deionized water or

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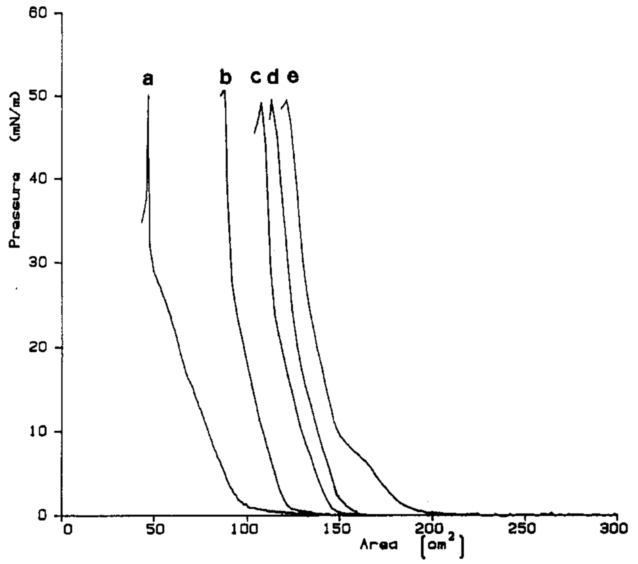

**Figure 1.** Pressure–area ($\pi$–$A$) isotherms for (a) pure **1** and the four **1**/stearic acid mixtures with molar ratios (b) 1:30, (c) 1:10, (d) 1:5, and (e) 1:1, performed on a pure water subphase at 20 °C and a barrier speed of 25 cm²/min.

0.1 mM $BaCl_2$ aqueous subphase at 20 °C. The spread monolayer was allowed to equilibrate for 5 min until the solvent evaporated; then the film was compressed until it collapsed as indicated by the isotherm. The quartz slides (2.5 × 7.5 cm) were cleaned by boiling in concentrated $HNO_3$ for several hours, removed, rinsed with deionized water, and then sonicated in chloroform for 45 min. The ITO plates were washed with chloroform before use.

The emission and the lifetime decay from solution were measured using a PTI spectrophotometer or Photonic Uv-22 nitrogen laser with 337-nm pulses. Emission spectra for film structures of 50 layers of 1:1, 1:5, and 1:20 **1**:stearic acid molar ratio solutions were also recorded using the same instruments. The UV–vis spectra were obtained using the Cary 14 spectrophotometer, the solution concentration was $\sim 10^{-5}$ M, and the absorbance of the film was measured as a function of the number of layers (12, 32, 48).

For the horizontal touch (HT) electrochemical measurements, the monolayer was first compressed on the trough, and the glassy carbon electrode was lowered horizontally onto the subphase surface, depositing the film on the electrode surface. The electrode was then raised off a few millimeters the CV run initiated. For the vertical dip (VD) cyclic voltammetry, the film was transferred to an ITO plate and subsequently reimmersed in an aqueous electrolyte solution.

## Results

**LB Film Properties.** The pressure–area ($\pi$–$A$) isotherms obtained from mixed monolayers of $Ir(ppy)_3$ and stearic acid indicate the formation of stable LB films at the surface of water (Figure 1). When the iridium compound solution (without stearic acid) is added to the surface of water, a dispersed monolayer capable of compression to a relatively high surface pressure before collapse is formed (Figure 1); however, this film could not be transferred to a substrate plate. The area occupied by each $Ir(ppy)_3$ molecule in the rigid mixed films is calculated to be 55 Å², and this value was consistent for the mixed films of **1**:stearic acid molar ratios 1:5, 1:10, 1:30, and 1:50. However, the area per iridium molecule calculated from the pure compound monolayer, 1:1, and the 1:2 **1**:stearic acid mixed layer is much smaller (~30 Å²).

**UV–Vis Absorption.** The absorption spectrum was measured for LB films of 1:5 **1**:stearic acid molar ratio. The 32-layer film of this mixture, deposited on a quartz plate at 25 mN/m surface pressure and 15 mm/min dipping speed with a transfer ratio very close to unity, gave a significant absorption (Figure 2). The absorbance of the mixed film was measured as a function of the number of layers deposited and was linearly dependent on the number of layers deposited on the substrate (Figure 3).

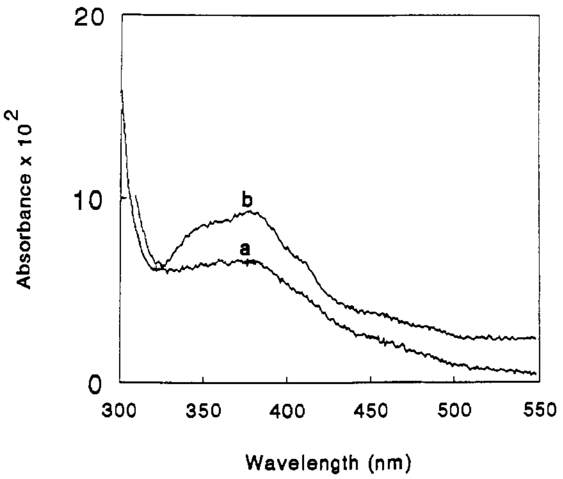

**Figure 2.** (a) Absorbance of 32 layers of a **1**/stearic acid mixture with a molar ratio of 1:5, deposited on a quartz plate at 25 mN/m surface pressure and a dipping speed of 15 mm/min. (b) Absorbance of **1** in $CH_3CN$ fluid solution ($8.4 \times 10^{-5}$ M) at room temperature.

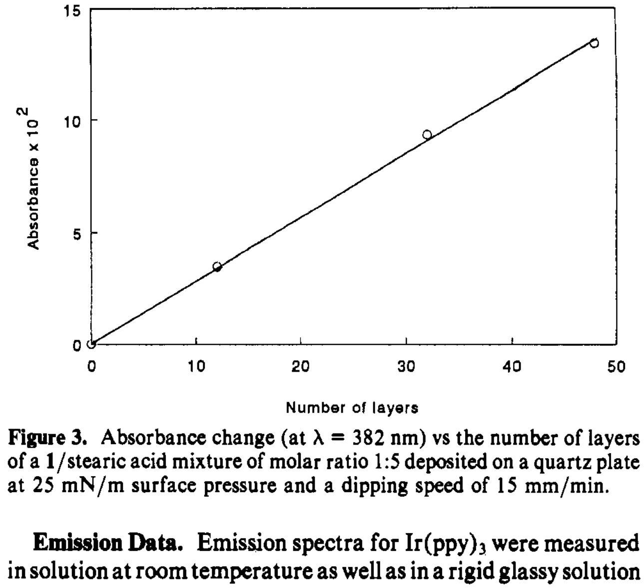

**Figure 3.** Absorbance change (at $\lambda$ = 382 nm) vs the number of layers of a **1**/stearic acid mixture of molar ratio 1:5 deposited on a quartz plate at 25 mN/m surface pressure and a dipping speed of 15 mm/min.

**Emission Data.** Emission spectra for $Ir(ppy)_3$ were measured in solution at room temperature as well as in a rigid glassy solution at 77 K. Blue shift in the emission is observed at both temperatures as the concentration of the complex in the solution matrix decreases (Figure 4). However, solvent change has no effect on the position of the emission peak. The intensity of the emission increases as the concentration decreases, which suggests self-quenching in the concentrated samples. The measured lifetime from a glassy sample of toluene/DMF (4:1 v/v) at 77 K is 5.8 $\mu$s (literature value is 5 $\mu$s).[11] Emission from 50-layer LB films of 1:20, 1:5, and 1:1 **1**:stearic acid molar ratios is shown in Figure 5. The relative intensity of the emission indicates the homogeneity of the films. The maximum of the peaks occurs at 543 nm, which resembles that from the solid powder of $Ir(ppy)_3$ (Figure 6).

**Electrochemistry.** Using the horizontal touch (HT) method, $Ir(ppy)_3$ exhibits an irreversible CV response for a 1:2 **1**:stearic acid molar ratio mixture compressed to 20 mN/m at the subphase surface. The anodic peak occurs at +990 mV vs AgCl/Ag, and the cathodic peak, at ~500 mV. The CV response disappears with repetitive CV scans (Figure 7). A monolayer structure deposited using the vertical dip (VD) method (1:2 ratio) also exhibits an irreversible CV response upon transfer to an electrochemical cell. Nine monolayers deposited using the VD method give a response that is approximately 13 times larger than the response for 1 monolayer (13.3:1). However, use of a monolayer and nine-layer system constructed from a 1:10 molar ratio

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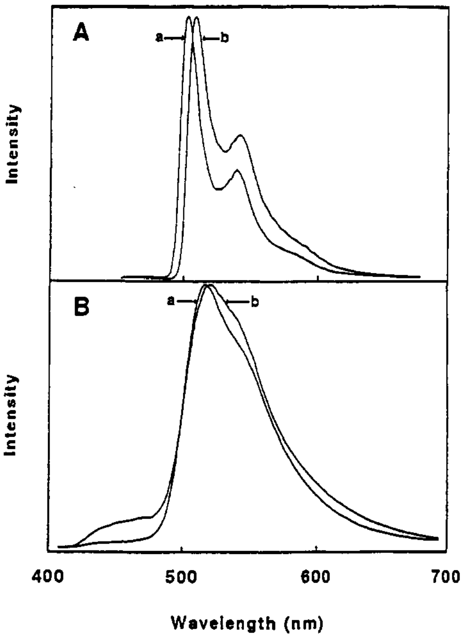

**Figure 4.** Emission spectra of $Ir(ppy)_3$ in toluene/DMF (4:1 v/v) solutions of concentrations (a) $1.68 \times 10^{-5}$ M and (b) $1.344 \times 10^{-3}$ M: (A) at 77 K; (B) at room temperature. Intensity is normalized in all spectra. $\lambda_{ex}$ = 400 nm.

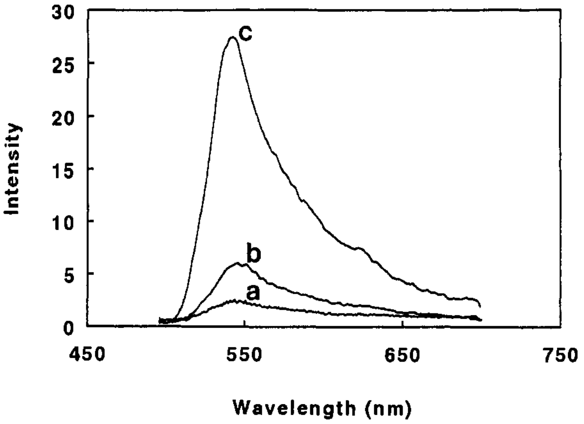

**Figure 5.** Room-temperature emission of 50-layer mixed LB films of **1**/stearic acid of molar ratios (a) 1:20, (b) 1:5, and (c) 1:1. $\lambda_{ex}$ = 400 nm.

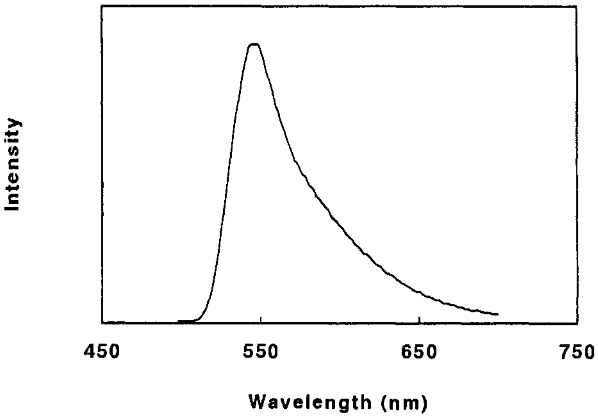

**Figure 6.** Room-temperature emission of $Ir(ppy)_3$ solid. $\lambda_{ex}$ = 400 nm.

produces a CV current ratio much less (2.5:1) than for the 1:2 ratio layer system.

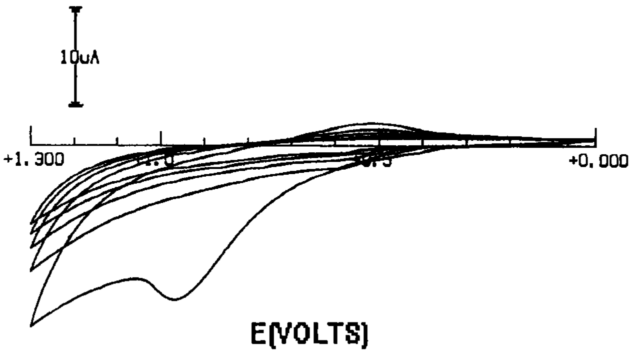

**Figure 7.** Cyclic voltammogram using the HT method for a 1:2 **1**:stearic acid molar ratio LB film on the surface of a 1 mM $Na_2SO_4$ aqueous subphase, showing the decrease in the response upon repetitive cycling.

## Discussion

Benzene solutions of $Ir(ppy)_3$ and stearic acid with molar ratios from 1:1 to 1:50 form compressible monolayers capable of transfer to a substrate when spread on the surface of the water subphase. The $\pi$–$A$ isotherms resulting from compressing the films at the surface of water (Figure 1) show three phase changes (gas–liquid–solid),[1] as expected for homogeneous films. The collapse pressure of these films is fairly high, ~50 mN/m. Assuming a spherical shape for the $Ir(ppy)_3$ molecule, the measured bond lengths Ir–C = 2.024 Å and Ir–N = 2.132 Å,[10] and the average C–C bond length of 1.2 Å, then the largest cross-sectional area of **1** is 62 Å$^2$. The average area occupied by each iridium molecule in the compressed mixed LB films was calculated by extrapolating the linear region of the isotherm of the LB films to zero surface pressure, which gives the total area occupied by both molecules, $Ir(ppy)_3$ and stearic acid. On the basis of the molar ratio and the molar concentration of each compound in the mother mixed solution and the assumption that the area occupied by each stearic acid molecule is 20 Å$^2$, the average molecular area of $Ir(ppy)_3$ is found to be 55 Å$^2$. However, the areas calculated from the isotherm of the pure iridium compound, 1:1, and the 1:2 mixed monolayer are rather small (~30 Å$^2$). We speculate that this might be due to aggregation that can occur for the Ir(III) molecules in the concentrated monolayer resulting from the increasing surface pressure, which pushes the metal complexes beneath the film surface. Although such a mechanical arrangement of the metal complex molecules takes place, homogeneous films are formed on the surface of water, especially when the mole fraction of stearic acid is high enough ($\geq$0.75), corresponding to a 1:3 **1**: stearic acid molar ratio solution mixture. The homogeneity of the films is verified by the absorbance of the film (after deposition on a quartz plate) as a function of the number of the layers deposited (Figure 3)[8] and by comparing the emission intensity of a multilayer mixed LB film of different molar ratios (Figure 5). From Figure 3, the linearity of the absorbance vs the number of layers of LB films indicates that the Ir(III) molecules are homogeneously dispersed in the stearic acid matrix. Also, the relative intensity of 50 layers of mixed LB films of 1:20, 1:5, and 1:1 **1**:stearic acid molar ratios (Figure 5a–c, respectively) indicates the homogeneity of the films. The mixed LB films produced on the surface of water can be transferred onto a quartz or ITO-coated substrate using the vertical dipping procedure with a transfer ratio very close to unity. However, the pure monolayer (Figure 1) of the iridium compound cannot be transferred onto any of the hydrophobic or hydrophilic substrates. We speculate that this is due to the aggregation of these molecules resulting in unusually large crystals that are too heavy to stick on the surface of the substrate.

The absorption spectra of multilayer mixed LB films of a 1:5 $Ir(ppy)_3$:stearic acid molar ratio and of $Ir(ppy)_3$ in solution are compared in Figure 2. The emission spectra of $Ir(ppy)_3$ in solution at 77 K and at room temperature are shown in Figure 4. A small blue shift in the emission spectra can be observed as the concentration of the complex is decreased. This phenomenon is not caused by the solvent since all of the solvents used (acetonitrile, acetone, methanol/ethanol mixture, and chloroform) exhibit this shift in the spectrum. The largest shift in the emission wavelength of this complex is from 545 nm (the maximum from the solid powder at room temperature) (Figure 6) to 502 nm (the maximum from a diluted solution of $1.68 \times 10^{-5}$ M at 77 K) (Figure 4A). A detailed study of this phenomenon will be presented later. The emission from homogeneous mixed LB films of 50 layers of 1:20, 1:5, and 1:1 **1**:stearic acid molar ratios occurs at 543 nm at room temperature (Figure 5a–c, respectively). Variation of the concentration of the metal complex in the mixed LB films has no effect on the spectroscopic properties of the multilayer films. No significant difference between the emission spectra of the mixed LB films with any molar ratio and the emission spectrum of the solid powder $Ir(ppy)_3$ can be observed.

In contrast to the organic solution (0.1 M TEAP–dimethylformamide) CV of **1**, which gives a reversible one-electron wave at 0.36 V (vs SCE),[12] the CV data for the LB film (Figure 7) show that the reduction wave for the Ir(III) complex is smaller than the oxidation wave, indicating an irreversible process. This can be due to the reaction of Ir(IV) with water or the loss of the charged complex from the substrate. However, the oxidized product would produce a cationic (Ir(IV)) complex that could ion-pair with the stearate anion. Consequently, we favor the $H_2O$ reaction rationale. Previous studies[13] have shown that electron transfer is diminished beyond ~24 Å from the surface of the ITO electrode. The large increase in current response at a nine-monolayer structure compared to the response for a monolayer is in contrast to the results[13] obtained for the multilayer (11-layer) film of $[Ru(tmbpy)_3]^{2+}$ at a 1:10 ratio of metal complex to stearic acid. The diameter of **1** for this study is approximately half that of the Ru(II) complex of the previous study.

## Conclusions

A new mixed LB film containing the neutral hydrophobic $Ir(ppy)_3$ complex, where ppy is 2-phenylpyridine, has been produced and transferred to various substrate plates for characterization. As for earlier films of charged hydrophobic complexes, the film collapse pressures are fairly high relative to that of pure fatty acid films. Absorption spectra of multilayer films give absorption maxima that correlate with solution spectra and with absorbance ($A$) values that are linear with the number of layers. The solution emission spectra at room temperature and 77 K produce a small but reproducible blue shift as the complex concentration is decreased. The film electrochemistry obtained for the vertical dip (VD) and the horizontal touch (HT) methods produce an irreversible oxidation wave at ~0.990 vs AgCl/Ag, which we speculate is due to the reaction of the Ir(IV) species with water. This is in contrast to the nonaqueous ($CH_3CN$) CV of $Ir(ppy)_3$, which gives a reversible one-electron wave at 0.36 V (vs SCE). The relatively high concentration of metal complex in the 1:2 molar ratio films enables efficient vertical charge transfer, in contrast to the behavior of mixed films[13] where the ratio of pseudospherical metal complex to fatty acid is small.

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