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Langmuir-Blodgett (LB) of Transition Metal Complexes Square Planar Platinum(II) Complexes

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Abstract

The flat Pt(Thpy)$_2$ complex, where Thpy is 2-(2-thienyl)-2-pyridine, forms a compressible LB film on the surface of pure water when it is mixed with stearic acid. The pressure-area isotherm of a mixture of Pt(Thpy)$_2$/stearic acid shows two plateaus in the solid phase region that corresponds to a horizontal and a vertical orientation of the Pt(Thpy)$_2$ molecules in the LB film on the surface of water. The areas calculated per molecule at the two orientations are (57 ± 2)Å^2 and (25 ± 1)Å^2. The Uv-vis absorption of the LB film of Pt(Thpy)$_2$/stearic acid mixture indicates that the Pt complex molecules disperse homogeneously between the stearic acid molecule in the film. The emission of the multilayer LB film of Pt(Thpy)$_2$/stearic acid shows a maximum at $\lambda = 566$ nm. Solution emission and lifetime decay data are also presented.

INTRODUCTION

The use of so called "supramolecular" assemblies or "organized aggregates"[1] has been suggested as a route to the development of molecular dimension switches and storage elements ultimately capable of utilization in molecular dimension devices including computers, energy conversion systems, sensors and microscopic communication systems. Aggregates containing both inorganic (primarily transition metal complex) and organic systems have been proposed. System strategies employed have utilized synthetic step by step assembly of molecular units,[2] self assembly[3] of systems and other approaches. A classical aggregate from the laboratory of Professor H. Kuhn[4] and continued through the efforts of Dr. D. Mobius is the Langmuir-Blodgett film. Here the use of amphiphilic water insoluble molecular species enables the production of monolayer and multilayer systems having a substantial degree of order. A favorite chemical constitutent of these aggregates has been the transition metal complex since the color and the redox properties of these materials affords a synthetic flexibility that permits a systematic perturbation of aggregate properties.

Our interest in molecular level switching and charge storage phenomena[5] originates from the recognition that localized charge separation can be produced in $[RuL_3]^{2+}$ and $[RuL_2L']^{2+}$ (L and L' are diimine chelate ligands) by both an electrochemical and photoexcitation perturbation. The desire for ordered systems with sufficient molecule concentration to enable molecular level interrogation resulted in examination of the LB strategy. Indeed the use of amphiphilic Ru(II) complexes containing long chain alkyl groups was first exploited by Whitten's group[6] and the Kuhn group[7] over twenty years ago. However, the chemical reactivity[7,8] of these molecule systems led to ambiguous and nonreproducible results. More recently Fujihira's group[9] has used amphiphilic long chain alkyl Ru(II) diimine complexes (no chemical reaction) to produce a molecular diode type system. While certainly an improvement on those ester systems giving unstable films because of a hydrolysis reaction,[7,8] the existence of the long chain alkyl function in the complex may limit the ability to create charge separated or energy transfer systems. Therefore the 1988 report[10] of stable ion pair LB film for the hydrophobic $[Ru(dp\text{-}phen)_3]^{2+}$ (dp-phen is 4,7-diphenyl -1,10-phenanthroline) with stearic acid was as useful. Subsequently we fabricated monolayer and multilayer mixed films[11] using $[Ru(t\text{-}mebpy)_3]^{2+}$ (t-mebpy is 4,4',5,5'-tetramethyl-2,2'-bipyridine), a hydrophobic cation, with stearic acid. In all these cases, the Ru(II) complex is essentially spherical in shape. The current results describe unusual LB film properties found for a neutral hydrophobic platinum(II) complex that, although the metal configuration is d^8, possesses a low lying charge transfer state superficially analogous to the localized MLCT state found in the $[Ru(bpy)_3]^{2+}$ species.

EXPERIMENTAL SECTION

Materials

Bis(2-(2-thienyl)-2-pyridine)platinum(II), $Pt(Thpy)_2$ was given to us by Dr. Alex von Zelewsky at the Institute of Inorganic Chemistry, University of Fribourg, Fribourg, Switzerland. The compound bis(diphenylphosphino)-ethane-5,6-dimethyl-1,10-phenanthrolineplatinum(II) bis(perchlorate), $[Pt(P\text{-}P)dmphen][ClO_4]_2$, is prepared according to the literature procedure[12] with some modification. The chloroform, DMF and acetonitrile are HPLC grade with purity of 99.9% and were Aldrich products. 1,1,1,3,3,3-hexamethyl-disilazane and the stearic acid are also purchased from Aldrich. All the chemicals were used as they were received without further purification. The quartz plates used were of dimensions (2.5 x 7.7) cm. The subphase water was freshly deionized and charcoal filtered.

Instrumentation

The LB films were prepared using a NIMA alternate layer trough. The emission and life time measurements were performed using LS-100 luminescence system (PTI). The Uv-vis absorptions were measured on Cary-14 spectrophotometer with computer update operating system.

Methods

The surface of the subphase is cleaned by spreading a monolayer film of stearic acid on the water and then vacuuming the film under pressure control. Solutions of total concentration of 10^{-3} M with different molar ratios (1:5; 1:7; 1:10; 1:20; 1:30 and 1:50) of Pt(II) complex/stearic acid were prepared in chloroform shortly before usage. The pressure-area (π-A) isotherms were performed by adding 50 µl of the prepared solutions on a subphase of deionized water or 0.1 mM $CdCl_2$ aqueous subphase at 20°C. The film is then squeezed at a barrier speed of 100 cm^2/min.

The quartz slides (2.5 x 7.7) cm were cleaned by standing them in concentrated HNO_3 bath overnight and then washed with chloroform and "sonicated" repeatedly with isopropanol and pure water. The hydrophobic surface on those slides has been prepared by standing them overnight in a covered beaker containing several drops of hexamethyldisilazane.

The emission and the lifetime decay were performed using the PTI spectrophotometer. The solution samples were deaerated by bubbling of pure nitrogen in the solution in the cuvette cell and then sealed under a continuous stream of nitrogen gas.

The Uv-vis spectra were performed using a Cary-14 spectrophotometer with a computer update operating system. The solution concentration was ~10^{-4} M while the absorbance of the film was measured as a function of the number of layers (50, 100, 150, 175).

RESULTS

The (π-A) isotherms obtained from different molar ratios of $Pt(Thpy)_2$ and stearic acid show two different solid phase changes at ca. surface pressure of (25-30) mN/m and (45-50) mN/m with a collapse pressure of (70-75) mN/m, while the (π-A) isotherm of a mixture of $[Pt(P\text{-}P)dmphen]^{+2}$ and stearic acid shows no plateau in the solid phase region. In both cases the phase change pressure and the collapse pressure are affected by increasing the molar ratio of the stearic acid in the solution mixture and by using the $CdCl_2$ in the subphase. The area per $Pt(Thpy)_2$ molecule calculated from the two plateaus in the solid phase region is (57 ± 2) and (25 ± 1) $Å^2$, and it is consistent for different molar ratios of $Pt(Thpy)_2$ in the solution mixtures. The largest area per $[Pt(P\text{-}P)dmphen]^{+2}$ ion calculated to be (62 ± 3)$Å^2$.

The Uv-vis spectrum of 50 layer LB film of $Pt(Thpy)_2$/stearic acid mixture shows absorption peaks at 423 and 296 nm. The absorbance increases linearly upon increasing the number of deposited layers.

The emission maximum of an LB film of $Pt(Thpy)_2$/stearic acid mixtures depends on the quality of the film, and is 566 nm for a multilayer film of 1:10 molar ratio of $Pt(Thpy)_2$ to stearic acid. The emission maximum of a solution of $Pt(Thpy)_2$ is solvent dependent[13] and, in all cases, occurs at longer wavelengths than the film even for a frozen sample (Table 1).

The lifetime decay of the Pt(Thpy)$_2$ solution is found to be longer than the reported values[13] at room temperature and at 77K (Table 2). The nitrogen lamp in the PTI is used for short lifetime measurements (nanosecond), while the xenon lamp is used for long lifetime measurements (microsecond).

Table 1
Emission data for Pt(Thpy)$_2$

	Literature[13]		Experimental	
	solvent	λ_{max} (nm)	solvent	λ_{max} (nm)
room temperature	nitrile*	578	CH_3CN	580
	$CH_3C_6H_{11}$	585	$CHCl_3$	585
77K	nitrile*	570	DMF	573
	$CH_3C_6H_{11}$	580		
solid sample at room temperature				585
LB film				566

Table 2
Lifetime data for Pt(Thpy)$_2$

	Literature[13]		Experimental	
	solvent	τ	solvent	τ
room temperature	nitrile*	2.2 μs	aerated CH_3CN	125 ns
	$CH_3C_6H_{11}$	3.2 μs	deaerated CH_3CN	11.7 ± 1.6 μs
77K	nitrile*	12.0 μs	DMF	18.2 ± 1.2 μs
	$CH_3C_6H_{11}$	10.0 μs		

* Propionitrile and butyronitrile (4:5 v/v)

DISCUSSION

A chloroform mixture of Pt(Thpy)$_2$ and stearic acid of molar ratios 1:5 down to 1:50 forms a good compressible monolayer film on the water surface. The pressure area (π-A) isotherm resulting from squeezing the film at the surface of water is an unusual one (Fig. 1). This isotherm shows two different changes in the solid phase region. The first change occurs at pressure of (25-30) mN/m while the second change occurs at pressure of (45-50) mN/m. The film at the surface of pure water is compressible up to a calculated pressure of 70 mN/m, and, beyond that pressure, the film collapses. However, the collapse pressure and the solid phase change pressures are affected by the molar ratio of stearic acid in the solution mixture, with collapse pressure increasing with increase of the acid in the solution mixture. The use of 0.1 mM $CdCl_2$ aqueous solution as a subphase increases the collapse pressure above 75 mN/m and also the pressure of the phase changes increases accordingly which means that the Cd^{+2} ions do stabilize the film by their interaction with the stearate ions from the stearic acid.

The changes in the solid phase region of the (π-A) isotherm suggest that the orientation of $Pt(Thpy)_2$ molecules is a function of the surface pressure and the areas calculated from different molar ratios of $Pt(Thpy)_2$ to stearic acid are consistent with a parallel and a perpendicular orientation (to the subphase) of the planar platinum complex. The areas calculated from the first and the second plateaus by extrapolating the linear region of the curve to zero surface pressure, assuming the area occupied by each stearic acid molecule to be 20Å^2, are (57 ± 2) and (25 ± 1)Å^2 per molecule, respectively.

For comparison, another square planar platinum complex $[Pt(P\text{-}P)dmphen][ClO_4]_2$ was used in a mixture with stearic acid to form an LB film on the surface of water. The (π-A) isotherm resulted from such a mixture shows no extra plateau in the solid phase region. This normal behavior of this positively charged platinum complex might be due to some ion-pair interaction between the Pt complex ion and stearic acid molecules. The maximum area per molecule of $[Pt(P\text{-}P)dmphen][ClO_4]_2$ was calculated from 1:50 molar ratio of $[Pt(P\text{-}P)dmphen]^{2+}$/stearic acid and found to be 62 ± 3 Å^2 using the same procedure mentioned above.

The film of 1:10 molar ratio of $Pt(Thpy)_2$/stearic acid formed on a 0.1 mM $CdCl_2$ aqueous subphase is reversible for a compression-expansion process up to a surface pressure of 30 mN/m at a barrier speed of 3 cm^2/min (Fig. 2).

The film from the surface of water subphase can be transferred to a solid hydrophobic substrate (quartz) at a pressure of 35 mN/m and a dipping speed of 50 mm/min with very good transfer ratio (> 80%). An attempt to transfer a good LB film of $Pt(Thpy)_2$/stearic acid mixture from the surface of water to a hydrophobic substrate at surface pressure where the $Pt(Thpy)_2$ molecules are perpendicularly oriented in the LB film (surface pressure of 47 mN/m) was difficult because of the high pressure. However, several layers of 1:10 molar ratio film mixture were deposited on the substrate at this pressure. The Uv-vis absorption and the emission of the film are the same as the film transferred at surface pressure of 35 mN/m.

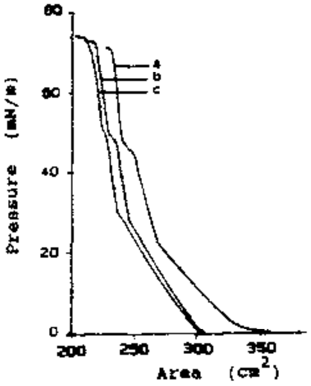

Fig.1. Surface pressure-area isotherm of Pt(Thpy)$_2$/ stearic acid mixtures with molar ratios of 1:10 (a); 1:30 (b); 1:50 (c)

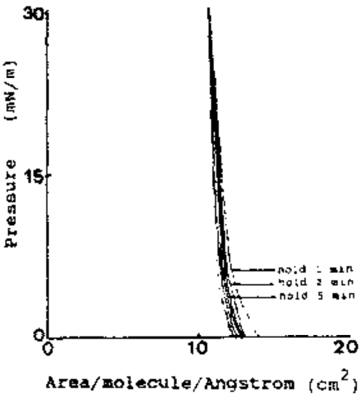

Fig.2. Compression-expantion cycling of 1:10 molar ratio of Pt(Thpy)$_2$/stearic acid spread on 0.1mM CdCl$_2$ subphase. Compression/expantion at 3cm^2/min.

The Uv-vis absorbance of 50 layers film (horizontal orientation) of 1:7 molar ratio of Pt(Thpy)$_2$/stearic acid shown in Figure 3. The MLCT band[13] appears to be slightly shifted to a lower energy in the film compared with the solution absorption spectrum (417 nm). The film absorbance was measured as a function of the number of layers and found to be linearly dependent on the

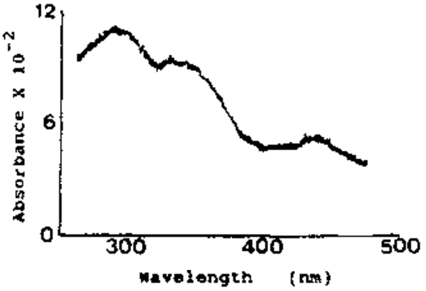

Fig.3. Absorbance of 50 layers of 1:7 molar ratio of Pt(Thpy)$_2$/ stearic acid deposited on a quartz plate.

number of layers deposited on the substrate (Fig. 4), which suggests that the platinum complex is dispersed homogeneously among the stearic acid molecules in the LB film.

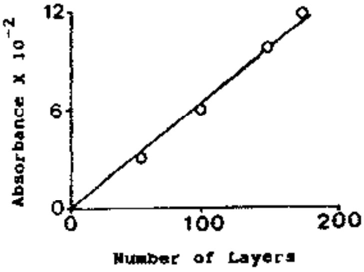

Fig. 4. Absorbance change of the MLCT band of a film of 1:10 molar ratio of $Pt(Thpy)_2$/stearic acid with the number of monolayers deposited.

The emission spectrum of a 140 layer film (horizontal orientation) of 1:10 molar ratio of $Pt(Thpy)_2$/stearic acid deposited on a hydrophobic quartz

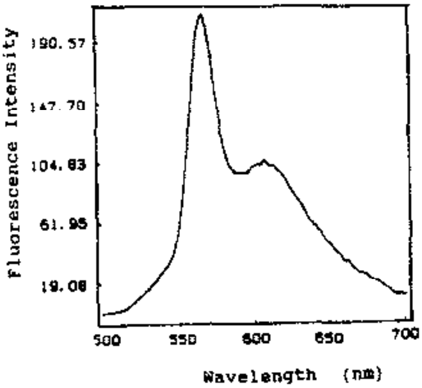

Fig. 5. Emission spectrum of LB film of 140 layers of $Pt(Thpy)_2$/stearic acid of molar ratio 1:10, exitation at 350nm.

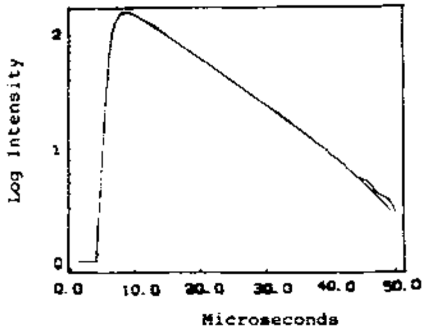

Fig.6. Initial decay of Pt(Thpy)$_2$ in deaerated CH$_3$CN at room temperature; exitation, 350nm; obsarvation, 585nm.

substrate shows a maximum at $\lambda = 566$ nm (Fig. 5). The emission from the film occurs at a higher energy than the solution or solid sample at room temperature and even that spectrum at low temperature (77K) (Table 1). No significant change in the emission spectra of films of different molar ratios of Pt(Thpy)$_2$/stearic acid was observed.

The lifetime of the platinum complex was measured at room temperature and for a frozen sample. The longest lifetime measured in aerated acetonitrile solution at room temperature using a nanosecond lamp (nitrogen lamp) was 125 ns. However, when a dilute acetonitrile solution is deaerated by bubbling with purified nitrogen for 10 minutes, the lifetime is extended to 11.7 μs (Fig. 6), while the literature value is 2.2 μs[13]. The lifetime of a frozen DMF solution at 77K is measured to be 18.2 μs (Table 2). Attempts to measure lifetimes of LB film were unsuccessful likely due to sensitivity problems.

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REFERENCES

1 "Supramolecular Photochemistry," NATOASI Series, ed. V. Balzani, Ch. 1, D. Reidel Publishing Co. (Dordrecht/Boston (1987).
2 Serroni, S. et al. J. Chemical Soc. Chem. Commun. 944 (1991).
3 Hickman, J.J.; et al. Science, 252 688 (1991).
4 Kuhn, H.; Mobius, D. Angew. Chim. (Int. Ed.) 10 620 (1971).

5 De Armond, M.K.; Myrick, M.L. Accounts Chem. Research 22 364 (1989).
6 Whitten, D.G.; Russell, J.L.; Schmehl, R. Tetrahedron 38 2455 (1982).
7 Seefeld, K.P.; Mobius, D.; Kuhn, H. Helv. Chim. Acta 60 2608 (1977).
8 Gaine G.L., Jr.; Behnken, P.E.; Valenty, L. J.J. Am. Chem. Soc. 100 6549 (1979).
9 Fujihira, M.; Nishiyama, K.; Yamada, H. Thin Solid Films 132 77 (1985).
10 Murakata, T.; Miyashita, R.; Matsuda, M. J. Phys. Chem. 92 6040 (1988)
11 Des Enfants, R.; Martinez, T.; De Armond, M.K. to be published in ACS Symposium Series, "Two and Three Dimensional Supramolecular Architecture," T. Bein (ed.) (1991).
12 Ken-To W.; Chi-Ming, C. J. Chem. Soc. Chem. Commun. 140 (1990).
13 Maestri, M.; Sandrini, D.; Balzani, V.; Chassot, L.; Jolliet, P.; Von Zelewsky, A. Chem. Phys. Letters 122 375 (1985).