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13. ABSTRACT (Maximum 200 words) The central theme of the four research areas has been and is intramolecular and intermolecular charge separation in materials, (metal complexes and oligomeric thiophene) directed towards the preparation of molecular assemblies useful in molecular electronics. The multielectron redox materials study has been completed and the generality of the charge localization scheme proposed by us for $[Ru(L_3)]^{2+}$ materials has been established for n=1 through 5 electrons. The one and two electron reduction are best adapted as "intramolecular" switching molecules. The liquid-liquid media has been established as an appropriate media for "intermolecular" charge separation using an external electric field to control the charge switching. The use of sol-gel media in the liquid-liquid experimental arrangement allows durable and portable charge separation assemblies. The oligomer-polymer materials provide a concentrated and durable molecular species capable of intermolecular and intramolecular charge separation at interfaces (liquid-liquid) and in Langmuir-Blodgett assemblies. The pendant Ru(II) complexes and the orthogonal thiophene oligomers both possess the perpendicular arrangement of π electron systems that can lead to charge storage and molecular switching. The mixed metal complex/fatty acid Langmuir-Blodgett films provide the organized molecular assembly system with the best potential for "molecular electronics." Our development of a technique for producing durable and portable LB films with a great range of metal complex types implies that this approach may be preferable to the fluid solution L-L-sol-gel approach.			
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**CHARGE STORAGE AND SWITCHING PHENOMENA WITH MOLECULAR
ASSEMBLIES OF METAL COMPLEXES**

FINAL REPORT

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May 31, 1993

U.S. ARMY RESEARCH OFFICE

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Table of Contents

I.	Preparation and Characterization of Multielectron Species	3
II.	Photoeffects for Liquid-Liquid and Sol-Gel Systems.....	5
III.	Soluble Oligomers and Polymers Incorporating Metal Complexes - Preparation and Characterization.....	6
IV.	Langmuir-Blodgett Films Containing Metal - Towards Molecular Electronics	8
	A. Molecular Electronics-Theory and Experiments	8
	B. Langmuir-Blodgett Film Methods and Materials	9
	C. Film Characterization	9
	D. Energy and Electron Transfer	11
	Estimation of Research Value.....	11
	List of Participants Supported Partially by ARO	12
	Publications	12

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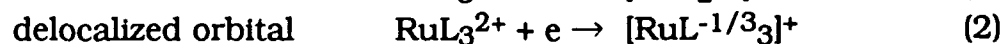
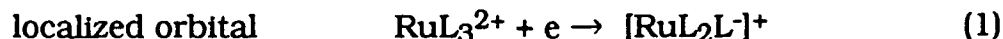
Charge Storage and Switching Phenomena with Molecular Assemblies of Metal Complexes

The report below briefly summarizes results in four related research areas:

- 1) Preparation and Characterization of Multielectron Species
- 2) Photoeffects for Liquid-Liquid and Sol-Gel Systems
- 3) Soluble Oligomers and Polymers
 - a) Metal Complexes
 - b) Thiophene
- 4) Langmuir-Blodgett Films Containing Metal Complexes - Molecular Assemblies for Molecular Electronics

I. PREPARATION AND CHARACTERIZATION OF MULTIELECTRON SPECIES

Background Results for One, Two and Three Electron Reduced Species The ESR, optical absorption and resonance Raman (RR) methods have been used to identify and characterize the orbital localization (eqns. 1,2) for $[\text{RuL}_3]^{2+}$ (parent) and $[\text{RuL}_2\text{L}']^{2+}$ (mixed ligand) type.



The ESR method has been central to the description of the redox orbital. ESR spectra for the one, two and three electron reduced species all give similar $g \sim 2$ and $S=1/2$ (Fig 1) spectra (RuL_3^{2+}) and exhibit a fluid solution temperature dependent line broadening which was the key to the localized orbital description of the reduced species. Our suggestion that the line broadening was the result of an electron hopping between the π electron systems of the individual chelate rings was corroborated by the ligand based intervalence (LBIT) measurement of Heath and our own RR of reduced $[\text{Ru}(\text{bpy})_3]^{2+}$. The magnitude of the activation energy ($700\text{-}1000 \text{ cm}^{-1}$) for the one electron reduction product is approximately one fourth of the LBIT energy as predicted for the limiting case intervalence system. However, the magnitude of E_a for the two electron species typically is one half that of E_a for the one electron species although the measured LBIT energy does not change for the two electron product.

The absence of hyperfine splitting ($a\vec{I} \cdot \vec{S}$) for the one, two and three electron reduction products ($n = 1, 2, \text{ and } 3$) and the absence of fine structure ($D\vec{S}_i \cdot \vec{S}_j$) for the two and three electron products for the reduced RuL_3^{2+} complexes were two puzzling results requiring rationale. Key to the answer to the first puzzle was the recognition that the kinetic process (electron hopping) occurring on the ESR time scale would result in the loss of typical $10^0\text{-}10^1$

gauss hyperfine (hfs) splitting. Consequently, the magnitude of E_a must be increased such that the hopping rate would diminish to permit the a|S interaction. Comparison of the cyclic voltammetry pattern for $[\text{Ru}(\text{bpz})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ indicated that, while similar, with each producing six-one electron waves, the $[\text{Ru}(\text{bpz})_3]^{2+}$ (bpz is 2,2'-bipyrazine) is shifted 0.6 volt positive. Since the localized orbital model predicts that the successive reduction electrons are placed into orbitals localized on the individual chelate rings, a mixed ligand complex as $[\text{Ru}(\text{bpy})_2(\text{bpz})]^{2+}$ should afford an opportunity for localizing an electron on the bpz that cannot hop to the bpy ligand since the barrier should be quite high. Generation of $[\text{Ru}(\text{bpz}^-)(\text{bpy})_2]^+$ by reduction at an appropriate potential produces a species that does give an ESR spectrum with hfs and whose $S=1/2$ contour does not broaden as the temperature is increased. A similar hfs structure is observed for the $[\text{Ru}(\text{bpz}^-)(\text{bpy})(\text{bpy})]^0$ product. The $[\text{Ru}(\text{bpz}^-)(\text{bpz})(\text{bpy})]^+$ complex does exhibit temperature dependent line broadening and no hyperfine structure; but the addition of a second electron to produce $[\text{Ru}(\text{bpz}^-)_2(\text{bpy})]^0$, as predicted, increases E_a so that hyperfine structure is observed. No temperature dependent line broadening is observed for this latter species. Verifying results have been obtained for mixed ligand complexes of bpy with the 2,2'-bipyrimidine ligand (bpm) and the 4-COOetbpy and 5-COOetbpy ligands (4-CO₂bpy is 4,4'-diethylcarboxy-2,2'-bipyridine) and 5-COOetbpy is 5,5'-diethylcarboxy 2,2'-bipyridine.

Results for four/five electron reduced species and more compounds - The ESR of the one electron reduction products for $[\text{Ru}(\text{CN})_4\text{bpy}]^{2+}$ and $[\text{Ru}(\text{NH}_3)_4\text{bpy}]^{2+}$ species have been determined and the a, hyperfine constant, values determined. These data are consistent with those "a" values (hyperfine constants) previously measured for mixed complexes of $[\text{Ru}(\text{bpy})_2\text{bpz}]^{2+}$ and $[\text{Ru}(\text{bpy})(\text{bpz})_2]^{2+}$.

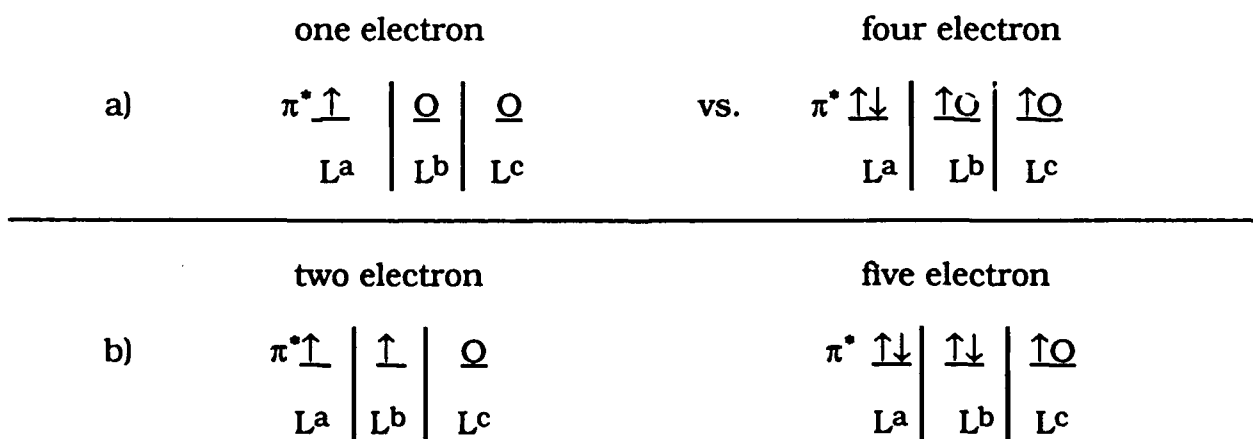


Figure 1. MO diagram of ML^n+ complex, (L^a , L^b and L^c are identical π diimine ligands) isolated from one another " \uparrow " is an electron, "O" is a vacant orbital site.

The ESR of the four and five electron reduction products of $[\text{Ru}(\text{bpz})_3]^{2+}$, $[\text{Ru}(4\text{-CO}_2\text{bpy})_3]^{2+}$ and $[\text{Ru}(5,5'\text{-dpbpy})]_3^{2+}$ have been measured. The g factors

obtained are similar to those of the one, two and three electron products with characteristics of a ligand radical and only small g anisotropy. However, the temperature dependent line broadening process for the one and two electron (interpreted as intramolecular electron hopping) is not apparent for these four and five species. The simple MO diagram (Fig. 1) in which the redox electrons are placed in empty π^* orbitals provided by the diimine ligands would, to a first approximation, be similar for the one and four electron species and the two and five electron species, that is, a comparable number of vacant sites for the "electron hopping" should be possible for the one and four and likewise for the two and five electron species.

As for the two and three electron reduced species half field ESR spectra at 77K produced no evidence for $S > 1/2$ species indicating that the reduction electron localized in individual π ligand orbitals and that coupling of spins on the individual rings does not occur. The determination of hyperfine structure at high temperatures for the $[\text{Ru}(\text{biq})_3]^{2-}$ (biq is 2,2'-biquinoline) and $[\text{Ru}(\text{pq})_3]^{2-}$ (pq is 2,2'-pyridylquinoline) (4e reduced species) is consistent with the absence of temperature dependant line broadening and implies that the thermal activation energy for electron hopping in these species must be large. ($E_a > 1400 \text{ cm}^{-1}$) (Two manuscripts produced)

II. PHOTOEFFECTS FOR LIQUID-LIQUID AND SOL-GEL SYSTEMS

Results The examination of photoeffects at the liquid-liquid interface commenced four years ago with the 6 month visit of Dr. Vladimir Marecek (Heyrovsky Institute of Physical Chemistry, Prague, Czechoslovakia). Dr. Marecek and Dr. Hofmanova-De Armond succeeded in the construction of a four electrode potentiostat and optical detection system (using lock-in amplifier detection) for donor and acceptor systems separated by the interface. The photo processes at the interface of two immiscible electrolyte solutions (ITIES) demonstrate that the interface was capable of blocking back electron transfer between an excited state metal complex, $[\text{Ru}(\text{bpy})_3]^{2+}$ and a suitable electron acceptor, in this case, methyl viologen (MV^{2+}). The comparison of the interface cyclic voltammetry and the photocurrent measured at the polarized interface enabled identification of the photoeffect as an electron transfer between interfacial $[\text{Ru}(\text{bpy})_3]^{2+}$ and the interfacial MV^{2+} . Two years ago Dr. Ondrej Dvorak, also from the Heyrovsky Institute, modified the photosystem and the detection system improving the sensitivity of the measurement to verify these initial results. Thus, the photocurrent was verified to be due to electron transfer at the interface, not from a bulk process. The initial measurement of a photopotential for the colored solution of a metal complex (thought to be monomolecular process) was found to result from a bimolecular process involving dissolved oxygen. We also succeeded in using impedance spectroscopy to determine the maximum rate constant, k , for the electron transfer process. The k was determined to be 10^2 - 10^3 , orders of magnitude larger than k for ion transfer at the ITIES. The efficiency of the electron transfer process was estimated to be 10-40% and is primarily determined by the extinction coefficient of the photoactive species and the surface concentration.

To establish the versatility of the charge transfer process at the ITIES for water and dichloroethane, the photoactive Ru(II) complex $[\text{Ru}(\text{bpz})_3]^{2+}$ (bpz is 2,2'-bipyrazine) was utilized with a series of reductive quenchers as organic

amines. The optical properties of $[\text{Ru}(\text{bpz})_3]^{2+}$ are nearly identical to those of $[\text{Ru}(\text{bpy})_3]^{2+}$ but the electrochemical properties of the species are different such that $[\text{Ru}(\text{bpz})_3]^{2+}$ is readily reduced and not oxidized whereas $[\text{Ru}(\text{bpy})_3]^{2+}$ has equal photoreduction and photooxidation capability. As for the $[\text{Ru}(\text{bpy})_3]^{2+}$ system, the charge transfer here is determined to occur in a thin layer in the interfacial region. This region is estimated to be several nanometers thick and the dc potential across this interface insures charge separation. Digital simulation demonstrates that bulk diffusion flux is negligible for these experimental conditions.

Most recently, the "charge separation at an interface" studies have been extended to include sol-gel systems. In the first study, transparent indium (tin) oxide (ITO electrodes were modified by a vanadium pentoxide gel layer prepared by hydrolysis of $\text{VO}(\text{OCH}_2\text{CH}_3)_3$. An anodic photovoltaic effect was induced by visible light. The use of ESR to determine the concentration of paramagnetic V^{IV} was useful in establishing a mechanism for the anodic photo effect.

A second sol-gel contribution utilized tetramethyl orthosilicate to produce a polysiloxane gel modifying the surface of platinum and ITO electrodes. The $[\text{Ru}(\text{bpy})_3]^{2+/3+}$ couple incorporated in the gel retains electrochemical and luminescence properties of the species in solution. Comparison of the electrochemical and luminescent properties of the $[\text{Ru}(\text{bpy})_3]^{2+}$ illustrate that only a fraction (~25%) of the metal complex is electrochemically active. This likely results from the fact that a substantial fraction of encapsulated complex is incorporated deep in the gel bulk and is not accessible to the solvent. Neither linear diffusion nor thin layer behavior fits the voltammetry curve shape for doped sol-gel films. Undoped films (~micron thickness) on platinum reduces the electron transfer for a H_2O redox species but does not prevent it, likely due to the porous character of the silica gel. Soaking the gel in water solution does not affect the gel film concentration but cycling the potential of the gel electrode in water does decrease the initial complex concentration. The gel film, doped or undoped, is destroyed by nonaqueous solvents. (Five manuscripts)

III. SOLUBLE OLIGOMERS AND POLYMERS INCORPORATING METAL COMPLEXES - PREPARATION AND CHARACTERIZATION

Background The electron spin resonance (ESR) of the reduction products of three polymers containing pendant $[\text{Ru}(\text{bpy})_3]^{2+}$ was reported earlier by us. As for the monomeric $[\text{Ru}(\text{bpy})_3]^{2+}$, the redox electrons are localized on single chelate rings and individual bpy (unreduced) and bpy^{-1} (reduced) species can be identified. Temperature dependent line broadening characteristics of inter-ring electron hopping is observed for the one electron species while, for the two and three electron reduction products, no line broadening is observed but hyperfine splitting can be measured. Such behavior indicates that the first two electrons enter orbitals localized on bpy rings while the third electron is localized in an orbital on the vinylbipyridine ligand (the linkage to the polymer backbone). Unlike the reduction products for many mixed ligand monomer cases, the $E_{1/2}$ and voltammetry wave spacings for the $[\text{Ru}(\text{bpy})_2(\text{pvbpy})]^{2+}$ (pvbpy=4-polyvinyl 2,2'-bpy) are similar to the parent $[\text{Ru}(\text{bpy})_3]^{2+}$ species. Consequently, temperature dependent line broadening and no hyperfine splitting would be expected for the two electron pendant Ru-complex if it

behaved as the monomeric parent complex. The neutral charge for this two electron reduced species may result in this species residing in a hydrophobic environment that effectively increases the barrier to hopping. Thus, in this case, the supermolecular environment does produce a significant perturbation upon the charge localization for this species.

Results The cyclic voltammetry of the heptamer thiophene (7-T) and the two dimer thiophenes have been determined (two ill-shaped oxidation waves are found for the heptamer) and experiments to produce totally electrolyzed samples done. For the heptamer, the narrow ESR line in methylene chloride suggests that the 0.1 millimolar thiophene sample is conducting. For the two orthogonal dimers (Si bridged and spiro C bridged), the broad irreversible CV wave suggests that the redox potentials for the one, two, three, and four electron oxidation waves overlap. This is consistent with the anomalous current/time curves measured for the constant potential electrolysis. Consequently, the chemical oxidation of the thiophene with anhydrous ferric chloride (eqn. 3) was used.



For the chemical oxidation, E_a for the two heptamer dimers are: (Si and spiro C) gave $E_a \sim 110 \text{ cm}^{-1}$, similar to the activation energy measured for the linear heptamer. These data suggest that the charge motion processes occurring for the two orthogonal dimers is similar to that in the heptamer. These E_a values suggest that charge hopping between the orthogonal halves of the two dimers cannot occur. The two electron oxidation of the two dimers produces a diamagnetic species, an unexpected result. The ESR and optical data were repeated to verify these data. The ESR results for the orthogonal thiophene dimers three thiophene in length are consistent with Aviram's suggestion that charge transfer between the two perpendicular halves of the monooxidized thiophene oligomers can be the basis of a molecular switch.

The pendant $[\text{Ru}(\text{biq})_2(\text{bvbp})]^{2+}$ complex has been synthesized and the absorption and emission spectra used to identify the presence of the $\text{Ru}(\text{biq})_2$ moiety in the complex. The luminescence spectra of the polymer complex is shifted to the red relative to the monomer analog $[\text{Ru}(\text{biq})_2\text{bpy}]^{2+}$. The CV pattern obtained for the polymer is as predicted from the monomer analog. The total electrolysis of this polymer complex material has been done and ESR spectra and temperature dependent ESR linewidth studies of the one, two and three electron product obtained.

Using a Meyer synthetic procedure, the $[\text{Ru}(\text{bpy})_2(\text{CO}_3)_2]^{-2}$ species was produced and reacted in acetic acid with the polybpy (Pbpy) oligomer to give the $[\text{Ru}(\text{bpy})_2(\text{Pbpy})]^{2+}$ pendant complex, an organic solvent soluble complex with a π electron backbone. Absorption and emission spectra in acetonitrile (AN) solvent gave bands that correlate with the $[\text{Ru}(\text{bpy})_3]^{2+}$ parent with an additional intense band of high energy. The CV in AN solvent is similar in overall shape and redox peak position to $[\text{Ru}(\text{bpy})_3]^{2+}$. The ESR spectra measured for the nominal two and three electron species is as expected with the spectrum showing the usual $S=1/2$ spectroscopy. Thus, the two electron reduced species would be written as $[\text{Ru}(\text{Pbpy})(\text{bpy})(\text{bpy})]^\ominus$. The narrow linewidth (5-7 gauss peak to peak) for the one electron reduction line suggests that the reduced Pbpy complex is a conductor with the first electron located on

the PbpY backbone of the $[\text{Ru}(\text{bpy})_2\text{Pbpy}]^{2+}$ complex. (Three manuscripts)

IV. LANGMUIR-BLODGETT FILMS CONTAINING METAL - TOWARDS MOLECULAR ELECTRONICS

Molecular Electronics-Theory and Experiments

A major fraction of the large number of film studies in the literature is motivated by the desire to produce a device or electronic function that can be related to the "molecular electronics" area. The focus on molecular dimension rectifiers, diodes and charge storage devices has, in large part, been generated by theoretical contributions, as the 1974 report of Aviram and Ratner who postulated an organic molecular rectifier of the D- σ -A (D is a donor, A an acceptor and σ , a covalent bond bridge between D and A. Metzger and Pannetta have developed a systematic synthetic approach to such a rectifier but to date have not succeeded in developing such a rectifier. Pertinent to these results are the experimental efforts of Aviram and coworkers to develop a molecular rectifier and to measure this process using an STM (scanning tunneling microscopy) tip as a detector. Although their initial rectification result was withdrawn, since they determined that the STM tip was touching the substrate surface, their use of the STM tip as a probe to monitor switching events was a significant contribution.

Interrogation of Nanoelectronic Structures. Currently, silicon based technology is routinely capable of producing 1 cm^2 chips with 16 megabits of information. This approach to a nanofabricated system proceeds from the large to the small system whereas the LB film and the SA methods proceed from the small to the large, so in spite of the remarkable capability of the Si based microelectronics industry, a role for molecular electronics in which the elements have molecule dimensions (1 nm) would seem to be possible.

Basically, two general approaches can be utilized both of which can, in theory, be viable: 1) molecular assembly interrogation and 2) single molecule (or electron) interrogation. This can involve two dimensional (monolayer) or three dimensional (multilayer) film structures, minimizing the measurement sensitivity problem (the READ problem) but thereby limiting the density of information storage. To achieve the ultimate in miniaturization the measurement of single molecule properties as "hole burning" must be utilized as discussed by Wild and colleagues. Key to the utility of this hole burning technique is the "Near Field Optical" phenomena examined by Lewis, Leiberman and Koppelman as well as Betzig. In the recent Science report, an optical near field technique provides an ability to interrogate single molecules (or layers of molecules).

For electrical interrogation of individual molecules, the single electron transfer (SET) (or Coulomb blocking) phenomenon could be utilized. The basic concept, recently described in a Scientific American article, utilizes a single small insulated tunnel junction between two metal electrodes. In at least one case, the use of an STM to probe a metal droplet on a metal oxide surface at 4K produces a V-I plot with sharply defined Coulomb steps.

An even more interesting (if true) result is that of Nejh who utilized a liquid crystal, 4,4'-n-heptyl cyanobiphenyl, on a platinum (111) crystal with an STM tip to measure an SET event that occurs at room temperature (294K).

Langmuir-Blodgett Film Methods and Materials

A large fraction of the work done with metal complex LB films have utilized classical amphiphilic metal complexes to make LB films. Our goal is to extend and generalize the LB film technique to include hydrophobic molecules with no long chain alkyl substituents. A systematic variation of charge, shape and metal ion in the complex has been utilized. We have produced monolayer and multilayer films (150 layers) of tris 4, 4',5,5'-tetramethyl-2,2'-bipyridine) $\text{Ru}^{\text{II}}([\text{Ru}(\text{tmbpy})_3]^{2+})$ on quartz plates. This pseudospherical cation complex produces ion-pair complexes with the stearate anion, much as the $\text{pRu}(\text{dpphen})_3]^{2+}$ LB film reported by Matsuda and coworkers. The pseudospherical (trisphenylpyridine) Iridium (III) $(\text{Ir}(\text{ppy})_3)$ complex is neutral and thus cannot form an ion-pair complex with the stearate anion. Nevertheless, monolayer and multilayer films of this can be produced over a wide range (1:1 to 20:1) of SA to metal complex.

Extending the hydrophobic metal complex to square planar geometry luminescent metal complexes, film results have been obtained for two hydrophobic Pt(II) complexes. The ion-pair film strategy was used for $[\text{Pt}(\text{P-P})(\text{Me}_2\text{-phen})]^{2+}$ where P-P is a chelating diphosphine and $\text{Me}_2\text{-phen}$ is 5,6-dimethyl-1, 10-phenanthroline. The transfer ratios for this mixed fatty acid-complex are greater than 0.9 and multilayer films having 150 layers were produced. Most recently the metal complex, $\text{Pt}(\text{Thpy})_2$ (Thpy is 2-(2-thienyl)-2-pyridine) was provided by Professor von Zelewsky (U. of Fribourg, Switzerland). A mixed stearic acid-metal complex from 50:1 to 2: to 1 gave stable reproducible films with transfer ratios greater than 0.9. Multilayer films having up to 150 layers can be produced.

Our recent focus has been upon development of new LB methods for producing more stable films and for producing LB films of water soluble metal complexes. Octadecylsilane (ODS) and the shorter chain dodecylsilane (DDS) have been used to dissolve the hydrophobic $[\text{Ru}(\text{tmbpy})_3]^{2+}$ and the LB apparatus used to produce multilayer siloxane films. Also "sandwich" type LB film assemblies have been made with four layers of pure siloxane, four layers of mixed $[\text{Ru}(\text{tmbpy})_3]^{2+}$ /stearic acid, followed by four more layers of pure siloxane. The ion-pair strategy was extended to produce a film from $[\text{Ru}(\text{bpy})_3]^{2+}$ ion dissolved in an aqueous solution on the surface of which stearic acid has been placed. By vertical dipping samples with up to 150 layers can be prepared.

Film Characterization

The past two and one half years have been spent examining various instrumental methods to determine their utility in characterizing the LB films and deciding which among the methods require some additional emphasis to improve their utility.

Pressure/area isotherms are routinely used to determine the presence of the metal complex in the mixed LB film prior to transfer from water surface. So, for example the charged Pt(II) complex, assumed to produce an ion paired complex, produces an isotherm which is shifted to larger "molecular areas" as the fraction of metal complex increases. This behavior is observed for film ratios varying from 2:1 to 50:1 (stearic acid/Pt complex) and molecular volumes indicate a horizontal molecular orientation to the substrate. For the neutral $\text{Pt}(\text{Thpy})$, the P/A isotherm indicates an additional phase change at high pressure for which the molecular area corresponds to the rotation of the

molecule from a horizontal to a vertical orientation.

For the films of the $[\text{Ru}(\text{bpy})_3]^{2+}$ produced by ion-pair interaction of subphase $[\text{Ru}(\text{bpy})_3]^{2+}$ with SA at the water-air interface, the pressure/area isotherm as function of metal complex concentration does not change from that of pure stearic acid. This behavior we have interpreted to indicate that the metal complex is beneath the SA head group. At the other extreme, the P/A behavior as a function of concentration of the implies that the Pt(II) complexes the $[\text{Ru}(\text{dpphen})_3]^{2+}$ and the neutral $\text{Pt}(\text{Thpy})_2$, implies that they are intercalated within the film. Other data (scanning microscopy, energy transfer) will be required to precisely locate the metal complex in the film for all of the ambiguous cases. Isotherm data for identification of an ordered film on the subphase surface was also utilized for the preparation of multilayer sol gel type films using the LB method. In all film examples above the collapse pressure of the stearic acid film as increased by the addition of the metal complex.

Spectroscopic Characterization Luminescence measurements of the film have been used in every mixed film produced since all of the metal complexes used do luminescence in solution. Correlation of the film and solution emission spectrum does verify: (1) the integrity of the metal complex and (2) the occurrence of structural perturbations by the film environment. Thus the absence of a emission structure change or significant intermolecular interaction of the $[\text{Ru}(\text{bpy})_3]^{2+}$ in the combined sol gel-LB film preparation is verified by the similarity of the solution and film emission contours of the Ru(II) complex. Absorption spectra as function of the number of layers have been obtained for the Pt(II) complexes, the $[\text{Ir}(\text{ppy})_3]$ and $[\text{Ru}(\text{tmbpy})_3]^{2+}$ metal complex films and used to argue that the linear change of absorbance with number of layers indicates homogeneous mixed films.

FT-IR has been utilized by us to characterize the $[\text{Ru}(\text{tmbpy})_3]^{2+}$ films and the $[\text{Ru}(\text{tmbpy})_3]^{2+}$ /sol gel LB film preparation. For the first case, the absence of the strong IR stretch of the ClO_4^- counter ion in the film preparation of $[\text{Ru}(\text{tmbpy})_3][\text{ClO}_4]_2$ and SA was used to argue that the ion-pair mechanism is operative. The acquisition of a PE 1720 spectrometer with an MCT detector and a grazing angle attachment has enabled us to utilize the local FT-IR system to calculate the tilt angle (angle of tilt from the perpendicular to the substrate) of the octadecylsilane (ODS) in the mixed matrix film. The angle calculated from appropriate equations was 15° , consistent with that of the typical siloxane pure film.

Electrochemical Characterization Cyclic voltammetry (CV) has been used as a qualitative measure for the Ru^{2+} films and the Ir^{3+} case. The oxidation of the $\text{Ru}^{\text{II}} \rightarrow \text{Ru}^{\text{III}}$ of the $[\text{Ru}(\text{tmbpy})_3]^{2+}$ film provided evidence that Ru^{II} complex is present in the film. For the $[\text{Ir}(\text{ppy})_3]$ film on ITO (vertical dip) on the glassy carbon electrode (horizontal touch method), the oxidation wave is irreversible (the $\text{Ir}^{\text{III}} \rightarrow \text{Ir}^{\text{IV}}$ process in acetonitrile solution is reversible).

Scanning Microscopy We have succeeded in obtaining molecular level AFM and STM resolution images of monolayers of stearic acid and mixed LB films of the $[\text{Ru}(\text{tmbpy})_3]^{2+}$ complex as well as the mixed LB films of the $[\text{Ir}(\text{ppy})_3]$ complex. We developed a procedure for the STM and AFM images:

- 1) Images are compared for
 - a) bare substrate
 - b) substrate plus fatty acid
 - c) substrate plus mixed

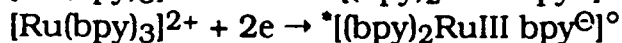
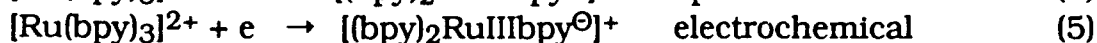
- fatty acid-complex layer
- 2) Images are obtained for both the constant height and constant current operating modes where possible
 - 3) Different substrate materials (ITO, Au, Si and Ag) are used when feasible.
 - 4) Distances of "molecule" images are compared with distances estimated from models and STM and AFM dimensions are correlated with area measurements from the LB isotherms.
 - 5) The image filtering procedure should not add structure to the film image but only clarify the structure of the unfiltered image.

These precautions do not necessarily provide insights into the modeling of the molecular image itself, in particular for STM where the image is really an electron density map which may not coincide with the molecule shape while the AFM technique images mainly the top layer. For the LB film, any ordered structure should not result from a template effect (as for the self acid matrix).

An AFM image (3 layers) of mixed Ir(ppy)₃ with SA shows a "tails up" image. The "heads up" AFM image (4 layers) of this same 6:1 SA/Ir(ppy)₃ is also obtained. The "tails up" image pattern and dimensions are nearly identical to the pure stearic acid "tails up" film. The "heads up" image of the mixed film suggests that an ordered pattern of Ir(ppy)₃ occurs near the hydrophilic head, perhaps beneath it. The spacing of the "heads up" image is larger than that of the "tails up" image.

Energy and Electron Transfer

Our solution data provides evidence that the propeller shaped tris-diimine complex shows charge localization in the individual propeller blades (spatially isolated orbitals) for both the excited state (Eqn. 4) and the reduced species (Eqn. 5).



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For the reduced species, six electrons can individually add to the three chelate rings, and ESR line broadening demonstrates intramolecular electron transfer between the chelate rings. These solution ESR data are necessary background detail for the production of electrolyzed LB films.

Electrochemical methods (CV) determine the qualitative and quantitative intermolecular charge transfer of the multilayer mixed films. Both the mixed [Ru(tm-bpy)₃]²⁺ and the Ir(ppy)₃ films coated on ITO electrodes appear to give CV behavior consistent with a tunneling electron transfer between the metal complex layers. The materials, techniques, instruments and expertise required to produce successful "molecular electronics" elements and devices have been detailed and will await appropriate funding to manifest significant results. (Eight manuscripts produced).

Estimation of Research Value

Any attempt to value basic research must suffer from the inability to precisely evaluate the effects of results and ideas in our practical society, both because of the need for the passage of time to convert the research to practical

products and because of the difficulty in assessing the value added by a piece of research. Consequently, the evaluation of current research must rely upon flawed quantitative data as "papers published, etc." At present sixteen papers have been published or accepted in refereed American Chemical Society journals and international journals and three more manuscripts will be submitted soon producing 19 papers for the \$250,000 award. This \$13K/paper rate is much less than the dollar/paper rate of ARO, NSF, DOE awardees as Myer, Turro etc. Indeed the dollar amount/paper of these researchers is more than three times that of these researchers.

While the argument can be made that the above is strictly a "quantitative" rather than a "quality" effect, some other data does occur that can amplify the "quality" fact. The author of this report, M.K. DeArmond, has in his 25+ years at North Carolina State and New Mexico State, two ambitious but less well known universities produced ~ 106 papers and trained some seventeen Ph.Ds and twelve postdoctoral scientists. As a measure of the "quality" factor, the survey by *Science Watch* April, 1992 of the science citation index for inorganic and analytical faculties during the 1986-1990 period ranks New Mexico State fifteenth in the world. Two Inorganic chemists (R. Wilkens and M.K. DeArmond) and one analytical chemist (J. Wang) can be determined to be the primary contributors to this recognition.

Another measure of the "quality" factor is the success of the graduates of the DeArmond program. Of the sixteen Ph.Ds granted, and twelve postdoctoral, three have faculty positions at major Universities (U. South Carolina, U. North Carolina (Charlotte),) six at National laboratories (Los Alamos, Battelle, Heyrovsky Institute, Prague) four in Industrial and government research labs (Nissan, EPA). Others are dispersed among colleges and industry in the U.S. and Europe.

List of Participants Supported Partially by ARO

- 1) Mr. James Diers, Physical Chemistry, June, 1993, Ph.D. received, (Postdoctoral at UC (Riverside))
- 2) Mr. Yuhao Sun, Ph.D. to be received, Inorganic Chemistry, August, 1993 (Postdoctoral at ?)
- 3) Mr. Hussein Samha, Ph.D. in Inorg. Chemistry, Ph.D. expected, May, 1994.
- 4) D. Anna H. DeArmond, postdoctoral, currently at New Mexico State University
- 5) Dr. Ondrej Dvorak, postdoctoral, currently at Heyrovsky Institute, Prague, Czech Republic

Publications

91. "Chromophoric Fine Tuning and the Interchromophoric Coupling Model in Ruthenium (II) Polypyridyl Complexes" (with R.L. Blakley, M.L. Myrick and R. Pittman), *J. Phys. Chem.*, **94**, (1990).
92. "Langmuir-Blodgett (LB) of Transition Metal Complexes - Square Planar Platinum(II) Complexes" (*Coord. Chem. Rev.* **III**, 73 (1991) (with H. Samha).
93. "Donor-Acceptor Proton Transfer Across the Interface of Two Immiscible

- Electrolyte Solutions", **J. Electro. and Chem.** 317, 299 (1991).
94. "Langmuir-Blodgett Films of Transition Metal Complexes" ACS Symposium Series, Supramolecular Architecture in Two and Three Dimension, (ed. by T. Bein), March, (1992) (with R. Des Enfants and T. Martinez).
 95. "Photoprocesses at the Liquid-Liquid Interface (III) Charge Transfer Details for Photoactive Metal Complexes", **Langmuir**, 8, 508 (1992) (with A.H. De Armond and O. Dvorak).
 96. "Photoprocesses at the Liquid-Liquid Interface IV Photooxidative Transfer with [Ru(bpzO₃)²⁺ Complexes", **Langmuir** 8, 955 (1992) (with O. Dvorak).
 97. "Langmuir-Blodgett Films of Pt(II) Complexes," **Langmuir**, 8, 2001 (1992) (with H. Samha and T. Martinez).
 98. "Photovoltaic Effect on Vanadium Pentoxide Gels Prepared by the Sol-Gel Method," **Chem. Materials**, 4, 1074 (1992) (with O. Dvorak and J. Diers).
 99. "Electrode Modification by the Sol-Gel Method", **J. Phys. Chem.**, 97, 2646 (1993) (with O. Dvorak).
 100. "Langmuir-Blodgett (LB) Films of Tris(-2-phenylpyridine) Iridium(III)" **Inorg. Chem.** (In press), (1992) (with H. Samha, F.O. Garice and R.J. Watts).
 101. "Multilayer Self Assembled Films Using the Langmuir-Blodgett Deposition Method," **J. Am. Chem. Soc.**, In Press, (1993) (with H. Samha).
 102. "Electron Microscopy of LB Films of Ru(II) Complexes," **Thin Solid Films**, In press (1993) (with O. Dvorak and A.H. De Armond).
 103. "Characterization of Unique Conducting Oligomeric Thiophene Materials," **Chem. Materials**, submitted, (1992) (with J. Diers, A. Diaz, J. Guay, and J. Tour).
 104. "Characterization of Mixed LB Films Containing Metal Complexes," **J. Phys. Chem.**, submitted, (1992) (with T. Martinez).
 105. "A Pendant Complex of Ru(bpy)₂²⁺ with an Oligomeric Bipyridine Backbone - A New Conducting Materials?" **J. Phys. Chem.**, submitted (1993) (with Y. Sun).
 106. "Incorporation of a Water Soluble Metal Complex into Fatty Acid LB Film by an Ion-Pair Process," **Langmuir**, In Press. 1993 (with O. Dvorak, H. Samha).