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Cite this: DOI: 10.1039/c0xx00000x

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PAPER

Optical and Electrochemical Properties of Covalent Assembled bis(4’-carboxylic phenyl terpyridyl) Ru(II)-Monolayer†

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Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x00.

Homoleptic monomolecular layers of optically-rich and redox-active Ru(II)-4’carboxylic-phenyl-2,2’:6’,2”-terpyridyl (**1**) have been fabricated on SiO_x-based substrates. The optical and redox properties of the films have been studied in detail. The molecular films showed high electrochemical and thermal stability. Combination of thermal and electrochemical stability of the surface-confined assemblies could be useful for potential applications in material science.

1 Introduction

Inorganic-organic hybrid materials (IOHMs) possess a number of fascinating physical properties like conductivity, magnetism, optics, to name a few, either individually or in myriad combinations.[1]This scenario makes them attractive for studying the “proof-of-principle” of the proto-type systems. However, for these materials to be applicable in real-world operations, the molecules need to be confined in space and time to have a better control over the molecular dynamics. Recent advances in this area have prompted to transfer the molecular properties from solution phase to solid substrates such as metal, quartz, glass, ITO-coated glass, silicon and semiconducting materials. Within this framework, molecular- based thin films is an up-and-coming research area owing to their stimulating applications in catalysis,[2] solar energy conversion,[3] and sensors.[4] Further, this methodology is being explored in fabrication of nanoscale electronic devices such as spintronics,[5] memory elements[6] as well as in (bio)-engineering.[7] In this connection, the research on solid-liquid or solid-gas interfaces is of the central importance, as it provides technology-generating properties in a way that is extraordinarily experienced in science and technology.[8] Within this, self-assembled monolayers (SAMs) have gained significant attention both from scientific and industrial communities. The self-assembled monolayers are the nano-objects with a number of useful features that link properties at the molecular level with numerous fascinating interfacial phenomena. This area of research is also well known as “molecular-based thin film chemistry”[9]. In particular, monolayer assembly with inorganic-organic materials is an emerging field in material science.[10] The monolayers have been developed as an excellent model surfaces as they provide expedient, flexible and simple molecular systems in the form of thin films through which the properties of surfaces can be altered readily. The fabrication of monolayers using metal complexes finds plenty of applications including optical, magnetic, catalytic, sensor, and electronic responses. The chemistry developed for surface modification mainly uses thiol or dithiols derivatives (either aliphatic or aromatic) on crystalline gold surfaces, extensively studied to date[11] and electrostatic interactions for charged surfaces.[12] However; these confined species suffer from the stability problem. To address the issue, stronger attachment of the molecules to the substrates are needed and covalent linking of the molecular component to the functionalized substrates is one such way. Therefore, recent developments where covalent assembled monolayers (CAMs) are formed using siloxane coupling layer (CL) have become more advantageous as far as stability issue is concerned.[13] To accomplish the immobilization process the substrates that have been used included Ni, Au, ITO-coated glass, quartz etc, is mostly unexplored.[14] On the other hand, reports on successful depositions of ruthenium-terpyridyl complexes on SiO_x-based substrates *via* covalent bond formation are fewer.[15] To address this present dearth, covalent assembled monolayers of an optically-rich and redox-active Ru(II)-terpyridyl complex have been fabricated on glass, ITO-coated glass substrates.

2 Experimental Sections

2.1 Materials

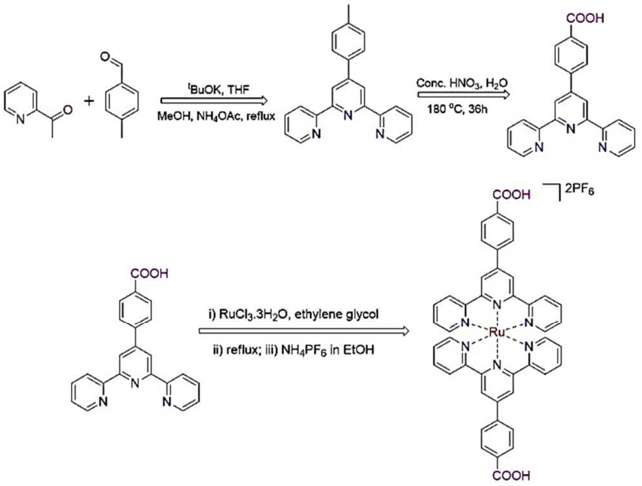
$RuCl_3.3H_2O$, p-tolualdehyde, 2-acetyl pyridine, NH_4PF_6, ferrocene, CD_3CN, DMSO-d_6, $CDCl_3$ and *n*-propyl trimethoxysilane were purchased from Sigma-Aldrich and used as received. Triethyl amine (Et_3N), ammonium acetate (NH_4OAc) was purchased from s. d. fine chemicals (Mumbai, India). Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and potassium tert-butoxide (^tBuOK) were purchased from Alfa-Aesar. ITO-coated glass substrates were purchased from VIN Karola Instruments (ρ=7-10 ohm^2). Soda-lime glass substrates were obtained from Chase Scientific Glass, India. Solvents (AR grade) were purchased from Merck and S. D. Fine Chemicals. The solvents were purified using literature procedures[16] and stored in N_2 filled glove box (O_2 < 2 ppm).

2.2 Physical Measurements

UV-Vis measurements were carried out on a double beam JASCO (Model V-670) spectrophotometer. 1.0 cm path length quartz cuvette equipped with a Teflon stopper was used for data collection. A bare glass substrate was used to compensate for background absorption. ^{1}H and ^{1}H-^{1}H NMR correlation spectra were recorded on JEOL 400 NMR (JNMECX 400P) using appropriate deuterated solvent. Electrochemical measurements were performed using a CH Instrument (Model 660D) electrochemical Workstation. Cyclic voltammograms (CV) of the complex were recorded in dry acetonitrile with $TBAPF_6$ as supporting electrolyte using a glassy carbon as working electrode (WE, ~ 0.2 cm^2), a Pt wire as counter electrode (CE) and Ag/AgCl (in 1 M KCl) as the reference electrode (RE). ITO-coated glass substrates (2.2 cm^2) were used as WE for the case of monolayer's electrochemical measurements. $TBAPF_6$ was dried at 100°C for 45 min before use. The solution was degassed with Ar for 30 min before measuring voltammograms.

2.3 Preparation of ligand and complex

The 4'-carboxyphenyl-terpyridyl was prepared by literature method[17, 18] which consists of two consecutive steps as shown in Scheme 1 and SI. The complex Ru(II)-4'carboxylic-phenyl-2,2':6',2"-terpyridyl was synthesized using a literature method.[19]



Scheme 1: Synthetic scheme for preparation of ligand and **1**.

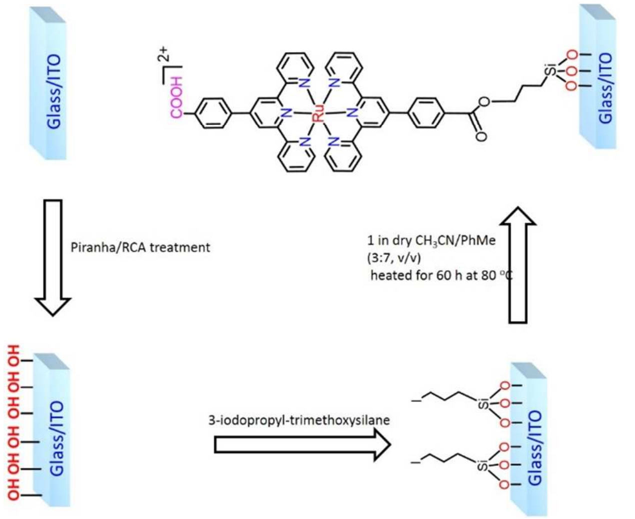
2.4 Preparation of 1-based covalent assembled monolayers

The fabrication of covalent assembled monolayers of **1** on SiO_x-based solid supports is schematically presented in scheme 2. ITO-coated glass substrates (22 mm × 10 mm) were cleaned by successive sonication in *n*-hexane, acetone, 2-propanol and dried under N_2 stream. Soda-lime glass substrates were cleaned by immersion in a "piranha" solution (composition of "piranha" soltution-7:3 (v/v) conc. H_2SO_4/30% H_2O_2) over 1h. [*Caution: "piranha" solution is an extremely dangerous oxidizing agent and should be handled carefully*]. Consequently, the glass substrates were rinsed repeatedly with deionized water and subjected to Radio Corporation of America (RCA) reagent (1:5:1 (v/v), NH_3•H_2O/H_2O/30% H_2O_2) at room temperature for 45 min. The substrates were then washed with water and dried under an N_2 stream. The glass and ITO-coated glass substrates were functionalized with 3-iodo-n-propyltrimethoxy-silane under N_2 atmosphere using Schlenk line technique.[20] The substrates were reacted with a dry *n*-pentane solution of 3-iodo-n-propyltrimethoxy-silane (200:1, v/v) for 45 min under N_2. Then the substrates were washed with dry *n*-pentane, and sonicated for 3 min with DCM and isopropanol to remove any physisorbed materials. The resulting coupling layers (CLs) were dried under a stream of N_2 followed by activating at 120ºC for 30 min. The functionalized substrates were loaded into a Teflon lined autoclave and immersed in acetonitrile/toluene (1:1, v/v) solution of **1** (0.5 mM) and thereafter placed in a programmable oven at 80ºC for 56h and cooled to room temperature. They were then rinsed with acetonitrile and sonicated for 3 min with acetonitrile and isopropanol followed by drying under N_2 before recording UV-vis spectra and cyclic voltammograms.

3 Results and Discussion

3.1 General procedure

In the present study, Ru-terpyridyl complex was chosen since, functionalized 2,2':6',2"-terpyridyl ligands (i) exhibit strong "chelate effect" towards transition metal ions, (ii) facile synthetic route, (iii) versatile coordination modes and (iv) its π-electron accepting nature stabilize the metal ions in lower oxidation states.[21] Similarly, functionalized terpyridyl complexes of transition metal ions (so called metallo-ligands) have several advantageous such as (i) robustness due to strong metal-to-ligand back bonding [dπ(M)-pπ(L)], (ii) tuneable photo-physical properties, and (iii) can be immobilized on various solid substrates employing free anchoring group.[22] The reaction time required to immobilize **1** onto SiO_x substrates was optimized by monitoring using UV−vis spectroscopy. It was observed that for a short reaction time (~10h), there was almost no growth, but with prolonged reaction (~60h) showed good coverage (see Fig. S6). Our group have been actively engaged to fabricate monolayers, dyads, oligomer films using terpyridyl-complexes with transition metal ions.[2b,6c,13c,15] The films were characterized by full battery of surface analysis techniques such as atomic force microscopic,



Scheme 2: Schematic representation of fabrication of covalent assembled monolayer of **1** on SiO_x. The process involves (i) Immobilization of 3-iodo-n-propyl-trimethoxysilane on a SiO_x substrate to form coupling layer (CL), and (ii) covalent bond formation using **1** to form monolayer.

ellipsometry, contact angle, X-ray photo-electron spectroscopy, near edge x-ray absorption fine structure. Here we investigate optical and electrochemical properties of the **1**-based monolayer.

3.2 UV-vis studies of 1-based monolayer. Formation of monolayer of **1** on glass substrates was examined by conventional UV-vis spectroscopy in the region λ = 300-800 nm under transmission mode. The UV−vis spectrum of **1**-based monolayer on glass substrate showed, in agreement with the previous reports,[2b,15] a pristine metal-to-ligand charge-transfer (^{1}MLCT) band at λ_{max} = 499 nm, which was red-shifted by $\Delta\lambda$ = 8 nm as compared to the spectrum of **1** in acetonitrile solution (Fig. 1). The shift in the position of the peak maxima could be the result of the covalent bond formation with iodo-terminated coupling layer. In the present case, the formation of the monolayer is believed to occur *via* the ester type bond formation, since the complex contains –COO$^-$ group which acts as a nucleophile and can readily substitute the labile I$^-$ of the coupling layer. These types of reactions are well known in organic chemistry.[23] The surface coverage of the monolayer on glass substrate, Γ was calculated to be ~8.5×10^{13} metallo-ligands/cm^2 (i.e., ~117 Å^2/metallo-ligand) from the UV−vis data assuming the same molecular extinction coefficient ($\varepsilon \approx 28{,}540$ cm^{-1} M^{-1}) as for the MLCT band at λ_{max} = 491 nm in acetonitrile solution. This coverage was estimated using the equation, $\Gamma = (N_A A_\lambda)/2\varepsilon_\lambda$, where N_A, A_λ and ε_λ are the Avogadro's number, absorbance and isotropic molar extinction coefficient, respectively. This coverage is in good accordance with the previously reported density values of uniform Ru(II)−polypyridyl complex and pyridyl-ligand-based covalent assembled monolayers.[24] Note that the molecular density is below a limit of ~1×10^{14} metallo-ligands/cm^2 obtained from theoretical value.[13c,15b] The full width at half maxima (FWHM) of the monolayer on glass substrate was estimated from UV-vis spectrum. The FWHM value of the monolayer was estimated at ~61 nm, which was higher ($\Delta\lambda$ = + 10 nm) than the corresponding metallo-ligand in acetonitrile solution. The broadening of the MLCT band can be ascribed as (i) restrictions in molecular motions on substrate, (ii) densely packing, and (iii) possible intermolecular π−π interactions between the surface-confined species.[25] Further, by extrapolating the ^{1}MLCT band in the UV−vis spectra,[26] the optical band gap (E_g) for **1**-based monolayer on glass substrate was estimated at 2.1 eV, which is found lower by 0.18 eV then the value estimated for metallo-ligand in acetonitrile.

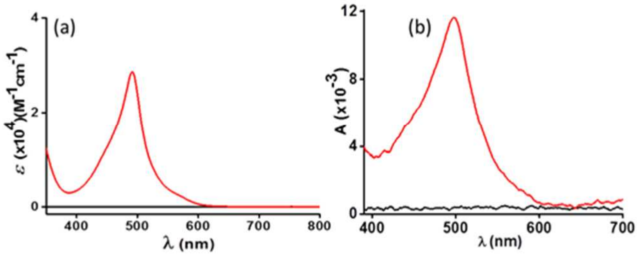


Fig. 1: (a) UV−vis spectra of **1** in acetonitrile and (b) **1**-based monolayer on glass substrate.

3.3 Electrochemical studies. The electrochemical behavior of the homoleptic monolayer of Ru(II)-terpyridyl complex was studied by cyclic voltammetry (CV). A reversible one electron (1e$^-$) redox process due to Ru$^{II/III}$ redox couple was observed from the monolayer on ITO-coated glass substrate. The voltammograms waves showed 1e$^-$ oxidation process at +0.94 V vs Pt reference (Fig. 2a) and +0.83 V vs Fc/Fc$^+$ reference (Fig. 2b). The half-wave redox potential of the monolayer layer, $E_{1/2}$, was estimated at +0.94 V vs Fc/Fc$^+$ and +0.90 vs Pt, which is in good agreement with the value reported for similar polypyridyl complex-based monolayers.[4b] The $E_{1/2}$ values remain almost constant throughout the scan rates (ν) 100-1000 mV s^{-1}.

A linear correlation (R^2 = 0.99-0.98) of the faradic current densities on the scan rates (ν) (Fig. 2c) indicates the redox process is not governed by diffusion controlled at solid-liquid interface rather unequivocally confirmed covalent immobilization of **1** (via ester bond formation) onto ITO electrode.[15] In addition, the stability of the redox species judged from almost unit value of the ratio of anodic to cathodic current density (I_{pa}/I_{pc}) as a function of scan rates (see Fig. S7). The peak-to-peak separation between the anodic and cathodic waves, ΔE_p was calculated at +30-40 mV over the scan rates (100 to 1000 mV s^{-1}). Lowering of ΔE_p further confirms ester bond formation between iodo-terminated coupling layers and –COOH-terminated **1**. The values of ΔE_p depend principally on two factors, i) the relative scan rate and ii) electron transfer rate. The absence of any substantial peak shift over the scan rates further suggests fast electron transfer within the electrochemical process. In general, higher the ΔE_p, lower the rates of interfacial electron transfer process. The values of ΔE_p and $E_{1/2}$ as a function of scan rates are summarized in Table S1. Full width at half-maximum (FWHM) measure for interaction of the surface bound species and estimated from the oxidation peak current at $\Delta E_{pa,1/2}$ = + 110-150 mV. The observed values deviate from an ideal Nernstian electrochemical process, $\Delta E_{pa,½}$ at room temperature as $\Delta Epa,½ = 90.6/n$ mV, where, n is the number of electron.[27] These deviations might be result of the redox site–site interactions and/or site heterogeneity.[28] Moreover, $\Delta E_{pa,½}$ is associated with parameter, $g = \alpha_o + \alpha_R - 2\alpha_{OR}$, where α_o, α_R, and α_{OR} are considered as the interaction parameters for oxidative site-oxidative site, reductive site-reductive site and oxidative site-reductive sites, respectively.[27] When $\alpha > 0$, it is deliberated as attractive interactions, while $\alpha < 0$ for repulsive ones. But at g = 0, we have $\Delta E_{pa,½} = 90.6/n$ mV; while $g < 0$, the $\Delta E_{pa,½} > 90.6/n$ mV. The observed larger values are ascribed to the strong redox site-redox site interactions. Further, the faradic current at scan rate of 300 mV s^{-1}, was employed to evaluate the molecular density. For instance, the surface coverage of **1** on ITO, Γ_S, calculated using the existing method,[28b] $I_p = n^2F^2\nu A\Gamma_s/4RT$ and found at 0.52×10^{14} metallo-ligands/cm^2, which is in good concurrence with the value obtained from UV−vis data (see above). Note that, the coverage of the molecular film suggests high charge (~$5\text{-}8 \times 10^{13}$ electrons/cm^2) can be accumulated. Additionally, ionization potential (IP) of Ru-center in the film was determined using equation,[29] IP = $-(E_{ox} + 4.44)$ eV and estimated at -5.27 eV, where E_{ox} was the corresponding oxidation potential of the Ru^{II}-center vs Fc/Fc$^+$. Electron transfer rate constant, K_{ET}, was calculated using Laviron's method[30] and found at ~ 4.1 s^{-1} for Ru-center. The relatively low K_{ET} value for the metal center is attributed to the low concentration (20 mM $TBAP_6$) of the electrolyte.[31] The discrete redox states can be reflected as a bit of information, being either "1" (at oxidation potential) or "0" (at reduction potential), which may find interest to be used as memory device.

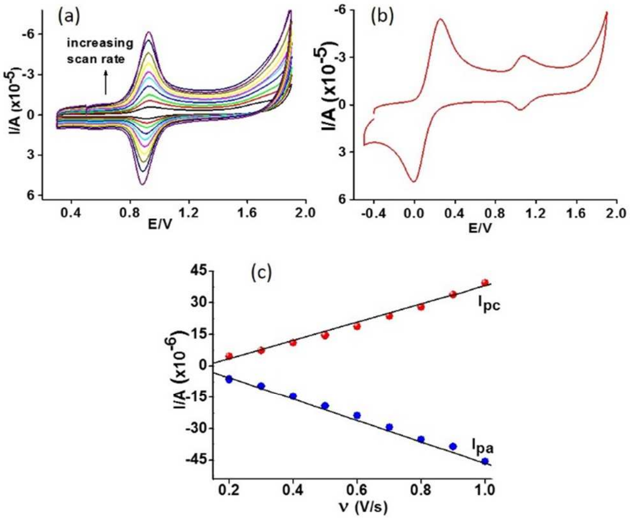


Fig. 2: (a) Cyclic voltammograms of **1**-based monolayer on ITO-coated glass using Pt-as pseudo reference electrode, (b) with ferrocene as internal standard, and (c) linear dependence (R^2 = 0.98-0.99) of anodic and cathodic current as a function of scan rates (V s^{-1}).

3.4 Stability of 1-based monolayer. The stability of the fabricated film was checked by optical and electrochemical means. The **1**-based monolayers were stable for months under dark as judged by UV-vis spectroscopy. It exhibited good mechanical durability, since washing the modified substrates with common solvents or mechanical abrasion could not deteriorate the molecules from the SiO_x-substrates. The films were found to be stable up to 180°C (Fig. 3a). It also showed tremendous thermal, temporal, and electrochemical stability. For instance, the modified substrates were subjected to thermal stress at 100°C for >2h and it showed only ~4-6% signal loss (see Fig. S8). Furthermore, cyclic voltammograms of **1** on ITO-coated glass substrates was recorded for 300 cycles at 100 mV s^{-1} and the film showed excellent redox stability, reversibility and did not deteriorate so much upon large numbers of "read−write" cycles (Fig. 3b).

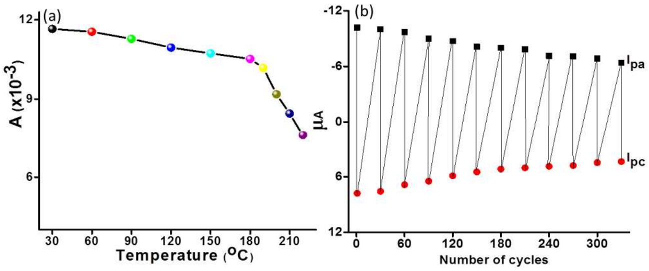


Fig. 3: (a) Ex-situ UV-vis monitoring of thermal stability of **1**-based molecular film on glass substrates and (b) redox stability on ITO-coated glass substrates measured at 100 mV s^{-1}.

A minimal loss in the faradic current was observed (~8- 10%). After the recording CVs, the electrolyte solution was verified by UV-vis and no optical signal was obtained. These studies demonstrate that there was no desorption or decomposition of the molecules to the electrolyte solution during the voltammetry experiments in the high potential range (up to +2 V). These results are highly fascinating since, such a stable film could open new avenue for design of opto-electronic materials.

4 Conclusions

The optical and electrochemical properties were investigated in detailed and compared with the corresponding solution properties. A red shift of 8 nm in the wavelength as compared to solution spectra has been observed. UV-vis along with cyclic voltammetry measurements clearly indicated ester bond formation of **1** with iodo-terminated silane coupling layers on glass, ITO-coated glass substrates. Covalent based monolayer techniques take advantage of the specific reactivity of the molecules. Covalent based monolayer techniques take advantage of the specific reactivity of the molecules. The present system showed excellent temporal, thermal and electrochemical stability.

5 Acknowledgements

Financial support from DST-Nano-Mission is gratefully acknowledged. The author sincerely thanks Council of Scientific and Industrial Research (CSIR), New Delhi, for senior research fellowship. The author acknowledges fruitful discussion with Dr. Vikram Singh, University of Delhi, India.

6 Notes and references

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†A tribute to late Prof. Tarkeshwar Gupta, University of Delhi.

Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

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