

THE STUDY OF PHOTOELECTRIC PROPERTIES OF COMPLEXES

DARPAN SINGH* AND VISHRUT CHAUDHARY**

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Abstract

A novel Re (I) complex, Re (CO)₃CIL (L=2-1- ethylbenzimidazol-2-yl pyridine), has been structurally characterized by single crystal X-ray diffraction analysis crystal data for C₁₇H₁₃ClN₃O₃Re: space group orthorhombic, Pbcn : a = 12.713 Å b = 15.103 Å c = 18.253 Å, Z=8. stable vacuum vapor deposition of the Re complex has been verified by UV-vis and infrared spectroscopy. A two layer electroluminescent device with configuration of ITO/TPD/Re (CO)₃CIL/Mg_{0.9}Ag_{0.1}/Ag has been fabricated, which gave a turn-on voltage of as low as 3V and a maximum luminance of 113 cd/m² at a bias voltage of 10.5V, and confirmed that the Re complex can function as a bright orange - red emitter and an electron transport material in an electroluminescent device.

Introduction

Luminescent Ru(II) and Re(I) metal complexes have attracted considerable attention due to their intriguing photophysical, photochemical, and excited state redox properties, and potential application in photonic and photo electronic devices. (Balzani, V; et al.- 1991). Recently there has been growing interest in electroluminescent (EL) devices with luminescent metal complexes as emitting layers since the first report on an organic EL device based on tris-(8- hydroxyquinolinato) - aluminium (AlQ). The luminescent metal complexes were usually introduced into EL devices as light - emitting layers by means of spin - coating, vacuum - deposition, Langmuir - Biedgett (LB), and self - assembling techniques. For obvious reasons, vacuum vapor deposition is the most appealing technique for making practical

*Research Scholar in Chemistry, Meerut College, Meerut & Lecturer in DIET Meerut (U.P.) India

** (Coresponding Author) Assistant Professor, Department of Chemistry, D.N. College, Meerut (U.P.) India

devices. Although many families of luminescent metal complexes have been reported for electroluminescent devices, e.g., Eu (III), Tb (III), Zn(II), Ru(II), Pt (II), Rh (I) and Re (I) complexes (Kido, J., et. al. - 1994, Gao. X.C.; 1998 and Li, Y.; - 2001, novel and vacuum volatile complexes are relatively scarce. Here we report a novel Re (I) complex capable of being vacuum deposited as the emitting layer of an electroluminescent device. The optical and X-ray crystal structure characterization and the electroluminescent properties of the Re (I) complex are reported.

Spectroscopy

Infrared spectra were recorded on a 7199 BFT - IR system. UV-vis spectra were obtained with a Shimadzu 240 spectro photometer. ¹H NMR spectra were measured on a Bruker ARX 400 using tetramethylsilane as an internal standard. Photo luminescence (PL) and electroluminescence (EL) spectra were measured with a Hitachi F-4500 fluorescence spectro photometer. The PL quantum yield of a degassed dichloromethane solution of the Re complex was calculated using eq(1),

$$\phi_s = \phi_{std} \frac{A_{std} I_s \eta_s^2}{A_s I_{std} \eta_{std}^2} \quad (1)$$

where ϕ_s and ϕ_{std} are the quantum yields of unknown and standard samples ($\phi_{std}=0.042$) for [Ru (bpy)²]. A_s and A_{std} (<0.1) are the solution absorbances at the excitation wavelength (λ_{ex}), I_s and I_{std} are the integrated emission intensities and η_s and η_{std} are the refractive indices of the solvents.

Cyclic Voltammetry

Cyclic voltammetry measurements were conducted on a model CH 600 voltammetry analyzer with a platinum plate as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a polished platinum wire as the counter electrode, at a scan rate of 0.1 V/s. The supporting electrolyte was 0.1 mol/dm³ tetrabutyl ammonium hexafluorophosphate (TBAH) in CH₃CN. The solution was deoxygenated with bubbling nitrogen for 15 min. Ferrocene was added at the end of each experiment to serve the internal reference. Its potential E⁰ was taken to be +0.425 V vs SCE (Gennett T.; et. al. 1995)

Electro Luminescence

The electro luminescent device was fabricated in the following two layer configuration: ITO/N V-diphenyl - N,N' - bis (3-methylphenyls - 1, 1' - biphenyl - 4,4' - diamine (TPD) (51 nm)/Re (CO)₃ CIL (56 nm) / Mg_{0.9} Ag_{0.1} (110nm) / Ag (60 nm). The device was fabricated by sequential vacuum deposition of TPD and the Re complex from molybdenum crucibles at rates of 0.1 - 0.4 nm/s and Mg: Ag alloy and Ag from tungsten wire baskets at rates of 0.1-1.0 nm/s onto an ITO - coated glass substrate belts a pressure of 1x10⁻³ Pa without breaching vacuum. The layer thickness was controlled in a vacuum with an IL - 1000 quartz crystal monitor and was also corrected by a dektak (Kido, J.; et.al.-2011) surface profile measuring system. The luminance was measured with a ST-86LA spot photometer and a close-up lens providing a focal spot of 5 mm at room temperature under ambient atmosphere.

Results and Discussion

Infrared Spectroscopy; IR spectroscopy is a powerful tool to monitor the vacuum deposition behaviour of materials. The FTIR spectra for the Re complex in a KBr pellet and film are compared in Fig. 1. The spectrum for the KBr pellet shows three CO stretching bands at 2019, 1985, and 1880 cm^{-1} . Which are consistent with the fac configuration at the rhenium center. The former band appears at 2017 cm^{-1} and the latter two bands appear as a single wide peak centered at 1889 cm^{-1} in the spectrum of a vacuum deposited film on CaF_2 . A heterocyclic C=N stretching frequencies are seen at 2916 and 2848 cm^{-1} for the film and at 2922 and 2852 cm^{-1} for the KBr pellet, respectively. These demonstrate stable vacuum deposition of the Re complex without significant thermal decomposition.

UV-vis spectroscopy; UV-vis spectroscopy has frequently been used to characterize vacuum-deposited films. In some cases, however, the UV-vis spectrum of the vacuum-deposited film could

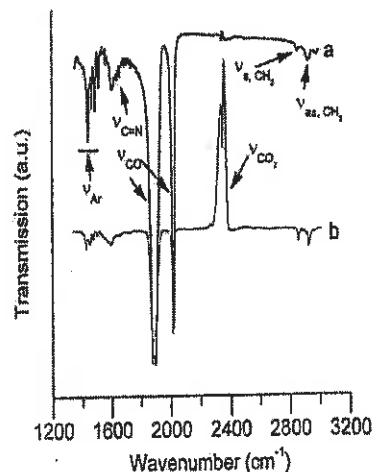


Figure 1. Infrared spectra of the Re complex in KBr pellet (a) and vacuum-deposited film (b).

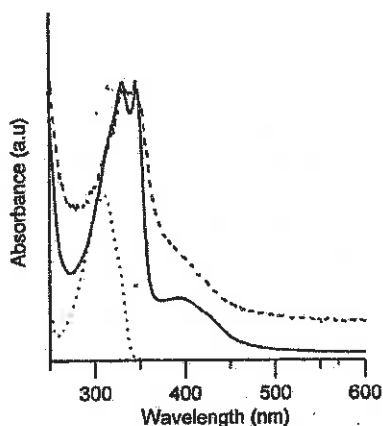


Figure 2. UV-vis spectra for the Re complex in a vacuum deposited film (dashed line) and chloroform solution (solid line), and for the ligand L in chloroform solution (dotted line).

be largely deformed compared to the solution spectrum due to the light scattering caused by inhomogeneous film thickness and distribution of particle dimensions.

Therefore one should be cautious in making any conclusion about the vacuum deposition stability of the materials solely relying on UV-vis spectroscopy. As shown in Fig. 2, the ultraviolet absorption spectrum of the Re complex in CHCl_3 exhibits two peaks at 331 and 347 nm due to intraligand $p \rightarrow p^*$ transitions which are red-shifted compared to the broad absorption peak at 310 nm for free ligand L in CHCl_3 and are almost the same as those for the film (330 and 346 nm). The visible absorption spectrum

of the chloroform solution appears as a broad absorption band centered at 400 nm which is ascribed to MLCT [$dp \rightarrow p^*-(L)$] transition and became ill-defined in the spectrum of the film. The film and the chloroform solution give almost the same onset absorption located at ~ 481 nm, which corresponds to an energy difference of 2.58 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) (Robinson, M.R.; et. al. - 2000).

Cyclic Voltammetry ; Cyclic voltammograms (Fig-3) of the Re complex show a couple of irreversible anodic waves at $E_{1/2} = 1.30\text{V}$ with an onset oxidation potential of + 1.22 V vs SCE, and a couple of quasi-reversible cathodic waves at $E_{1/2} = 1.40$ V with an onset reduction potential of - 1.32 V vs SCE. The anodic waves were associated with a Re^{I} -based oxidation process ($\text{Re}^{\text{I}}/\text{Re}^{\text{II}}$), and the cathodic waves with a L-based reduction process ($[\text{Re}^{\text{I}}\text{Cl}(\text{CO})_3(\text{L})]/[\text{Re}^{\text{I}}\text{Cl}(\text{CO})_3(\text{L})]$). From the onset oxidation [$E_{\text{onset}}(\text{Ox})$] and reduction [$E_{\text{onset}}(\text{Red})$] potentials, HOMO and LUMO energy levels of the Re complex were calculated (E_{HOMO} or $E_{\text{LUMO}}/\text{eV} = -4.74 - E_{\text{onset}}(\text{Ox})$) or $E_{\text{onset}}(\text{Red})$) to be - 5.96 and -

3.42 eV with respect to the vacuum level, respectively, based on a calculated value of - 4.74 eV for SCE with respect to the zero vacuum level (Bard, A.J.; et. al. - 1980). The gap between the LUMO

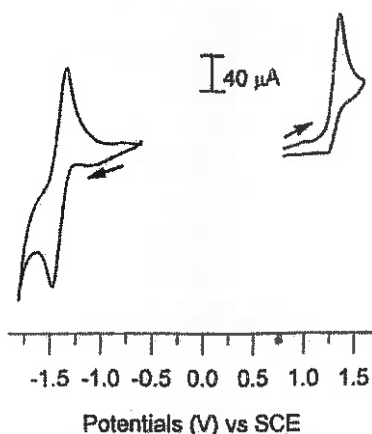


Figure 3. Cyclic voltammograms of the Re complex ($\text{CH}_3\text{CN}/0.1 \text{ mol/dm}^3$ TBAH) at 0.1 V/s.

and the HOMO energy levels was thus derived to be 2.54 eV, which is well in agreement with that (2.58 eV) obtained from the UV-vis spectroscopy.

Photoluminescence and Electroluminescence; Photo-luminescence (PL) spectra for the Re complex in compressed powder, vacuum-deposited film, and chloroform solution, and electroluminescence (EL) spectrum for the device ITO/ $\text{N,N}'$ -diphenyl- $\text{N,N}'$ -bis-(3-methylphenyl)-1,1'-biphenyl-4,4'-di-amine (TPD) (51 nm)/ $\text{Re}(\text{CO})_3\text{CIL}$ 56nm/ $\text{Mg}_{0.9}\text{Ag}_{0.1}$ (110nm)/Ag (60nm) are compared in Fig 4. upon excitation of a degassed dichloroform solution of the Re complex at 400 nm, a PL quantum yield of 0.11% was obtained based on eq (1).

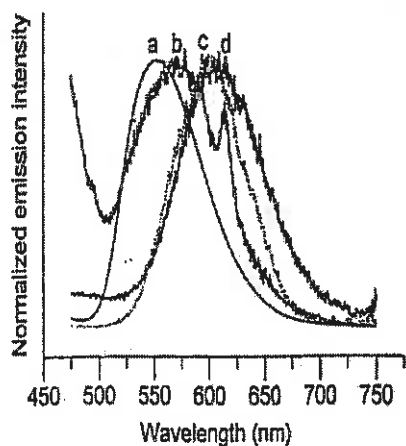


Figure 4. PL spectra for the Re complex in compressed powder (a), vacuum-deposited film (b), and chloroform solution (c), and EL spectrum for the device with a configuration of (+)ITO/TPD/ $\text{Re}(\text{CO})_3\text{CIL}/\text{Mg}_{0.9}\text{Ag}_{0.1}/\text{Ag}(-)$ at a bias voltage of 6 V (d).

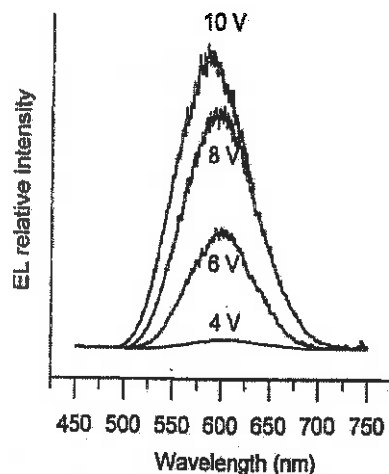


Figure 5. Bias voltage dependent EL spectra of the device with a configuration of (+)ITO/TPD/ $\text{Re}(\text{CO})_3\text{CIL}/\text{Mg}_{0.9}\text{Ag}_{0.1}/\text{Ag}(-)$.

In sharp contrast to the PL spectrum peaked at 363nm ($\lambda_{\text{exc}}=340\text{nm}$) for ligand L in chloroform, PL maxima for the Re complex in the powder, vacuum-deposited film, and chloroform solution were found to be 550, 573 and 606 nm, respectively, while the electroluminescent device gave orange-red light emitting with the EL spectra depending on bias voltages (Fig-5), e.g., 600 nm for a bias voltage

of 6V and 586 nm for 10 V, indicating that the recombination of holes and electrons occurred in the Re complex layer and excitations produced subsequently excited the Re (I) complex. However, the obvious difference observed between the EL and PL spectra indicates that the electron-induced excited state is different from the photo-induced excited state. A small blue shift (10 nm) was also observed for a Ru (bpy)₃ (ClO₄) based electroluminescent device. When the bias voltages increased from 3.1 to 9.4 V, and a 12-nm blue shift was observed for a spin-coated film based electroluminescent device with Re (CO)₃ Cl (mbpy) (mbpy=4, 4' - dimethyl bi-pyridine) as the light - emitting layer upon the bias voltages increased from 1.5 to 6.5 V. The EL spectra for our electroluminescent device were red-shifted compared with the PL spectra for the powder and the vacuum-deposited film. The EL spectra, however, were blue-shifted at bias voltages equal to or lower than 8 V and almost the same at the bias Voltages equal to or higher than 10V, compared with the PL spectrum of the chloroform solution. Red shift in the EL spectra compared with the PL spectra of the films were also observed for the Re (CO)₃ Cl (mbpy)- based device. Also, a large red shift (50 nm) in the Ru (bpy)₃ (ClO₄) based EL spectra was observed relative to the acetonitrile and the aqueous solutions.

A possible explanation for the relatively large variations observed between the EL and PL spectra of Ru (bpy)₃ (ClO₄)₂ has been given as follows: electrons and holes were injected into the metal center and bpy ligand from the opposite electrodes, respectively, and electric field-driven electron and hole hopping occurred until these were localized on a single molecule producing the excited state of the Ru (II) complex. In addition to this mechanism, formation of aggregates, interface energy transfer between the Re complex and TPD, and the change in the microenvironment of the Re complex induced by the applied electric field, as governed by the rigidochromism rule well-documented for

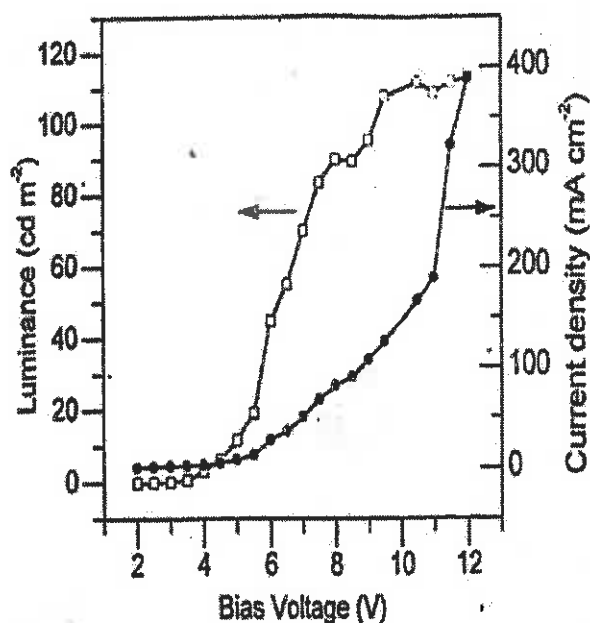


Figure 6. Current density-voltage and luminance-voltage curves of the device with a configuration of (+)ITO/TPD/Re(CO)₃Cl/Mg_{0.9}Ag_{0.1}/Ag(-).

the Re (I) complexes, may be operative in our EL device. It is hard to make a definite conclusion at the present stage. The luminance-voltage and current density voltage curves of that electroluminescent device are shown in fig-6.

It shows that the luminescence increased with increasing injection currents and bias voltages. The device exhibited a low turn-on voltage of ~3V and a rectification ratio greater than 10⁴ at 12V. The maximum external EL quantum efficiency of 0.09% photons/electrons and luminous efficiency of 0.9 lm/w were obtained at 6.0V. At a bias voltage of 10.5 V and current density of 166 mA/cm², a maximum luminance 0.2 lm/w and an external EL quantum efficiency of 0.03%. The maximum luminance for the present device is

comparable to that of the EL devices we recently reported with Tb (III) and Eu (III) complexes as light-emitting layers. The maximum luminous efficiency is close to the level for the commercially available lighting diodes or ZnS- based EL devices.

To best understand the device performance observed, an energy diagram of the EL device is given in Fig 7. The HOMO and LUMO energy levels for the TPD and work functions for ITO anode and

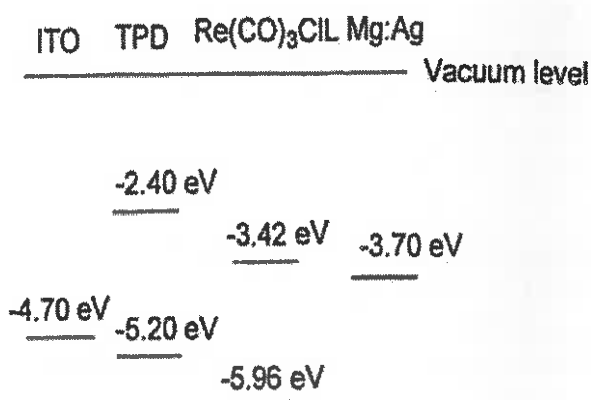


Figure 7. An energy level diagram of the EL device of (+)ITO/TPD/Re(CO)₃CIL/Mg_{0.9}Ag_{0.1}/Ag(-).

Mg:Ag cathode were taken from ref 4e. It is generally accepted that EL originates from the excitation of the light-emitting layer by the excitations produced by the recombination of electrons and holes which are injected from the cathode and the anode, respectively. The balanced injection and transport of holes and electrons are therefore crucial for achieving high quantum efficiency. It can be seen from fig.7 that the barrier for electron injection from the Mg:Ag cathode to the Re complex

layer is only 0.28 eV (the energy difference between the work function of Mg:Ag and LUMO of the Re complex), indicating that the Re complex we synthesized is a good electron transport material. The low turn-on voltage observed for the present EL device is due to the small barrier for electron injection from the Mg:Ag electrode to the Re complex layer. The barrier for electron injection from the Re Complex to the TPD layer is as high as 1.02 eV. So, the TPD layer can effectively block the electrons so that the electrons injected from the Mg:Ag electrode can be effectively confined to the Re complex emitting layer. On the other hand, the barriers for hole injection from the ITO anode to the TPD layer and from the TPD layer to the Re complex layer are 0.52 and 0.76 eV, respectively and these two values are much less than the barrier (1.26 eV) for direct hole injection from the ITO anode to the in a one-layer device of ITO/Re(CO)₃CIL/Mg_{0.9}Ag_{0.1}/Ag. Here the TPD played a role like a "ladder" in facilitating stepwise hole transport, similarly to Cu-phthalocyanine (Van Slyke, S.A.; et. al.-2006) and starburst molecules (Itano, K.; et. al.-2008) which were used as buffer layers for hole injection in organic electroluminescent devices. In short, the TPD layer acted as both a hole transport and an electron blocking layer, and the Re complex as an electron transport layer facilitating more balanced carrier injection from the anode and cathode. This resulted in an increase in the recombination probability of electrons and holes in the Re complex layer and accordingly a reduction in the quenching probability of excitations created by the recombination of electrons and holes at the boundary between the Re complex and the ITO electrode. As anticipated the one-layer device without the hole transport TPD layer showed substantially low luminance.

In conclusion, a newly synthesized Re(I) complex was successfully applied for a vacuum-deposited film-based electroluminescent device. Bright range-red light emitting with a low voltage drive was demonstrated in the electroluminescent device. Good electroluminescent characteristics are due to rational design of the device configuration, and stable vacuum deposition and good electron transport properties of the Re complex. Efforts are being directed forward improving the hole transport and photoluminescent properties of the complexes.

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