To my loving parents
Declaration of the candidate

The work described in this thesis was carried out by me under the supervision of Dr. P.M. Jayaweera and a report on this has not been submitted to any University for another degree.

07-08-2002
Date

S.S. Palayangoda
Declaration of the supervisor

I certify that the above statement made by the candidate is true and that this thesis is suitable for submission to the university for the purpose of evaluation.

7/8/2002
Date

Dr. P.M. Jayaweera
Dept. of Chemistry
University of Sri Jayawardenepura
Gangodawila - Nugegoda,
SRI LANKA
SPECTROSCOPIC AND ELECTROCHEMICAL STUDIES OF IRON(II) AND COBALT(II) COMPLEXES;
POTENTIAL DYE MATERIALS FOR NANO-POROUS PHOTOVOLTAIC DEVICES

By

SUJEEMA SENARATH PALAYANGODA
[ B.Sc.(Chemistry) sp., USJ, Sri Lanka ]

Thesis submitted in partial fulfillment of the requirements for the Degree of Master of Philosophy in Chemistry of the Faculty of Applied Science, University of Sri Jayewardenepura, Nugegoda, Sri Lanka.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF CONTENTS</td>
<td>i</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>x</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xi</td>
</tr>
</tbody>
</table>

## CHAPTER -1

**INTRODUCTION**

1. Theoretical Background 1
   1.1 Solar cells 1
   1.2 Energy band gap of solids 3
   1.3 Fermi level 5
   1.4 Charge carriers 7
      1.4.1 Photo-excitation 7
      1.4.2 Thermal excitation 7
      1.4.3 Doping 7
   1.5 Conductivity of a semiconductor 8
      1.5.1 Electronic conductivity 8
      1.5.2 Ionic conductivity 8
   1.6 Dye sensitization 9
      1.6.1 Kinetics of the semiconductor electrode/electrolyte interface 11
1.7 Efficiency of a Photo Electrochemical Cell
  1.7.1 Drawbacks of the efficiency of the Photo Electrochemical Cell
1.8 Properties of electronically excited states of transition metal complexes
  1.8.1 Criteria for classification of the excited state
  1.8.1.1 Metal centered (MC) excited states
  1.8.1.2 Metal-to-Ligand Charge Transfer (MLCT) states
  1.8.1.3 Ligand Centered (LC) excited states
  1.8.2 Transition metal complexes as dye material for solar cells
    (Photovoltaic cells)
1.9 Fate of a dye molecule in a Photo Electrochemical Cell
1.10 Acid-base switching of alizarin and quinalizarin sensitized nano-porous
    Photovoltaic devices
1.11 Cyclic Voltammetry
  1.11.1 Data interpretation
1.12 Computational Chemistry
  1.12.1 HyperChem software package
  1.12.2 Building and displaying molecules
  1.12.3 Optimizing the structure of molecules
  1.12.4 Molecular Mechanics (MM+)
  1.12.5 Semi-empirical methods of quantum chemistry
    1.12.5.1 General background
    1.12.5.2 Molecular geometry
    1.12.5.3 Calculating electronic potential energy
    1.12.5.4 Features of semi-empirical method
1.12.5.5 Range of semi-empirical methods
1.12.5.6 ZINDO/1 (Zerner's Intermediate Neglect of Differential Overlap) method
1.12.5.7 Selecting options for ZINDO/1 method
1.12.5.8 Single point calculation
1.12.5.9 Contour plots
1.12.5.10 Total electron density calculations (charge density)

CHAPTER -2

Experimental

2.1 Chemicals and Solvents

2.2 Preparation methods

2.2.1 Preparation of conducting glass plates (CTO) for applying TiO_2 layer
2.2.2 Deposition of TiO_2 on conducting glass plates
2.2.3 Preparation of Fe(II)(C_2O_4)_3bromopyrogallol red complex
2.2.4 Preparation of [Co(1,10-Phen)_2] Cl_2 complex
2.2.5 Preparation of Co(1,10-Phen)_2bromopyrogallol red and Co(1,10-Phen)_2catechol violet complexes
2.2.6 Preparation of I^-/I_3^- electrolyte
2.2.7 Coating procedure of dye on semiconductor films
2.2.8 Preparation of acidic and basic ethanolic solutions
2.2.9 Measuring the photocurrent and photovoltage values of acidic medium and basic medium dye coated photovoltaic cells
CHAPTER -3

Results and Discussion

3.1 Preparation of a dye sensitized photovoltaic cell

3.2 Preparation of a metal complexes

3.3 Comparison of spectroscopic properties of Fe(II)(C₂O₄)₂bromopyrogallol red complex with bromopyrogallol red free ligand

3.4 Spectroscopic and photovoltaic properties of Co(II)(1,10-phen)₂ bromopyrogallol red and Co(II)(1,10-phen)₂ catechol violet complexes

3.5 Emission and absorption properties of Co(II)(1,10-phen)₂ catechol violet and catechol violet ligand in methanolic solution

3.6 Acid-base switching of alizarin and quinalizarin sensitized nano-porous photovoltaic devices
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Average photocurrent, voltage and cell efficiency values for two dye materials [iron(II)(C₂O₄)₂ bromopyrogallol red and bromopyrogallol red free ligand</td>
<td>52</td>
</tr>
<tr>
<td>2.2</td>
<td>Heat of formation values of cobalt(II) (1,10-phen)₂bromopyrogallol red and cobalt(II) (1,10-phen)₂catechol violet</td>
<td>56</td>
</tr>
<tr>
<td>2.3</td>
<td>Average photocurrent, voltage and cell efficiency values for two dye materials [cobalt(II) (1,10-phen)₂bromopyrogallol red and [cobalt(II) (1,10-phen)₂catechol violet]</td>
<td>62</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Classification of solids and semiconductors</td>
<td>4</td>
</tr>
<tr>
<td>1.2</td>
<td>Charge distribution of semiconductor after ionization</td>
<td>6</td>
</tr>
<tr>
<td>1.3</td>
<td>Mechanism of dye sensitization</td>
<td>10</td>
</tr>
<tr>
<td>1.4</td>
<td>Ruthenium polypyridyl type molecule</td>
<td>12</td>
</tr>
<tr>
<td>1.5</td>
<td>The charge separation at the interface of particulate film and the electrolyte</td>
<td>13</td>
</tr>
<tr>
<td>1.6</td>
<td>The photocurrent conversion efficiency curve</td>
<td>15</td>
</tr>
<tr>
<td>1.7</td>
<td>Mechanisms within the cell</td>
<td>20</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic layout of action spectra set up</td>
<td>37</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic layout of cyclic voltammetry set-up</td>
<td>39</td>
</tr>
<tr>
<td>3.1</td>
<td>The mechanism of surface complexation of dye with TiO₂</td>
<td>42</td>
</tr>
<tr>
<td>3.2</td>
<td>Triphenylmethane type molecules</td>
<td>45</td>
</tr>
<tr>
<td>3.3</td>
<td>iron(II)(C₂O₄)₂bromopyrogallol red complex</td>
<td>47</td>
</tr>
<tr>
<td>3.4</td>
<td>Absorption spectra of iron(II)(C₂O₄)₂bromopyrogallol red and bromopyrogallol red in methanol</td>
<td>48</td>
</tr>
<tr>
<td>3.5</td>
<td>Cyclic voltammograms of (a) iron(II)(C₂O₄)₂bromopyrogallol red and bromopyrogallol red in aqueous solution containing 1×10⁻³ M KNO₃ as the supporting electrolyte.</td>
<td>50</td>
</tr>
<tr>
<td>3.6</td>
<td>Photocurrent action spectra for nanocrystalline TiO₂ films coated with iron(II)(C₂O₄)₂bromopyrogallol red and bromopyrogallol red</td>
<td>51</td>
</tr>
</tbody>
</table>
Figure 3.7 Photocurrent - voltage curves for iron(II)(C\textsubscript{2}O\textsubscript{4})\textsubscript{2} bromopyrogallol red complex and bromopyrogallol red ligand

Figure 3.8 The time development of the photocurrent when cells were illuminated with 750 W/m\textsuperscript{2} solar simulator

Figure 3.9 Most probable structures of cobalt(II)(1,10-phen)	extsubscript{2}bromopyrogallol red and cobalt(II)(1,10-phen)	extsubscript{2}catechol violet molecules.

Figure 3.10 Absorption spectra of cobalt(II)(1,10-phen)	extsubscript{2}bromopyrogallol red and cobalt(II)(1,10-phen)	extsubscript{2}catechol violet in ethanol.

Figure 3.11 Reflectance spectra (a) cobalt(II)(1,10-phen)	extsubscript{2}bromopyrogallol red and (b) cobalt(II)(1,10-phen)	extsubscript{2}catechol violet complexes on TiO\textsubscript{2} surface

Figure 3.12 Action spectra cobalt(II)(1,10-phen)	extsubscript{2}bromopyrogallol red and cobalt(II)(1,10-phen)	extsubscript{2}catechol violet complexes on TiO\textsubscript{2} surface.

Figure 3.13 Photocurrent-voltage curves for cobalt(II)(1,10-phen)	extsubscript{2} bromopyrogallol red and cobalt(II)(1,10-phen)	extsubscript{2} catechol violet.

Figure 3.14 Emission spectra of cobalt(II)(1,10-phen)	extsubscript{2}catechol violet and catechol violet free ligand.

Figure 3.15 Energy level diagram of cobalt(II)(1,10-phen)	extsubscript{2} catechol violet complex.

Figure 3.16 Molecular structures of alizarin (1,2-dihydroxyanthroquinone) and quinalizarin (1,2,5,8-tetrahydroxyanthroquinone)
Figure 3.17 Acid-base effect on observed photocurrent and photovoltage responses of alizarin and quinalizarin coated photocell

Figure 3.18 Contour plots of HOMO, LUMO of protonated and deprotonated forms of alizarin and quinalizarin
ACKNOWLEDGEMENTS

I would like to express my sincerest thanks to my supervisor, Dr. P.P.M. Jayaweera, dept. of Chemistry, University of Sri Jayewardenepura for his expert supervision, helpful advice and constant encouragement during the course of this research work.

My thanks are due to Prof. K. Tennakone and Dr. R. Senadeera, Institute of Fundamental Studies, Kandy for their support. I would also like to thank technical staff at the Department of Chemistry, University of Sri Jayewardenepura and Institute of Fundamental Studies, Kandy, Sri Lanka.

Special thanks go to Prof. A.P. De Silva, School of Chemistry, Queens University of Belfast and Dr. Daya Barlo, Department of Physics, University of Colombo for their kind help to get Elemental Analysis data and Mass Spectral data respectively.

I would also like to thank colleagues in the Physical Chemistry research laboratory, Department of Chemistry, University of Sri Jayewardenepura, Mr. R.G.C.R. Gamage, Miss. P.I. Godakumbura and Mr. C.N. Weeraman, and Mr. P.V.V. Jayaweera, Photochemistry laboratory, I.F.S. for their support and friendship over the last two years.

Finally, the University of Sri Jayewardenepura and National Science Foundation, Sri Lanka are greatly acknowledged for all the support and financial assistance (Grant No. RG/98/C/05).
ABSTRACT

Metallochromic triphenylmethane type dyes (bromopyrogallol red and catechol violet) have attracted attention of many scientists due to their potential ability to chelate with a number of transition metal centers. The dye materials belonging to this class is capable of producing high photocurrents and photovoltages when used as sensitizers in nano-porous TiO₂ photovoltaic cells. However, slow photo-degradation of dye molecules and low photocurrent conversion efficiencies have been the major problem.

Complexation of a triphenylmethane ligand with a transition metal center shows enhanced photovoltaic properties when compared with the photovoltaic cells coated by free triphenylmethane ligand only. Electrochemical and absorption spectroscopic data suggest that the nature of the lowest electronic transition of such a complex as a π* (ligand) ← d π (metal), metal to ligand charge transfer transition. Photovoltaic cells coated with these transition metal complexes show higher stability for photo-degradation and incident photocurrent conversion efficiencies with a UV radiation blocking filter.

When catechol violet is complexed with Co²⁺(1,10-phen)₂ moiety, it shows emission as well. Experimental and theoretical data suggest that the emission of this complex occurs from an upper ligand centered state and not from a low lying MLCT state.

1,2-dihydroxyanthraquinone or 1,2,5,8-tetrahydroxyanthraquinone can be used as sensitizing dye material in nano-porous solar cells, not only they produce fairly high photocurrent and photovoltage, when exposed to light, but also those properties show high sensitivity to the protonation and deprotonation of the 2 hydroxy group of the ligand when the pH value of the solvent is changed. Semi-empirical computational studies have shown that fine tuning of HOMO-LUMO orbitals are responsible for the sensitivity.
Chapter-01

INTRODUCTION
INTRODUCTION

1. Theoretical Background

1.1 Solar cells

In present world, the total usage of whole energy is $2.5 \times 10^{14}$ MJ/year. It can be predicted that a significant enhancement of energy usage within near future. About 98% of the energy supply depend on fossil fuel resources, which are depleting rapidly. It has been predicted that these fuel resources will be completely wiped out within next century\(^{(1)}\). Therefore, it is important to execute new research methodology to invent alternative energy sources to overcome future energy crisis. Another important aspect is that any alternative energy sources must be environmental friendly as far as possible.

Since all energy sources except nuclear energy have originated from solar energy, there is a clue to develop alternative energy sources using Sunlight. There are more supportive evidence to concentrate solar energy conversion as an effective energy source. It is plentiful, clean and non-polluting. Earth continuously receives sunlight at the rate of $6 \times 10^{18}$ MJ/year. This value is 3000 times greater than the annual energy consumption in the whole world\(^{(1)}\). Scientists have tried and are still trying to develop apparatus, solar cells, that can convert solar energy into chemical energy and electrical energy.

The conventional solar cells were made by Paul Rappaport, D. Chapin and G. Pearson at Bell Labs, USA in 1954. They used direct band gap materials such as Si semiconductors\(^{(2)}\). These cells use p-n junctions which marks the barrier between regions of electron and hole conduction. Electrons and holes created \textit{via} the absorption
of light in a silicon wafer, diffuse at different rates in n-doped and p-doped materials. This result is an accumulation of electrons and holes at the junction. More cost-effective technologies, which use thin films of such materials as amorphous silicon deposited on glass, are under development. The cost of production of conventional solar cells is very high, that limits their usage especially in the third world countries. Apart from this reason, there are several other disadvantages, such as:

1. Reflection of incident light at the interface.
2. Recombination of the photo-induced electrons and holes.
3. Insufficient light absorption.

An amount of 50-60 MW of solar cells are currently produced whole world in each year, no technology has produced low cost commercially available, efficient and reliable modules that can be used on the exterior of buildings\(^3\).

Use of sensitization processes in solar cells has also been explored. Very first work was done by researchers such as Meier, Tributsh, Memming and Gerischer\(^3\). Last decade, a Swiss research group has combined several concepts to produce a low cost 7% efficient solar cell\(^3\). The cell, which is called a nanocrystalline dye sensitized solar cell or photovoltaic cell, is remarkable in that it resembles natural photosynthesis in two respects.

1. It uses an organic dye to absorb light and transduce solar energy.
2. It uses multiple layers to improve the absorption and collection efficiency over that of thicker layers.
It is one of a new class of devices called molecular electronic devices and has considerable advantages when compared with conventional silicon solar cells. These advantages are:

1. Incident sunlight can be reached on the dye layer without significant loss.
2. A junction between n-type or p-type with electrolyte can be made in direct ways.
3. The cells have the ability to convert solar energy directly into various useful forms such as electrical energy, chemical energy and so on.

1.2 Energy Band gap of solids

The energy band formed from the lowest unoccupied molecular orbital is called the conduction band (CB). The CB lies above the valance band (VB), which is occupied by electrons. Broadness of the conduction band is higher than that of the valance band. Energy difference between the lowest energy level of the conduction band and the highest energy level of the valance band is called the band gap (Eg).

According the band gap, solids can be classified into three main groups (Figure 1.1). Those are metals, insulators and semiconductors. When the conduction band and the valance band overlaps, it is called a metal. But insulators and semiconductors have some extent of band gap.
Semiconductors can be further classified into two groups.

(a) Intrinsic semiconductors e.g., Si, Ge

(b) Extrinsic semiconductors e.g., ZnO, CdS, TiO₂

Figure 1.1 Classification of solids and semiconductors
1.3 Fermi level

An important concept in the description of semiconductor electrode is that of the Fermi level, \( E_f \), which is defined as the energy where the probability of a level being occupied by an electron is \( \frac{1}{2} \) \(^{(5)}\).

For an intrinsic semiconductor at room temperature, \( E_f \) lies essentially midway between the CB and VB within the forbidden gap region (Figure 1.2a). For an extrinsic semiconductor, the location of \( E_f \) depends on the doping level. For moderately or heavily doped n-type materials, \( E_f \) lies slightly below the CB edge (Figure 1.2b). Similarly, for moderately or heavily doped p-type materials, \( E_f \) lies just above the VB edge (Figure 1.2c) \(^{(6)}\).
Figure 1.2 Charge distribution of semiconductor after ionization

- $E_c$ - conduction band edge
- $E_v$ - valence band edge
- $E_f$ - fermi level
- $E_d$ - energy level of donor atoms
- $E_a$ - energy level of acceptor atoms

- Hole
- Electron
- fixed negative charge
- fixed positive charge
1.4 Charge carriers

Semiconductors behave as an insulator at low temperature if they are made from perfect crystals. But one can make semiconductors conductive either by adding extra electron into the CB or by removing electron from the VB. In order to obtain these conditions, one of these methods must be executed on semiconductors. Those are the photo-excitation, thermal excitation and doping. 

1.4.1 Photo excitation

If the energy of incident photons are greater than that of corresponding $\lambda_{bg}$ (corresponding wavelength for band gap excitation), electron can migrate from VB to CB. Then a hole is create in VB.

1.4.2 Thermal excitation

This method is more suitable for narrow band gap ($E_g < 0.5$ eV) semiconductors. When heat is supplied electron migrate from VB to CB.

1.4.3 Doping

Addition of acceptor atoms or donor atoms into an intrinsic semiconductor is called doping. Then the semiconductor becomes an extrinsic semiconductor. This process leads new energy level with in the band gap region. According the position of new energy level and the type of the dopent extrinsic semiconductors can be divided as n-type and p-type semiconductors.
1.5 Conductivity of a semiconductor\(^{(11,12)}\)

Semiconductors show two types of conductivities namely electronic conductivity and ionic conductivity. Both are temperature and purity govern conductivities.

1.5.1 Electronic conductivity

\[ \sigma = en_{c} \mu \]

where,

- \( \mu \) - mobility of electron
- \( e \) - electronic charge
- \( n_{c} \) - the number of charge carriers contribute to conductivity
- \( \sigma \) - conductivity

1.5.2 Ionic conductivity

Ionic conductivity occurs in a semiconductor when they have either a large number of crystal defects or large interstitial cavities. The temperature dependence of ionic conductivity is usually expressed by the Arrhenius equation.

\[ \sigma = \sigma_{0} \exp (-\Delta E / k_{b} T) \]

where,

- \( \Delta E \) - thermal activation energy
- \( \sigma \) - conductivity at temperature \( T \) K
- \( k_{b} \) - Boltzmann constant
- \( T \) - absolute temperature
- \( \sigma \) - conductivity at temperature 0 K
1.6 Dye sensitization

One of the interesting phenomena of photoelectrochemical cell (PEC) is dye sensitization. Some n-type semiconductors adsorb dyes on their surfaces. When the adsorbed dye is excited by light, the excited electrons in the dye transfer to the conduction band of the semiconductor and flow into the bulk. The dye sensitization was first reported by Greischer and Tributch. The mechanism now explained is as follows:

The dye monomolecularly adsorbed on the n-type semiconductor surface absorbs light and its electron is injected into the CB, which flows along the potential gradient formed in the depletion layer. In the presence of a reducing agent in the solution, a steady photocurrent flows because the reducing agent supplies electrons for the dye. Figure 1.3 illustrates the mechanism of dye sensitization.
Figure 1.3 Mechanism of dye sensitization.
1.6.1 Kinetics of the semiconductor electrode/electrolyte interface.

During the past decades, the utilization of thin semiconductor films made from colloidal suspension of semiconductor particles as light harvesting electrodes in photoelectrochemical cells have received much attention. Even though in a colloidal suspension in which the semiconductor nanocrystallites (20 ~ 50 Å) show the properties of short circuit microelectrodes, under band gap excitation, thin semiconductor films made from the colloidal particles are capable of exhibiting photoelectrochemical properties similar to polycrystalline semiconductor films\(^{(13)}\). For example, Gratzel and co-workers have shown that the porous TiO\(_2\) film prepared from colloidal particles is efficiently sensitized by Ruthenium polypiridine type (Figure 1.4) dyes containing carboxyl groups or sulfonic groups\(^{(14,15)}\). It has been pointed out that the mechanism of photocurrent generation in such a thin film is considered to be different from the conventional photoelectrochemical cells in which the single or poly crystalline semiconductor electrodes are being employed. In particulate electrodes, charge separation can only be achieved due to the different transferring rates of photoinduced electrons and holes at the solution interface\(^{(16-21)}\). Figure 1.5 illustrates the charge separation at the interface of particulate film and at the electrolyte.
Figure 1.4 Ruthenium polypyrindyl type dye
Figure 1.5 The charge separation at the interface of particulate film and the electrolyte.
1.7 Efficiency of a Photo Electrochemical Cell

The efficiency of a PEC can be studied by using three important parameters: they are

1. Open circuit voltage \( V_{oc} \)
2. Short circuit current \( I_{sc} \)
3. Fill factor \( ff \)

1. Open circuit voltage

The voltage which is measured at open circuit, is called the open circuit voltage i.e., the voltage is measured using a high resistance voltmeter so as to draw a minimum current. This represents the power that can be obtained under open circuit condition.

2. Short circuit current

The current measured under short circuit conditions is called the short circuit current.

3. Fill factor

The rate at which the current approaches it’s limiting short circuit value is called the fill factor, which is given by the following equation

\[
\text{Fill factor} = A / I_{sc} \times V_{oc}
\]

An efficient PEC must have maximum \( I_{sc} \) and \( V_{oc} \) value. The efficiency of the cell can be defined as follows.

\[
\text{Efficiency} = (I \times V)_{\text{max}} \times (ff) \times 100 / P_{m}
\]

Where,

\[
P_{m} = \text{Incident photon flux}
\]

\[
A = (I \times V)_{\text{max}} = \text{Maximum power}
\]
Figure 1.6 shows the efficiency curve, which is used to calculate the efficiency of a dye.

\[(I_{\text{max}} \times V_{\text{max}})\]

Figure 1.6 The efficiency curve
1.7.1 Drawbacks of the efficiency of the Photo Electrochemical Cell

1. *Reflection of light*

A part of the sunlight incident on solar cells is reflected at the surface. Hence a considerable amount of energy is lost on the cell surface.

2. *Insufficient light absorption*

When the optical path is not sufficiently long, the transmitted light is not completely absorbed.

3. *Insufficient charge separation*

The electron-hole pairs are separated by an electric field in the semiconductor and they are led to the external circuit. But all the photogenerated electron-hole pairs do not contribute to the photocurrent.

4. *Recombination process*

Only the absorb energy is useful to create photoinduced charge carriers in both bands. Photoinduced charge carriers recombine rapidly through the surface states unless the electrons are carried away quickly to create useful electric current.

1.8 Properties of electronically excited states of transition metal complexes

The excited states initially formed by the absorption of photons is the Franck-Condon (FC) state, and they have the ground state molecular structure and same spin multiplicity. Vibrational lifetimes are very short (\(10^{-10}\) s) in condensed phases and hence any chemical reaction that occurs from these FC states must occur very rapidly. Such processes from the FC states are rarely observed in inorganic photochemistry.
Luminescence and photochemistry occur from "thermally relaxed" electronically excited states. The term "thexi state" was proposed to describe an electronically excited state of a metal complex by Adamson\(^{(0)}\). The energy and the geometry of the excited state differ from those of the ground state. Hence, the reactivity of respective states can be understood undoubtedly.

1.8.1 Criteria for classification of the excited states

Magnetic resonance and magnetic susceptibility measurements of complexes in the ground state reveal the presence of one or more unpaired electrons and hence serve as a guide to assigning configurations as being due to strong or weak field. Due to their short-lived nature, the excited states are not amenable to magnetic studies. Features of absorption, emission and reactivity patterns are used for guidance\(^{(22-27)}\).

1.8.1.1 Metal centered (MC) excited states

These states involve transitions localized on the central metal ion as their name implies. Absorption bands are usually observed in fluid solution, are devoid of structure and range in intensity from extremely weak to medium strength. d-d transitions are very weak due to forbidden changes in spin multiplicity. The shape of the d-d absorption band also reveals the orbital promotional nature of the associated transition. The energy of the MC excited state depends on the σ-donor and π-acceptor properties of the ligands, the steric crowding around the metal and the bite angle with ligands such as bipyridine.

The emission is broad (Gaussian shaped) and structureless. The temperature dependence is rather pronounced, so that MC emission is rarely observed in fluid
solution. The mean decay time is strongly temperature-dependent. The quantum yield is generally quite low, but can be improved by removing high frequency vibrations from the coordination sphere.

1.8.1.2 Metal-to-Ligand Charge Transfer (MLCT) states.

The intense colors of metal complexes with π conjugated ligands are due to π* ← d transitions. Since the π* ← d promotions are responsible for CT transition both singlet and triplet, both (π* ← d)1 and (π* ← d)3, are predicted. These bands are generally broad. The energy of the MLCT states depend on the reduction potential of the ligand involved in the MLCT transition, the oxidation potential of the metal in the complex and the charge separation caused by the transition.

The emission is intense and highly structured. The temperature dependence of the lifetime and emission intensity is sufficiently weak that the luminescence is observable at room temperature in a rigid matrix and sometimes in fluid solution. The quantum yield of the luminescence is high, often exceeding 10% \((28-32)\). When the complex is asymmetrical and possesses a static dipole moment, the energy of the emission band can be shifted markedly by changing the polarity of the medium.

1.8.1.3 Ligand-Centered (LC) excited states

An emission spectrum originating from a ligand centered excited state is generally structured as that from the MLCT state. It is possible to distinguish the two types of emissions on the grounds of energy and lifetime. The LC state emission of the complex is like the corresponding \((\pi ← \pi^*)^3\) emission that can usually observed from the
uncoordinated ligand under the same conditions. The emission occurs close to the emission of the free ligand whereas the MLCT emission can occur at much lower energies.

The LC emission is much less influenced by the heavy metal ions, so that it maintains its spin-forbidden character to a greater degree than the MLCT.

1.8.2 Transition metal complexes as dye material for solar cells (Photovoltaic cells) as dye material

At the initial stage, the researchers were used several organic molecules as dyes in photovoltaic cells. Extensive efforts have been made in various laboratories to modify the semiconductor surface with various sensitizing organic dyes. These dyes are directly adsorbed on the semiconductor surface either by electrostatic interaction or by charge transfer interaction. Functional groups such as carboxylic and hydroxy are useful for binding the dyes to semiconductor surface. The interaction between the semiconductor surface and the dye molecules often results in spectral changes which include displacement or broadening of the absorption bands, appearance of new charge transfer bands and changes in the molar extinction coefficient of absorption. Although there are many suitability of organic dyes, there are some drawbacks, such as rapid recombination of charge carriers and photodecomposition of the dye.

To overcome the above problems a more efficient system would be a cell sensitized through a charge capturing mechanism (Figure 1.7), such as a metal-ligand charge transfer (MLCT) transition where charge recombination is much less probable.
Figure 1.7 Mechanisms within the cell
1.9 Fate of a dye molecule in a Photoelectrochemical cell

Dye molecules contain unsaturated kernel and chromophores. Some of these chromophores of dye molecule are important for absorption, sensitization and imparting color to the substrate. They are called auxochromes. Such properties of the molecule are given by $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. Whereas, $\pi \rightarrow \pi^*$ transitions are predominant.

Dye molecule (D) absorbs photon from sunlight and it excites from the ground level $S_0$ to the excited level $S^*$ (singlet or triplet). $D^*$ oxidizes and injects an electron into the conduction band (in an anodic process) of n-type semiconductor. This $D^+$ accepts an electron from $I^-$ of the redox couple $I^-/I_3^-$, regenerating the dye, and diffusion controlled migration of $I^-$ to the cathode maintains the equilibrium of the redox couple.

$$D + hv \rightarrow D^*$$
$$D^* \rightarrow D^+ + e^-$$

To conduction band

$$D^+ + I^- \rightarrow D + I^-$$
$$I^- + e^- \rightarrow I^-$$
1.10 Acid-base switching of Alizarin and Quinalizarin sensitized nano-porous photovoltaic devices

One of the important requirements of an information storage system or a molecular switching effect is the existence of two stable forms of a molecule that can be interconverted conveniently (33). During the past decade a large number of research articles have been published (34) and most of the systems are based on cis-trans isomerization or cyclization of organic systems. However, when it comes to designing of any practical molecular electronic device, these systems have shown several drawbacks. For any practical device, output of certain molecular properties must be interconverted (on / off) by means of a simple technique and with a very good reproducibility of the output signal. When alizarin (1,2-dihydroxyanthroquinone) or quinalizarin (1,2,5,8-tetrahydroxyanthroquinone) were used as sensitizing dye materials in nano-porous solar cells, not only they produce fairly high photocurrents and photovoltages when exposed to the light, but also those properties show high sensitivity to the protonation and deprotonation of the 2 hydroxy group of the ligand.
1.11 Cyclic Voltammetry

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron transfer reactions and on coupled chemical reactions or adsorption processes. Cyclic voltammetry offers a rapid location of redox potentials of the electroactive species and convenient evaluation of the effect of media upon the redox process.

Cyclic voltammetry consists of scanning linearly the potential of a stationary working electrode using a triangular potential wave form. Single or multiple cycles can be used to obtain information. That depends on the information that one is seeking. The potentiostat measures the current with respect to the applied potential through out the potential sweep. The resulting plot of current vs potential is named as a cyclic voltammogram.

1.11.1 Data interpretation

Reversible system

The cyclic voltammogram is characterized by several important parameters. At 25°C the peak current for a reversible couple is given by the Randles-Sevcik equation:

\[ I_p = (2.69 \times 10^5)n^{3/2} ACD^{1/2} \nu^{1/2} \]

Where,

A - area of the electrode
The ratio of the reverse-to-forward peak currents, $I_{r} / I_{f}$, is unity for a simple reversible couple. This peak ratio can be strongly affected by chemical reactions coupled to the redox process.

The position of the peaks on the potential axis ($E_p$) is related to the formal potential of the redox process. The formal potential for a reversible couple is centered between $E_{p,a}$ and $E_{p,c}$:

$$E^0 = \frac{(E_{p,a} + E_{p,c})}{2}$$

The separation between the peak potentials for reversible is given by $^{(35)}$:

$$\Delta E = E_{p,a} - E_{p,c} = 0.059/n \text{ V}$$

The peak separation can be used to determine the number of electrons transferred, and as a criterion for a Nernstian behavior $^{(35)}$. A fast one-electron process exhibits a $\Delta E_p$ of about 59 mV. Both the cathodic and anodic peak potentials are independent of the scan rate.
**Irreversible and Quasi-reversible systems**

For irreversible processes, the individual peaks are reduced in size and widely separated. Totally irreversible systems are characterized by a shift of the peak potential with the scan rate: \(^{(36)}\)

\[
E_p = E^0 - \frac{RT}{\alpha n_a} F [0.78 - \ln(k^0/D^{1/2}) + \ln(\alpha n_a F v/RT)^{1/2}]
\]

Where \(\alpha\) is the transfer coefficient and \(n_a\) is the number of electrons involved in the charge-transfer step. \(E_p\) occurs at potentials higher than \(E^0\), with the overpotential related to \(k^0\) and \(\alpha\). Independent of the value \(k^0\), such peak displacement can be compensated by an appropriate change of the scan rate. The peak potential and the half-peak potential (25 °C) will differ by 48/\(\alpha n\) mV. So the voltammogram becomes more drawn out as \(\alpha n\) decrease \(^{(37)}\).

\[
I_p = (2.99 \times 10^5) n (\alpha n_a)^{1/2} \Lambda C D^{1/2} v
\]

The peak current is still proportional to the bulk concentration, but will lower in height.

For quasi-reversible systems (with \(10^{-1} > k^0 > 10^{-5}\) cm/s), the current is controlled by both the charge and mass transport. The shape of the cyclic voltammogram is a function of \(k^0/\pi a D^{1/2}\) (where \(a = nFv/RT\)). The voltammograms of a quasi-reversible system are more drawn out and exhibit a larger separation in peak potentials compared to a reversible system \(^{(38)}\).

Cyclic voltammograms can be used to assign the electron transfers of the dye materials such as \(\pi^* \rightarrow \pi, \pi^* \rightleftharpoons d\) and so on.
1.12 Computational Chemistry

Computational chemistry is a new discipline of chemistry. Its advent and popularity have paralleled improvements in computing power during the last several decades. As with other disciplines in chemistry, computational chemistry uses tools to understand chemical reactions and processes. Scientists use computer software to gain insight into chemical processes. Although computational chemists frequently develop and refine software tools, their primary interest is in applying software tools to enhance chemical knowledge.

Computational chemists face a challenge to characterize and predict the structure and stability of chemical systems in order to estimate energy differences between different states and to explain reaction pathways and mechanism at the atomic level. Meeting these challenges could eliminate time consuming experiments.

Empirical information has been based on for software tools of computational chemistry. One needs to understand the nature of the database and techniques in order to use these tools (39-42).

1.12.1 HyperChem software package

HyperChem is a versatile molecular modeler an editor and a powerful computational package. It offers many types of molecular and quantum mechanics calculations.
1.12.2 Building and displaying molecules

HyperChem is versatile computational package. It helps to build and display molecules easily. Using the drawing tool, a two dimensional (2D) representation of a molecule can be obtained. Then three dimensional (3D) structure of the molecule can be obtained using model builder. The model builder adds implicit hydrogens to the molecule at our request. Individual bonds, bond geometries, angles, torsions, and atomic charges also can be measured during model building or after model building\(^{(43)}\).

1.12.3 Optimizing the structure of molecules

Well defined molecular structure is needed to calculate the properties of a molecule. A calculation often requires a structure that represents a minimum on a potential energy surface. Hyperchem contains several geometry optimizers to do this. One can then calculate single point properties of a molecule or use the optimized structure as a starting point for subsequent calculations.

1.12.4 Molecular mechanics (MM+)

Molecular mechanical force fields use the equations of classical mechanics to describe the potential energy surfaces and physical properties of molecules. Those molecular mechanical force field calculations are approximated to the simple harmonic motions. Hence these calculations can not describe the bond breaking or bond formation. But molecular mechanical calculations can be used to initial optimization of molecules with in a short time, which can be then used to further optimization by semi empirical calculation\(^{(43-45)}\).
1.12.5 Semi-empirical methods of quantum chemistry

Semi-empirical methods have evolved over the last three decades. Using today’s microcomputers, they can produce meaningful, often quantitative, result for large molecular system (45-47).

1.12.5.1 General background

Molecules consist of electron and nuclei. Most applications of quantum chemistry separate the motion of the nuclei from the motion of electrons [Born-Oppenheimer approximation]. The approximation results in a model of nuclei moving on a potential energy surface with electrons adjusting instantly to changes in nuclear positions. Nuclear motion is constrained by the interaction of nuclei and electrons. At any position of the nuclei, potential energy is the sum of the repulsion among the positively charged nuclei and attractions arising from the electrons.

1.12.5.2 Molecular geometry

The most important chemical structures are stable, equilibrium molecular geometries and transition states. Equilibrium geometry of a molecule describes the coordinates of a deep minimum on a potential energy surface. A set of atoms may have a number of potential energy minima, each corresponding to a different isomer of the molecular system. Other, less deep minima may correspond to intermediates in chemical reactions.
1.12.5.3 Calculating electronic potential energy

Electronic energy must be computed by solving the quantum mechanical Schrödinger equation\(^ {48}\). The lowest energy solution of this equation is called the ground state wavefunction. Semi-empirical molecular orbital methods provide approximate solutions of the Schrödinger equation; the ground state wavefunction and certain low energy excited states.

1.12.5.4 Features of semi-empirical method

- Do not require information about the location or geometry of bonds in a molecular system.
- Parameters for elements are independent of the chemical environment. In contrast, parameters used in molecular mechanics methods often depend on the chemical environment.
- Semi-empirical methods can be used to describe the bond breaking.
- Hyperchem can perform semi-empirical molecular orbital calculations on molecules containing hundreds or more atoms. There is no restriction on the number of atoms, but larger structures may require excessive computing time.

1.12.5.5 Range of semi-empirical methods

The semi-empirical methods in Hyperchem differ in how they approximate the Schrödinger equation and how they compute potential energy\(^ {48-50}\).

Example; Extended Huckel method does not explicitly consider the effects of electron-electron repulsion but incorporates repulsion into a single electron potential. This
simplifies the solution of the Schrodinger equation and allows Hyperchem to compute
the potential as the sum of the energies for each atom.

1.12.5.6 ZINDO/1 (Zerner’s Intermediate Neglect of Differential Overlap) method

The ZINDO/1 method is the most suitable semi-empirical method in Hyperchem
for determining structures and energies of molecules with first or second row transition
metals (48-50).

The ability to perform molecular orbital calculations on metals is extremely useful
because molecular methods are generally unable to treat metals. This is because metals
have a wide range of valences, oxidation states, spin multiplicities and have unusual
bonding situations such as d,p back bonding.

1.12.5.7 Selecting options for ZINDO/1 method

Following options were selected from the semi-empirical dialog box to set
conditions for the calculation (49-52).

(i) Convergence criteria

Convergence limit and iteration limit specifies the precision of the
calculation. Convergence limit refers to the differences in energy (in
kcal/mol) between two successive SCF cycles (Self Consistence Field
calculation). Iteration limit specifies the maximum number of cycles
allowed to reach that goal. If the calculation exceeds the iteration limit
before it reaches the convergence limit, then there is most likely convergence failure.

(ii) Charge, Spin and Excited state

Specify the charge and spin multiplicity in the semi-empirical options dialog box. Closed shell molecules have a multiplicity of one (a singlet). A radical with one unpaired electron, has a multiplicity of two (a doublet). A molecular system with two unpaired electrons usually (a triplet) has a multiplicity of three. In some cases, however such as a biradical, two unpaired electrons may also a singlet.

(iii) UHF and RHF

Hyperchem can compute open shell (non-singlet) systems with either the half electron RHF or UHF method.

RHF – Restricted Hartree Fock

UHF – Unrestricted Hartree Fock

Use the RHF wave function for singlet electronic states, such as the ground states of stable organic molecules. The UHF wave function is most often used for multiplicity’s greater than singlets. In this case, the space orbitals for alpha electrons need not be the same as for beta electrons. But use the UHF method for singlet states only to avoid potential energy discontinuities when a covalent bond is broken and electrons can unpair.
1.12.5.8 Single point calculation

Hyperchem always computes the electronic properties for the molecule at the last step of geometry optimization. However, a separate single point calculation is required if a calculation with the configuration interaction is required for an optimized geometry.

A single point calculation determines molecular properties such as energy or spin density of a defined molecular structure. Normally these calculations are for stationary points on a potential energy surface; can use either molecular or quantum mechanical methods for single point calculations. The calculation provides energy and the gradient of that energy. The gradient is the root mean square of the derivative of the energy with respect to Cartesian coordinates. The size of the gradient can provide qualitative information to determine if the structure is close to a minimum.

1.12.5.9 Contour plots

Hyperchem allows the visualization of two dimensional contour plots for a certain number of variables. These contour plots show the values of a spatial variable (a property $f(x,y,z)$ in normal three dimensional Cartesian space) on a plane that is parallel to the screen.

1.12.5.10 Total electron density (charge density)

Hyperchem can display a contour map of the total charge (electron) density. Semi-empirical methods available from Hyperchem do not include inner shell electrons. The charge density shows only the valance charge density.
Chapter-02

EXPERIMENTAL
Experimental

2.1 Chemicals and Solvents

Analytical grade Aldrich and BDH chemicals were used for all synthetic work and preparation work. Double distilled solvents and deionized distilled water were used. Nitrogen was used to make an inert environment throughout the synthetic procedure.

TiO₂, commercial name DEGUSSA, was used as the n-type semiconductor.

2.2 Preparation methods

2.2.1 Preparation of conducting glass plates (CTO) for applying TiO₂ layer

Commercial name “Tec glass” CTO glass plates were used. Sheet resistance was approx. 20 Ω cm². Surface area of a plate was 2.5 cm². Then plates were well cleaned by washing with 0.05 M KOH, 0.05 M HNO₃, propen-2-ol and distilled water respectively. Plates were dried using hot air. Each plate was covered except 1 cm² using aluminum foil.

2.2.2 Deposition of TiO₂ on conducting glass plates

Suitable amount of Degussa TiO₂ powder was finely ground using pestle and mortar or using a sonicator. Then the ground Degussa powder was dissolved in ethanol until suitable viscosity was obtained. Covered plates were placed on a hot plate around 100°C and the above solution was sprayed until the thickness of the TiO₂ layer was translucent. Then plates were sintered in a 450°C preheated box furnace for 30 minutes.
2.2.3 Preparation of Fe(II)(C_2O_4)_2bromopyrogallol red complex

Bromopyrogallol red (BPR) and di(aqua)bis(oxalato)iron(II) [which was prepared by precipitating the complex in aqueous medium by adding oxalic acid to an aqueous solution of ferrous ammonium sulfate.] were mixed and refluxed for 2 hours in methanol. The resultant mixture was evaporated and the dark black solid product obtained was washed several times with acetone to remove any unreacted BPR.

2.2.4 Preparation of [Co(1,10-phen)_2]Cl_2

CoCl_2.4H_2O and 1,10-phenanthroline were mixed in 1:2 molar ratio in 100 ml of methanol. This mixture was refluxed hours under a nitrogen atmosphere. The resulting mixture was reduced to a volume of 20 ml and decanted into 200 ml of acetone. Then the mixture was cooled. After few minutes pink color [Co(1,10-phen)_2]Cl_2 crystals were filtered out.

2.2.5 Preparation of [Co(1,10-phen)_2]bromopyrogallol red and [Co(1,10-phen)_2] catechol violet complexes

Co(1,10-phen)_2 was dissolved in 100 ml of methanol and bromopyrogallol red or catechol violet(CatV) was mixed (1:1molar ratio) with it slowly over 30 minutes period. Above mixture was refluxed (5 hrs) and reduced to a volume of around 20 ml and decanted into a saturated sodium chloride solution. After few minutes a dark reddish brown precipitate was formed. The precipitate was filtered and washed with cold methanol.
2.2.6 Preparation of I/I$_3$ electrolyte

Ethylene carbonate liquid (7.3 ml) which was obtained by melting ethylene carbonate solid and acetonitrile (2 ml) were mixed well. 1.5 g of tetrapropyl ammonium iodide and 6 ml of above mixture were mixed and shake few minutes. After mixing 0.12 g of I$_2$ was added into it.

2.2.7 Coating procedure of dye on semiconductor films

Semiconductor films were kept immersed in a dye solution, containing 5% ethanol. Different levels of dye adsorption on semiconductor plates were achieved, by varying the duration of immersion in the dye solution or changing the dye concentration.

2.2.8 Preparation of acidic and basic ethanolic solutions

Trichloroacetic acid and triethylammine were used to prepare the acidic and basic methanolic solutions. The pH values of the solutions are 2.5 and 9.5 respectively.

2.2.9 Measuring the photocurrent and photovoltage values of acidic and basic medium dye coated photovoltaic cell

Protonation and deprotonation of the coated dye was carried out by immersing the dye coated TiO$_2$ plates in trichloroacetic acid and triethylammine in methanolic solutions for 5 minutes respectively. Normal procedure was carried out to assemble the cell.
2.3 Instruments and Techniques

2.3.1 Absorption and Reflectance spectra

Absorption spectra were recorded using PERKIN ELMER-551 double beam spectrophotometer and reflectance spectra were recorded using SHIMADZU UV-3000 double beam spectrophotometer equipped with part No 037-7003 for reflectance measurements.

2.3.3 Photo-current action spectra

Photo-current action spectra (i.e. dependence of the observed photo-current as a function of excitation wavelength) were monitored using Nikon monochromator Auto-scanner AS-C 101 equipped with Stanford Research lock-in-amplifier. Figure 2.1 illustrates the block diagram of photocurrent action spectra set-up.
Figure 2.1 Schematic layout of action spectra set-up
2.3.4 Emission spectra

Emission spectra were recorded using a SHIMADZU model RF 5000 spectrofluorimeter.

2.3.5 Cyclic voltammograms

Cyclic voltammograms were recorded using an EG & G Princeton applied research instrument potentiostat/galvanostat, model: Versastat II. Solution was degassed for 20 minutes by bubbling nitrogen prior to the scans. Supporting electrolyte was $1 \times 10^{-1}$ M KNO$_3$. Teflon shrouded Pt electrode was used as the working electrode and scan rate was 100 mVs$^{-1}$. Figure 2.2 illustrates a schematic layout of cyclic voltammetry set-up.
Figure 2.2 Schematic layout of cyclic voltammetry set-up
2.3.6 Solar simulator

SUNTEST CPS PLUS model Atlas solar simulator was used to expose the cells with and without UV radiation.

2.3.7 HyperChem quantum mechanical calculations\(^{(40-45)}\)

(i) The model diagram was drawn initially.
(ii) Using molecular mechanics force field, (MM+) parameters, initial geometry was optimized.
(iii) Secondary and final geometry was optimized using a semi-empirical quantum mechanical calculation. In this study ZINDO/1 parametric method was used.
(iv) Log file was opened and it gives the calculated data for the system.
(v) Single point energy calculation was done to calculate the total energy for the fully optimized geometry.
(vi) Energy data for the system was obtained by opening the log file.
Chapter-03

RESULTS AND DISCUSSION
RESULTS AND DISCUSSION

3.1 Preparation of a dye sensitized photovoltaic cell

Initial, cleaning process of conducting Tin oxide (CTO) glass plates is very important in order to get a good binding surface for nanocrystalline colloidal particles of TiO₂. Diluted acid can be used to react with basic contaminant and vice versa and propan-2-ol used to remove any organic substances on the CTO surface.

The TiO₂ layer is prepared from nanocrystalline colloidal particles of TiO₂ through a well-controlled annealing process. Charge separation and charge collection are two key steps in the processing of sunlight to electricity and both take place on the textured TiO₂ film. The morphology and the structure of the layer play important roles and it is important that procedures for the preparation of the TiO₂ layer takes into account the delicate of this annealing process. Annealing is carried out to create physical contacts between the various TiO₂ particles and to make the bulk resistively of the film low. Large annealing time is undesirable because it can cause sintering and reduce the porosity of the film. The preparation of the TiO₂ film indeed is a delicate process and large differences in the performances of the film can be observed if strict procedure is not adopted. Figure 3.1 illustrates the surface complexation mechanism with a dye molecule. Dye is tightly adsorbed on TiO₂ as a result of complexation with Ti⁴⁺ ions on the surface. Ti³⁺ ions on the surface of TiO₂ are bonded to hydroxyl groups.

Several criteria can be used to measuring the efficiency of the cell. The efficiency means that how many monochromatic photons are converted into
electrons (photocurrent). That is given by the incident photon-to-current conversion efficiency (IPCE) \(^{(32)}\).

![Figure 3.1 The mechanism of surface complexation of dye with TiO\(_2\)](image-url)

\[
\text{CH} \quad + \text{HO- Ti}^{4+} \quad \rightarrow \quad \text{CH} + \text{H}_2\text{O} + \text{H}^+ 
\]
The IPCE is mainly determined by three factors.

(a) Light harvesting ability of the dye material
   (Depends on the spectral and photophysical properties of the dye)

(b) The charge injection yield
   (Depends on the excited state redox properties and the lifetime)

(c) The charge collection efficiency
   (Depends on the structure and morphology of the TiO₂ layer)

Apart from good visible light absorption properties a key requirement for the sensitizer is its excited state redox potential. The excited state should have enough driving force to inject electrons into the conduction band.

Another important aspect is that the dye must have a less charge recombination properties and less photo-degradation in order to enhance the current voltage properties and to maintain it with time. If charge-capturing mechanism such as MLCT or MMCT is used above requirement can be obtained.

Triphenylmethane dye molecule having –OH groups attached to the phenyl ring have shown strong ability to chelate with number of transition metal ions. Metallochromic triphenylmethane type dyes have been subjected for many studies in the area of trace metal analysis because of its binding ability. Figure 3.2a and 3.2b show the two triphenylmethane molecules that were used for this research work. Triphenylmethane molecules involve ligand centered (LC)
electronic transitions for the electron injection process. [Say for an example LUMO orbital of the sensitized dye to the CB of the TiO$_2$ semiconductor. The nature of the LUMO orbital plays an important role when considering the photovoltaic properties of the cell.]
(a) Bromopyrogallol red  
(b) Catechol violet

Figure 3.2 Triphenylmethane molecules
But these molecules have received very little attention as potential solar energy capturing pigments in dye sensitized nano-porous photovoltaic cells. However, recent studies have indicated that triphenylmethane type materials are potential candidates for dye sensitized nano porous photovoltaic devices. One of the main advantage is that the availability of several dye materials with the same structural skeleton. Since the molecule is a nonplaner itself, different substituent groups attached to the phenyl rings influence the torsion angles between three phenyl rings. This will directly affect the π orbital symmetry. For an example, bromopyrogallol red and catechol violet have different torsion angles. Therefore, upon excitation the location of the electron (localization/delocalization) would be subjected to further investigation.

3.2 Preparation of metal complexes

Moisture free solution was used to dissolve the reactants and inert atmosphere was maintained in order to keep the low oxidation state of the metal. Unless MLCT charge capturing mechanism can not be expected. Final product was washed several times with moisture free suitable solvents to remove unreacted free ligands.

3.3 Comparison of spectroscopic properties of Fe(II)(C₂O₄)₂bromopyrogallol red complex with bromopyrogallol red free ligand

Bromopyrogallol red free ligand has a strong absorption peak at 540 nm in the visible region. This molecule strongly binds with TiO₂ semiconductor surface
as shown in Figure 3.1. Structure of Fe(II)(C₂O₄)₂bromopyrogallol red complex is shown in Figure 3.3.

Aqueous medium absorption spectra of both iron(II) complex and bromopyrogallol red free ligand are shown in figure 3.4. According to the absorption spectrum, lowest electron transition of bromopyrogallol red ligand (540 nm) can be assigned to a transition $\pi^* \leftarrow \pi$. But the Fe(II) metal complex has a peak at 690 nm. This band extends to the 900 nm region. Therefore, it is clear from these results that the lowest electronic transitions of both molecules are different.

Another important fact is that the oxalato ligand acts as a spectator ligand. Since the absorption spectrum of Fe(II)(C₂O₄)₂(H₂O)₂ has no peaks in the visible region, hence spectroscopic properties of Fe(II)(C₂O₄)₂bromopyrogallol red complex and bromopyrogallol red free ligand can be easily interpreted.

Figure 3.3  Fe(II)(C₂O₄)₂bromopyrogallol red complex
Figure 3.4 Absorption spectra of Fe(II)(C₂O₄)₂ bromopyrogallol red (-------) and bromopyrogallol red (-----) in methanol
Cyclic voltammograms for both iron(II)(C₂O₄)₂bromopyrogallol red and bromopyrogallol red free ligand in 1 × 10⁻³ M KNO₃ solution are shown in Figure 3.5. Reference electrode was Ag/AgCl electrode. Quasi-reversible reduction waves were observed for both molecules at ~430 mV. An irreversible oxidation occurred at 628 mV only for free ligand. According to above observations, there is no effect on reduction waves when Fe(II)(C₂O₄)₂ bind with bromopyrogallol red. Hence, observed reduction waves for both molecules can be assigned to reductions of bromopyrogallol red ligand base. Therefore, the electronic transition tailing out to 900 nm region of the spectrum for iron(II) complex is most likely to be a π*(BPR) ← dπ(Fe), MLCT transition.

Figure 3.6 illustrates the photocurrent action spectra for iron(II) complex and bromopyrogallol red free ligand. In bromopyrogallol red spectrum, there are two peaks appearing at 362 nm and 625 nm. The peak at 362 nm can be attributed to the sensitization through TiO₂ band gap excitation and 625 nm peak for the dye sensitization. Iron(II) complex also has two peaks at 580 nm and 698 nm. But 362 nm peak has disappeared due to large surface dye concentration. Similar behaviour has been observed for the Ru complexes sensitized nono-porous photovoltaic devices. When photocurrent action spectra and aqueous medium absorption spectra are considered a red shift (690 nm → 698 nm) can be observed. This type of red shift can be observed for bis(bipyridyl)Ru(II) complexes. This effect was attributed to the lowering of energy of π* orbital due to delocalization. Hence 690 nm → 698 nm red shift can be interpreted as to the delocalization of π* orbitals of the bromopyrogallol red part of the complex chelated with Ti⁴⁺ ion.
Figure 3.5 Cyclic voltammograms of (a) iron(II)(C₂O₄)₂bromopyrogallol red and (b) bromopyrogallol red in aqueous solution containing 1X 10⁻³ M KNO₃ as supporting electrolyte. Working electrode: Teflon shrouded Pt electrode; scan rate 100 mVs⁻¹.
Figure 3.6 Photocurrent action spectra for nanocrystalline TiO$_2$ films coated with (a) Fe(II)(C$_2$O$_4$)$_2$ bromopyrogallol red and (b) bromopyrogallol red.
Figure 3.7 shows the I/V curves (efficiency curves) for both complex and the free ligand. Calculated percentage cell efficiencies are 0.2 and 0.3 respectively. When UV radiation (<348 nm) was blocked the cell efficiencies give approx. equal reductions, around 0.67%. This can be attributed to the fact that iron(II) complex and free ligand have a similar action spectra in the visible region. Average short circuit photocurrent ($I_{sc}$), open circuit voltage ($V_{oc}$) and cell efficiency values are given in Table 2.1.

Current voltage values for the complex of ferrous ammonium sulfate with bromopyrogallol red is comparable to the current voltage values of iron(II)(C$_2$O$_4$)$_2$ bromopyrogallol red complex. According to these results there is no significant role of the spectator oxalato ligand on the current–voltage properties. These results clearly indicate that the enhancement of the cell efficiency due to the iron(II) complex is a result of the MLCT character.

Figure 3.8 illustrates the time development curve of both iron(II) complex and bromopyrogallol red free ligand. Cells were exposed to a 750 Wm$^{-2}$ solar simulator with or without UV filter. Rapid decay can be observed without the UV filter because UV light generates electrons and holes in TiO$_2$ and these are readily accepted by oxygen molecules to form peroxides. This is a reason for initial rapid degradation and liquid redox couple ($I^-/I_3^-$) act as a catalyst.

**Table 2.1**

Average photocurrent, voltage and cell efficiency values for two dye materials:

(illumination: 750 Wm$^{-2}$ solar simulator)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Photocurrent(mA/cm$^2$)</th>
<th>Photovoltage(mA/cm$^2$)</th>
<th>Cell Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromopyrogallol red</td>
<td>0.83</td>
<td>411</td>
<td>0.20</td>
</tr>
<tr>
<td>Iron(II) complex</td>
<td>1.23</td>
<td>423</td>
<td>0.29</td>
</tr>
</tbody>
</table>

52
Figure 3.7  Photocurrent–voltage curves for (a) Fe(II)(C$_2$O$_4$)$_2$ bromopyrogallol red and (b) bromopyrogallol red
Figure 3.8 The time development of the photocurrent when cells were illuminated with 750 W/m² solar simulator for: (a) Fe(II)(C₂O₄)₂bromopyrogallol red (b) bromopyrogallol red (c) Fe(II)(C₂O₄)₂bromopyrogallol red with a UV blocking filter (d) bromopyrogallol red with a UV blocking filter.
3.4 Spectroscopic and photovoltaic properties of [Co(II)(1,10-phen)$_2$

bromopyrogallol red] and [Co(II)(1,10-Phen)$_2$catechol violet] complexes

In the previous study Fe(II)(C$_2$O$_4$)$_2$ bromopyrogallol red was synthesized. Oxalato ligand acts as a spectator ligand only because it has no chromophores in the visible region. Therefore, it doesn’t give a contribution to enhance the current voltage properties of the cell. Where as, 1,10-phenanthroline ligand has chromophores in the visible region. So such a ligand could give a contribution to enhance the current voltage properties of the cell (54). But Fe(II)(1,10-phen)$_2$ can not be synthesized because Fe(II)(1,10-phen)$_3$ is the only product from at any molar ratio of Fe: 1,10-phen.

Co$^{2+}$ ion can be used to form Co(II)(1,10-phen)$_2$ easily using CoCl$_2$ and 1,10-phenanthroline. So [Co(II)(1,10-phen)$_2$ bromopyrogallol red] and [Co(II)(1,10-phen)$_2$ catechol violet] were synthesized. Computational data suggested that the binding positions of bromopyrogallol red and catechol violet are 4,5 and 3,4 respectively. All possibilities and considered respective $\Delta H^0_f$ values are given table 2.2. The complexes Co(II)(1,10-phen)$_2$ bromopyrogallol red and Co(II)(1,10-phen)$_2$ catechol violet hereafter refer as BPR complex and CatV complex respectively. Absorption spectra of both complexes are shown in figure 3.10. Inserted figure shows the absorption spectra of the corresponding free ligands. Bromopyrogallol red ligand has a peak at 438 nm and 540 nm. Whereas the relevant complex has no 438 nm peak and it has a peak at 565 nm, which is extended towards 900 nm region. Catechol violet has no such a sharp peak whereas its complex has a weak absorption peak at 608 nm region.
Both bromopyrogallol red and catechol violet ligands of the Co(II) complexes readily bind with nonoporous colloidal TiO$_2$ surface. Both complexes produce a bluish color on the TiO$_2$ surface, whereas bromopyrogallol red and catechol violet free ligand give red color when they bind with TiO$_2$. This clearly indicates that the dye molecule binds with TiO$_2$ are different.

Diffuse reflectance spectra of the two dye complexes are shown in figure 3.11. Reflectance and absorption spectra of bromopyrogallol red complex have same peak maximum. But the reflectance spectrum is extended up to around 1000 nm region. According to literature this type of extension is due to the charge transfer between the bromopyrogallol red complex and the TiO$_2$ molecules. The reflectance and absorption spectra of catechol violet complex do not show such a broad effect.

Table 2.2 Heat of formation values of cobalt(II)(1,10-phen)$_2$ bromopyrogallol red (CoBPR-phen) and cobalt(II)(1,10-phen)$_2$ catechol violet (CoCatV-phen)

<table>
<thead>
<tr>
<th>Component</th>
<th>Total Energy (Electronic Energy)</th>
<th>Core-Core Interaction</th>
<th>Heat of Formation</th>
<th>Gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoBPR-phen</td>
<td>$-353544.43$ (kcal/mol)</td>
<td>$-321187.26$ (kcal/mol)</td>
<td>$-19387.33$ (kcal/mol)</td>
<td>$4.80$ (kcal/mol/Ang)</td>
</tr>
<tr>
<td>CoCatV-phen</td>
<td>$-563.39$ (a.u.)</td>
<td>$2910058.74$ (kcal/mol)</td>
<td>$3263603.18$ (kcal/mol)</td>
<td>$-3263603.18$ (kcal/mol)</td>
</tr>
</tbody>
</table>
### (CoBPR-phen 2'-3')

**ENEnergies and Gradient**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energy</td>
<td>-353189.27</td>
</tr>
<tr>
<td>Total Energy</td>
<td>-562.83</td>
</tr>
<tr>
<td>Binding Energy</td>
<td>-29303.17</td>
</tr>
<tr>
<td>Isolated Atomic Energy</td>
<td>-323886.09</td>
</tr>
<tr>
<td>Electronic Energy</td>
<td>-3408135.27</td>
</tr>
<tr>
<td>Core-Core Interaction</td>
<td>3054946.00</td>
</tr>
<tr>
<td>HE Energy Correction</td>
<td>-47.60</td>
</tr>
<tr>
<td>Heat of Formation</td>
<td>-19385.44</td>
</tr>
<tr>
<td>Gradient</td>
<td>3.50</td>
</tr>
</tbody>
</table>

### (CoBPR-phen 5-6)

**ENEnergies and Gradient**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energy</td>
<td>-353030.82</td>
</tr>
<tr>
<td>Total Energy</td>
<td>-562.57</td>
</tr>
<tr>
<td>Binding Energy</td>
<td>-29144.73</td>
</tr>
<tr>
<td>Isolated Atomic Energy</td>
<td>-323886.09</td>
</tr>
<tr>
<td>Electronic Energy</td>
<td>-3371097.58</td>
</tr>
<tr>
<td>Core-Core Interaction</td>
<td>3018066.76</td>
</tr>
<tr>
<td>HE Energy Correction</td>
<td>-37.11</td>
</tr>
<tr>
<td>Heat of Formation</td>
<td>-19227.00</td>
</tr>
<tr>
<td>Gradient</td>
<td>3.95</td>
</tr>
</tbody>
</table>

### (CoBPR-phen 4-5)

**ENEnergies and Gradient**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Energy</td>
<td>-353040.99</td>
</tr>
<tr>
<td>Total Energy</td>
<td>-562.59</td>
</tr>
<tr>
<td>Binding Energy</td>
<td>-29154.90</td>
</tr>
<tr>
<td>Isolated Atomic Energy</td>
<td>-323886.09</td>
</tr>
<tr>
<td>Electronic Energy</td>
<td>-3249366.42</td>
</tr>
<tr>
<td>Core-Core Interaction</td>
<td>2896325.42</td>
</tr>
<tr>
<td>HE Energy Correction</td>
<td>-35.55</td>
</tr>
<tr>
<td>Heat of Formation</td>
<td>-19237.17</td>
</tr>
<tr>
<td>Gradient</td>
<td>4.29</td>
</tr>
</tbody>
</table>
CoCatV-phen 3'-4')

ENERGIES AND GRADIENT
Total Energy = -324824.79 (kcal/mol)
Total Energy = -517.63 (a.u.)
Binding Energy = -29217.84 (kcal/mol)
Isolated Atomic Energy = -295606.95 (kcal/mol)
Electronic Energy = -2889775.19 (kcal/mol)
Core-Core Interaction = 2564950.39 (kcal/mol)
Heat of Formation = -19261.34 (kcal/mol)
Gradient = 5.93 (kcal/mol/Ang)

CoCatV-phen 3-4)

ENERGIES AND GRADIENT
Total Energy = -324269.42 (kcal/mol)
Total Energy = -516.74 (a.u.)
Binding Energy = -28963.64 (kcal/mol)
Isolated Atomic Energy = -295305.77 (kcal/mol)
Electronic Energy = -2884933.98 (kcal/mol)
Core-Core Interaction = 2560664.56 (kcal/mol)
HE Energy Correction = -33.81 (kcal/mol)
Heat of Formation = -19059.24 (kcal/mol)
Gradient = 5.76 (kcal/mol/Ang)
Figure 3.9  Structures of (a) Co(II)(1,10-phen)$_2$ bromopyrogallol red and (b) Co(II)(1,10-phen)$_2$ catechol violet molecules.
Figure 3.10 Absorption spectra of (a) cobalt(II)(1,10-phen)$_2$ bromopyrogallol red and (b) cobalt(II)(1,10-phen)$_2$ catechol violet in ethanol. Inserted figures: (a) and (b) absorption spectra of free bromopyrogallol red and catechol violet respectively.
Figure 3.11 Reflectance spectra of (a) cobalt(II)(1,10-phen)$_2$ bromopyrogallol red and (b) cobalt(II)(1,10-phen)$_2$ catechol violet complexes on TiO$_2$ surface. Recorded with diffuse reflectance assembly using TiO$_2$ metal oxide as the reference.
It indicates that there is no significant charge transfer interaction between catechol violet complex and TiO₂ surface.

Photocurrent action spectra of both complexes are shown in Figure 3.12. Both spectra have a similar shape but different photocurrent intensities. Table 2.3 shows short circuit currents (Isc) and open circuit voltages (Voc) and efficiency of the both complexes. Figure 3.13 illustrates the I/V curves for both complexes. It shows the clear difference about the current generation of both dye coated cells.

AM1 computational calculations performed using HyperChem software have revealed that the bromopyrogallol red and catechol violet ligands are non-planer molecules. The two phenyl rings (i.e. phenyl rings with the -SO₃H group and the gallol ring) in cobalt(II)(1,10-phen)₂bromopyrogallol red has a improper torsion angles of ca. 86 and 59 degrees with respect to the quinone ring. The angle for the cobalt(II)(1,10-phen)₂catechol violet is ca. 77 and 60 degrees.

According to absorption, reflectance and photocurrent action spectra, The difference of the observed photocurrent values are clearly comparable. These results clearly show that the bromopyrogallol red complex is a better sensitizer than catechol violet complex.

Table 2.3

Average photocurrent, voltage and cell efficiency values for the two dye materials: 240 Wm⁻² CFL daylight bulb.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Photocurrent (mA/cm²)</th>
<th>Photovoltage (mV/cm²)</th>
<th>Cell efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromopyrogallol red complex</td>
<td>3.20</td>
<td>463</td>
<td>1.1</td>
</tr>
<tr>
<td>Catechol violet complex</td>
<td>0.48</td>
<td>368</td>
<td>0.6</td>
</tr>
</tbody>
</table>
Figure 3.12 Action spectra of (a) cobalt(II)(1,10-phen)$_2$ bromopyrogallol red and (b) cobalt(II)(1,10-phen)$_2$ catechol violet complexes on TiO$_2$ surface.
Figure 3.13 Photocurrent-voltage curves for (a) cobalt(II) (1,10-phen)$_2$bromopyrogallol red and (b) cobalt(II) (1,10-phen)$_2$catechol violet.
3.5 Emission and absorption properties of Co\(^{2+}\)(1,10-Phen)\(_2\) catechol violet and catechol violet ligand in methanolic solutions.

Catechol violet complex shows moderately intense emission in methanolic solution. Figure 3.14 shows the emission spectra of [Co(II)(1,10-Phen)\(_2\) catechol violet] complex in dotted line and uncoordinated free ligand in solid line. There is a 12 nm red shift between emission spectra of complex and free ligand. Inserted figure shows absorption spectra of both complex and the free ligand. The complex has a weak electronic transition at 603 nm and extends to IR side of the spectrum. This is a characteristic to a low lying \(\pi^* \leftrightarrow d_e\), Metal to Ligand Charge Transfer (MLCT) transition (33).

When structured nature, emission intensity and \(\lambda_{\text{max}}\) are considered the observed emission of 435 nm suggest that the lowest electronic transition of the free ligand is ligand based. Expected MLCT emission of the complex can not be detected as well. But complex shows an emission peak at 447 nm. These results suggest that emission of the complex is originating from a ligand-centered (LC) transition and not from a MLCT state which would expect to lie at a wavelength higher than 603 nm.

AM1 semi-empirical quantum mechanical computational calculations (HyperCube Autodesk Release 4.0 of HyperChem) have indicated that the catechol violet ligand is not a planner molecule. Three phenyl rings have a \textit{ca.} 28\(^0\) of torsion angle. This will effectively reduce the overlap of ligand-centered \(\pi\) orbitals and \(d_e\) orbitals of Co(II). Hence, restricting the non-radiative fast electron transfer to the MLCT state. Consequently, emission is resulting from an upper ligand centered state (Figure 3.15).
Figure 3.14 Emission spectra of (a) cobalt(II)(1,10-phen)$_2$catechol violet and (b) catechol violet free ligand. Inserted figure: corresponding absorption spectra, solvent, methanol.
Figure 3.15 Energy level diagram of cobalt(II)(1,10-phen)$_2$catechol violet complex.
3.6 Acid-Base switching of Alizarin and Quinalizarin sensitized nano-porous Photovoltaic devices.

One of the important requirements of an information storage system or a molecular switching effect is the existence of two stable forms of a molecule that can be interconverted conveniently\(^\text{13,14}\). Most of such systems are based on cis-trans isomerization or cyclization of organic systems. However, when it comes to designing any practical molecular electronic device, these systems have shown several drawbacks. For any practical device, output of a certain molecular properties must be interconverted (switch on/off) by means of a simple technique and with a very good reproducibility of the output signal.

Figure 3.16 shows the structures of (a) Alizarin and (b) Quinalizarin molecules.

![Structures of Alizarin and Quinalizarin](image)

(a) Alizarin  
(b) Quinalizarin

**Figure 3.16**
They have two and four chelating positions respectively. Previous studies have revealed that ruthenium(II)bis(bipyridine)alizarin type complexes can undergo acid catalyzed 1,2 and 1,9 linkage isomerization. But alizarin and quinalizarin have no evidence to show that similar acid catalyzed linkage isomerization for the TiO₂ surface. Figure 3.17 shows acid-base effect on observed photocurrent and photovoltages on the photocell.

ZINDO/1 computational calculations were performed using HyperChem Auto Desk Release 4.0 software. Contour plots and energy diagram obtained for the LUMOs and HOMOs for the alizarin and quinalizarin coordinated Ti(IV) are shown in Figure 3.18. Molecular orbital calculations clearly indicate the localized nature of the electron density of LUMOs on the Ti(IV) center for the surface bound alizarin and quinalizarin complexes, when they are either protonated or deprotonated. Striking feature is that the relative energy levels of the LUMOs and HOMOs with respect to the conduction and valance bands of TiO₂. Protonation of the 2-hydroxy group bring down the relative energy of the LUMOs by about 3.51 eV and 3.38 eV for its deprotonated form for the alizarin and quinalizarin respectively. In the case of HOMO level it is about 6.81 eV and 5.54 eV respectively. Deprotonation of the 2-hydroxy has reduced the energy gap between the HOMO and LUMO orbitals by about 3.30 eV and 2.16 eV. Therefore it shows that deprotonation of 2-hydroxy group will cause the shift of both LUMO and HOMO levels well above the conduction band. Resulting the drop in observe photocurrent and photovoltage values.
Figure 3.17 Acid-base effect on observed photocurrent and photovoltage responses on the photocell
Energy level diagram of protonated and deprotonated alizarin and quinalizarin

Alizarin

<table>
<thead>
<tr>
<th>Acid form</th>
<th>Base form</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO</td>
<td>HOMO</td>
</tr>
<tr>
<td>-1.656 eV</td>
<td>1.651 eV</td>
</tr>
</tbody>
</table>

Quinalizarin

<table>
<thead>
<tr>
<th>Acid form</th>
<th>Base form</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUMO</td>
<td>HOMO</td>
</tr>
<tr>
<td>-2.164 eV</td>
<td>1.223 eV</td>
</tr>
</tbody>
</table>

Figure 3.18 Contour plots of HOMO LUMO of protonated and deprotonated alizarin and quinalizarin 0.5 Å above the molecular surface
REFERENCES


CONCLUSION

Complexation of triphenylmethane type molecules with transition metal centers such as cobalt(II) and iron(II) shows increased cell efficiencies when compared with similar cells constructed by coating respective free ligand. Absorption and cyclic voltammetry data suggest that the lowest transition has a MLCT character in these metal complexes. When visible light harvesting chromophores such as 1,10-phenanthroline ligands are incorporated into the complex, they produce enhanced photocurrents when compared with non-absorbing chromophores such as oxalato unit in the complex. The study clearly indicates that the way forward in developing dye sensitized photovoltaic devices is by harvesting solar energy through a charge capturing mechanism. In any such mechanism, the lowest electronic transition should have a charge transfer character to the chromophore that binds with n-type semiconductor such as TiO₂.

AM1 and ZINDO/I semi-empirical computational studies have shown that triphenylmethane ligands are generally non-planar molecules having different torsion angles. When they bind with transition metal centered moieties, it leads to high torsion angle. This will effectively increase the non-radiative electron transfer to the MLCT state, resulting in a better overlap of ligand and metal centered orbitals. Therefore, much improved communication results between the transition metal center and Ti⁴⁺ ion via low-lying MLCT state.

The thesis also reports the effect of pH on hydroquinone type dye coated solar cells and their photovoltaic properties. Deprotonation of the 2-hydroxy group of alizarin and quinalizarin shifts the relative energy positioning of the HOMO and LUMO orbitals well above the conduction band of the TiO₂. Hence causing drastic
drop of observed photocurrent values. Once the 2-hydroxy group is protonated relative energy positions adjust in a way that efficient electron transfer process could result. Remarkable finding this that the reproducibility of the pH effect on observed photocurrent and experiments are underway to develop this technique to produce an efficient molecular switches.
LIST OF PUBLICATIONS ARISEN IN THE DURATION OF STUDY


4. P.M. Jayaweera, S.S. Palayangoda, R.G.C.R. Gamage, K. Tennakone, Co²⁺(1,10-phen)₂-triphenylmethane type dye complexes and their sensitization properties in nano-porous photovoltaic cells, Accepted, *Journal of Current Science*


78