International Journal of Scientific Research and Modern Education (IJSRME)
ISSN (Online): 2455 – 5630 & Impact Factor: 3.110
National Conference on Recent Trends in Applied Chemistry (NCRTAC–2016)
Easwari Engineering College, Ramapuram, Chennai, Tamilnadu

SCHIFF BASE TRANSITION METAL COMPLEXES AS SENSITIZER IN DYE-SENSITIZED SOLAR CELL

S. Bharathi*, I. R. Celine Rose, M. P. Kannan***, D. Mohan******
& A. Jeya Rajendran*****
Advanced Materials Research Laboratory, Department of Chemistry,
Loyola College, Chennai, Tamilnadu

Abstract:

Tetradentate N_2S_2 *type Schiff base ligand, Benzil bis (4-methyl-3-thiosemicarbazide) (L-BMTSC) was synthesized by the condensation of benzil with 4-methyl-3-thiosemicarbazide and was complexed with transition metals, Co and Zn. The ligandand complexes were characterized by spectral analysis and thermal studies. The complexes were found to be neutral and are tentatively proposed to show octahedral geometry. The synthesized complexes were used as sensitizer to study the efficiency of dye sensitized solar cell (DSSCs) and were compared with the standard ruthenium dye. The solar cell was fabricated using CdSeas photo cathode,* TiO_2 *as photo anode and* I^-/I_3^- *as electrolyte. The sensitizers (Ruthenium dye,* $[CoLCl_2]2H_2O$ *and* $[ZnLCl_2]$*) were varied and the conversion efficiency of solar cell was investigated. The* $[CoLCl_2]2H_2O$ *is expected to show conversion efficiency nearer to the standard ruthenium dye.*

Key Words: Schiff Base, Sensitizer, Dye Sensitized Solar Cell & Conversion Efficiency

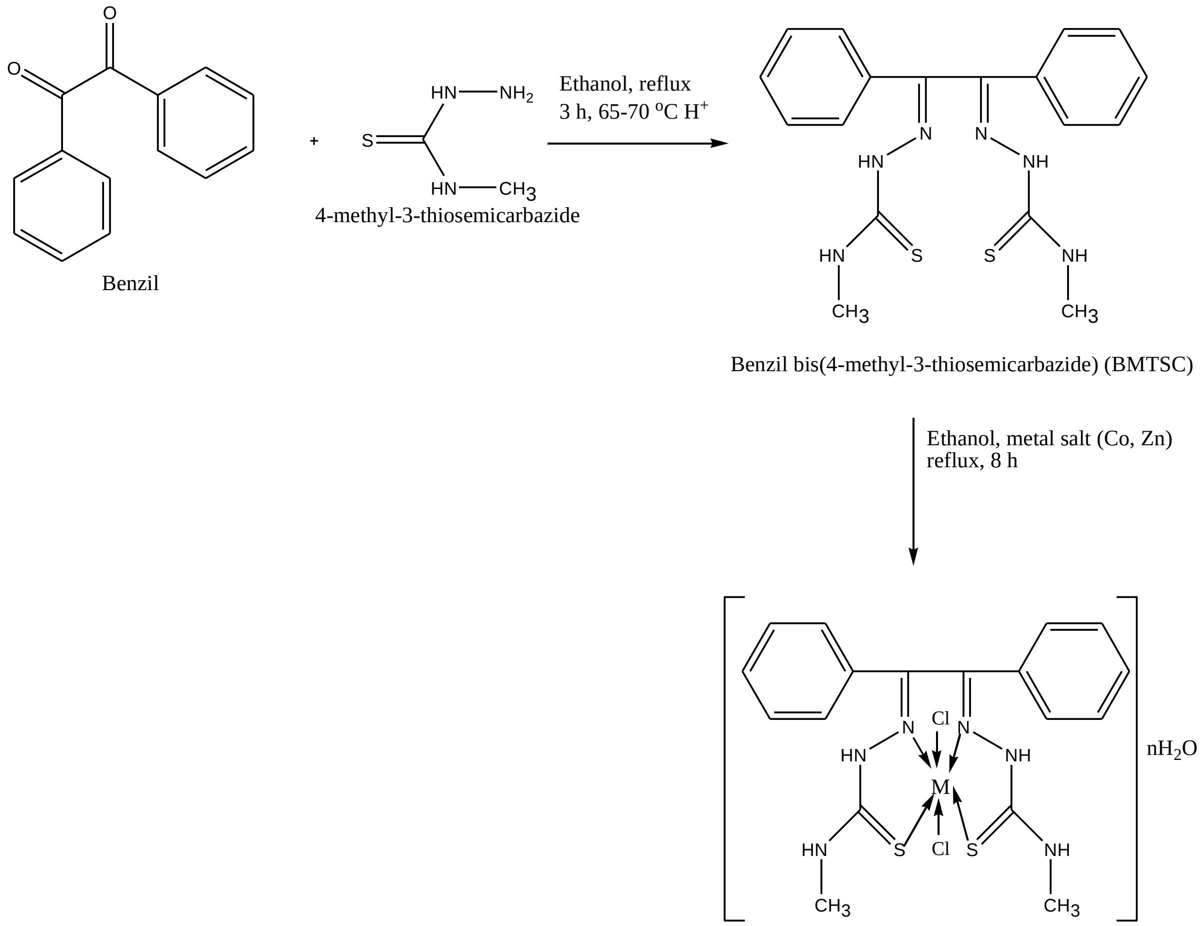
Introduction:

Schiff baseligands and their complexes of transition metals have been investigated extensively for many years because of their importance in many applications [1-4]. These complexes have important contribution in the development of catalysis, magnetism, molecular architectures and materials chemistry. Complexes also can be used as sensitizers or dyes in DSSCs as they absorb visible radiations and undergo charge transfer transitions. DSSC sare the devices for the conversion of visible light into electricity and have attracted much attention as low cost photo voltaic cells and become rapidly expanding field with potential applications [5-7].DSSCs contain four components: an electrode covered by sensitizer which absorbs solar energy; a conductive oxide layer which is transparent and allows charge transfer from electrode; counter electrode which returns the charge from the external circuit back to the cycling circuit in the cell; redox electrolyte layer which reduces the energy supplied from sensitizers [8]. By altering any one of these components, the efficiency of the DSSCs can also be altered accordingly.

In DSSCs, the dyeasasensitizer plays key rolein absorbing light and transforming solar energy into electric energy. Ruthenium complexes have received particular interest asphotosensitizers in DSSC application due to their favorable photoelectron chemical properties and high stability in the oxidized state, making practical applications feasible [9]. DSSCs are widely concentrated in research as an alternative of silicon based solar cells due to their simple structure, low production cost and wide applications. Among these advantages the low efficiency of DSSCs compared to silicon based solar cells has limited their commercial implementations [10, 11]. Thus, there is a need to increase the efficiency of DSSC’s with cost effectiveness. The efficiency of DSSCs can be altered by many ways among which the sensitizer has a key role in absorbing the light and transforming it into electrical energy. In the present work, Schiff base transition metal complexes were synthesized, characterized and were used as sensitizers in DSSCs to evaluate the power conversion efficiency of the solar cell.

Synthesis of Ligand and Complexes:

The synthesis of ligand and complexes are shown in scheme 1. Hot ethanolic solution of 3-methyl-4-thiosemicarbazide and ethanolic solution of benzil in 2:1 molar ratio were mixed in the presence of few drops of conc. HCl with constant stirring. This mixture was refluxed at 60-70 °C for 3 h [12]. The completion of the reaction was confirmed by the TLC. The solution was evaporated to form brown solid which was further washed with cold ethanol and dried. Hot ethanolic solution of corresponding metal salts ($CoCl_2.6H_2O$ and $ZnCl_2$) was mixed with hot ethanolic solution of ligand in 1:1 molar ratio and the mixture was refluxed for 8 h at room temperature. On evaporating the solvent, grey and yellow colored complexes were separated out as Co and Zn complexes respectively. The physical properties of ligand and complexes are given in table 1.



Scheme 1: Synthesis of BMTSC (L), $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$

Fabrication of Solar Cell Using TiO_2/CdSe Film:

CdSe nano particles were synthesized, characterized and reported earlier [11] which was used as counter electrode in fabrication of solar cell. Solar cell was fabricated using TiO_2 as photoa node and CdSe as photocathode or counter electrode. Homogenous TiO_2 paste was prepared by dissolving 0.5 g TiO_2 in 1mL of water and acetone and a monolayer of TiO_2 paste was coated on fluorine doped tin oxide (FTO) glass (3.5 cm x 2 cm) by doctor blading technique [14] and sintered at 300 °C for 3 h. Ruthenium dye, $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$ as sensitizers and I^-/I_3^-solution as an electrolyte.

Instrumentation:

All chemicals (ethanol, benzil, 4-methyl-3-thiosemicarbazide, $CoCl_2.6H_2O$, $ZnCl_2$) were purchased from avra and spectrochem chemicals which are of analytical grade and were used directly without any further purification. Molar conductivities in three solvents (ethanol, methanol and acetone) at room temperature were measured by using systronic digital conductivity meter. Electronic spectra were recorded in the region 200-800 nm using Jasco UV-visible spectrophotometer. Mass spectra were performed on a JEOL-AccuTOF JMS-T100LC mass spectrometer equipped with a custom-made electro spray interface (ESI). EPR spectra were recorded on a Varian E112 EPR spectrometer for X-band at room temperature. The thermal studies were carried out using TA instruments-Discovery model thermal analyzer with a temperature range from room temperature to 1200 °C. The current-voltage measurement of solar cell was carried on GS610 YOGOKAWA source measure unit.

Results and Discussion:

The ligand and complexes were soluble in ethanol, methanol, acetone and few organic solvents and insoluble in water, diethyl ether. Color, yield and melting point for the ligand, complexes and molar conductivity of complexes in three solvents (ethanol, methanol and acetone) at room temperature are given in table 1. The complexes were neutral and non-electrolytic in nature. The mass of the ligand and complexes were confirmed by mass spectrum and the molecular ion peak obtained is given in table 1.

Table 1: Physical properties of the ligand and complexes

Compound	Color	Yield (%)	Mass peak value	M.pt. (°C)	Molar conductivity ($S.cm^2.mol^{-1}$)			μ eff (BM)
					Ethanol	Acetone	Methanol	
BMTSC (L)	Light Brown	88	385	88-90	-	-	-	-
$[CoL(Cl_2]2H_2O$	Grey	78	551	116-120	0.7	0.7	0.7	1.85
$[ZnLCl_2]$	Yellow	79	447	188-190	0.5	0.9	0.4	-

Spectral Characterization:

The electronic spectrum of BMTSC, $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$ were recorded in ethanol at 10^{-6} M concentration (fig 1). The geometry of the metal complexes has been deduced from electronic spectra of the complexes. The ligand exhibits a single broad absorption band from 210-300 nm which corresponds to intra ligand transitions ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) which on complexation with metal splits into two peaks and also shifts to higher wavelengths suggesting coordination of the nitrogen and oxygen atoms of the ligand to the metal ion. The electronic spectra of $[CoLCl_2]2H_2O$complex shows two broad absorption maxima at 350-550 nm and 600-700 nm which are assigned to ${}^2E_g \rightarrow {}^2B_{1g}$ and ${}^2E_g \rightarrow {}^2A_{1g}$ respectively which is the characteristic of low spin distorted octahedral geometry around the metal ions [15].

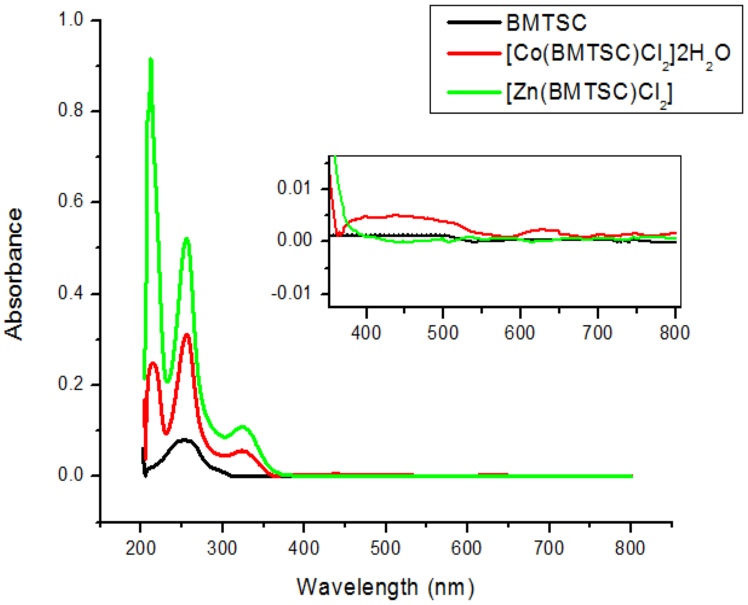


Figure 1: Electronic spectrum of BMTSC, $[CoLCl_2]2H_2O$. $[ZnLCl_2]$

The decomposition patternof BMTSC, $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$(Fig 2, table 2) at 5°C min^{-1} heating rate under N_2 atmosphere was studied from thermal (TG) studies. The ligand undergoes complete decomposition in two stages. The first stage from 25-250 °C showed loss of C_6H_5-C-C-C_6H_5 molecule followed by the second stage decomposition from 250-600 °C showed loss of two N-NH-CS-NH-CH_3moieties.

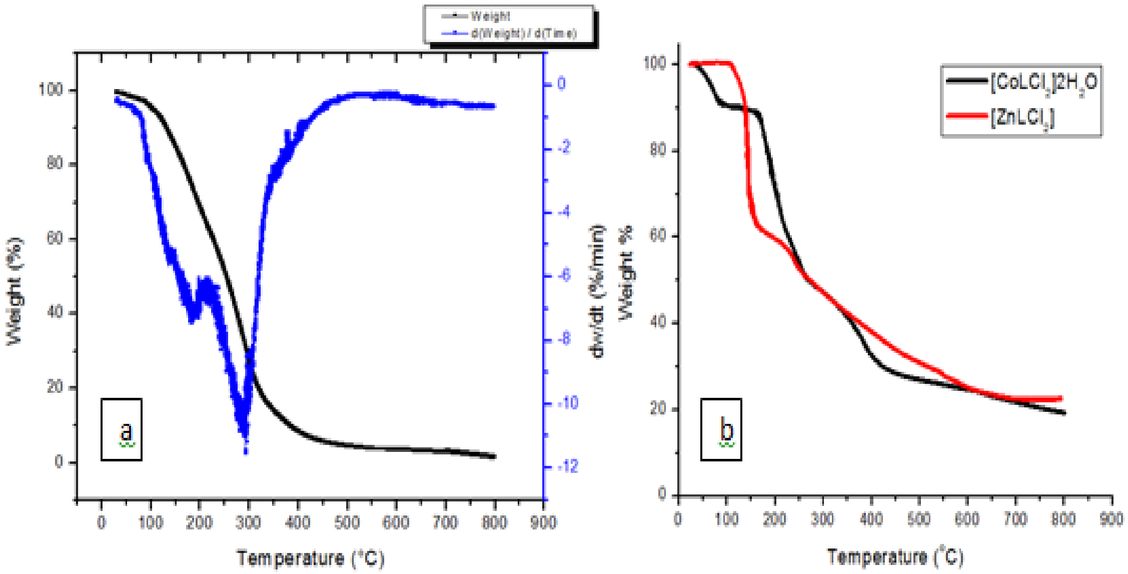


Figure 2: TGthermogram of a) BMTSC, b) $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$

The complexes show different decomposition pattern from ligand. $[CoLCl_2]2H_2O$ shows loss of lattice water molecules from 35-80 °C which is not seen in $[ZnLCl_2]$ and is stable up to 110 °C. Loss of C_6H_5-C-C-C_6H_5 and two Cl atoms are observed from 130-260 °C and 110-180 °C for $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$ respectively followed by loss of two N-NH-CS groups from 260-450 °C and 180-400 °C for $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$ respectively. The last stage of decomposition shows loss of two NH-CH_3 groups from

450-740 °C and 400-750 °C for $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$ respectively leaving oxides of metal as residue.

Table 2: Decomposition pattern of BMTSC, $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$

Compound	Decomposition stage	Temperature range (°C)	Weight lost		Assignments
			% Expt	% Cal.	
BMTSC(L)	1	25-250	43	46	C_6H_5-C-C-C_6H_5
	2	250-600	57	54	2 N-NH-CS-NH-CH_3
$[CoLCl_2]2H_2O$	1	35-80	7	6	Lattice H_2O
	2	130-260	43	45	C_6H_5-C-C-C_6H_5, 2Cl
	3	260-450	22	24	2 N-NH-CS
	4	450-740	10	11	2 NH-CH_3
	Residue	Above 750	18	14	Oxide of cobalt
$[ZnLCl_2]$	1	110-180	43	45	C_6H_5-C-C-C_6H_5, 2Cl
	2	180-400	21	27	2 N-NH-CS
	3	400-750	17	12	2 NH-CH_3
	Residue	Above 750	19	16	Oxide of residue

The X-band EPR spectra of $[CoLCl_2]2H_2O$ complex (Fig 3) was recorded in solid state at room temperature at 9.2 GHz under the magnetic field strength 330 mT. The spectrum of $[CoLCl_2]2H_2O$ complex shows a sharp peak and a broad signal with minimum hyperfine splitting interaction with the nuclei.The spin Hamiltonian parameters of the complex were calculated from the spectra as $g_{\parallel}$(2.29), $g_{\perp}$ (2.07) and g_{av} (2.14);$A_{\parallel}$ (8.5 x 10^{-3} cm^{-1}), $A_{\perp}$ (8.2 x 10^{-3} cm^{-1}) and A_{av} (8.3 x $10^{-6}cm^{-1}$). The geometric parameter, G was measured using Hathaway expression[16] and value was found to be 2.43 indicating considerable interaction between the metal centers. The g-factor was calculated from spin Hamiltonian parameters and found to be 320 which further contribute to the distorted octahedral geometry of the complex. The magnetic moment (μ) calculated from the g-value was found to be 1.85 B.M for Co(II) complex in low spin d^7 configuration [16].

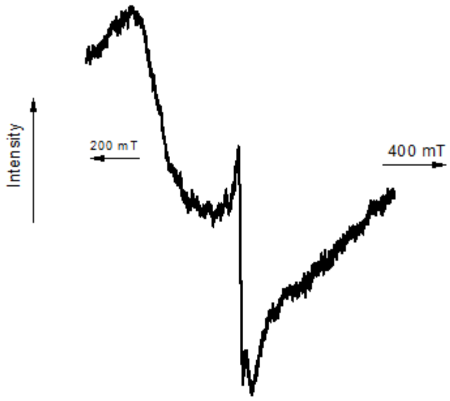


Figure 3: EPR spectrum of $[CoLCl_2]2H_2O$

Photovoltaic Performance:

The photovoltaic performance of solar cell was illustrated by a J-V curve (Fig. 4) and the photovoltaic parameters i.e., short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and power conversion efficiency (η) estimated from these curves are given in table 3. The difference in the parameters indicates that the power conversion efficiency (η) of solar cell is dependent on the sensitizers. The short circuit current (J_{sc}) and fill factor (FF) are high for $[CoLCl_2]2H_2O$-CdSe cell compared to ruthenium-CdSe cell indicating high light harvesting capacity of the cell in presence of this sensitizer.

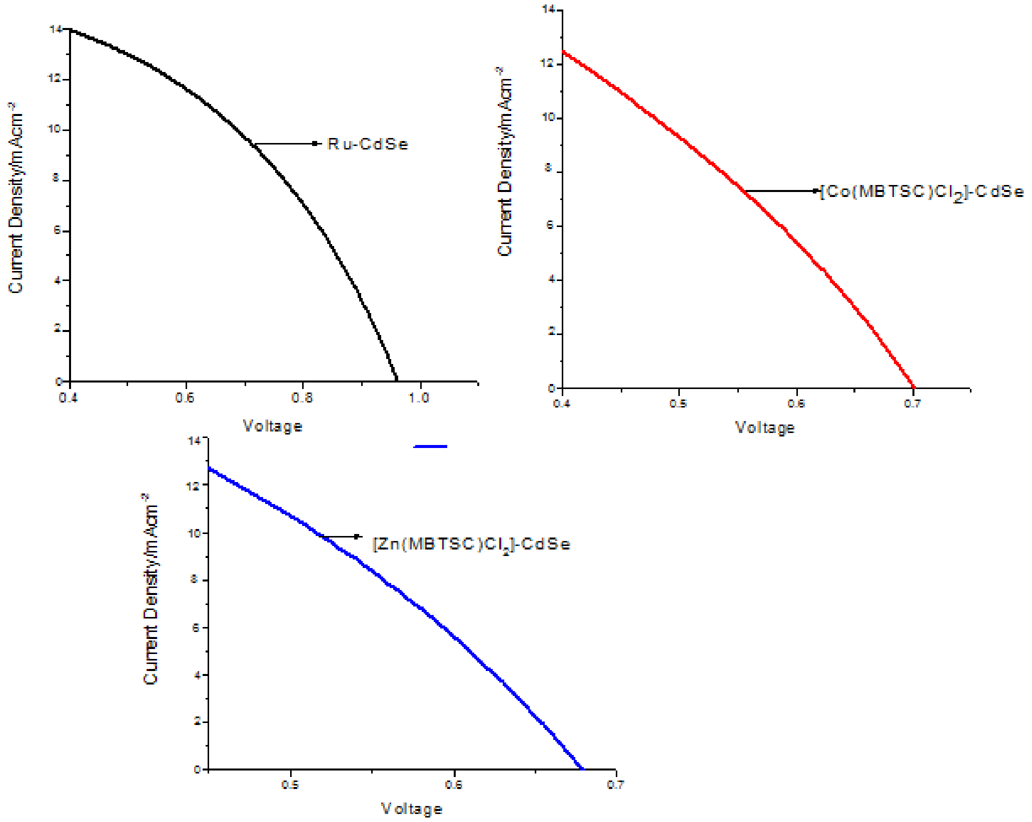


Figure 4: J-V curve of CdSe based DSSC

Table 3: Photovoltaic parameters of CdSe based DSSC

Parameters	Ru-CdSe	$[CoLCl_2]2H_2O$-CdSe	$[ZnLCl_2]$-CdSe
V_{oc} [mV]	1.0	0.74	0.58
J_{sc} [μA]	17.4	17.9	12.4
FF [%]	0.565	0.590	0.501
η [%]	2.7	2.01	1.02

The efficiency of a solar cell is defined as the output power density divided by the input power density. If the incoming light has a power density P_{in}, the efficiency will be

$$\eta = {}^{P_m}\!/_{P_{in}} = \frac{J_{sc}.V_{oc}.FF}{P_{in}}$$

The fill factor, FF is defined as the ratio of the maximum power output product (P_m) to the product of short circuit photo current and open circuit voltage.

$$FF = \frac{P_m}{J_{sc}\ X\ V_{oc}} = \frac{J_{mp}\ X\ V_{mp}}{J_{sc}\ X\ V_{oc}}$$

Where J_{mp} and V_{mp} represents the photocurrent and photovoltage corresponding to the maximal power point respectively. The four quantities J_{sc}, V_{oc}, FF and η are used to characterize the performance of a solar cell.

The efficiency of solar cell for different sensitizer are calculated and given in table 3. The $[CoLCl_2]2H_2O$ – CdSe cell shows 2.01 % efficiency which is nearer to the standard ruthenium dye (2.7 %). Due to high values of J_{sc} and FF for $[CoLCl_2]2H_2O$ –

CdSe cell, the efficiency can be further increased by altering other possible factors in fabricating the solar cell.

Conclusion:

Complexes of Co and Zn tetradentate N_2S_2 type Schiff base ligand were synthesized and characterized by spectral analysis and thermal studies. The complexes are predicted to be neutral and show distorted octahedral geometry. DSSC was fabricated using CdSe as photocathode, TiO_2 as photoanode, I^-/I_3^- as the electrolyte and the sensitizers were varied. The sensitizers used were ruthenium dye and the synthesized complexes; $[CoLCl_2]2H_2O$ and $[ZnLCl_2]$. The photovoltaic parameters were calculated from J-V curve and it was found that the short circuit current (Jsc) and fill factor (FF) were high for $[CoLCl_2]2H_2O$-CdSe cell than the ruthenium-CdSe cell. The efficiency of $[CoLCl_2]2H_2O$-CdSe cell(2.01 %) is also nearer to the standard ruthenium dye (2.7 %).

References

1. Chandra S, Raizada S, Tyagi M, Gautam A., “Syhthesis, Spectroscopic and antimicrobial studies on bivalent Nickel and Copper complexes of Bis(thiosemicarbazone)”, Bioinorg. Chem Appl., 2007.
2. Casas J S, Garcia-Tasende M S, Sordo J, “Main group metal complexes of semicarbazones and thiosemicarbazones - A structural review,” Coord. Chem. Reviews, 2000; 209 (1) :197–261.
3. Govindraj M, Vijayakumar K, Nair V N, Simon A V, “Synthesis characterization and biological activity Benzimidazole derivatives”, IJERME, 2016; 1(1).
4. Arunachalam T, Vijayakumar K, Sithiravel R, Akshayaa P, “synthesis, Characterization, biological screening of some novel triazole derivatives”, IJERME, 2016; 1(1).
5. Lee B, Kim J,“Enhanced efficiency of dye-sensitized solar cells by UV–O_3 treatment of TiO_2 layer”,Curr. Appl. Phys. 2009;9: 404–408.
6. Durr M, Schmid A, Obermaier M, Rosselli S, Yasuda A, Nelles G,“Low-temperature fabrication of dye-sensitized solar cells by transfer of composite porous layers”,Nature 2005;4: 607–611.
7. Jun Hyuk Yang, Chung Wung Bark, Kyung Hwan Kim, HyungWook Choi, “Characteristics of the Dye-Sensitized solar Cells using TiO_2 nanotubes treated with $TiCl_4$”, Materials, 2014; 7: 3522-3532.
8. Meidan Ye, Xiaoru Wen, Mengye Wang, James locozzia, Nan Zhang et. al., “Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes”, Materials, 2015; 18(3): 155-162.
9. Saha S, Das T K, Bhattacharya R, “Fabrication of ZnSe based dye sensitized solar cell and its characterization” IMPACT: IJRANSS), 2016; 4(1): 1-8.
10. Yang J H, Bark C W, Kim K H, Choi H W, “Characteristics of the Dye-Sensitized Solar Cells Using TiO_2 Nanotubes Treated with $TiCl_4$,Materials,2014; 7: 3522-3532.
11. Hug H, Bader M, Mair P, GlatzelT, “Natural pigments in dye-sensitized solar cells Biophotovoltaics”, App. Energy,2014; 115: 216–225.
12. Calatayud G D, Escolar F J, Elena Lopez-Torres, Mendiola M A, “Facile and selective synthesis of 4-methyl and 4-phenylthiosemicarbazide (= N-methyl and N-phenylhydrazinecarbothioamide) derivatives of Benzil (= 1, 2 – Diphenylethane-1,2-dione)”, Helvetica ChimicaActa, 2007; 90: 2201 – 2216.

13. Celine rose I R, Sathish R, Jeya Rajendran A, Sagayaraj P, “Effect of reaction time on the synthesis of cadmium selenide nanoparticles and the efficiency of solar cell”, J. Mater. Environ. Sci., 2016; 7(5): 1589-1596.
14. W. A. Tisdale, K. J. Williams, B. A. Timp, D. J. Norris, E. S. Aydil, X. Y. Zhu, “Hot-electron transfer from semiconductors nanocrystals”, Science, Vol. 328, pp. 1543-1547, 2010.
15. Gopalan R, Ramalingam V., “Concise coordination chemistry”, Copyright, 2001.
16. Anitha C, Sheela C D, Tharmaraj P, Hema V V., “Synthesis, spectroscopic characterization and biological activities of metal complexes of 4-((4-chlorophenyl)diazenyl)-2-((p-tolylimino)methyl)phenol”, J. Chem., 2013.