

Research Article

Organic-Ruthenium(II) Polypyridyl Complex Based Sensitizer for Dye-Sensitized Solar Cell Applications

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Received 25 April 2011; Accepted 26 May 2011

Academic Editor: Surya Prakash Singh

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A new high molar extinction coefficient organic-ruthenium(II) polypyridyl complex sensitizer (**RD-Cou**) that contains 2,2',6,6'-tetramethyl-9-thiophene-2-yl-2,3,5,6,6a,11c-hexahydro1H,4H-11oxa-3a-aza-benzoanthracene-10-one as extended π -conjugation of ancillary bipyridine ligand, 4,4'-dicarboxy-2,2':6',2''-bipyridine, and a thiocyanate ligand in its molecular structure has been synthesized and completely characterized by CHN, Mass, ¹H-NMR, UV-Vis, and fluorescence spectroscopies as well as cyclic voltammetry. The new sensitizer was tested in dye-sensitized solar cells using a durable redox electrolyte and compared its performance to that of standard sensitizer **Z-907**.

1. Introduction

The increasing demand for power supply as well as environmental concern for the consumption of fossil fuel have triggered a greater focus all over the world on renewable energy sources over the past decades [1]. In this context, solar energy appears to be very attractive alternate: covering 0.16% of the earth with 10% efficient solar conversion systems would provide power nearly twice the world's consumption rate of fossil energy [2]. For this reason, dye-sensitized solar cells (DSSC) have emerged as one of the most promising candidates because of its cost-effective manufacturing, a respectable high efficiency and a remarkable stability under the prolonged thermal and light soaking dual stress among various photovoltaics [3–5]. A typical DSSC system consists of a nanocrystalline semiconductor that adsorbs a sensitizer on its surface, a Pt-counter electrode, and a redox mediator. The photosensitizer plays a crucial role in achieving higher photoconversion efficiency and has been actively studied globally. A wide variety of sensitizers have been studied for DSSC that includes various metal complexes, organic

molecules, porphyrins, and phthalocyanines and so forth [6–9]. But only ruthenium-based sensitizers could have marked their way towards commercialization because of their high photoconversion efficiencies. The most successful ruthenium charge transfer sensitizers employed in such cells are *bis*(tetrabutylammonium)-*cis*-di(thiocyanato)-*N,N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenium(II) (the N719 dye) and trithiocyanato 4,4'4''-tricarboxy-2,2':6',2''-terpyridine ruthenium(II) (the black dye) produced solar-energy-to-electricity conversion efficiencies (η) of >11% [10–13]. The high efficiency of these complexes are attributed to its suitable ground- and excited-state energy levels with respect to the nanocrystalline TiO₂ conduction band energy and matching redox properties with the I⁻/I₃⁻ redox couple. However, the durability of these devices is very low due to the leakage of volatile liquid redox electrolytes. In order to improve the device durability, one has to replace the liquid redox electrolyte with either quasisolid or solid redox electrolyte. Gratzel and coworkers have designed an alternative amphiphilic ruthenium(II) complex (**Z-907**) in order to suit for quasisolid redox electrolytes [14, 15].

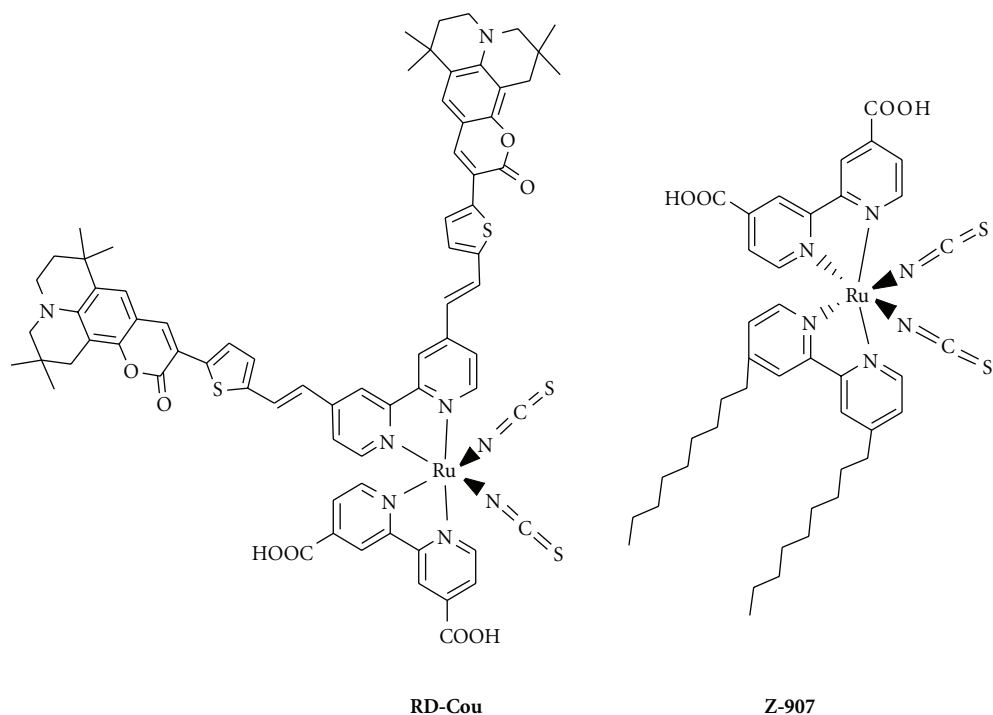


FIGURE 1: Molecular structure of RD-Cou and Z-907.

In order to further improve the efficiency of DSSC devices based ruthenium(II) sensitizers one has to improve its near-IR absorption because of its absorption maxima restricted at around 550 nm and more over the molar absorption coefficient of ruthenium(II) complexes are low causing use of thicker TiO₂ layers which further has disadvantage of achieving higher open circuit potential. Hence, research to find optimum ruthenium-based sensitizers has been focused primarily on enhancing the molar absorption coefficient as well as broadening of the metal-to-ligand charge transfer band. For this reason, Gratzel and coworkers have increased the molar extension coefficient of ruthenium(II) complexes by introducing extended π -conjugation concept in the molecular structure [16, 17]. We have also adopted the same concept for increasing the molar extinction coefficient and reported a few ruthenium(II) polypyridyl complexes [18–20]. Thiophene-derived units are good candidates for increasing the conjugation length of the ancillary ligand to improve the light harvesting ability of a ruthenium complex [21]. In surge, we have synthesized a new type of ruthenium sensitizer consisting of a donor (hole transport) Coumarin moiety bridged to the pyridyl groups by thiophene which resulted in extended π -conjugation and broadening in the metal-to-ligand charge transfer transition. The reason that we have chosen Coumarin as an organic moiety is that it has absorption in 450 nm region where ruthenium(II) has minimum absorption and more over this class sensitizers have already shown good efficiency in DSSC devices. It is known in the literature that the introduction of donor organic moiety in ruthenium(II) polypyridyl complexes can enhance the spectral response and, therefore, conversion

efficiency of the DSSC based on it [22–24]. The bipyridine carboxylic acid has been used as the anchoring media onto nanocrystalline TiO₂ surface and the thiocyanate ligands to tune the redox properties of the ruthenium centre. Here in this paper, we report the synthesis, characterization, and photovoltaic studies of new ruthenium complex-based supersensitizer **RD-Cou** as shown in Figure 1 and compare its efficiency with that of **Z-907**.

2. Experimental

2.1. Synthesis. 4,4'-dicarboxylic acid-2,2'-bipyridine (**Bpy-acid**), 4,4'-diethyl ester phosphonate-2,2'-bipyridine (**Bpy-phosphonate**), and formyl coumarin (**Cou-S-CHO**) were synthesized according to the procedures reported in the literature [25, 26].

2.1.1. Synthesis of Bpy-Cou (L). The ligand **Bpy-Cou (L)** was synthesized by using Wittig-Horner reaction [27]. NaH (26 mg, 1.09 mmol) was added to a solution of **Bpy-phosphonate** (100 mg, 0.21 mmol) and **Cou-S-CHO** (196 mg, 0.48 mmol) in 150 mL of dry tetrahydrofuran (THF). The resulting reaction mixture was refluxed overnight under nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and then filtered. The filtrate is concentrated, and the obtained solid is washed with methanol and dried to get the desired product in pure form of 75% yield. Elemental analysis of Anal. Calcd. for C₆₀H₅₈N₄O₄S₂% (963): C, 74.81; H, 6.07; N, 5.82. Found: C, 74.90; H, 6.05; N, 5.85. ¹H NMR (CDCl₃): δ , ppm 9.08 (d, 2H), 8.6 (d, 2H), 8.4 (s, 2H), 7.9 (d, 2H), 7.7 (d, 2H),

7.6 (s, 2H), 7.25 (d, 2H), 7.1 (d, 2H), 6.8 (s, 2H), 3.6 (m, 4H), 3.2 (m, 4H), 1.9–2.1 (m, 4H), 1.4 (m, 4H), 0.9–1.3 (s, 24H). ESI-MS: m/z 962 $[M]^+$. UV/Vis., (ethanol): (λ_{\max} , ϵ $M^{-1} \text{ cm}^{-1}$) = 473 (18,006).

2.1.2. Ru(L)(p-cymene)(Cl)₂. A mixture of ligand **Bpy-Cou L** (0.53 g, 1.25 mmol) and $[\text{Ru}(\text{Cl})_2\text{-(p-cymene)}]_2$ was dissolved in ethanol: chloroform (8:2 v/v) mixture. The resultant reaction mixture was refluxed for 4 hours under nitrogen atmosphere. Evaporation of the solvent under reduced pressure afforded the pure complex as an orange solid.

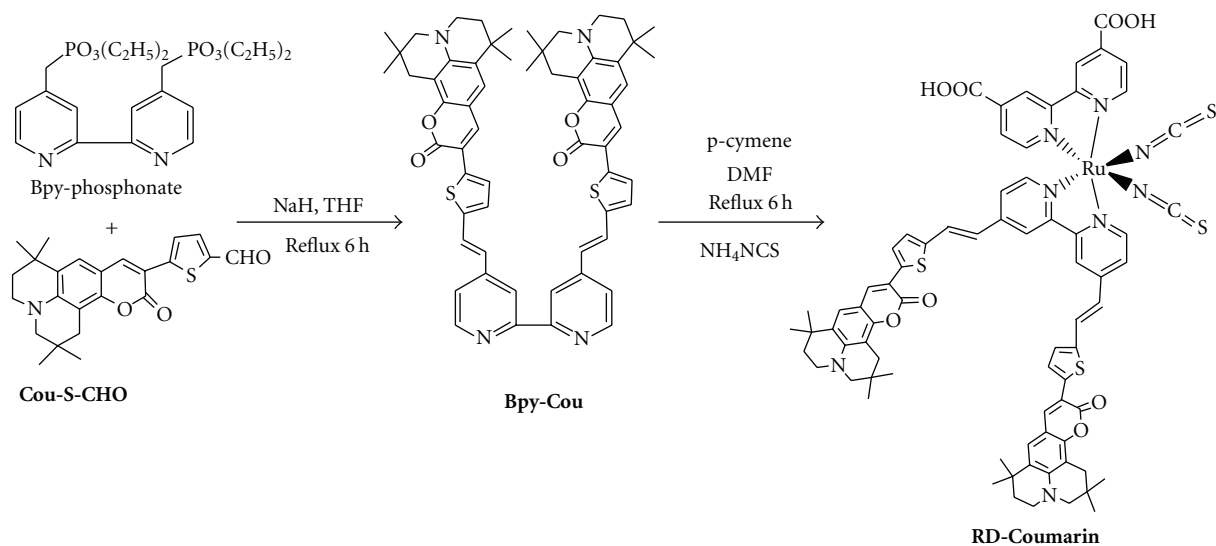
2.1.3. Synthesis of RD-Cou Dye. 4,4'-dicarboxylic acid-2,2'-bipyridine (75 mg, 0.308 mmol) was dissolved in dry DMF at 80°C. To this DMF solution of **Ru(L)(p-cymene)(Cl)₂** complex (350 mg, 0.154 mmol) was added. The reaction mixture was refluxed under nitrogen atmosphere for 4 h and then cooled to 80°C. To the reaction mixture was added aqueous NH_4NCS (362 mg, 4.77 mmol in 10 mL of H_2O) and then heated for further 2 h at 140°C and cooled to room temperature. The solvent DMF was evaporated under reduced pressure, and water was added. The resulting purple solid was filtered and washed with water. The crude complex was dissolved in basic methanol (with tetrabutylammonium hydroxide (TBAOH)) and further purified on a Sephadex LH-20 column with methanol as eluent. The main band was collected, concentrated, and precipitated with dilute acidic methanol to obtain pure desired complex. Elemental analysis of Anal. Calcd. for $\text{C}_{74}\text{H}_{66}\text{N}_8\text{O}_8\text{RuS}_4$ (1424.29): C, 62.21; H, 4.94; N, 7.84. Found: C, 66.70; H, 5.03; N, 7.90. ESI-MS ($\text{C}_{90}\text{H}_{109}\text{N}_9\text{O}_8\text{RuS}_4$): m/z 1670 $[\text{M}-2\text{H}]^+$ IR (KBr) cm^{-1} : 3390, 2958, 2870, 2102, 1964, 1610, 1540, 1464, 1365, 1355, 1231, 1056, 879, 784, 696. $^1\text{H NMR}(\text{CD}_3\text{OD})$: 9.08 (d, 4H), 8.67 (d, 4H), 8.16 (s, 2H), 7.70 (d, 2H), 7.25 (m, 6H), 7.00 (m, 4H), 6.96 (d, 2H), 3.35 (s, 4H), 3.27 (s, 4H), 2.47 (s, 4H), 1.77 (s, 4H), 1.25 (m, 24H). UV/Vis (ethanol): (λ_{\max} , ϵ $M^{-1} \text{ cm}^{-1}$) = 498 (16,046), 384 (13,521).

2.2. Characterization Methods. UV-Vis spectra were measured in a 1 cm pathlength quartz cell using a Shimadzu model 1700 spectrophotometer. Steady state fluorescence spectra were recorded on a Spex model Fluoromax-3 spectrofluorometer using a 1 cm quartz cell. Solutions having optical density at the wavelength of excitation (λ_{ex}) \sim 0.11. The $^1\text{H NMR}$ spectra were recorded at 300 MHz on a Bruker 300 Avance NMR spectrometer with X-WIN NMR software. The ^1H spectra were referenced to tetramethylsilane. ESI mass spectra were recorded on a Water Quattro Micro (Water Inc, USA). The infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrophotometer. The spectra of the solid samples were recorded by dispersing the sample in Nujol mull or as KBr wafers. Cyclic and differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. Cyclic voltammetric experiments were performed on 1 mM dye solution in acetonitrile at scan rate of 100 mV/s using 0.1 M tetrabutylammonium perchlorate

(TBAP) as supporting electrolyte. The working electrode is glassy carbon, standard calomel electrode (SCE) is reference electrode, and platinum wire is an auxiliary electrode. After a cyclic voltammogram (CV) had been recorded, ferrocene was added, and a second voltammogram was measured. Thermogravimetric measurements were carried out on a Mettler Toledo TGA/SDTA 851e instrument heating rate at $10^\circ\text{C min}^{-1}$ with 10 mg of sample under nitrogen atmosphere. DFT calculations were done for the ground-state optimization of **RD-Cou** at B3LYP/6-31g(d) using Gaussian 03 [28].

2.3. Device Fabrication. A screen-printed single- or double-layer film of interconnected TiO_2 particles was used as mesoporous negative electrode. A 10 μm thick film of 20-nm-sized TiO_2 particles were first printed on the fluorine-doped SnO_2 (FTO) conducting glass electrode and further coated by a 5- μm -thick second layer of 400-nm-sized light scattering anatase particles. The detailed preparation procedures of TiO_2 nanocrystals, pastes for screen printing, and nanostructured TiO_2 film have been reported in the literature procedure [29–31]. A cycloidal TiO_2 electrode (\sim 0.74 cm^2) was stained by immersing it into a dye solution containing **RD-Cou** or **Z907** sensitizer (300 μM) in ethanol solvent overnight. After washing with ethanol and drying by air flow, a sandwich cell was prepared using the dye-sensitized electrode and platinum-coated conducting glass electrode as the counter electrode. The latter was prepared by chemical deposition of platinum from 0.05 M hexachloroplatinic acid. The two electrodes were placed on the top of each other using a thin polyethylene film (50 μm thick) as a spacer to form the electrolyte space. The empty cell was tightly held, and edges were heated to 130°C to seal the two electrodes together. The active surface area of the TiO_2 film electrode was ca. 0.74 cm^2 . The redox electrolyte was introduced into the cell through a predrilled hole of the counter electrode, which was later closed by a cover glass to avoid the leakage of the electrolyte solution. The redox electrolyte is ionic liquid electrolyte, and the composition is 0.2 M I_2 , 0.5 M guanidinium thiocyanate (GuSCN), and 0.5 M N-methyl benzimidazole (NMB) in a 65/35 v/v% mixture of 1-propyl-3-methylimidazolium iodide/1-Ethyl-3-methyl-imidazolium tetracyanoborate $[\text{PMII}/\text{EMIB}(\text{CN})_4]$ (Z580) [15].

2.4. Photoelectrochemical Measurements. The photovoltaic performance of the dye-sensitized nanocrystalline TiO_2 cells was determined using the simulator SOLARONIX SA SR-IV unit Type 312. The spectral response was determined by measuring the wavelength dependence of the incident photon-to-current conversion efficiency (IPCE) using light from a 100-W xenon lamp that was focused onto the cell through a double monochromator. The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2420 digital source meter, and a 1000-W xenon lamp was used as the irradiation source. The spectral output of the lamp is set matched the AM 1.5 solar spectrum in the region of 350–750 nm (mismatch 1.9%).



SCHEME 1

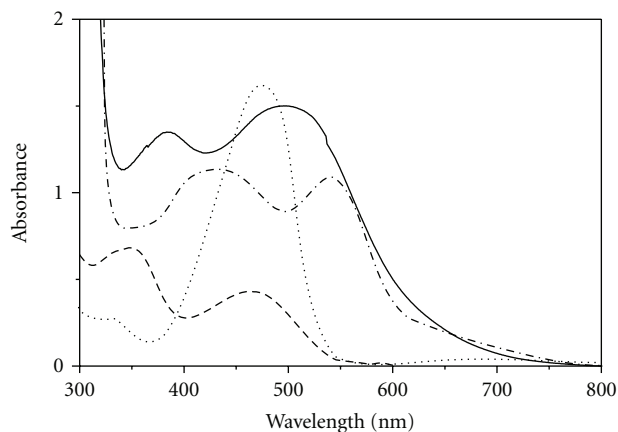


FIGURE 2: Electronic absorption spectra of (···) **Cou-S-CHO**, (---) **Bpy-Cou (L)**, (—) **RD-Cou**, and (-·-·) **Z-907** in ethanol solvent.

3. Results and Discussion

3.1. Synthesis and Characterization. The details of the synthetic strategy adopted for the synthesis of **RD-Cou** complex is shown in Scheme 1, and **Z-907** was synthesized according to the literature method [14]. Both **Bpy-phosphonate** and **Cou-S-CHO** were synthesized as per the reaction procedures reported in the literature [23, 24]. The C=C double bond was introduced at 4, 4' positions of the bipyridine ligand, starting from **Bpy-phosphonate** with **Cou-S-CHO** using a Wittig-Horner reaction [27]. The ligand **Bpy-Cou (L)** was completely characterized by using elemental analysis, Mass, IR, and ^1H NMR spectroscopies. Finally, the **RD-Cou** complex was synthesized by refluxing *p*-cymene complex and **Bpy-Cou (L)** in ethanol:chloroform mixture to get the corresponding chlorocomplex. The chlorocomplex with **Bpy-acid** and aq. ammonium thiocyanate refluxed in DMF to get the desired complex after sephadex column purification. The complex **RD-Cou** was completely characterized

by the elemental analysis, ESI-MS, IR, UV-Visible, and fluorescence spectroscopies as well as cyclic voltammetry. ESI-MS spectrum consists of a molecular ion peak at 1670 (*m/z*) which corresponds to the presence of a one TBA molecule in its molecular structure.

Figure 2 shows the absorption spectra of **Cou-S-CHO**, **Bpy-Cou (L)**, **RD-Cou**, and **Z-907** in ethanol, and the corresponding data are presented in Table 1. The absorption maximum of coumarin in **Cou-S-CHO** is located at 470 nm. In **Z-907**, the absorption maximum at 540 nm belongs to the metal-to-ligand charge-transfer transition in singlet manifold ($^1\text{MLCT}$). The absorption maximum of **RD-Cou** is centered at 498 nm with a molar extinction coefficient of $16,046 \text{ M}^{-1} \text{ cm}^{-1}$. From Figure 1, it is clear that the absorption of **RD-Cou** is very broad not like typical ruthenium(II) polypyridyl complexes. This is due to the presence of coumarin moiety in its molecular structure, which absorbs at 470 nm. The absorption maxima of **RD-Cou** is bathochromic shift (540 nm in **Z-907** to 498 nm in **RD-Cou** is hypsochromic) when compared to that of the standard sensitizer **Z-907**. The absorption maximum at 387 nm belongs to the intraligand $\pi-\pi^*$ transitions of bipyridine ligand. Figure 2 depicts the absorption spectra of **RD-Cou** adsorbed onto 6- μm -thick TiO_2 film. The absorption features of the ruthenium complex in solution as well as when anchored onto TiO_2 surface are identical except for a slight red shift in the absorption maxima due to the interaction of anchoring groups with the surface as well as further broadening [32]. The emission spectra of **RD-Cou** were measured in ethanol solvent at room temperature and are shown in Figure 3. Excitation of lower energy MLCT transition of **RD-Cou** sensitizer produces an emission centered at 690 nm. The excited singlet state energy (E_{0-0}) of **RD-Cou** was calculated from the onset of absorption spectrum and was found 1.65 eV. However, the emission of **RD-Cou** sensitizer was quenched when adsorbed onto the TiO_2 film as a consequence of electron injection from the excited state of Ru(II) into the conduction band of TiO_2 .

TABLE 1: UV-visible emission and electrochemical data.

Sensitizer	λ_{\max} , nm, $\epsilon(\text{mol}^{-1} \text{cm}^{-1})^a$	λ_{em} , nm ^b	$E_{1/2}$ V versus SCE ^c		E_{0-0} , eV ^d	E_{ox}^*	
			Ox	Red			
RD-Cou	498 (16,046)	690	0.72	-1.05	-1.47	1.65	-0.93
Z-907	540 (10,040)	720	0.65	-0.98	-1.64	1.62	-1.02

^aSolvent: ethanol, Error limits: λ_{\max} , ± 1 nm, $\epsilon \pm 10\%$. ^bSolvent: ethanol, λ_{\max} , ± 1 nm. ^cSolvent: DMF, Error limits: $E_{1/2} \pm 0.03$ V, 0.1 M TBAP. ^dError limits: 0.05 eV.

With a view to evaluate HOMO-LUMO levels of **RD-Cou**, we have carried out the electrochemistry by adopting the cyclic and differential pulse voltammetric techniques in acetonitrile solvent using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte and compared their data with that of the standard sensitizer **Z-907** in Table 1. When the potential is scanned between 0 and 1.0 V, chemically reversible redox waves with formal potentials at 0.65 and 0.72 V (versus SCE) were observed, which can be attributed to the one-electron oxidation of ruthenium center in both dyes. Compared to the standard **Z-907** dye, the metal center oxidation of **RD-Cou** is anodically shifted by 70 mV indicating the electron-poor character of the new ligand as a result of the insertion of Coumarin moiety on extended π -conjugation. It also undergoes two reductions at -1.05 and 1.47 V, corresponding to the one electron reduction of anchoring ligand. Furthermore, for a sensitizer in DSSC, the LUMO energy level should be compatible with the conduction band edge energy of the TiO_2 photoanode (0.80 V versus SCE), and its HOMO should be sufficiently low in energy to accept electrons from the I^-/I_3^- -based redox electrolyte (0.2 V versus SCE). The excited oxidation potential of **RD-Cou** is -0.93 V and that of standard sensitizer **Z-907** is -1.02 V, which is above the conduction band of TiO_2 . In **Z-907**, the excited state oxidation potential is sufficiently higher than that in **RD-Cou**, as a result electron injection into the TiO_2 conduction band is more efficient, and it should lead to a better conversion efficiency than **RD-Cou**.

To know the electronic distribution of **RD-Cou** sensitizer, we performed DFT calculations of the electronic ground state of **RD-Cou** sensitizer using mPW1PW91 method for the geometry optimization with LANL2DZ basis function on Ru and 6-31 g(d) basis function on C, H, N, O and S. As can be seen from the Figure 5, occupied orbitals HOMO, HOMO-1 and HOMO-2, have the electron delocalized over the Ru(II) metal and -NCS ligand. The LUMO, LUMO+1, and LUMO+2 are π^* orbitals delocalized over the bipyridine carboxylic acid ligand facilitating electron injection from the excited state of **RD-Cou** sensitizer to the conduction band of TiO_2 . These results are in good agreement with other ruthenium(II) polypyridyl complexes reported in the literature [16, 17].

3.2. Photovoltaic Measurements. The performance of newly synthesized **RD-Cou** as a sensitizer with a sandwich-type nanocrystalline TiO_2 was determined from measurements on photovoltaic cells using an ionic liquid redox electrolyte, that is, 0.2 M I_2 , 0.5 M guanidinium thiocyanate (GuSCN), and 0.5 M N-methyl benzimidazole (NMB) in a 65/35 v/v%

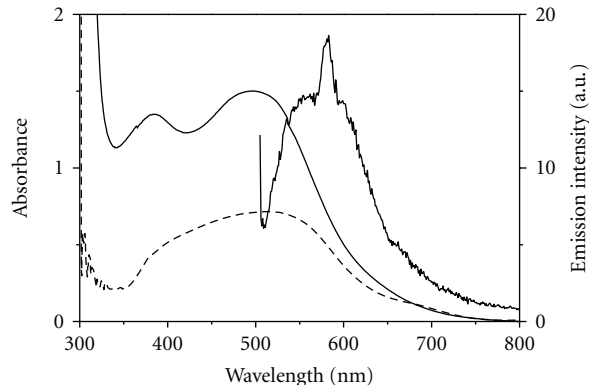
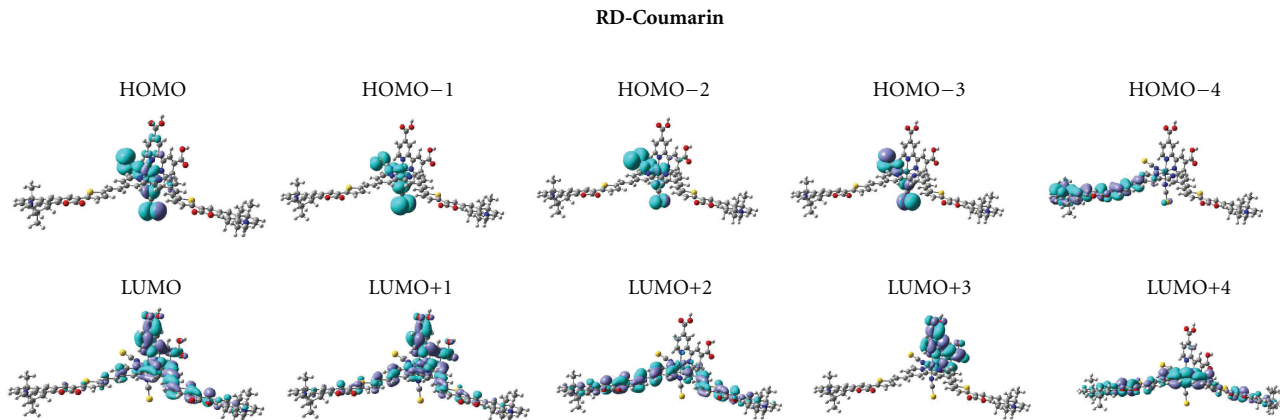
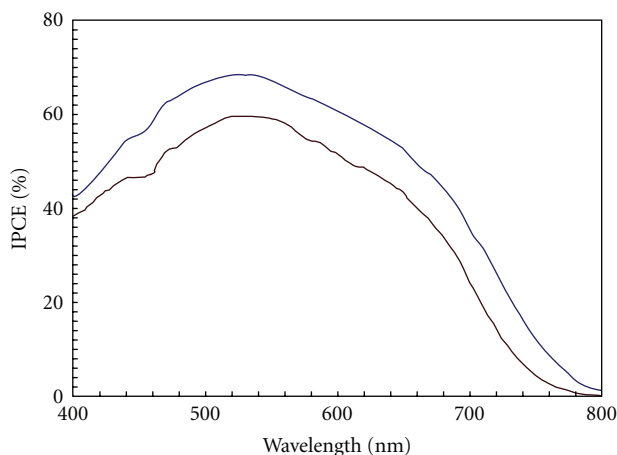


FIGURE 3: Absorption (—) and emission spectra in ethanol and absorption (---) spectra adsorbed onto a 6 μm thick TiO_2 film of **RD-Cou**.

mixture of 1-propyl-3-methylimidazolium iodide/1-Ethyl-3-methyl-imidazolium tetracyanoborate [PMII/EMIB(CN)₄] (Z580) and compared its performance with that of standard sensitizer **Z-907** under similar test cell conditions. The additive guanidinium thiocyanate in redox electrolyte is to improve the V_{oc} by reducing the dark current [33]. We assume that in our case, also guanidinium thiocyanate in Z580 redox electrolyte is responsible for improvement in V_{oc} . 1-Ethyl-3-methylimidazolium tetracyanoborate (EMIB(CN)₄) is an ionic liquid of a low viscosity (19.8 cP at 20°C) and high chemical and thermal stability. By using this redox electrolyte with this composition, Gratzel and coworkers have observed an efficiency of 6.4% [15]. Figure 5 illustrates the photocurrent action spectra of **RD-Cou** and **Z-907**, where the incident monochromatic photon-to-current conversion efficiencies (IPCE) values are plotted as a function of excitation wavelength. The IPCE was calculated according to the following equation:

$$\text{IPCE}(\%) = 1240 \left(\frac{J_{\text{sc}}}{\lambda \phi} \right) \times 100, \quad (1)$$

where λ is the wavelength (nm), J_{sc} is the photocurrent density under short circuit conditions (mA/cm^2), and ϕ is the incident radiative flux (mW/cm^2). We have observed IPCE values of 60 and 68% using **RD-Cou** and **Z-907** sensitizers, respectively. From Figure 4, it is clear that the photocurrent action spectrum resembles the absorption spectra except for a slight red shift by ca. 10 nm in both **RD-Cou** and **Z-907**. The photoresponse of thin films displays a broad spectral response covering the entire visible spectrum up to 800 nm in both the sensitizers.

FIGURE 4: Molecular orbital spatial orientation of **RD-Cou**.FIGURE 5: Photocurrent action spectra of (brown line) **RD-Cou** and (blue line) **Z-907** using **Z-580** redox electrolyte.TABLE 2: Photovoltaic performance of **RD-Cou** and **Z-907**^a.

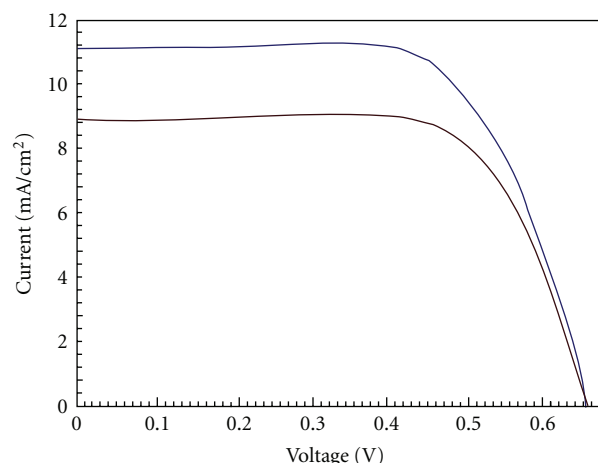
Sensitizer	Electrolyte ^b	J_{sc} (mA/cm ²) ^c	V_{oc} (mV) ^c	ff ^c	η (%)
RD-Cou	Z580	8.80	650	0.68	4.24
Z-907	Z580	11.97	650	0.68	5.20

^aPhotoelectrode: TiO₂ (10 + 5 μ m and 0.74 cm²); ^belectrolyte: 0.2 M I₂, 0.5 M guanidinium thiocyanate (GuSCN), and 0.5 M N-methyl benzimidazole (NMB) in a 65/35 v/v% mixture of 1-propyl-3-methylimidazolium iodide/1-Ethyl-3-methyl-imidazolium tetracyanoborate [PMII/EMIB(CN)₄]. ^cError limits: J_{sc} : ± 0.20 mA/cm², V_{oc} = ± 30 mV, ff = ± 0.03 .

Figure 6 shows the photocurrent-voltage characteristics of **RD-Cou** and **Z-907** using **Z-580** as redox electrolyte under 1.0 sun irradiation (1000 W/m²), and corresponding data are shown in Table 2. The solar-energy-to-electricity conversion efficiency (η), under white-light irradiation can be obtained from the following equation:

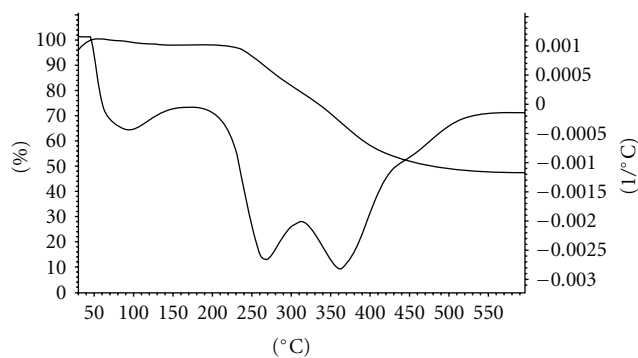
$$\eta [\%] = \frac{J_{sc} [Am^{-2}] \cdot V_{oc}[V] \times ff}{I_0 [Wm^{-2}]} \times 100, \quad (2)$$

where I_0 is the photon flux (e.g., 1000 W m⁻² for 1.0 sun), J_{sc} is the short-circuit photocurrent density under irradiation,

FIGURE 6: Current-voltage characteristics: (brown line) **RD-Cou** and (blue line) **Z-907** using **Z-580** redox electrolyte.

V_{oc} is the open-circuit voltage, and ff represents the fill factor. We have observed an overall conversion efficiency of 4.24% under 1.0 sun irradiation ($J_{sc} = 8.80$ mA/cm², $V_{oc} = 650$ mV, ff = 0.68) using **RD-Cou** as sensitizer. Under similar test cell conditions, the device based on **Z-907** sensitizer [$J_{sc} = 11.97$ mA cm⁻², $V_{oc} = 650$ mV, and ff = 0.68] shows a photovoltaic conversion efficiency of 5.20%. The low efficiency of **RD-Cou** when compared with that of standard sensitizer **Z-907** is probably due to poor hole transport property from coumarin moiety to Ru(II).

3.3. Thermal Studies. We have examined the thermal stability of new ruthenium(II) polypyridyl sensitizer and compared their thermal stability with that of the standard sensitizer **Z-907**, using thermogravimetric analysis. Figure 7 shows the thermal behavior of **RD-Cou**. From the Figure, it is clear that the sensitizer **RD-Cou** is stable up to 220°C. The initial weight loss between 200 to 250°C is attributed to the removal of the carboxyl group. In contrast, the standard sensitizer **Z-907** is stable up to 200°C.



Conversion	
(°C)	(%)
28.56	0
91.74	1.07
154.92	1.79
218.11	3.12
281.29	12.07
344.47	25.83
407.66	41.61
470.84	48.28
534.02	50.73
597.2	51.76

FIGURE 7: TG/DTG curves of **RD-Cou** with heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen.

4. Conclusions

In conclusion, we have designed and synthesized a new Coumarin-Ruthenium(II) polypyridyl complex having an extended π -conjugation. The new complex was completely characterized by elemental analysis, ESI-MS, IR, UV-Visible, and fluorescence spectroscopies as well as cyclic voltammetry. The performance of new sensitizer was tested in dye-sensitized solar cells using a durable redox electrolyte and compared with that of standard sensitizer **Z-907**. The low efficiency of device based on **RD-Cou**, when compared to **Z-907**, is probably due to poor hole transport property from coumarin moiety to Ru(II).

Acknowledgments

The authors are thankful to the IICT-Aisin Cosmos collaborative project for financial support of this work. L. Giribabu is thankful to the project SR/S1/IC21/2008 for partial financial support of this work. V. K. Singh and Ch. V. Kumar are thankful to Council of Scientific and Industrial Research (CSIR) for a fellowship.

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