Metal Complex Dyes for Dye-Sensitized Solar Cells: Recent Developments

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Ruthenium complexes are widely used as sensitizers in Dye-Sensitized Solar Cells. Structural diversities of these complexes, their synthesis , and other properties are discussed in this article.

1. Introduction

Dye-sensitized solar cells (DSSC) provide a technically and economically credible alternative concept to present day p–n junction photovoltaic devices. In contrast to the conventional systems where the semiconductor acts as light absorbent and charge carrier transport, the two functions are separated in DSSC. Light is absorbed by a sensitizer anchored to the surface of a wide-band semiconductor. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the solid. Carriers are transported in the conduction band of the semiconductor to the charge collector. The use of broad absorption band sensitizers in conjunction with nanocrystalline oxide films permits harvesting of a large fraction of sunlight. Nearly quantitative conversion of incident photons into electric current is achieved over a large spectral range extending from the UV to the near IR region. Overall solar (standard AM 1.5) to current conversion efficiencies (IPCE) over 10% have been reached and there are good prospects to produce these cells at lower cost than conventional devices. The working principle of DSSC is shown in *Figure* 1.

Recent developments (last ten years) in ruthenium complex and other metal complex dyes for DSSC are discussed here.

2. Dye Sensitizers

Dye sensitizers serve as solar energy absorbers in DSSC, which
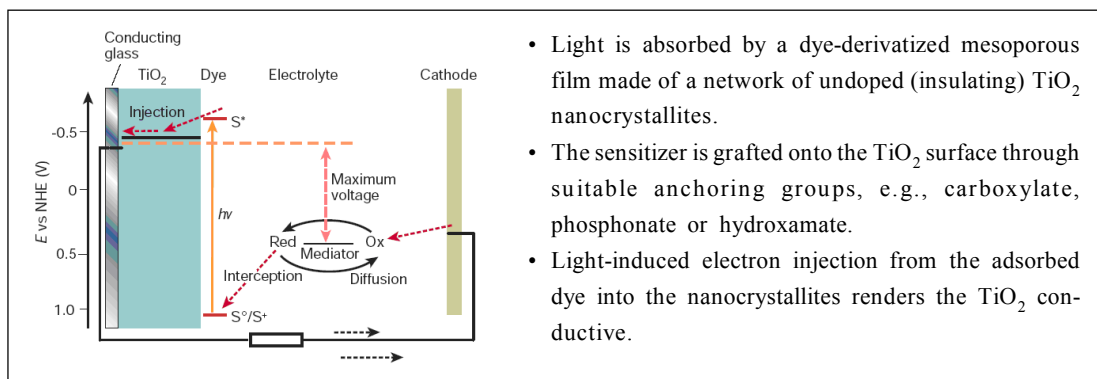
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- Light is absorbed by a dye-derivatized mesoporous film made of a network of undoped (insulating) TiO_2 nanocrystallites.
- The sensitizer is grafted onto the TiO_2 surface through suitable anchoring groups, e.g., carboxylate, phosphonate or hydroxamate.
- Light-induced electron injection from the adsorbed dye into the nanocrystallites renders the TiO_2 conductive.

Figure 1. Light harvesting by nanocrystalline TiO_2 films.

control the light harvesting efficiency and the overall photoelectric conversion efficiency. An ideal sensitizer for dye-sensitized solar cells should absorb all the light below a threshold wavelength of about 920 nm. In addition, it should be firmly grafted to the semiconductor oxide surface and inject electrons into the conduction band with a quantum yield of unity. Its redox potential should be sufficiently high so that it can be regenerated rapidly via electron donation from the electrolyte or a hole conductor. Finally, it should be stable enough to sustain at least 10^8 redox turnovers under illumination corresponding to about 20 years of exposure to natural light. The best photovoltaic performance in terms of both conversion yield and long-term stability has so far been achieved with polypyridyl complexes of ruthenium and osmium. The sensitizers used in DSSC are divided into two types, *viz*., organic dyes and inorganic dyes according to the structure. Inorganic dyes include metal complexes, such as polypyridyl complexes of ruthenium and osmium, metal porphyrin, phthalocyanine and inorganic quantum dots, while organic dyes include natural and synthetic organic dyes.

2.1 Ruthenium Complexes

Compared with organic dyes, inorganic metal complex dyes have high thermal and chemical stability. Among these complexes, polypyridyl ruthenium sensitizers were widely used and investigated for their high stability and outstanding redox properties and good response to natural visible sunlight. The sensitizers anchored on the surface of semiconductor film electrode with

carboxylate or phosphonate group enable the electron injection into the conduction band of the semiconductor. Polypyridyl ruthenium dyes may be divided as carboxylate polypyridyl ruthenium dyes, phosphonate ruthenium dyes, and polynuclear bipyridyl ruthenium dyes. The difference between the first two types of sensitizers lies in their adsorption groups. The first two types of sensitizers differ from the third type in the number of metal centres. The carboxylate polypyridyl ruthenium dye is a level structure, which enables the electron injection into the conduction band of the semiconductor quantitatively.

Ruthenium polypyridyl complexes are synthesized by reaction of polypyridyl ligand with ruthenium trichloride. The synthesis of polypyridyl ligands is well reported in literature. The synthetic route to obtain 2,2'-bipyridineand 2,2':6',2"-terpyridine is given in *Scheme* 1.

Most well-known Ru complexes for DSSCs are **N3**, **N719**, **N749** and **Z907.** (See *Table* 2, pp.824–825 for structures.) **N3** has two bipyridine and two thiocyanato (NCS) ligands. It absorbs up to
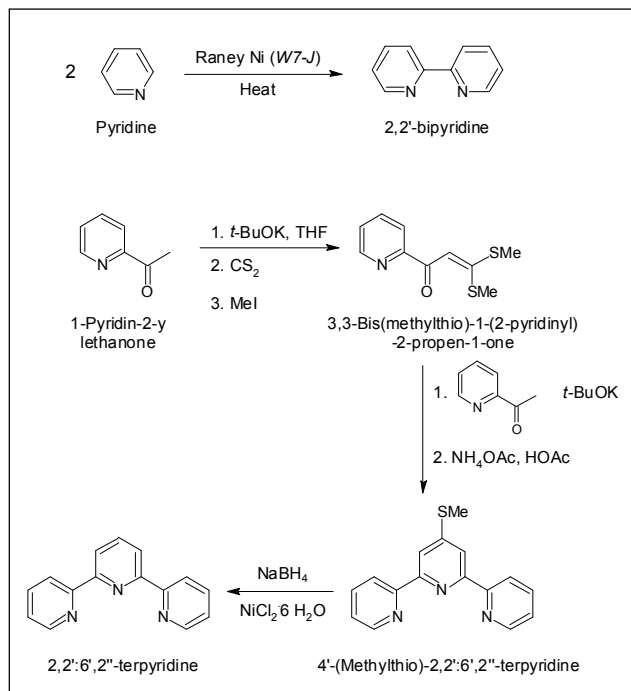
Scheme 1.

800 nm radiation due to the loosely-attached NCS groups. Even though the dye provides high J_{sc} (short circuit current), it does not give high V_{oc} (open circuit voltage). **N719** dye has the same structure as **N3** dye but has TBA$^+$ (tetrabutylammonium) instead of H$^+$ at two carboxyl groups. The difference in V_{oc} is rationalized as due to the difference in proton concentrations at the surfaces. Since **N3** dye can provide at most four protons per dye, which can adsorb at the basic sites of the TiO$_2$ surface and shift the E_{cb} (conduction-band-edge energy level) to positive.

N749 dye, which is called black dye, has achieved the maximum absorption up to 860 nm, and showed performance similar to **N3** and **N719** dyes. However, the absorption coefficient of **N749** is lower than **N3** and **N719** dyes. These low-absorption coefficients require thicker TiO$_2$ electrodes to adsorb more dye molecules on TiO$_2$. The increase of the thickness has disadvantages in view of electron transport and open circuit voltage, that is, J_{sc} and V_{oc} could decrease. V_{oc} of the DSSC using **N749** is somehow lower than **N719**, which cannot be explained by proton effect. Based on these, **N749** has not shown higher efficiency than **N719**.

Z907 has different features than others. DSSCs using **N3** and **N719** have shown degradation during long-term operation. This is because water molecules penetrate into the electrolyte and desorb the dyes from the TiO$_2$ surface. **Z907** has hydrophobic alkyl chains attached to one of the bipyridine ligands and it keeps water molecules away from the chemical bonds between the dye and TiO$_2$. Durability tests showed stable performance of the DSSCs with Z907 for 1000 h under light irradiation. Thus, in recent years, amphiphilic ruthenium dye represented by **Z907** and high-molar-extinction-coefficient ruthenium sensitizers represented by **K19** became the focus of research. *Table* 1 shows the molecular structure and the photovoltaic performance of solar cells. Also see Section 2.3 for details.

In spite of the considerable advantages carboxylate polypyridyl ruthenium sensitizers are easily desorbed from the surface in the aqueous solution when the pH value is less than 5. The phosphonate

> The phosphonate group of the phosphonate polypyridyl ruthenium sensitizers, used to anchor to the surface of the semiconductor, hardly desorbs from the semiconductor surface even at high pH value.

Dye	Abs (nm) ε (10^3m^{2}mol^{-1})	IPCE[a] (%)	Short Circuit Current, J_{sc} (mA/cm^2)	Open Circuit Voltage, V_{oc}(mV)	Fill Factor FF	Efficiency, η (%)
N3	534(1.42)	83	18.20	720	0.730	10.00
N719	532(1.40)	85	17.73	846	0.750	11.18
Black Dye	605(0.75)	80	20.53	720	0.704	10.40
Black Dye	-	80	20.90	736	0.722	11.10
Z907	526(1.22)	72	13.60	721	0.692	6.80
Z907	526(1.22)	72	14.60	722	0.693	7.30
K8	555(1.80)	77	18.00	640	0.750	8.64
K19	543(1.82)	70	14.61	711	0.671	7.00
N945	550(1.89)	80	16.50	790	0.720	9.60
Z910	543(1.70)	80	17.20	777	0.764	10.20
K73	545(1.80)	80	17.22	748	0.694	9.00
K51	530(1.23)	70	15.40	738	0.685	7.80
HRS-1	542(1.87)	80	20.00	680	0.690	9.50
Z955	519(0.83)	80	16.37	707	0.693	8.00

[a] Incident photon to current conversion efficiency.

group of the phosphonate polypyridyl ruthenium sensitizers, used to anchor to the surface of the semiconductor, hardly desorbs from the semiconductor surface even at high pH value, though it is not in conjugation with the polypyridyl plane due to their non-planar structures. This is a disadvantage to the injection of electrons. The first phosphonate polypyridyl ruthenium dye (**Complex 1**) had the lifetime of excited state of 15 nanoseconds and the Langmuir adsorption coefficient of 8×10^6, which is 80 times larger than that of the **N3** dye. The incident photon-current conversion efficiency of **Complex 1** achieves a maximum of 70% at the wavelength of 510 nm. The phosphonate polypyridyl ruthenium analogue of **Z907** gained a conversion efficiency of more than 8% for solar cells based on it.

The ester linkage of the dye to the TiO$_2$ is susceptible to hydrolysis if water adsorbs on the TiO$_2$-surface. For this reason, in **N3**-based Ru-complexes two of the four carboxylic groups were replaced by long alkyl chains. In these sensitizers the conjugated

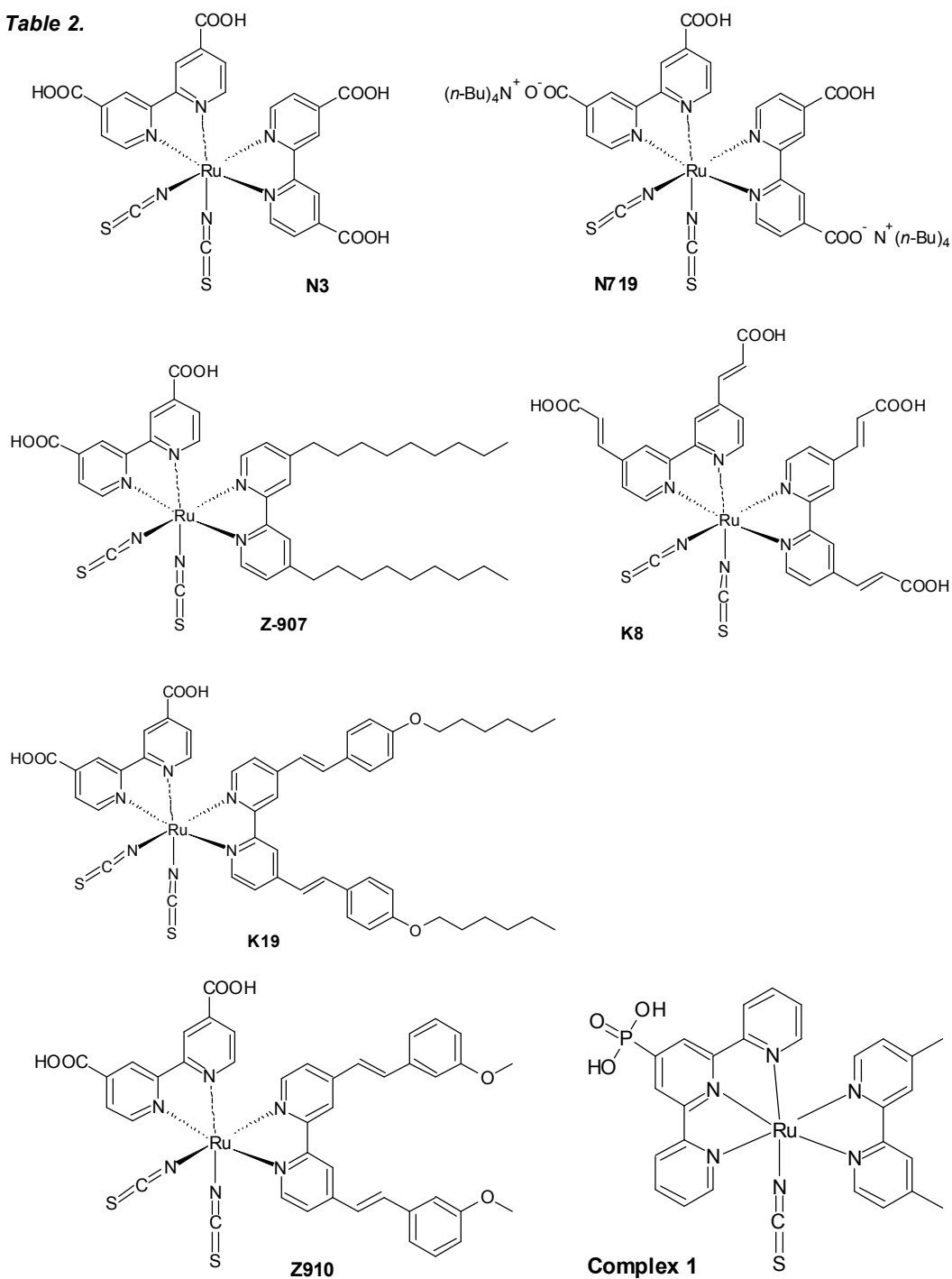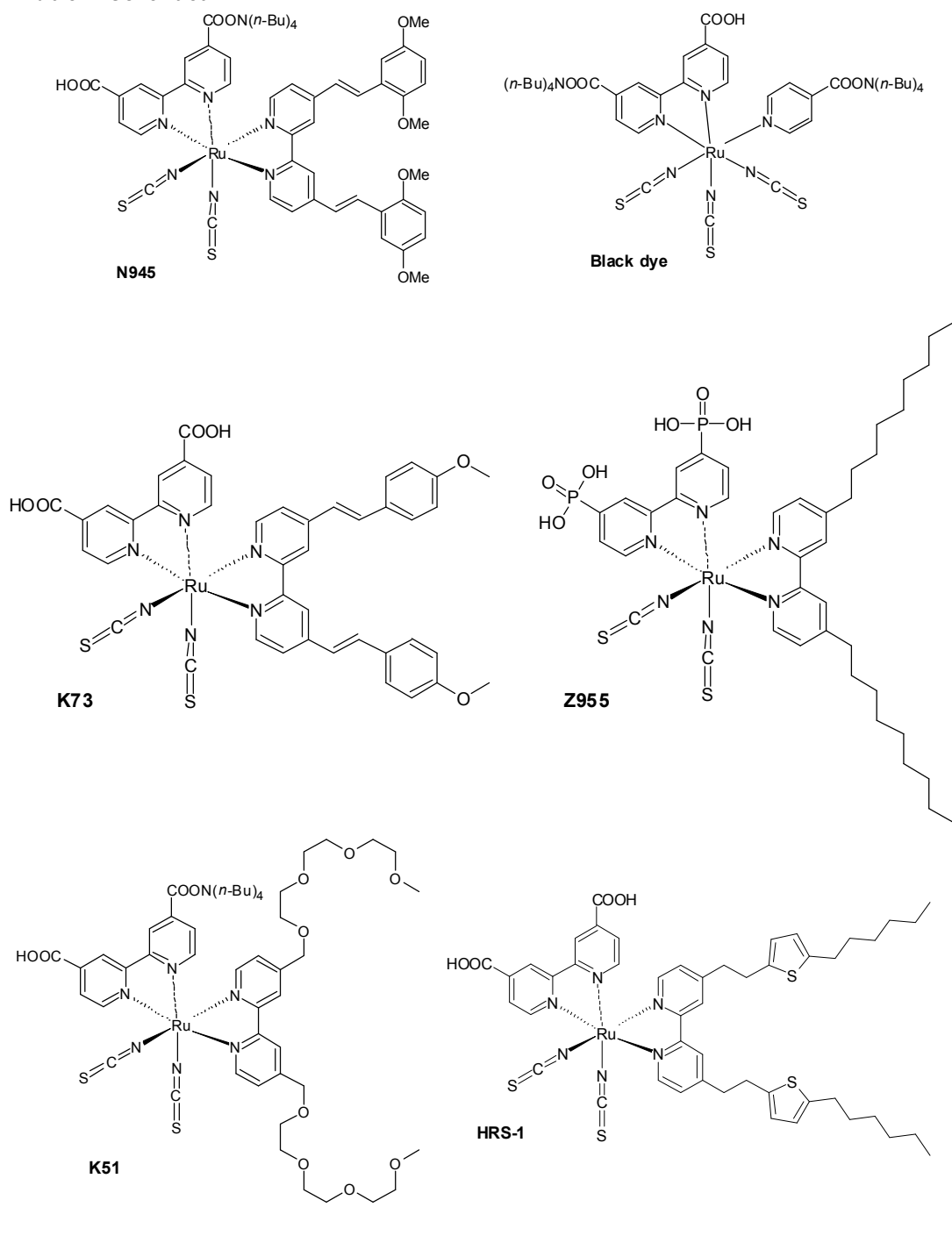*Table 1. Absorption spectra and photoelectric performance of different polypyridyl ruthenium (II) complexes.*

Table 2.

N3

N7 19

Z-907

K8

K19

Z910

Complex 1

Table 2. Continued

N945

Black dye

K73

Z955

K51

HRS-1

π-system of the bipyridyl-ligand is smaller and thus the absorption coefficient is typically lower. However, the initial conversion efficiencies are still reasonably good and range from 7.3% for **Z907** (with 9 carbon atoms) to 9.6% for **N621** (with 13 carbon atoms). The main advantage of these dyes is their extraordinary stability. For example, **Z907**-sensitized DSSCs passed 1000 h at 80 °C in darkness and at 55 °C under illumination without any degradation.

Polynuclear complexes have been employed in order to increase absorption coefficients. However, these bulky sensitizers require more space on the TiO_2 surface and penetrate less easily in the small cavities of the nanocrystalline TiO_2 than the mononuclear complexes. Hence, for polynuclear complexes, the increased absorption coefficients in solution do not necessarily lead to enhanced light absorption on the TiO_2 electrode due to the reduced surface concentration of the bulkier sensitizer molecules on the nanoporous TiO_2.

Sensitization with any one single dye is limited, since its absorption spectrum hardly matches with the solar emission spectrum. Co-sensitization of several dyes with different spectral responses, instead of a single dye, was used for wide-band-gap semiconductors. A series of squaraine dyes (derivatives of sqaric acid) are used as co-sensitizer with ruthenium polypyridyl complexes. That improved efficiency by 13% of dye-sensitized solar cells compared to those sensitized with simple ruthenium polypyridyl complexes. By co-sensitization of squaraine dye and polypyridyl ruthenium dye in a proper ratio, the spectral response scope was widened and the photovoltaic performance of dye-based solar cells was improved.
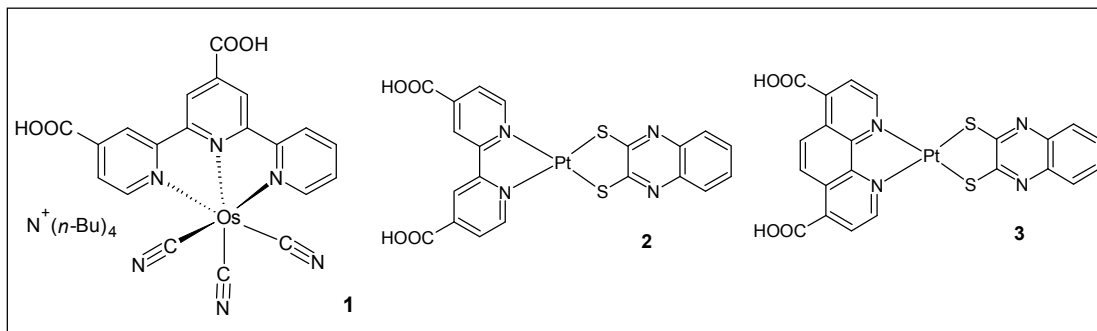
2.2 Other Metal Complexes

Several attempts were made to replace Ru with other metals, such as Os^{II}, Pt^{II}, Re^{I} Cu^{I}, and Fe^{II}. The osmium complex represented by structure **(1)** exhibited reversible $Os^{II} \rightarrow Os^{III}$ oxidation process with $E_{1/2} = 663$mV in methanol. The maximum incident

photon to current conversion efficiency (IPCE) for this osmium complex was found to be 50% lower than that of Ru-complex (black dye), but photochemical stability of osmium complex was superior as compared to black dye.

Square-planar platinum(II)-based dyes (**2** and **3**) containing 4,4'-dicarboxy-2,2'-bipyridine and quinoxaline-2,3-dithiolate ligands provided efficient sensitization of nanocrystalline TiO_2 solar cells over a wide visible range, generating a short-circuit photo-current of 6.14 $mAcm^{-2}$ and 5.02 $mAcm^{-2}$ and an open-circuit potential of 600 mV and 615 mV respectively under simulated AM 1.5 solar irradiation. Solar energy conversion efficiency for dyes **1** and **2** were found to be 2.6% and 2.33% respectively.

A series of chlorotricarbonyl rhenium(I) complexes (**4–6**) based on banzathiazole derivatives have been reported. Compared to other rhenium(I) 2,2'-bipyridine complexes, these were found to have red-shifted absorption because the heterocyclic ligands have lower π to π^* energy levels. These dyes exhibited solar energy conversion efficiencies of 1.72%, 1.46% and 1.43% respectively.

7   **8**

9
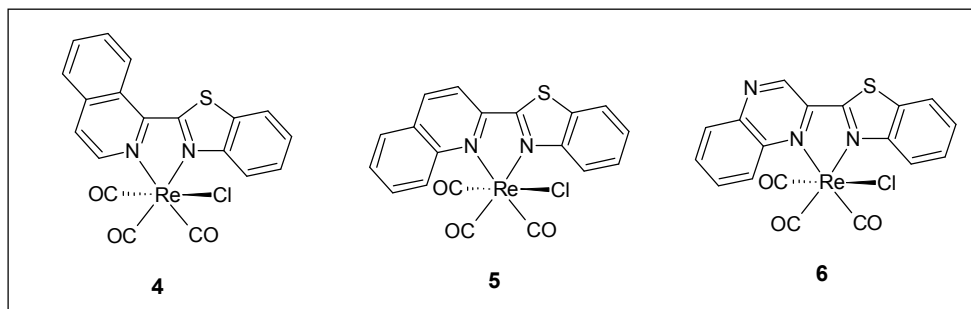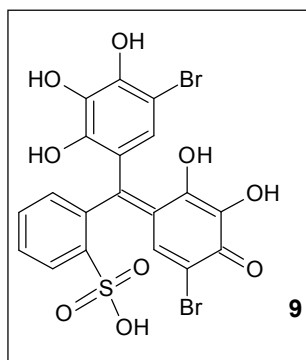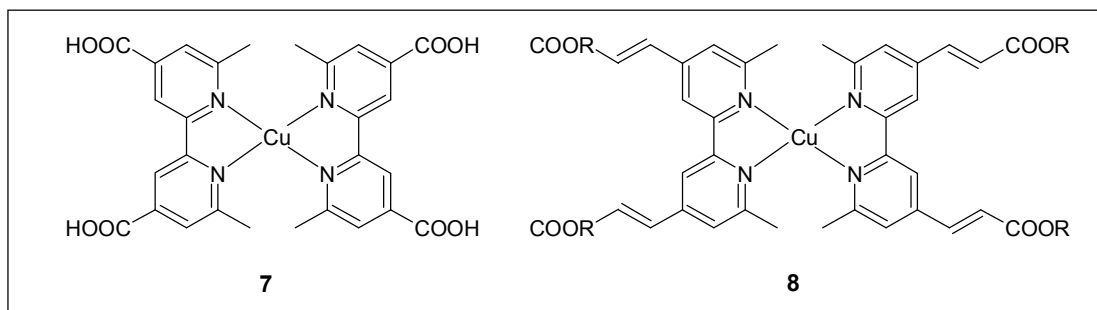
Copper(I) complexes of 6,6'-disubstituted-2,2'-bipyridines (**7** and **8**) have been reported to be effective sensitizers for TiO_2. These dyes showed surprisingly high incident photon to current efficiencies (IPCE) for DSSCs. Current–voltage characteristics of these dyes were compared with that of N719 and were found to have solar conversion efficiency of 1.9% and 2.3% respectively.
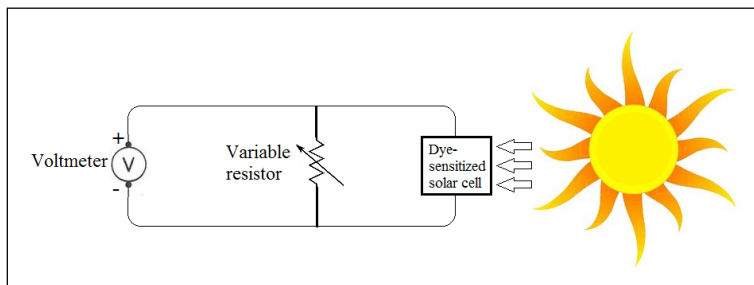
Complexation of bromopyrogallol red ligand (**9**) with di(aqua)bis(oxalato)iron(II) moiety, $[Fe(II)(H_2O)_2(C_2O_4)]^{2"}$, showed enhanced photovoltaic properties when compared with the photovoltaic cells coated by bromopyrogallol ligand only. However, the latter showed higher stability towards photodegradation. Its solar cell efficiency was 0.29%, and 0.24% by blocking the UV radiation.

2.3 *Performance Evaluation of Dye-sensitized Solar Cells*

Once the solar cell has been fabricated, it has to be evaluated for a number of parameters which provide its performance information in the real world applications. These include IPCE (Incident Photon to Current Efficiency or Quantum Efficiency), I_{sc} (short circuit current), V_{oc} (open circuit voltage), *FF* (fill-factor) and *h* (power conversion efficiency). These parameters can be determined by following the procedure described below.

1.   Connect the solar cell in series with a variable resistor. Connect a voltmeter across the variable resistor to determine the voltage across the resistor (*Figure* 2).

2. Upon irradiation (by using light source such as halogen lamp or Xe lamp), DSSC will generate electricity. Initially, keep the resistance value to maximum and record the corresponding voltage in the voltmeter. Reduce the resistance value and record the voltage. Continue to reduce the resistance value till the voltage becomes zero. Calculate the corresponding current at recorded points by using the formula:

Current (I) = Voltage (V) / Resistance (R).

3. Plot voltage (on x-axis) vs. current (on y-axis) as shown in *Figure* 3.

4. Calculate fill-factor by using the formula:

$$FF = \frac{I_m \times V_m}{I_{sc} \times V_{oc}} = \frac{P_m}{I_{sc} \times V_{oc}}.$$
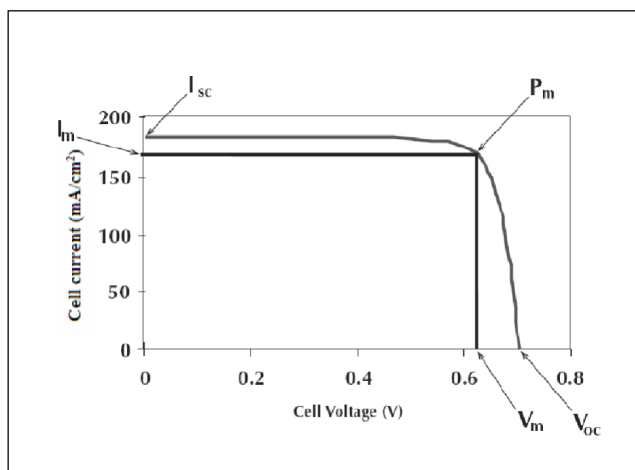
Figure 3. Current–Voltage characteristics of a typical solar cell I_m and V_m are the maximum cell current and maximum cell voltage respectively at the maximum power point (P_m) and $P_m = I_m \times V_m$.

5. Calculate power conversion efficiency by using the formula:

$$\eta = \frac{\text{outputpower}}{\text{inputpower}} \times 100$$

$$= \frac{P_m \, (\text{mW}/\text{cm}^2)}{\text{Light intensity} \, (\text{mW}/\text{cm}^2)} \times 100$$

$$= \frac{I_{sc} \, (\text{mA}/\text{cm}^2) \times V_{oc} \, (\text{V}) \times FF}{\text{Light intensity} \, (\text{mW}/\text{cm}^2)} \times 100 \, .$$

Conclusion

Ruthenium complexes offer several advantages in terms of performance characteristics of Dye-Sensitised Solar Cells. However, their availability and cost prohibit the use on a large scale. In fact scaling up of the energy harvesting itself is a key issue in this area. Research work is in progress in evaluating innocuous complexes like iron complexes.

Suggested Reading

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