

## Dye-sensitized solar cells: A brief overview

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### Abstract

The aim of this brief review is to give a short and simple overview of the dye-sensitized solar cell technology from the working principles to the first commercial applications. It emphasizes the role of the sensitizer and the strategies to improve the performances of the dye as well as some recent development aiming to answer specific issues.

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### 1. Introduction

One of the biggest challenges ahead of human kind is to replace the fossil fuel with renewable energy sources while keeping pace with the worldwide increasing thirst for energy because of increasing population and rising demand from developing countries. This challenge has to be answered with a low-cost solution using abundantly available raw materials. The Sun is an obvious source of clean and cheap energy, already used by Nature to sustain almost all life on Earth. Therefore harnessing the power of the Sun with photovoltaic technologies appears to be the only reasonable large scale answer to the energy challenge.

Up to now, commercially available photovoltaic technologies are based on inorganic materials, which require high costs and highly energy consuming preparation meth-

ods. In addition, several of those materials, like CdTe, are toxic and have low natural abundance. Organic photovoltaic can avoid those problems. However, the efficiencies of organic-based photovoltaic cells are still at the moment a long way behind those obtained with purely inorganic-based photovoltaic technologies.

Conventional organic photovoltaic devices use a donor and an acceptor type of organic materials, which form a heterojunction favoring the separation of the exciton into two carriers. Those formed carriers are then transported to the electrodes by the same organic materials that are used for the generation of an exciton. That is a material for classical organic photovoltaic devices should have both good light harvesting properties and good carriers transporting properties which is a difficult task to achieve. On the other hand, The dye-sensitized solar cell (DSSC) technology separates the two requirements as the charge generation is done at the semiconductor-dye interface and the charge transport is done by the semiconductor and the electrolyte. That is spectral properties optimization can be done by modifying the dye alone, while carriers transport properties can be improved by optimizing the semiconductor and the electrolyte composition.

The first sensitization of a photoelectrode was reported in 1887 (Moser, 1887). However, the operating mechanism

*Abbreviations:* IPCE, incident monochromatic photon-to-current conversion efficiency; LUMO, lowest unoccupied molecular orbitals; HOMO, highest occupied molecular orbitals;  $V_{OC}$ , open-circuit potential;  $J_{SC}$ , short circuit current;  $ff$ , fill factor; dc bpy, 4,4'-dicarboxy-2,2'-bipyridine; dc biq, 4,4'-dicarboxy-2,2'-biquinoline; ppy, phenylpyridine; UV-vis, ultraviolet-visible; CIGS, copper indium gallium selenide; DSSC, dye-sensitized solar cell.

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by injection of electrons from photo-excited dye molecules into the conduction band of the n-type semiconductor substrates dates only from the 1960s (Gerischer and Tributsch, 1968). The concept developed in the following years with first the chemisorption of the dye on the surface of the semiconductor (Dare-Edwards et al., 1981; Tsuborama et al., 1976) and then the use of dispersed particles to provide a sufficient interface area (Duonghong et al., 1984; Desilvestro et al., 1985). At the moment, champion cells using ruthenium complexes exhibit around 11% power conversion efficiency under AM1.5 conditions (Nazeeruddin et al., 2005).

Overall, DSSC is considered as a low cost and promising solution to solve the energy problem.

## 2. Working principle

The actual dye-sensitized solar cell contains broadly five components: (1) a mechanical support coated with Transparent Conductive Oxides; (2) the semiconductor film, usually  $\text{TiO}_2$ ; (3) a sensitizer adsorbed onto the surface of the semiconductor; (4) an electrolyte containing a redox mediator; (5) a counter electrode capable of regenerating the redox mediator like platine. A schematic representation of the dye-sensitized solar cell is shown in Fig. 1.

Due to its multiple advantages, titanium dioxide became the semiconductor of choice for the photoelectrode. It is low cost, widely available, and non-toxic. Ruthenium complexes such as  $[\text{Ru}(4,4'\text{-dicarboxy-2,2'\text{-bipyridine ligand}})_3]$  were employed as sensitizer very early on and are still now the most commonly used sensitizer. Finally, the main redox couple used is triiodide/iodine.

Fig. 2 shows the operating principles of the dye-sensitized solar cell. The first step is the absorption of a photon by the sensitizer  $S$  (Eq. (1)), leading to the excited sensitizer  $S^*$  which injects an electron into the conduction band of the semiconductor, leaving the sensitizer in the oxidized state  $S^+$  (Eq. (2)). The injected electron flows through the semiconductor network to arrive at the back contact and then through the external load to the counter electrode to reduce the redox mediator (Eq. (3)) which in turn regenerates the sensitizer (Eq. (4)). This completes the circuit.

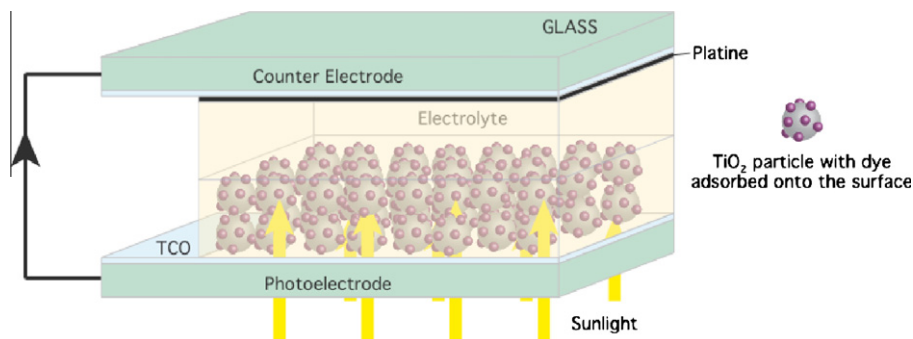


Fig. 1. Schematic representation of the dye-sensitized solar cell.

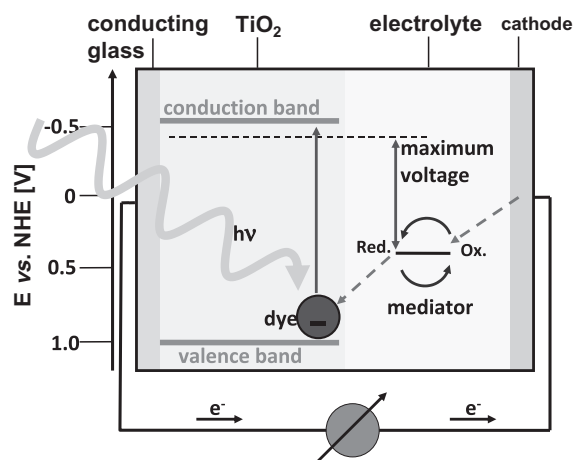
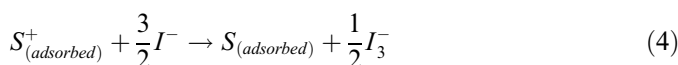
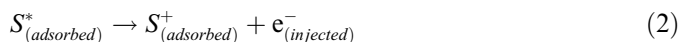
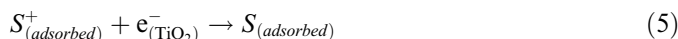


Fig. 2. Operating principles and energy level diagram of dye-sensitized solar cell.

Under illumination, the device constitutes a regenerative and stable photovoltaic energy conversion system.



Some undesirable reactions resulting in losses in the cell efficiency occur. They are the recombination of the injected electrons either with oxidized sensitizer (Eq. (5)) or with the oxidized redox couple at the  $\text{TiO}_2$  surface (Eq. (6)).



The total efficiency of the dye-sensitized solar cell depends on optimization and compatibility of each of these constituents, in particular on the semiconductor film along with the dye spectral responses (Barbé et al., 1997). A very important factor is the high surface area and the thickness

of the semiconductor film which leads to increased dye loading, thus optical density resulting in efficient light harvesting (Rothenberger et al., 1999).

The incident monochromatic photon-to-current conversion efficiency (IPCE), sometimes referred to also as the “external quantum efficiency” (EQE), is an important characteristic of a device. In particular, using devices with same architecture, it is possible to compare the light-harvesting performance of sensitizers. It is defined as the number of electrons generated by light in the external circuit divided by the number of incident photons as a function of excitation wavelength as in equation (7) (Hagfeldt and Grätzel, 1995):

$$\begin{aligned} \text{IPCE}(\lambda) &= \frac{\text{Photocurrent density}}{\text{Wavelength} \times \text{Photon flux}} \\ &= \text{LHE}(\lambda) \times \varphi_{inj} \times \eta_{coll} \end{aligned} \quad (7)$$

where  $\text{LHE}(\lambda)$  is the light-harvesting efficiency at wavelength  $\lambda$ ,  $\varphi_{inj}$  is the quantum yield for electron injection from the excited sensitizer in the conduction band of the  $\text{TiO}_2$ , and  $\eta_{coll}$  is the efficiency for the collection of electrons.

The overall conversion efficiency ( $\eta$ ) of the dye-sensitized solar cell is determined by the photocurrent density ( $J_{SC}$ ), the open-circuit potential ( $V_{OC}$ ), the fill factor ( $ff$ ) of the cell and the intensity of the incident light ( $I_s$ ), (Eq. (8)) (Nazeeruddin et al., 1993).

$$\eta_{global} = \frac{J_{SC} \cdot V_{OC} \cdot ff}{I_s} \quad (8)$$

The open-circuit photo-voltage is determined by the energy difference between the Fermi level of the solid under illumination and the Nernst potential of the redox couple in the electrolyte (Fig. 2). However, the experimentally observed open-circuit potential ( $V_{OC}$ ) for various sensitizers is smaller than the difference between the conduction band edge and the redox couple. This is generally due to the competition between electron transfer and charge recombination pathways. Knowledge of the rates and mechanisms of these competing reactions are vital for the design of efficient sensitizers and thereby improvement of the devices (Cahen et al., 2000; Ferber and Luther, 2001; van de Lagemaat and Frank, 2000). The fill factor  $ff$  is defined as the ratio of the maximum power  $P_{max}$  obtained with the device and the theoretical maximum power, that is  $P_{th} = J_{SC} \cdot V_{OC}$ .  $J_{SC}$  is the short circuit current and  $V_{OC}$  is the open-circuit voltage. The fill factor  $ff$  can then take values between 0 and 1. It reflects electrical and electrochemical losses occurring during operation of the DSSC.

It can be seen that the photophysical and electrochemical properties of the sensitizer will mainly define the performances of the device. First through the oxidation potential which set the maximum open-circuit voltage possible and second through the absorption properties, which dictate the short circuit current. Finally, overall electron transfer dynamics will influence losses.

### 3. Molecular sensitizers

#### 3.1. N3 and N719: The archetype

While several transition-metal complexes as well as metal-free organic dyes have been tested (Bessho et al., 2008; Hagberg et al., 2008; Kim et al., 2008; Hara et al., 2003; Islam et al., 2001; Geary et al., 2005; Wong et al., 2007; Ferrere and Gregg, 1998; Sauvé et al., 2000; Asbury et al., 2000; Baranoff et al., 2010), the best photovoltaic performances both in terms of conversion yield and long term stability has so far been achieved with polypyridyl complexes of ruthenium in which two ligands  $L = 4,4'$ -dicarboxy-2,2'-bipyridine and thiocyanate ligands have been used. Thus, the ruthenium complex *cis*- $\text{RuL}_2(\text{NCS})_2$ , (**1**) known as N3 dye, has become the paradigm of heterogeneous charge transfer sensitizer for dye-sensitized solar cells (Nazeeruddin et al., 1993). The role of the carboxylate groups is to allow immobilization of sensitizer to the film surface via the formation of bidentate coordination and ester linkages, whilst the ( $-\text{NCS}$ ) groups enhance the visible light absorption.

The N3 dye exhibits absorption maxima (extinction coefficient) at 400 nm ( $1.41 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 535 nm ( $1.45 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) of MLCT (metal-to-ligand charge transfer) character, that is the excitation of the dye involves the transfer of an electron from the metal to the  $\pi^*$  orbital of the surface anchoring carboxylated bipyridyl ligand.

To obtain high light to electric power conversion efficiencies, the short-circuit photocurrent ( $J_{SC}$ ) and open-circuit potential ( $V_{OC}$ ) of the solar cell have to be optimized. The performance of the three sensitizers **1**, **2** and **3** that contain different degrees of protonation were studied on nanocrystalline  $\text{TiO}_2$  electrodes (Nazeeruddin et al., 1999). Fig. 3 shows the photocurrent action spectra obtained with a monolayer of these complexes coated on  $\text{TiO}_2$  films. As the conduction band of the  $\text{TiO}_2$  is known to have a Nernstian dependence on pH (Yan and Hupp, 1996; Tachibana et al., 2001), it is expected that the protonation state of the dye which originally contains 4 protons, will influence the energy level of the  $\text{TiO}_2$  conduction band, hence the efficiency of the device. The fully protonated sensitizer **1** charges the  $\text{TiO}_2$  surface positively by transferring its protons upon adsorption. The electric field associated with the surface dipole generated in this fashion enhances the adsorption of the anionic ruthenium complex and assists electron injection from the excited state of the sensitizer into the titania conduction band, favoring high photocurrents (18–19  $\text{mA/cm}^2$ ). However, the open-circuit potential (0.65 V) is lowered due to the positive shift of the conduction band edge induced by the surface protonation.

The opposite is true for the sensitizer **3** that carries no protons: it shows high open-circuit potential compared to complex **1**, due to the relative negative shift of the conduction band edge induced by the adsorption of the anionic complex, but as a consequence the short-circuit photocurrent is lower. Between those two extremes, there should

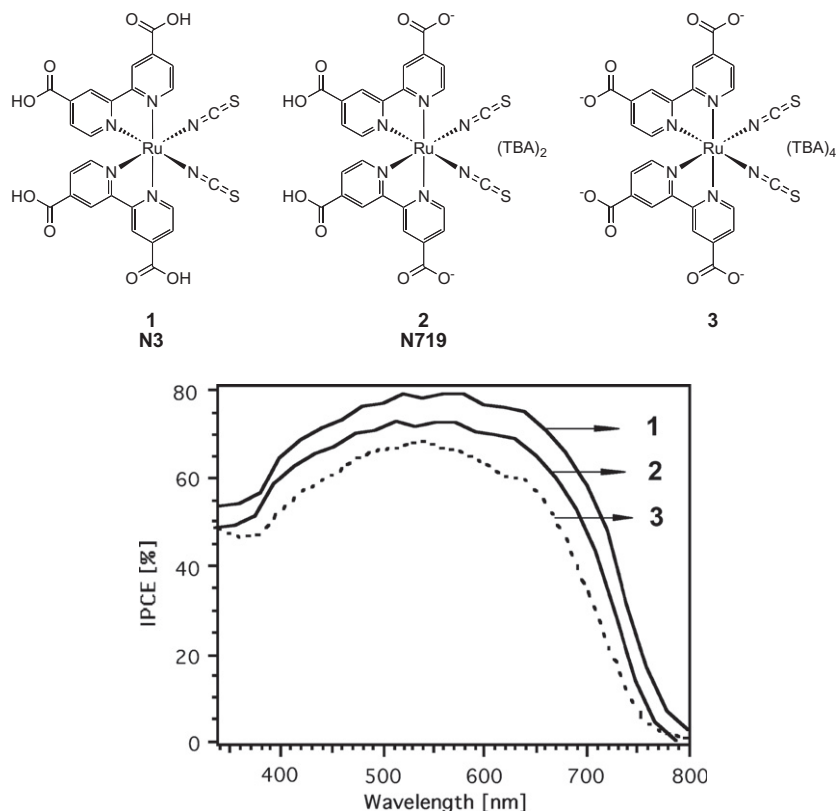


Fig. 3. Photocurrent action spectra of nanocrystalline  $\text{TiO}_2$  films sensitized by complexes **1**, **2** and **3**. The incident photon-to-current conversion efficiency is plotted as a function of wavelength.

be an optimal degree of protonation of the sensitizer for which the product of short-circuit photocurrent and open-circuit potential is maximized.

The incident monochromatic photon-to-current conversion efficiency (IPCE) is plotted as a function of excitation wavelength. The IPCE value in the plateau region is 80% for complex **1**, while for complex **3** it is only about 66%. This difference is even more pronounced in the red region. Thus, at 700 nm the IPCE value is twice as high for the fully protonated complex **1** as compared to the deprotonated complex **3**. Consequently the short-circuit photocurrent drops from 18–19  $\text{mA}/\text{cm}^2$  for complex **1**, to only about 12–13  $\text{mA}/\text{cm}^2$  for complex **3**. However, there is a trade off in photovoltage, which is 0.9 V for complex **3**, as compared to 0.65 V for complex **1**. Nevertheless, this is insufficient to compensate for the current loss.

Photovoltaic performance data obtained with a sandwich cell under illumination by simulated AM1.5 solar light using complex **2** are shown in Fig. 4. At one sun the sensitized solar cell exhibited  $17.73 \pm 0.5$  mA current, 846 mV potential and fill factor 0.75 yielding an overall conversion efficiency of 11.18%. Hence, the photovoltaic performance of complex **2** carrying two protons is superior to that of compounds **1** and **3** that contain four or no protons, respectively. The doubly protonated form of the complex is therefore preferred over the other two sensitizers for sensitization of nanocrystalline  $\text{TiO}_2$  films.

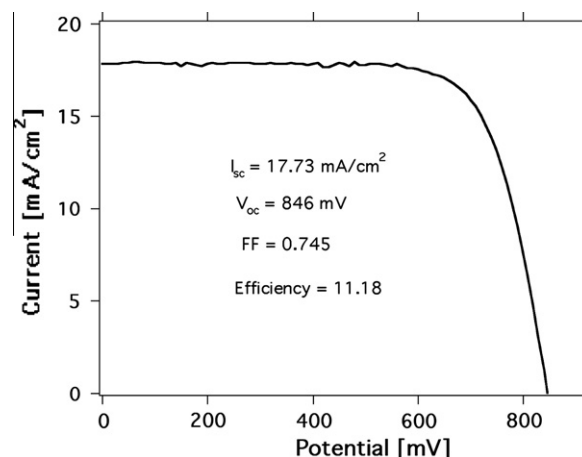
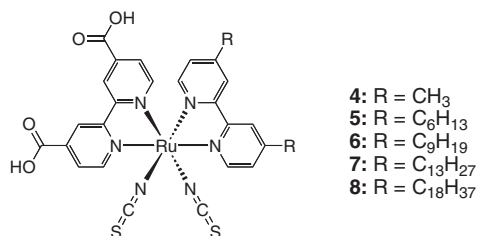


Fig. 4. Photocurrent–voltage curve of a solar cell based on complex **2**. The cell was equipped with an anti-reflective coating. The conversion efficiency in full AM1.5 sunlight illumination ( $100 \text{ mW cm}^{-2}$ ) is 11.18%. The cell is masked with black plastic to avoid the diffusive light leaving an active cell area of  $0.158 \text{ cm}^2$ .

### 3.2. Hydrophobic sensitizers

Due to the chemical nature of the anchoring groups, the water-induced desorption of the sensitizer from the  $\text{TiO}_2$  surface is an other crucial aspect in dye-sensitized solar cells as it impacts the long term stability of the device. To overcome this problem, alkyl chains are grafted onto one bipyridine

conferring hydrophobic properties to the complexes (**4–8**). The absorption spectra of these complexes show broad features in the visible region and display maxima around 530 nm. The performance of these hydrophobic complexes as charge transfer photosensitizers in nanocrystalline TiO<sub>2</sub> based solar cell shows excellent stability towards water-induced desorption (Nazeeruddin et al., 2001).



In addition, those sensitizers have shown to considerably suppress the recombination reactions as described in Eqs. (5) and (6). The rate of electron transport in dye-sensitized solar cell is a major element of the overall efficiency of the cells. The injected electrons into the conduction band from optically excited dye, can traverse the TiO<sub>2</sub> network and can be collected at the transparent conducting glass or can react either with oxidized dye molecule or with the oxidized redox couple (recombination). The reaction of injected electrons into the conduction band with the oxidized redox mediator gives undesirable dark currents, reducing significantly the charge-collection efficiency, and thereby decreasing the total efficiency of the cell.

Several groups have tried to reduce the recombination reaction by using sophisticated device architecture such as composite metal oxides as the semiconductor with different band gaps (Tennakone et al., 1999; Chandrasekharan and Kamat, 2000). Gregg et al. have examined surface passivation by deposition of insulating polymers (Gregg et al., 2001). We have studied the influence of spacer units between the dye and the TiO<sub>2</sub> surface with little success (Nazeeruddin and Graetzel, 2002). Nevertheless, by using TiO<sub>2</sub> films containing hydrophobic sensitizers that contain long aliphatic chains (**4–8**) the recombination reaction was suppressed considerably (Schmidt-Mende et al., 2005; Nazeeruddin et al., 2005). The most likely explanation for the reduced dark current is that the long chains of the sensitizer interacts laterally to form an aliphatic network, like a shield, thereby preventing triiodide from reaching the TiO<sub>2</sub> surface.

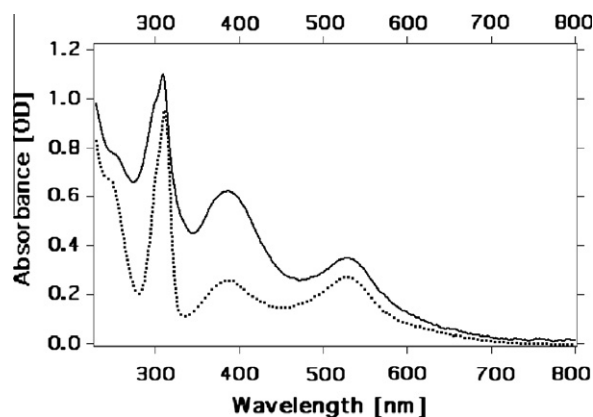


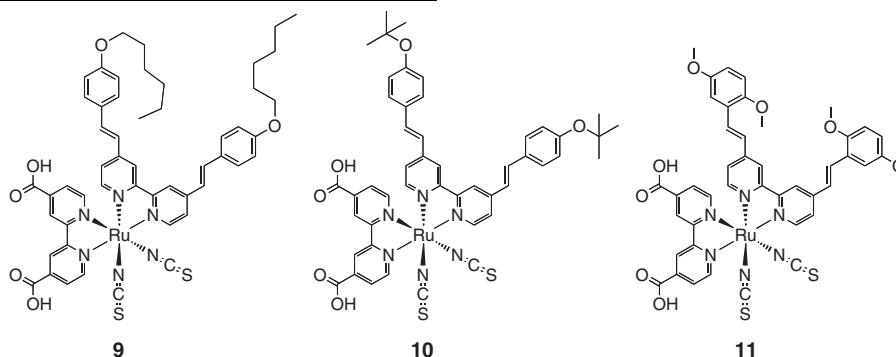
Fig. 5. Comparison of absorption spectra of complexes **1** and **11** in ethanol.

### 3.3. High molar extinction coefficient sensitizers

Due to its simple chemical structure and excellent performances, complex **1** has become a paradigm in the area of dye-sensitized nanocrystalline TiO<sub>2</sub> films (Nazeeruddin et al., 2005). Therefore the vast majority of sensitizers are based on its design. In spite of this, the main drawback of this sensitizer is the lack of absorption in the red region of the visible spectrum and also relatively low molar extinction coefficient. Therefore, sensitizers with high molar extinction coefficient have been particularly sought after. A new series of high molar extinction coefficient sensitizers (**9–11**) featuring alkyloxy groups has been synthesized and utilized in dye-sensitized solar cells. The purpose of 4,4'-bis((*E*)-2,5-dimethoxystyryl)-2,2'-bipyridine ligand that contains extended  $\pi$ -conjugation with substituted methoxy groups is to enhance molar extinction coefficient of the sensitizers, and furthermore to provide directionality in the excited state by fine tuning the LUMO level of the ligand with the electron-donating alkoxy groups.

The absorption spectra of complexes (**9–11**) are dominated by the metal-to-ligand charge transfer transitions in the visible region, and the lowest allowed MLCT bands appearing at 400 and 545 nm. The molar extinction coefficients of these bands being close to 35,000 and 19,000 M<sup>-1</sup> cm<sup>-1</sup>, respectively, are significantly higher than N3 (Fig. 5).

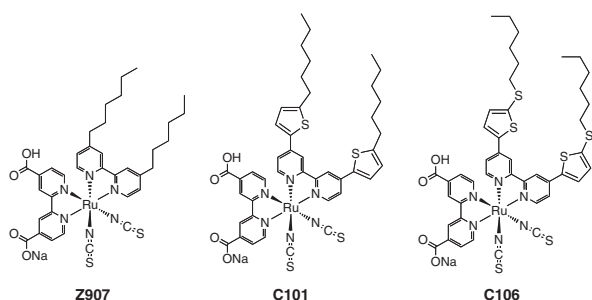
The photovoltaic data of these sensitizers using an electrolyte containing 0.60 M butylmethylimidazolium iodide (BMII), 0.03 M I<sub>2</sub>, 0.10 M guanidinium thiocyanate and



0.50 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio: 85:15), exhibited a short-circuit photocurrent density of  $16.50 \pm 0.2 \text{ mA/cm}^2$ , with an open-circuit voltage of  $790 \pm 30 \text{ mV}$  and a fill factor of  $0.72 \pm 0.03$ , corresponding to an overall conversion efficiency of 9.6% under standard AM1.5 sunlight and demonstrate stable performance under light and heat soaking at  $80^\circ\text{C}$  (Wang et al., 2005).

### 3.4. Supersensitizers

In the recent years, a design intermediate between hydrophobic sensitizers and high molar extinction coefficient sensitizer appears. It is based on heteroleptic sensitizers with a ligand incorporating thiophene moieties to increase significantly the spectral properties of the complex and alkyl chains to shield the  $\text{TiO}_2$  surface from the redox mediator (Cao and Bai, 2009).



As the extinction coefficients of those sensitizers are much higher than **N719**, it is possible to decrease the thickness of the semiconductor film. This results in an improvement of the open-circuit voltage as well as the fill factor, translating into high efficiencies of 10% and more.

Those very recent sensitizers already exhibit performances similar or superior to **N719**. Therefore it is expected that optimization of the device in the coming years will result in conversion efficiencies close to 12%.

### 3.5. Cyclometallated ruthenium complexes

The thiocyanate ligands are usually considered as the most fragile part of the ruthenium dyes. First because it is

a monodentate ligand, therefore it is easier to decoordinate than a bidentate ligand like bipyridine. Second it is an ambidentate ligand which can attach at either the sulfur atom or the nitrogen atom. Efforts have been made in the past to replace those ligands without great success as the efficiencies obtained for the devices remain well below 10%.

A promising result was obtained recently by replacing the thiocyanate by a cyclometallated 2,4-difluorophenylpyridine, yielding the complex **YE05** (Fig. 6) (Bessho et al., 2009). Such ligand is widely used in iridium emitters for organic light emitting devices (OLEDs) (Baranoff et al., 2009). The spectral response is significantly red shifted when compared to **N719** as can be seen in the IPCE spectrum which reach a maximum over 80% at 600 nm extending to 800 nm. It originates from the absorption spectrum where three absorption bands can be observed in the visible instead of the two usually obtained with thiocyanate based ruthenium complexes. In addition, the lowest energy MLCT band in **YE05** is red-shifted by 25 nm when compared to **N719**, with overall remarkable high molar extinction coefficient exceeding substantially that of **N719** over the whole visible domain. This is due to the cyclometallated ligand, which is a stronger donor than the two thiocyanate groups. It results in the stronger destabilization of the highest occupied molecular orbital (HOMO) than the lowest unoccupied molecular orbital (LUMO). The presence of the two fluorine atoms allows the fine-tuning of the redox potential of the sensitizer. Overall, **YE05** produces a short-circuit photocurrent of  $17 \text{ mA/cm}^2$ , a  $V_{OC}$  of 800 mV, and a fill factor of 0.74, corresponding to a conversion efficiency of 10.1% under AM1.5 standard sunlight. Thus, **YE05** emerges as a prototype for thiocyanate-free cyclo-metalated ruthenium complexes, exhibiting remarkable spectral and stability properties.

## 4. Outlook

Inspired by the principle of natural photosynthesis, Dye-Sensitized Solar cells have become a credible alternative to solid-state p–n junction devices. Conversion efficiencies over 11% and 15% have already been obtained with single junction and tandem cells, respectively, on the laboratory

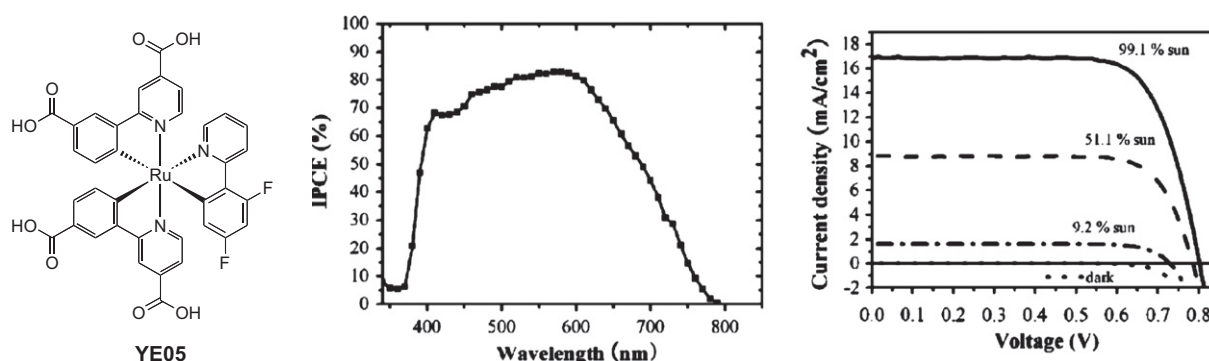


Fig. 6. **YE05** chemical structure and IPCE spectrum (left) and photocurrent voltage curves (right) under various light intensities of AM1.5 sunlight.

scale, with still ample room for further amelioration. Future improvement will focus on the  $J_{SC}$  by extending the light response of the sensitizers in the near IR spectral region. Gains in the  $V_{OC}$  are expected from introducing ordered oxide mesostructures and controlling the interfacial charge recombination dynamics. The mesoscopic cells are well suited for a whole realm of applications ranging from the low power market to large-scale applications. Their excellent performance in diffuse light gives them a competitive edge over silicon in providing electric power for stand-alone electronic equipment both indoor and outdoor. In addition, contrary to amorphous silicon, which suffers from degradation due to the well-known Staebler-Wronski effect, the intrinsic stability of the DSC has been confirmed by extensive accelerated light soaking tests carried out over the last decade. Application of the DSC in building integrated PV has already started and will become a fertile field of future commercial development.

### Acknowledgment

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