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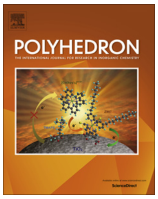

Ruthenium complexes with tridentate ligands for dye-sensitized solar cells

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ABSTRACT

Since the first report of black dye, ruthenium complexes with tridentate ligands have attracted attention due to their ability to harvest photons in the near infrared. Herein we review this family of sensitizers for dye-sensitized solar cell focusing on their chemical structures and properties. We briefly highlight their performance in photovoltaic devices.

1. Introduction

Our society consumes approximately 18 terajoules of energy per second, about 100 times the amount utilized a century ago. During this period, the availability of cheap energy from fossil fuels has supported a phenomenal development in technology and, overall, has resulted in a significant improvement of our quality of life, if only from a material point of view.

Unfortunately fossil fuels are becoming more expensive and our rate of energy consumption continues to increase due to growing population and rising demand from developing countries. One of the biggest challenges faced by our society is therefore to replace fossil fuels with a vast, renewable, and affordable energy source while keeping pace with the world's rapidly increasing energy requirements. Furthermore, this challenge has to be answered with an economically and energetically low-cost solution using abundantly available and safe raw materials.

The sun is a particularly attractive source of energy. Nearly 89 petajoules of solar energy reach the Earth's surface every second which amounts to 4000 times our current energy consumption. As a result, the challenge of converting sunlight into electricity, photovoltaics, continues to be a very active topic in research.

Commercially available photovoltaic technologies are based on inorganic materials, the processing of which requires high costs and is highly energy consumptive. Furthermore, many of those materials can be toxic and have a low natural abundance. Organic photovoltaics do not have such issues as the materials are based mainly on carbon and hydrogen atoms, meaning they can easily be disposed of. However, the efficiencies of organic-based photovoltaic cells are a long way behind those obtained by their purely inorganic counterparts.

Conventional organic photovoltaic devices are based on a heterojunction formed by a donor and an acceptor. This architecture is necessary to enhance the spliting of the exciton into two charge carriers, which are then transported to the electrodes by the same materials which are used for the generation of the exciton. Consequently, materials for organic photovoltaic devices should be able to both harvest light and transport charge carriers efficiently, a difficult task to achieve.

The dye-sensitized solar cell (DSC) has key advantages over silicon based solar cells such as the low-cost of fabrication, low embodied energy cost, and the higher efficiency at low insolation level [1,2]. It also has important advantages over organic solar cells, as the generation of charge carriers and the transport of these charges are achieved by different materials [3,4].

DSCs are constructed from five key components: (1) a mechanical support coated with transparent conductive oxides (TCO); (2) a n-type semiconductor film of TiO_2; (3) a sensitizer chemically adsorbed onto the surface of the semiconductor; (4) an electrolyte containing a redox shuttle; (5) a counter electrode to regenerate the redox shuttle [4,5].

A schematic of the operating principles of the DSC is shown in Fig. 1. First, upon absorption of a photon, the sensitizer S is excited to S^*, which injects an electron into the conduction band of the

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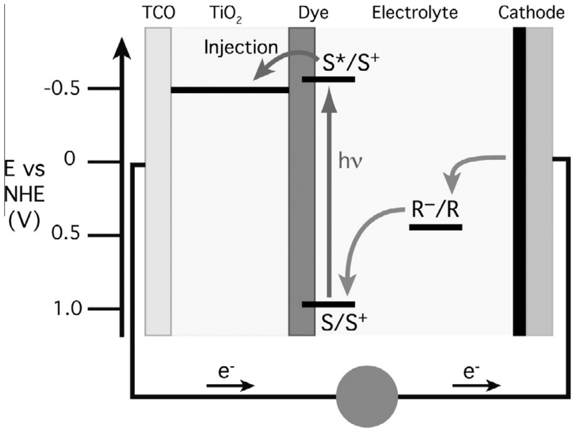


Fig. 1. Operating principles and energy level diagram of the DSC; S/S$^+$/S* = sensitizer in the ground, oxidized, and excited state; R$^-$/R = redox mediator.

semiconductor. The resulting oxidized dye S$^+$ is regenerated by the redox mediator, which is in turn reduced at the cathode.

$$\eta = \frac{J_{ph} \cdot V_{OC} \cdot ff}{P_{irr}} \tag{1}$$

The power conversion efficiency (η) of the device is related to the photocurrent density (J_{ph}) also refered as short circuit current density (J_{sc}), the open circuit potential (V_{OC}), the fill factor (ff) of the cell, and the intensity of the incident light (P_{irr}), (Eq. (1)).

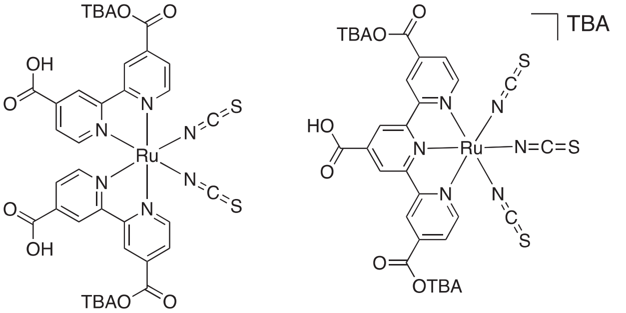
The sensitizer is a key component for high efficiency devices as it dictates the light harvesting capability of the device (related to J_{ph}) and participates in the electron transfer dynamics (related to V_{OC} and ff). Therefore optimization of the photophysical and electrochemical properties of the sensitizer has been the subject of intensive work.

Historically, polyimine ruthenium complexes have had a particular importance and were central to the early successes of the DSC [3,5], resulting in champion cells with 11% power conversion efficiency under AM1.5 conditions [6]. In particular since black dye was first reported, ruthenium complexes with tridentate ligands have attracted attention due to their ability to harvest photons in the near infrared. Herein we review this family of sensitizers for dye-sensitized solar cell focusing on their chemical structures and properties. We briefly highlight their performance in photovoltaic devices.

2. Archetype ruthenium dyes: N719 and N749

Several transition-metal complexes have been tested as sensitizers for DSCs [7–16]. Within this large family of sensitizers, the best photovoltaic performances both in terms of conversion yield and long term stability have so far been achieved with complexes of ruthenium in which polypyridine (substituted with carboxylic acid functional anchoring groups) and thiocyanate ligands have been used (see Fig. 2).

The ruthenium complex cis-Ru(dcbp)$_2$(NCS)$_2$, dcbp = 4,4′-dicarboxy-2,2′-bipyridine, known as **N3** dye, has become the paradigm for heterogeneous charge transfer sensitizers in dye-sensitized solar cells [17]. The doubly deprotonated version, **N719**, offers an improvement in the device performance due to the impact of the protons on the properties of the complex and on the conduction band of the titania. The role of the carboxylate groups is to anchor the sensitizer onto the surface of the semiconductor film via the formation of bidendate coordination and ester linkages. The thiocyanate groups stabilize the dye t_{2g} orbitals, finely tune the oxidation potential of the dye to match the potential of the iodide/triiodide redox mediator and also enhance the visible light absorption. Under AM 1.5 solar light, a DSC using **N719** exhibited 17.73 ± 0.5 mA current, 846 mV potential and a fill factor of 0.75 yielding an overall conversion efficiency of 11.18% [6].



N719

N749
black dye

Fig. 2. Archetypal polypyridine ruthenium complexes for DSCs. TBA = tetrabutyl ammonium.

N719 exhibits absorption maxima (extinction coefficient) at 395 nm (1.43 × 10^4 M^{-1} cm^{-1}) and 535 nm (1.47 × 10^4 M^{-1} cm^{-1}) due to metal-to-ligand charge transfer (MLCT) transitions involving the t_{2g} metal orbitals and the π^* orbital of the bipyridyl ligand [18]. The absorption depends on the pH of the solution and the absorption maxima are blue shifted upon deprotonation (Fig. 3a). Most importantly, in device conditions, the spectral response of **N719** barely exceeds 780 nm, while the optimum threshold for single junction converters is 920 nm.

N749, or black dye, was developed to absorb more of the visible spectrum. It uses a terpyridine ligand, 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine (tctpy), and three –NCS. When going from Ru(bpy)$_3^{2+}$ (bpy = 2,2′-bipyridine) to Ru(tpy)$_2^{2+}$ (tpy = 2,2′:6′,2″-terpyridine), the absorption maximum is red shifted from 452 to 474 nm [19]. An even larger red shift of absorption is observed between **N719** (535 nm) and **N749** (610 nm) [20]. This effect is attributed to the modification of the polypyridyl ligands and to the additional –NCS group, which supplies a further negative charge to the metal center and destabilizes the HOMO energy level (E_{ox} = 0.85 and 0.66 V *versus* SCE for **N719** and **N749**, respectively), which in turn reduces the optical bandgap. The absorption spectrum of **N749** also depends on the pH of the solution and is blue-shifted upon deprotonation (Fig. 3b) [20]. A nanocrystalline photoelectrochemical cell sensitized by **N749** resulted in η = 10.4% with V_{OC} = 0.72 V, J_{ph} = 20.53 mA m^{-2} and ff = 0.704 [20]. Optimization of the device leads to a conversion efficiency slightly above 11% [21,22]. Despite the spectral response reaching 920 nm, which is the ideal value for single junction cells, the conversion efficiency improvement over **N719** is not as significant as one might expect. This is due to the lower driving force of dye regeneration by the electrolyte and a lower coupling with the TiO$_2$ density of states lowering the injection efficiency compared to **N719** [23,24].

3. RuL(NCS)$_3$ type of complex with L = tridentate ligand

The unique near infrared sensitization of titania by black dye triggered a lot of interest and engendered many studies on this particular sensitizer. Yet most chemical modifications of black dye have only recently been reported.

Complexes **1**–**3** (Fig. 4) utilize the same strategy of extending the conjugation of the terpyridine ligand to further increase the response in the near infrared [25,26]. The synthesis of the complexes follows a two-step procedure: the terpyridine ligand is first refluxed with ruthenium trichloride in ethanol to afford RuLCl$_3$,