A Study on Ruthenium polypyridyl complexes Vs Metal free organic molecules: Efficient sensitizers for dye sensitized solar cell applications

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Abstract: Organic molecules are found to be potential alternative sensitizers to ruthenium complexes based on structural versatility, electronic and physical properties. In this key note address the synthesis and application of variety of ruthenium complexes as well as metal free organic molecules synthesized in our laboratory as sensitizers in DSSCs will be discussed. Dye sensitized solar cells (DSSC) are currently great interest because of low cost, easy fabrication and environment-friendly compared to conventional solid-state p–n photovoltaic devices. The sensitizer is one of the key components in achieving high efficiency and durability of the device. Ru(II) polypyridyl complexes are widely used as sensitizers for DSSC with an efficiency >11%. However, ruthenium complexes are expensive due to rarity of the metal and lack of molar absorption coefficients in the red region of the visible spectrum.

Key words: renewable energy, solar cells, ruthenium, sensitizers

Description

The sensitizer plays a key role for the DSSCs to achieve higher conversion efficiency (η) and have been extensively studied by researchers all over the world. Dye-sensitized solar cells (DSSCs) are one of the most attractive alternatives for developing new renewable energy sources because of their high conversion of sunlight to electricity and low production cost.[1] The first high performance polypyridyl Ru complexes, such as *cis*-di(thiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium(II), coded as N3 and its salt form of N719 (Fig.1) have shown the higher short-circuit current due to broad UV-vis absorption and the enough long excited-state lifetime, resulted in obtaining the respectable η value (>10%) and higher stability.[2]

Dyes attached to TiO_2 through carboxylic acid groups are susceptible to desorption from the surface under the action of trace quantities of water and have serious consequences on the long-term stability of the devices. It has been reported that dyes with attached hydrophobic chains can display an enhanced stability towards desorption from TiO_2 induced by water in the liquid or gel.[3] DSSC based on Z907 (Fig. 1) using a polymer gel I^-/I_3^- electrolyte was shown to combine a cell efficiency of 6.1% with excellent stability to both prolonged thermal stress and light soaking that matched the criteria required for the outdoor use of solar

cells. However the ε of this sensitizer (12.2×10^3 M^{-1} cm^{-1}) is somewhat lower than that of the standard N719 dye. Subsequently, efforts were focused on the development of high molar extinction coefficient, amphiphilic ruthenium sensitizer by several groups including our group, with a motivation to enhance device efficiency.[4] In this direction extended π-conjugation on electron donating ancillary ligand of the ruthenium complex gave better results for high molar extinction coefficient sensitizers (eg. K77, K19, HRD dyes, MC dyes *etc*) (Fig. 1). These dyes were demonstrated as highly efficient, stable sensitizers for DSSC. For example, in search of new sensitizers we combined the structural features of K19 and HRD1 and synthesized a sensitizer *cis*-Ru(II)(4,4′-bis(3,5-di-*tert*-butyl-4-hexyloxystyryl)-2,2′-bipyridyl) (4,4′-dicarboxy-2,2′-bipyridyl) (NCS)$_2$, named as MC119[5] (Fig. 1), and showed superior performance over champion N719.

To improve the light harvesting property we synthesized a symmetrical sensitizer, named as BDF, using fluorene chromophore and we achieved superior performance over Z907. With this encouraging performance further we synthesized a BPFC sensitizer by tethering di-*tert*-butylcarbazole (hole transporting material) antenna on peripheral of the BDF sensitizer, but unfortunately we obtained lesser conversion efficiency which could be attributed to increased molecular size of the sensitizer. We found that, using conventional symmetric bipyridines on ruthenium sensitizers, one can either increase light-harvesting ability and red-shift the metal to ligand charge transfer (MLCT) band by incorporating π-conjugation or improve electron donating/hole transport properties by derivatizing with a desirable chromophore. Whereas the unsymmetrical bipyridine ligand concept allows the possibility of a large variety of bipyridine ligands with varied structural features. In this regard four novel unsymmetric bipyridine ligand L1-L4 have been designed and successfully synthesized based on "*one bipyrine-triple advantages*" concept. (1) The increasing light harvesting ability and red shift the MLCT band while providing aromatic stability avoiding isomerisation (unlike in double bonds). (2) The hexyl chain provides hydrophobic environment to the sensitizer, increases the solubility, and prevent approach of redox electrolyte in the vicinity of TiO$_2$ reducing recombination. (3) The alkyl groups at two *ortho* and *para* positions of the phenyl ring serve as electron pumping and red shift the absorption. Using these ligands a series of heteroleptic ruthenium complexes MC103-MC106 (Fig. 1) were synthesized and successfully utilized for DSSC application.[6] The efficiencies of 9.56, 9.58, 8.34, and 8.32% have been obtained for MC103, MC104, MC105, and MC106 respectively, while under similar fabrication and measurement conditions, standard N719 showed 7.2% efficiency.

Much effort has been made to increase stability of a device, towards the

development of sensitizers, electrode and photoanode material. A way to improve the stability is the development of a dye without or with lesser number thiocyanate (SCN) ligands because monodentate SCN is believed to provide the weakest dative bonding within the metal complexes, making the sensitizer To further improve the device efficiency using this class of ruthenium [3+2+1] complexes, we replaced the symmetrical ancillary bipyridine ligand of mLBD dye with novel unsymmetrical bipyridine ligands. We thus synthesized four novel mixed unsymmetrical ligand dyes (MC107-MC110) and one mixed symmetrical ligand dye (MC111) (Fig. 1).[8] The sensitizers having alkyl thiophene on bipyridine performed better than the sensitizers with alkyl bithiophenes. We successfully demonstrated that by careful design of unsymmetrical bipyridine ancillary ligands, the optical properties of the sensitizer can be effectively tuned for better light harvesting in DSSCs without increasing the bulk. Furthermore, the sensitizer with alkyl thiophene and triisopropyl groups on the bipyridine ligand exhibited a higher short-circuit current (16.81 mA cm^{-2}).

Homoleptic dye such as N719 can absorb on TiO_2 using carboxylic anchoring groups residing on different bipyridines, whereas heteroleptic dyes necessarily adsorb *via* carboxylic groups residing on the same bipyridine. With this point, we designed and synthesized a novel mixed bipyridine ligand, MC112 complex (Fig. 1)[9], and the new design rule allows us to

unstable. In this way we reported two Ru(II) terpyridyl- based mixed ligand dyes, mLBD1 and mLBD2 (Fig. 1).[7] These two sensitizers exhibited better solar energy conversion efficiencies with good thermal stability as compared to the standard black dye.

engineer both light-harvesting and interfacial properties in the same dye. This sensitizer was used in DSSCs, yielding efficiency of 7.6% under standard AM 1.5 sunlight and an excellent device stability. The mixed bipyridine ligand allowed MC112 binding to TiO_2 to occur *via* three anchoring carboxylic groups, thus exhibiting similar interfacial properties to those of the N719 dye. DFT/TDDFT calculations were performed on the new dye revealing the peculiar photovoltaic properties of the MC112 dye are related to its anchoring mode.

However, there are still many problems to be addressed in terms of non-abundant Ru metal, its environmental issues and difficulty and high cost involved with purification of ruthenium complexes. On the other hand, Metal-free organic sensitizers can be synthesized rather inexpensively, and their absorption properties can be easily tuned by suitable molecular design. High extinction coefficients and expansion of the absorption into the near-IR region can be achieved with the well-known structure-property relationships of color chemistry. The theoretical calculations and computer simulations of photo physical properties of metal free organic

dyes are easier when compared to metal complexes like Ru and Os. Due to this reason a lot of effort has been paid to develop metal free organic dyes.

Most of the organic dyes have been constructed based on donor-spacer (π)-acceptor (D-π-A) like structure and usually have a rod-like configuration. This type of structure is favorable for photoinduced electron transfer from donor to acceptor through linker, to the conduction band of semiconductor, and also we can increase the light harvesting ability by extending the π-conjugation either increasing methine unit or by the introduction aromatic rings such as benzene, thiophene, furan *etc.* We can tune the photophysical properties of these organic dyes by varying donor, linker and acceptor groups. Record efficiencies up to 10.3% has been reported by using organic dyes.[10] Moreover in conjunction with transition metal-based electrolytes, organic dyes have been shown to clearly outperform Ru(II)-based dyes. The performance of organic dyes in DSCs can still be further enhanced. The photocurrent could be increased with a stronger optical response of the dyes in the near infrared (IR) region, and the photovoltage could be increased by blocking interfacial recombination between injected electrons in the mesoporous TiO_2 and the redox couple, which is substantial for some organic dyes.
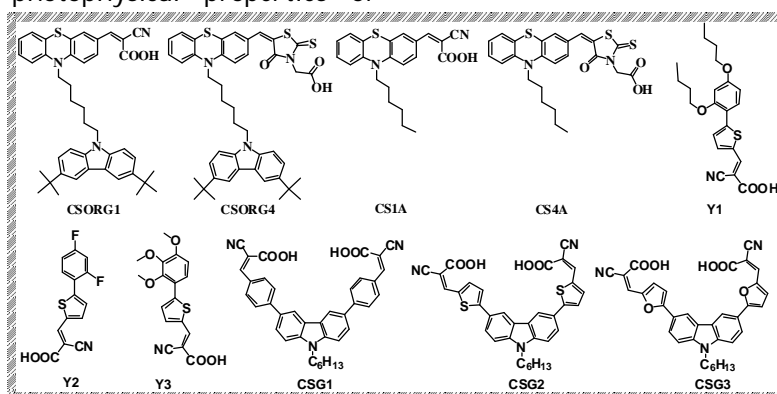

Figure 2: Organic sensitizers used in dye sensitized solar cell application

The advantages of organic dyes prompted us to design and synthesize two simplest organic dyes, coded as **Y**2 and **Y**3, (Fig. 2) for application in DSSCs.[11] The IPCE of the sensitizers **Y**2 and **Y**3 in a device reaching up to 67% and 82% were achieved. The organic sensitizer with 3,4,5-trimethoxy phenyl (**Y**3) as donor moiety obtained better conversion efficiency of 3.30% whereas the sensitizer **Y**2 showed comparatively lower efficiency of 1.02%. In contrast to reported sensitizers, these sensitizers are the simplest and particularly **Y**2 has fluorine substituted on donor moiety. The low η of **Y**2 is attributed to

the lack of absorption in the region >400 nm.

Organic dyes with a narrow spectral response have interesting applications as well. From a commercial point of view, DSSCs with a variety of colors allow for aesthetically appealing small-scale PV products or building-integrated PV panels. A combination of dyes with small absorption windows can also be used in cocktail DSSC systems, where the TiO_2 is co-sensitized by several dyes to achieve a panchromatic response.[12]

We succeeded in designing and synthesizing two small, simple donor–acceptor type co-adsorbents **Y**1 and **Y**2 (Fig. 2) and used as co-adsorbents in black dye based test cells.[13] Among the two, the novel co-adsorbent **Y**1 distinguished itself by integration of three advantages into one small and simple molecule: offsetting the competitive visible light absorption due to I_3^-, adjusting the distance between dyes to avoid aggregation, and reducing the recombination of electrons in the TiO_2 film. The distinct properties of co-adsorbent **Y**1, enabled DSSCs sensitized with black dye to perform with high efficiency. A public research center AIST certified the cell's efficiency to be 11.4%. These results emphasize the importance of the strategy that integrates multiple functions into one co-adsorbent to improve the device performance and will facilitate further improvement of efficient DSSCs through the enhancement of the IPCE in the IR wavelength region.

With the concept of Forster energy transfer (FRET),[14] we have reported the synthesis, photovoltaic characterization and computational modeling of two organic phenothiazine dyes, (Fig. 2) obtained by linking, *via* a hexyl chain, a donor carbazole (CZ) moiety to the phenotiazine (PTZ) core, which is anchored to the TiO_2 surface either through a cyanoacrylic acid (**CSORG**1) or a rhodanine-3-acetic acid (**CSORG**4).[15] The introduction of the CZ donor was shown to remarkably enhance the photovoltaic performances of the rhodanine-based dye (**CSORG**4), compared to the corresponding simple PTZ dye (**CS4A**), with more than a two-fold increase in the overall efficiencies. On the other side, the CZ did not bring beneficial effects in the case of the cyanoacrylic-based sensitizers, even yielding a slightly lower efficiency for **CSORG**1, compared to **CS1A**. Computational modeling studies confirm the possible occurrence of FRET from CZ to PTZ in both molecules, although with a possibly larger Förster radius (higher energy transfer rate) in the rhodanine-based dye, possibly accounting for the increase in the light absorption and the increase in the generated photocurrent in the $350-400$ nm window.

We also studied the optical properties of **CS1A** in two distinct solvents such as DCM, THF and also

on TiO_2 respectively.[16] The UV-Visible absorption spectra of **CS1A** recorded in THF solution, presents two bands centered at 438 and 316 nm. When changing the solvent from THF to DCM, the main absorption peak shifted to 463 nm. Upon adsorption of **CS1A** onto TiO_2, the main visible absorption band appears slightly broadened and red-shifted, with an λ_{max} at 442 nm. Such shifts can either be originated from aggregation of surface adsorbed dye and/or solvatochromism in the initial dye solution. These results suggest that salvation plays a major role in determining the optical properties of this class of organic dyes. Understanding the origin of these spectral changes along with their possible effect on charge-transfer properties is important for the further improvement of DSSCs, allowing the design of more efficient dyes, which minimize the use of antiaggregating coadsorbents.

In another case we designed and synthesized three metal-free organic di-anchoring dyes (**CSG**1–**CSG**3) (Fig. 2) for application in DSSCs.[17] These dyes share the CZ moiety and cyanoacrylic acid as the common electron donor and anchoring group with different linker moieties such as benzene, thiophene, or furan. In this case we observed that the η's were sensitive to the π-bridging linker moiety. The results based on photovoltaic experiments show that dye with a benzene linker exhibit a higher open-circuit voltage compared to thiophene and furan linker. Among the three dyes, DSSCs based on thiopene linker exhibited the best overall conversion efficiency.

This study demonstrates that a proper molecular design, by accurate selection of donor, π-linker, acceptor and anchoring groups, combined with a high-level computational modeling of the structural and optical/electronic properties of the dye-sensitized interface, may provide remarkable advances toward the high efficiency.

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