Molecular engineering of carbazole functionalized ruthenium dyes for efficient dye-sensitized solar cells

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Abstract
A new ruthenium complex, coded HMP-12, incorporating an antenna ligand composed of the sequential connection of a conjugated segment and carbazole hole-transport moiety was synthesized. This dye exhibits a lower energy metal-to-ligand charge transfer (MLCT) band centered at 536 nm with a high molar absorption coefficient of \(21.43 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}\). Nanocrystalline ZnO dye-sensitized solar cells employing HMP-12 show good conversion efficiency (4.46%). It was found that the difference in light-harvesting properties between Rut-B1, HMP-11 and HMP-12 is associated mainly with dye structure. The power conversion efficiency of solar cells based on HMP-11 is 4.11% while the Rut-B1 delivered a lower efficiency of 3.57% under the same device fabrication and measuring conditions.

Keywords: dye-sensitized solar cells, ruthenium complexes, conjugated ligands

Classification numbers: 6.03, 6.04

1. Introduction

Increasing energy demand and concerns about climate changes have led to a focus on renewable energy sources in recent years. Dye-sensitized solar cells (DSSCs) have attracted much interest for their high performance in converting solar energy to electricity at low cost [1]. The photosensitizer plays an important role in determining the stability, light-harvesting capability and the total cost of DSSCs. Presently the most important photosensitizers are ruthenium dyes [2, 3], yielding up to 11.3% [4]. Progress in optimizing the ruthenium-based sensitizers for DSSCs has mainly focused on enhancing the light-harvesting ability to match the solar irradiation [5] and on multiplying the specific functionalities for improving the thermal resistance [6] or retaining the photoinduced interfacial charge separation between the dye-sensitized n-type semiconductor and electrolyte [7].

Recently, efficient ruthenium sensitizers endowed with an ancillary ligand consisting of a conjugated segment and a carbazole hole-transporting unit have enhanced the spectral response and therefore the conversion efficiency of the DSSCs based on them [8, 9].

To further improve the light harvesting capacity of this class of sensitizers and at the same time test the merit of the carbazole-containing ruthenium dyes, we have designed a new ruthenium sensitizer cis-[Ru(H\(_2\)dcbypy)(L)(NCS)]\(_2\), coded HMP-12 (figure 1), endowed with a similar antenna function, where H\(_2\)dcbypy=4,4'-dicarboxylic acid-2,2'-bipyridine and L=4,4'-bis-[4-(3,6-dimethoxy-N-carbazolyl)-phenyl-2-vinyl]-2,2'-bipyridine. The photovoltaic performance of HMP-12 in DSSCs was investigated and compared with previous dyes.

2. Experimental

2.1. Materials and instrumentation

All materials were reagent grade and were used as received. All synthetic reactions were carried out under a nitrogen atmosphere unless otherwise noted. Solvents were purified...
according to the published methods. TiO$_2$ nanoparticles were purchased from Solaronix S A (Nanoxide-T, Lausanne, Switzerland). Fluorine-doped tin oxide (FTO) electrodes with a sheet resistance of 8 $\Omega$ per square were supplied by Samsung Corning Co., Korea. $^1$H-NMR spectra were recorded on a Varian INOVA 400 MHz NMR spectrometer in chloroform-d (CDCl$_3$) or dimethylsulfoxide-d$_6$ (DMSO-d$_6$). Electrospray ionization mass spectrometry (ESI-MS) was performed on a Hewlett-Packard 1100 liquid chromatography/mass spectrometry (HP 1100 LC/MS) system with acetonitrile as solvent and fast atom bombardment mass spectrometry (FAB-MS) on a JMS-700 high resolution mass spectrometry (JMS-700 HRMS) instrument. Absorption spectra were recorded on an OPTIZEN 2120 UV-Vis spectrophotometer. The electrochemical measurements were performed under nitrogen atmosphere and the electrolyte used was 0.1 M tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$) in acetonitrile. Cyclic voltammetry (CV) was recorded using a three-electrode system consisting of Ag/Ag$^+$ (0.01 M AgNO$_3$, 0.1 M Bu$_4$NBF$_4$, CH$_3$CN) as the reference electrode, a platinum wire as counter electrode and a FTO/TiO$_2$/Dye photoelectrode as the working electrode. All potentials are calibrated by the ferrocene/ferrocenium (Fc/Fc$^+$) couple potential ($E = +212$ mV versus Ag/AgNO$_3$).

2.2. Solar cell fabrication

Photoanodes of the DSSCs were prepared from a colloidal suspension of nanosized TiO$_2$ particles (Nanoxide-T, Solaronix, average size of 20 nm) by a doctor blade technique. The electrodes were sintered at 500 $^\circ$C for 30 min in air to obtain TiO$_2$ films with thickness of 8 $\mu$m measured by a Dektek 6M Stylus Profiler. These electrodes were immersed in solution containing 0.5 mM of ruthenium dye for one day while still hot (80 $^\circ$C). Chenodeoxycholic acid (1 mM) was added into the dye solution as a coadsorbent to prevent dye aggregation [10]. Solvents for the dye solutions were DMF:$t$-BuOH (3 : 7) for Rut-B1, tetrahydrofuran (THF) for HMP-11, and CH$_3$CN:$t$-BuOH (1 : 1) for HMP-12. Platinum-coated counter electrodes were prepared by spreading a drop of $5 \times 10^{-3}$ M H$_2$PtCl$_6$ (Fluka) solution in isopropanol on the surface of FTO glass and were treated in an oven at 400 $^\circ$C for 15 min. The two electrodes were assembled using 25 $\mu$m thick Surlyn polymer (Dupont, 1702) and held tightly at 120–130 $^\circ$C to seal the cell. The electrolyte was composed of 0.1 M lithium iodide, 0.1 M iodine, 0.5 M 4-$t$-butylpyridine and 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide in acetonitrile. The photovoltaic characterization was carried out by illuminating the cell with a 1000 W Xenon lamp (Spectra-Physics) as a solar simulator. The light source was calibrated to 100 mW cm$^{-2}$ by a National Renewable Energy Laboratory (NREL) standard, Si solar cell equipped with a KG-5 filter to approximate AM 1.5G light intensity. An active area of about 0.32 cm$^2$ was irradiated. The current-voltage curves were obtained by measuring the photocurrent of the cell using a Keithley mode 2400 digital source meter (Keithley, USA) under an applied external potential scan.

3. Results and discussion

The electronic absorption spectra of Rut-B1, HMP-11 and HMP-12 measured in dimethylformamide DMF are given in figure 2. HMP-12 shows three absorption bands centered at 295, 374 and 536 nm, respectively. The band at 295 nm is assigned to the overlap of intraligand $\pi-\pi^*$ transitions
of 4,4′-dicarboxylic acid-2,2′-bipyridyl anchoring ligand and that of the ancillary ligand [11]. Another band centered at 374 nm also contains two components: the π−π* transition of the ancillary ligand and one of the metal-to-ligand charge transfer (MLCT) transition for HMP-12. The molar extinction coefficient (ε) of the lower energy MLCT band centered at 536 nm is 21.43 × 10^3 (M−1 cm−1). Compared to its predecessor, HMP-11, the ε value of HMP-12 is similar. Both HMP-11 and HMP-12 show red shift of maximum absorption and higher extinction coefficients of the MLCT band than those of Rut-B1 due to the second N-phenyl carbazole attached to the ancillary ligand, increasing both the electron donating ability and extension of π-conjugation of ancillary ligands. The absorption and electrochemical data are summarized in table 1.

DSSC devices based on a nanostructured TiO2 electrode, using HMP-12 sensitizer, were characterized by a J−V curve and compared with HMP-11 and Rut-B1 (figure 3). Photovoltaic parameters are summarized in table 2.

The DSSC device based on HMP-11 provides a short circuit current density (JSC) of 9.06 mA cm−2, an open circuit voltage (VOC) of 0.63 V, and a fill factor (FF) of 0.716, yielding an overall conversion efficiency of 4.11% under illumination with AM 1.5G light intensity (100 mW cm−2). Under the same condition, the efficiency obtained with the Rut-B1 sensitized cell is only 3.57%, the JSC, VOC and FF being 7.64 mA cm−2, 0.64 V and 0.731, respectively. The major difference in the photovoltaic performance between these two cells is the JSC, and this arises from the higher peak molar extinction coefficient of HMP-11 compared to that of Rut-B1 and a red shift in the absorption. The HMP-11 with one more N-phenyl carbazole donor attached to the ancillary ligand shows a positive effect on the device performance. The enhanced extinction coefficient due to the extension of conjugation length provides a possible way to improve the power conversion efficiency of DSSCs.

We also compared the photovoltaic performance of the HMP-12 with HMP-11 dye. The JSC of the two devices are similar but HMP-12 shows higher VOC (0.68 V) than that of HMP-11 resulting in improved efficiency from 4.11 to 4.46%. The ancillary ligand of HMP-12 contains methoxy substituents at the 3, 6 positions of carbazole moieties as a modification of HMP-11 dye. This modification implies the retardation of the charge recombination between injected electron and electron acceptor (I3−) in the electrolyte, resulting in improved open circuit voltage (VOC) of DSSCs based on HMP-12 (0.68 V). Attaching methoxy substituents on carbazole further optimizes the structure of the ruthenium dye.

4. Conclusion

In summary, we have reported a new ruthenium sensitizer, HMP-12, with an antenna consisting of the electron-rich alkyl-substituted carbazole. The cell based on this new sensitizer with a volatile liquid electrolyte exhibits a 4.46% conversion efficiency under AM 1.5G light intensity. This cell shows enhanced VOC compared to that of HMP-11 and both VOC and JSC compared to those of Rut-B1. By optimizing the structures of ruthenium complexes, new sensitizers could be investigated with increased molar extinction coefficients, effective charge recombination suppression and favorable energy levels.

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References

[1] O’Regan B and Grätzel M 1991 Nature 353 737
[2] Kay A, Nazeeruddin M K, Rodicio I, Humphry-Baker R, Muller E, Linska P, Vlachopoulos N and Grätzel M 1993 J. Am. Chem. Soc. 115 6382
[3] Chen C Y, Wu S J, Wu C G, Chen J G and Ho K C 2007 Adv. Mater. 19 3888
[4] Gao F, Wang Y, Shi D, Zhang J, Wang M, Jing X, Humphry-Baker R, Wang P, Zakeeruddin S M and Grätzel M 2008 J. Am. Chem. Soc. 130 10720
[5] Gao F, Wang Y, Zhang J, Shi D, Wang M, Humphry-Baker R, Wang P, Zakeeruddin S M and Grätzel M 2008 Chem. Commun. 23 2635
[6] Wang P, Klein C, Humphry-Baker R, Zakeeruddin S M and Grätzel M 2005 J. Am. Chem. Soc. 127 808
[7] Handa S, Wietasch H, Thelakkat M, Durrant J R and Haque S A 2007 Chem. Commun. 17 1725
Nguyen H M, Nguyen D N and Kim N J 2010 Adv. Nat. Sci.: Nanosci. Nanotechnol. 1 025001
[8] Chen C Y, Chen J G, Wu S J, Li J Y, Wu C G and Ho K C 2008 Angew. Chem. 120 7452
Nguyen H M, Choi J W, Heo J H, Oh J W, Nguyen D N and Kim N J 2010 J. Nanosci. Nanotechnol. 10 6811
[9] Chen C Y, Pootrakulchote N, Wu S J, Wang M, Li J Y, Tsai J H, Wu C G, Zakeeruddin S M and Grätzel M 2009 J. Phys. Chem. C 113 20752
[10] Kay A and Grätzel M 1993 J. Phys. Chem. 97 6272
[11] Balzani V, Juris A, Venturi M, Campagna S and Serroni S 1996 Chem. Rev. 96 759
[12] Chen C Y, Lu H C, Wu C G, Chen J G and Ho K C 2007 Adv. Funct. Mater. 17 29