

A novel ruthenium sensitizer with a hydrophobic 2-thiophen-2-yl-vinyl-conjugated bipyridyl ligand for effective dye sensitized TiO₂ solar cells

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A hydrophobic and 2-thiophen-2-yl-vinyl-conjugated ruthenium complex, *cis*-Ru(dhtbpy)(dcbpy)(NCS)₂ [dhtbpy = 4,4'-di(hexylthienylvinyl)-2,2'-bipyridyl; dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl], was newly designed, synthesized and applied successfully to sensitization of nanocrystalline TiO₂-based solar cells, giving a conversion efficiency of 9.5% under irradiation with AM 1.5 solar light.

Dye-sensitized nanocrystalline TiO₂ solar cells (DSCs) have attracted considerable interest because of their high conversion of sunlight to electricity and low production and material cost.^{1,2} In these DSCs, sensitizing dye molecules must be chemically adsorbed on the porous nanocrystalline TiO₂ surfaces, and harvest solar light ranging from the UV to visible and near-IR regions just like photovoltaic semiconductor diode interfaces. Up to now, the most investigated efficient sensitizers are ruthenium complexes,^{3–6} which show effective charge separation at the metal to ligand (Ru-bpy) and ligand to metal (SCN–Ru) absorption bands in the visible solar light region. Among the ruthenium sensitizers, the fairly stable N719 dye (Bu₄N)₂[Ru(dcbpyH)₂(NCS)₂] has the highest efficiency for solar power conversion in DSCs.⁷ In addition, as exemplified by Z907, the introduction of a long hydrophobic alkyl group to the ruthenium sensitizing dye molecules resulted in thermal and long-term stability.⁶

On the other hand, some organic dye sensitizers have been developed for DSCs, giving respectable incident photon to current efficiency (IPCE) partly due to the high molar extinction coefficient of the conjugated π -bonds coupled with the aromatic ring.⁸ Our strategy of designing sensitizing molecules is to introduce a π -conjugated group into the ruthenium complex sensitizers as a kind of hybrid of a ruthenium sensitizer with an organic sensitizer. The noteworthy dye K-19, which was developed by Grätzel's group,⁹ can be regarded as a hybridized ruthenium sensitizer composed of dcbpy, SCN and the bpy conjugated with phenylenevinylene groups. Such a bpy ligand enables the π -conjugation to extend through the complexes, giving higher molar extinction coefficients when compared to N3 and N719. With these viewpoints in mind, we successfully designed a new bpy ligand, 4,4'-di(hexylthienylvinyl)-2,2'-bipyridyl, to replace one of the dcbpy ligands in the N3 ruthenium sensitizer,³ Ru(dcbpyH)₂(NCS)₂. The resulting new hybridized ruthenium sensitizer (coded

HRS-1, Fig. 1) showed excellent IPCE in the wider visible region. The DSC fabricated using HRS-1 as a sensitizer presents higher light to electron conversion efficiency compared to that using the N719 sensitizer under comparable conditions.

The new ligand, 4,4'-di(hexylthienylvinyl)-2,2'-bipyridyl, was prepared by deprotonation of 4,4'-dimethyl-2,2'-bipyridyl followed by addition of 5-hexylthiophene-2-carbaldehyde. For the synthesis of HRS-1 dye, microwave assisted one-pot synthetic procedures were successfully employed as follows: under MW irradiation in the dark, 4,4'-di(hexylthienylvinyl)-2,2'-bipyridine and dichloro(*p*-cymene)ruthenium(II) dimer were heated in DMF¹⁰ at 70 °C for 10 min. To this solution was added 4,4'-dicarboxy-2,2'-bipyridyl, and the mixture was MW-irradiated for another 10 min. Finally, NH₄SCN was added and the reaction was MW-irradiated for 10 min. After evaporation of DMF, water was added to the residue, and the solid was filtered and washed with water. The resulting crude product was dissolved in tetrabutylammonium hydroxide (TBAOH)-methanol solution, and purified on Sephadex LH-20 with methanol as eluent. The main band was collected and acidified to get the precipitate, which was filtered, washed with water and analyzed.

Fig. 2 shows the electronic absorption spectra of HRS-1 and standard N719 sensitizers in ethanol. The spectrum of the HRS-1 sensitizer shows two absorption peaks at 371 and 542 nm in the visible region, which are due to metal to ligand charge transfer transitions (MLCT). The molar extinction coefficients of these two bands are 42.4×10^3 and 18.7×10^3 M cm⁻¹, respectively. The molar extinction coefficient of the lowest energy absorption band of sensitizer HRS-1 increases by 33% and its absorption maximum wavelength is red-shifted about 10 nm when compared with that of sensitizer N719. Such high molar extinction coefficients and red shift result from the extension of the π -conjugation in the complex due to the introduction of two hexylthienylvinyl moieties on one of the bipyridyl ligands.

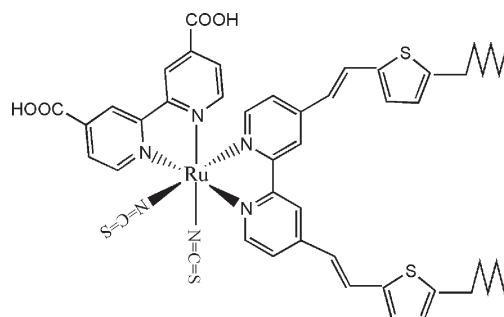


Fig. 1 Molecular structure of the new sensitizer, HRS-1.

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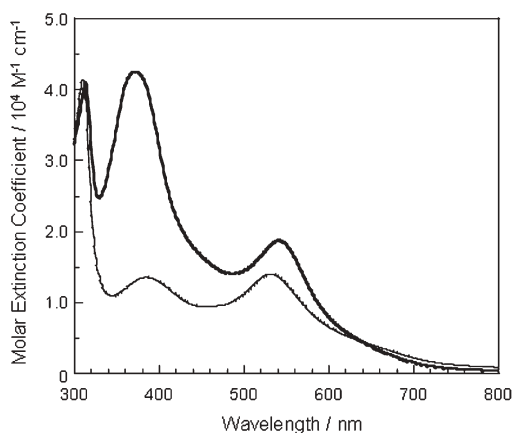


Fig. 2 Absorption spectra of the HRS-1 sensitizer (bold line) and standard N719 sensitizer (thin line) in ethanol.

The oxidation potential of HRS-1 was obtained using a Pt electrode in DMF with 0.1 M tetrabutylammonium perchlorate. The HRS-1 dye molecule revealed a reversible, one-electron oxidation process at $E_{1/2} = 0.34$ V *versus* the ferrocene/ferrocenium couple (Fc/Fc⁺). The potential is shifted cathodically by 0.11 V, compared to that of the N719 molecule. This reversibility of the ruthenium(III)/(II) couple in HRS-1 will contribute to its stability when employed in DSCs. The difference in oxidation potential between HRS-1 and N719 is attributed to the electron-donating properties of the thienyl groups in the 4,4'-di(hexylthienylvinyl)-2,2'-bipyridyl ligand.

For preparation of the photoelectrochemical devices, two layers of TiO₂, a main layer and a scattering layer, were prepared by screen printing TiO₂ pastes on a fluorine-doped SnO₂ conducting glass substrate (FTO, 10 Ω □⁻¹, Nippon Sheet Glass). The main layer (thickness: 12 μm, TiO₂ particle size: 20 nm) and the scattering layer (thickness: 4 μm, TiO₂ particle size: 400 nm, purchased from Catalysts & Chemicals Ind. Co., Ltd. (CCIC) in Japan) were prepared from two different TiO₂ colloids. The TiO₂ colloid with an average TiO₂ particle size of 20 nm was prepared by hydrolyzing titanium tetraisopropoxide in the presence of acetic acid, followed by autoclaving with a little nitric acid at 250 °C for 12 h as described in the literature.¹¹ The first layer of TiO₂ was heated at 450 °C for 30 min. after coating, and the second layer was heated at 520 °C for 20 min. The resulting film was further treated with 0.04 M TiCl₄ aqueous solution as reported.¹² The dye solutions were prepared in a 1 : 1 v/v acetonitrile-*tert*-butyl alcohol solvent mixture at a concentration of 0.3 mM. For the HRS-1 dye solution, 2 mM chenodeoxycholic acid was added to the dye solution to prevent HRS-1 molecular aggregation during adsorption on the TiO₂ surface. For comparison, N719 was chosen as a standard sensitizer. Sintered TiO₂ electrodes were placed and left in the dye solution at room temperature for 20 h. Pt-sputtered FTO glass was used as a counter electrode. An electrolyte composed of 0.1 M LiI, 0.05 M I₂, 0.6 M 1-propyl-3-methylimidazolium iodide, and 0.5 M *tert*-butylpyridine in a mixture of acetonitrile and valeronitrile (1 : 1, v/v) was employed for DSC fabrication.

The photovoltaic performance of the devices were recorded under irradiation with AM 1.5 (100 mW cm⁻²) simulated solar light (YSS-50A, Yamashita Denso Co. Ltd.) as shown in Fig. 3.

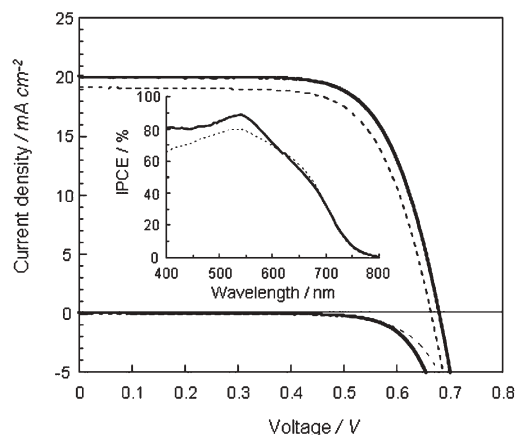


Fig. 3 Photocurrent density–voltage curves of the dye-sensitized solar cells sensitized with HRS-1 (bold) or N719 (dotted) measured under AM 1.5 light illumination (100 mW cm⁻²). The inset is the photocurrent action spectrum of the cells.

The active area was 0.14 cm² without employing a mask. The inset in Fig. 3 shows the action spectrum of monochromatic incident photo to current conversion efficiencies (IPCE) for DSCs with the HRS-1 and N719 sensitizers. Note that the IPCE value of the cell using N719 is somewhat lower compared to the short-circuit photocurrent density (J_{sc}) appearing in the I - V curve since the cells are not the same. In the case of sensitizer HRS-1, IPCE values of more than 80% were observed in the range up to 575 nm with maximum peaks at around 540 nm. When reflection and absorption losses of the FTO glass substrate are considered, the net conversion efficiency in this range is almost unity.

The photovoltaic performances of DSCs with these sensitizers are listed in Table 1. The short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (ff) of the device with the HRS-1 sensitizer under AM 1.5 (100 mW cm⁻²) irradiation are 20 mA cm⁻², 0.68 V, and 0.69, respectively, which gives an overall conversion efficiency (η) of 9.5%. From the Table, we can find that the devices for the two sensitizers present similar values of open-circuit voltage and fill factor. When J_{sc} is compared to those of N719 based DSCs, the device with sensitizer HRS-1 shows a higher value, which may be partly ascribed to the increase in molecular extinction coefficient and the red shift in the absorption spectrum. Although N719 based DSCs still has the highest conversion efficiency, up to 10–11%,⁷ the higher conversion efficiency for the HRS-1 based device will be expected if an anti-reflector layer is employed to increase the light harvesting on the glass surface, and the TiO₂ electrode structure and electrolyte composition are further optimized.¹² As reported by Wang *et al.*,⁹ the N719-based DSCs presented poorer long term stability under

Table 1 Photovoltaic performance of DSCs under AM 1.5 light illumination (100 mW cm⁻²) with N719 and HRS-1 as sensitizer, respectively

Sensitizer	V_{oc}/V	$J_{sc}/\text{mA cm}^{-2}$	ff	η (%)
N719	0.66 ± 0.020	19 ± 0.3	0.70 ± 0.007	8.9 ± 0.22
HRS-1	0.68 ± 0.003	20 ± 0.5	0.69 ± 0.006	9.5 ± 0.24

prolonged thermal stress and light illumination. This was explained as dye desorption from the surface of the TiO₂ electrodes. Now it is well known that the presence of a hydrophobic moiety on the bipyridyl ligand in ruthenium sensitizers can effectively prevent water-induced desorption of the sensitizing molecules. The two hydrophobic hexyl chains on the HRS-1 molecule can effectively hinder water molecule penetration into the interface of the HRS-1 molecules and TiO₂, leading to the long-term stability of DSC devices. Preliminary tests showed that the color of the HRS-1 sensitized TiO₂ film remains almost unchanged for several hours, even in dilute aqueous sodium hydroxide solution, while the color of N719-dyed TiO₂ electrodes disappeared immediately under the same conditions.

In conclusion, the novel 2-thiophen-2-yl-vinyl conjugated ruthenium sensitizer (HRS-1) shows respectable light harvesting performance in the visible-light region, and a reversible, one-electron oxidation process. The HRS-1 based DSCs give a higher solar light to electricity conversion efficiency compared to N719-based DSCs under comparable conditions.†

Notes and references

† 4,4'-Di(hexylthienylvinyl)-2,2'-bipyridine: light yellow powder, ¹H NMR (CD₃COCD₃): δ 8.62 (d, 2H), 8.57 (s, 1H), 7.72 (d, 2H), 7.53 (d, 2H), 7.18 (d, 2H), 6.95 (d, 2H), 6.83 (2H). HRS-1 complex: black powder, ¹H NMR (DMSO-d₆) in the aromatic region: δ 9.44 (d, 1H), 9.16 (d, 1H), 8.97 (s, 1H), 8.83 (s, 1H), 8.79 (s, 1H), 8.69 (s, 1H), 8.24 (d, 1H), 8.00 (d, 1H), 7.97 (d, 1H), 7.87 (d, 1H), 7.78 (d, 1H), 7.72 (d, 1H), 7.58 (d, 1H), 7.36 (d, 1H), 7.27 (d, 1H), 7.14 (d, 1H), 7.09 (d, 1H), 6.90 (d, 1H), 6.82 (d, 1H), 6.80 (d, 1H). MS-ESI *m/z*: 1001.5 (M – H)⁺.

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