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Synthesis and characterization of cross-linkable ruthenium dye with ion coordinating property for dye-sensitized solar cells

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ABSTRACT

Crosslinkable ruthenium complex dye, Ru(2,2'-bipyridine-4,4'-bicarboxylic acid)(4,4'-bis((4-vinyl benzyloxy)methyl)-2,2'-bipyridine)(NCS)₂ (denoted as Ru-S dye), was synthesized and characterized using ¹H-NMR, ¹³C-NMR, Fourier transform infrared (FTIR) and UV/vis spectroscopies.The power conversion efficiency of dye-sentitized solar cell (DSSC) using Ru-S and liquid electrolyte containing lithium iodide (LiI) reached 7.53% under standard global AM 1.5 full sunlight, which is partly attributed to Li⁺ being coordinated by Ru-S as verified by ATR-FTIR spectroscopy. As Ru-S was further crosslinked with glycerol propoxylate triacrylate (GPTA), not only 89% of dye retained on TiO₂ mesoporous surface after rinsed by 0.1 N NaOH aqueous solution, the power efficiency was also increased to 7.88%. As poly(methyl acrylate) was used to gel the electrolyte system, the power efficiency of DSSC with Ru-S dye was 6.96% but increased to 7.57% after crosslinking with GPTA. Notably, both DSSCs showed a good long-term stability after one month storage.

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1. Introduction

Mesoscopic dve sensitized solar cells (DSSC) reported in 1991 by O'Regan and Grätzel [1] have attracted intensive interest due to their flexibility of device design, relatively high conversion efficiency and inexpensive fabrication processes compared to the amorphous silicon solar cells. To improve the photovoltaic performance of the DSSC, great effort has been paid to the development of sensitizers, electrolytes, and photoanode materials [2-7]. Various structural modifications to the ruthenium dye have been attempted, such as tethering additional conjugate moieties on bipyridyl ligand for increasing the light absorption and tethering hydrophobic aliphatic long chains on bipyridyl ligand for prolonging the service life [8-14]. Recently, to overcome the desorption problem of ruthenium dyes from TiO2 mesoporous surface, a crosslinkable ruthenium dye with aliphatic side chains carrying allyl end groups on one of the bipyridyl ligands has been synthesized [15]. However, owing to the low reactivity of allyl groups, as it was crosslinked with methyl acrylic acid (MAA), the dye only retained 77% on the TiO₂ mesoporous surface after immersion in 0.1 N NaOH solution, which is typically employed to remove the ruthenium dye for the measurement of dye content on the TiO_2 mesoporous layer.Besides, because the aliphatic side chains are too long, they tend to retard the dye adsorption on TiO_2 and hinder the dye regeneration process upon excitation by sunlight. The power conversion efficiency of DSSC using Ru-C dye is only 5.18% [15].

It has been frequently reported that the presence of lithium cations (Li⁺) in the liquid electrolyte is capable of increasing the photocurrent of DSSCs [16–20]. However, because the surface of TiO₂ mesoporous film is negatively charged during operation of DSSC, Li⁺ may intercalate or adsorb onto the surface of TiO₂ layer, resulting in a positive shift of the TiO₂ conduction band and consequently causing a dramatic drop of open-circuit voltage for the cell [21]. To refraining Li⁺ from the TiO₂ surface adsorption, the ruthenium sensitizers were often designed with the ethylene oxide groups tethering on one of their bipyridyl ligands to coordinate Li⁺ [22–24]. For example, the ruthenium dye with a bipyridine ligand tethering two triethyleneoxide methyl ether groups, denoted as K51 [21]. However, because the triethyleneoxide methyl ether groups are hydrophilic, K51 dye is highly soluble in polar solvent.

In this contribution, we designed a novel ion-coordinating crosslinkable ruthenium dye system, which contains an ion-coordinating crosslinkable Ru(2,2'-bipyridine- 4,4'-bicarboxylic acid)(4,4'-bis((4-vinyl benzyloxy)methyl)-2,2'- bipyridine)(NCS)₂, denoted as Ru-S and glycerol propoxylate triacrylate (GPTA), an ion-coordinating crosslinker with the chemical structure shown below





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Ru-S carries two styryl crosslinkable groups which are an electron donor, whereas GPTA carries three acrylic groups, an electron acceptor. The crosslinking reaction rate will be increased if they form a charge–transfer complex [25]. The power conversion efficiency of dye-sentitized solar cell (DSSC) using Ru-S and liquid electrolyte containing lithium iodide (LiI) reached 7.53% under standard global AM 1.5 full sunlight. As Ru-S was crosslinked with GPTA (the product is designated as Ru-S-cross-GPTA), not only 89% of dye retained on TiO₂ surface as compared to 28% of uncrosslinked Ru-S after immersion in 0.1 N NaOH aqueous solution, but the power efficiency was also increased to 7.88%.

2. Experimental section

2.1. Materials

All solvents and chemicals were obtained from Acros and Aldrich. Ru-S was synthesized on the basis of typical one-pot synthetic method developed for heteroleptic polypyridyl ruthenium complexes [26]. The synthesis scheme is illustrated in Fig. 1 with the detail synthesis procedure shown in the supporting information.

2.2. Fabrication of DSSCs

DSSCs were fabricated using fluorine-doped tin oxide (FTO) glass (20–25 Ω /sq) as a substrate for photoelectrode. A mesoporous anatase TiO₂ layer coated on the FTO glass was prepared by sol-gel process as suggested in the literature [27]. In general, 72 mL titanium tetraisopropoxide (TTIP) was added to 430 mL of 0.1 M HNO₃. After vigorously stirring for 30 min, the solution was heated to 85–90 °C and kept stirring for 8 h for peptization. After filtering to remove the large particles, the solution was placed in an autoclave for reaction at 240 °C for 12 h. After cooling, it was concentrated to 13 wt% of TiO₂. Poly(ethylene glycol) was then added to the solution in 30 wt% of TiO₂ weight. After further stirring for 5 h to obtain TiO₂ paste, it was spread on the FTO glass subtract using a glass rod and an adhesive tape was used as a spacer to control the thickness to \sim 120 µm. The photoelectrode was obtained by heating the dried TiO₂ paste on the FTO glass in an oven at 450 °C for 30 min and repeating the coating and heating process two more times to complete the sintering process.

An active area of 0.25 cm² was selected from the TiO₂ sintered electrode, immersed in a solution of acetonitrile and tertiary butanol (volume ratio of 1:1) containing 3×10^{-4} M of Ru-S for 24 h, rinsed with acetone, and dried. To crosslink Ru-S with GPTA in optimal practice condition, two drops of 1×10^{-3} M GPTA mixing with 1×10^{-4} M azobisisobutyronitrile (AIBN) in acetonitrile were applied on top of the Ru-S layer. The crosslinking reaction was immediately performed under UV exposure at 300 W m⁻² for 1 min followed by heating at 80 °C for 30 min. The counter electrode was fabricated by sputtering a thin Pt layer with a thickness of ~ 100 nm



Fig. 1. Synthesis scheme of Ru-S.



on indium tin oxide (ITO, with a sheet resistivity of 8–10 $\Omega/sq)$ glass plate.

The liquid electrolyte systems containing $0 \sim 0.2$ M LiI and $0.5 \sim 0.7$ M 1-methyl-3-propyl-imidazolium iodide (PMII), 0.05 M I₂, 0.5 M 4-*tert*-butylpyridine (TBP) and 0.1 M guanidinium thiocyanate (GuNCS) in 3-methoxypropylnitrile (MPN) were applied to the dye-sensitized electrode. To fix the total concentration of I⁻ ions in MPN at 0.7 M, the concentration of PMII was varied responding to the alteration of LiI concentration. The thickness of liquid electrolytes was controlled at 60 µm using a spacer. The assembly of DSSCs was done by pressing the counter electrode against the electrolyte-filled dye-sensitized electrode.

On the other hand, PMA latex powder prepared by soap-free emulsion polymerization [28–30] was used to gel the liquid electrolyte system at an amount of ~25 vol% of MPN. The final concentrations of PMA-gelled electrolyte system were 0.5 M Lil, 0.05 M I₂, and 0.5 M TBP. To seal the DSSCs, a hot melt sealing foil SX1170-60 (SOLARONIX) was center-cut and placed on top of the counter electrode to form a frame for enclosing the coated dye, and then the photoelectrode was placed on top of the frame. Both electrodes were assembled by melting the sealing foil with heat.

The gelled electrolyte system after heating to fluid was injected from a small filling hole which was pre-drilled on the counter electrode. At last, the filling hole was sealed with hot melt foil.

2.3. Analytical methods

Nuclear magnetic resonance spectra were recorded on a Bruker AVANCE 500 spectrometer at 298 K by utilizing deuterated chloroform and dimethyl sulphoxide (d₆-DMSO) as solvents. Elemental analysis was conducted by HERAEUS VarioEL EA, NCH elemental analysis instrument. UV-vis absorption spectra were recorded on a Jasco model 555 spectrometer. Fourier-transform infrared (FT-IR) spectra were recorded on a Jasco model 480 Fourier-transform infrared spectrometer and ATR-FTIR spectra were recorded on a ThermoNicolet NEXUS470 Fourier-transform infrared spectrometer. Photovoltaic characterization of all the DSSCs was carried out by illuminating the cell at full sunlight (100 mW cm^{-2}) with a 1000 W ozone-free Xenon lamp equipped with a water-based IR filter and AM 1.5 filter (Newport). The open-circuit voltage (V_{oc}) and photocurrent-voltage characterization plots were recorded with a potentiostat/galvanostat (PGSTAT 302N, Autolab, Eco-Chemie, the Netherlands).

3. Result and discussion

3.1. Characterization and crosslinking property of Ru-S

Fig. 2 shows the ¹H NMR spectrum of Ru-S with the enlarged aromatic region and asigned proton peaks. Due to different electronical environment, the symmetrical pyridyl ring protons in a bipyridine ligand have two different reasonance peaks, indicating that the ligands are coordinated to ruthenium ion in *cis*-hetero-leptic complex form [31]. The vinyl protons of styryl groups can be clearly observed at δ = 5.24, 5.82, and 6.72 ppm. Fig. 3 shows the ¹³C NMR spectrum of Ru-S with the asigned carbons for the aromatic, carboxlic acid, –NCS and styryl groups. Twenty resonance peaks in the aromatic region from two bipyridine ligands, twelve peaks from two stryrl benzen rings, two peaks from two carboxylic acids, and two peaks from two –NCS groups also supported that the ligands are coordinated to ruthenium ion in *cis* form. The resonance



Fig. 3. ¹³C-NMR spectrum of Ru-S.



Fig. 4. FTIR spectra of Ru-S before and after crosslinked with AIBN initiator.

peaks at $\delta = 114$ and 136 ppm were contribued by the vinyl carbons of styryl groups.

FTIR spectrum of Ru-S in KBr pallet is shown in Fig. 4. The absorption band observed at 2100 cm⁻¹ was contributed by the stretching of –NSC groups and that at 1730 cm⁻¹ was contributed by carboxylic acid groups. The absorption bands contributed by the vinyl groups of Ru-S dye can be clearly seen at 910 and 3070 cm⁻¹. To investigate the reactivity of vinyl groups, a drop of the Ru-S solution with AIBN initiator (1 mol% of Ru-S) in acetonitrile was placed on the glass slide, which was immediately polymerized under UV exposure at 300 W m^{-2} for 1 min and followed by heating at 80 °C for 30 min to remove the remaining solvent. The crosslinked Ru-S which could not be dissolved in any solvent was ground with KBr for FTIR measurement. Compared to the untreated Ru-S by normalizing the spectrum to the major absorption band at 2100 cm^{-1} (see Fig. 4), the vinyl peaks at 910 and 3070 cm⁻¹ were significantly reduced, and the peaks at 2852 cm^{-1} and 2930 cm^{-1} contributed by -CH- and -CH₂- appeared, indicating that the vinyl groups have been open for crosslinking reactions.

Moreover, Ru-S is more facile to crosslink with GPTA than by itself owing to the possible formation of "charge-transfer complexes" [25]. Fig. 5 shows the ATR-FTIR spectra of Ru-S-cross-GPTA and Ru-S on



Fig. 5. ATR-FTIR spectra of Ru-S and Ru-S-cross-GPTA, respectively adsorbed on ${\rm TiO_2}$ mesoscopic film.



Fig. 6. UV-vis absorption spectra of Ru-S and Ru-S-cross-GPTA before and after immersion in 0.1 N NaOH aqueous solution.

the TiO₂ mesoporous layer. The possessed additional ester and ether peaks at 1732 cm⁻¹ and 1234 cm⁻¹ contributed by GPTA for Ru-Scross-GPTA compared to Ru-S were observed. The extent of crosslinking density for Ru-S and Ru-S-cross-GPTA on the TiO₂ mesoporous layer respectivly were investigated by immersing the crosslinked samples in the 0.1 N NaOH aqueous solution for 1 min. After fully rinsed with water and acetonitrile, they were subjected to measure the UV-vis absorption spectroscopy. Fig. 6 shows the results in comparion with their UV-vis absorption spectra before immersion. 89% of Ru-S-cross-GPTA dye still remained on the TiO₂ mesoporous layer as estimated by the absorption peak at 500 nm, whereas the pristine Ru-S had only 28% remained and the crosslinked Ru-S by itself with AIBN initiator has 62% remained [32]. Because the ruthenium dyes anchored to the TiO₂ mesoporous surface using two carboxylic groups through the coordination modes such as unidentate mode, chelating mode, and bridging bidentate mode [33–35], the styryl group away from the TiO₂ surface would be easy to crosslink with GPTA.

3.2. Li⁺ coordinating property of Ru-S

Ru-S and Ru-S-cross-GPTA are capable of coordinating $\rm Li^+$ ions because both contain ether linkages. Fig. 7 shows the ATR-FTIR



Fig. 7. ATR-FTIR spectra of (a) Ru-S dye adsorbed on TiO_2 mesoporous film, (b) the Ru-S dye in (a) after adding a few drops of 0.25 M Lil in acetonitrile on top and dried, and (c) the Ru-S dye in (b) after washed with pure acetonitrile.



Fig. 8. Photocurrent-voltage plots of the DSSCs with (a) Ru-S and (b) Ru-S-cross-GPTA, respectively with various concentrations of Lil in the liquid electrolyte.

spectrum of Ru-S dye adsorbing on the surface of the TiO₂ mesoporous film, which has been subtracted a spectrum of "blank" TiO₂ mesoporous reference film for the background correction. The broad peak at 1050–1200 cm⁻¹ is derived from the ν (C–O) stretch of the methylene oxide group. A few drops of 0.25 M lithium iodide in acetonitrile solution were then added onto the Ru-S dye and fully dried. The change of IR spectrum was monitored, which was also shown in Fig. 7. The peak at the v(C–O) stretch (1050–1200 cm⁻¹) became broader owing to the appearance of the additional peak at 1070 cm⁻¹. According to the literature [21], the v(C–O) stretch at 1106 cm⁻¹ shifted to lower energy (1078 cm⁻¹) after coordination with lithium ions v(C–O...Li+). The similar trend was also observed in our case. As the sample was washed with acetonitrile to remove Lil and dried, the original peak is restored (see Fig. 7).

In order to investigate the effect of $\rm Li^+$ coordination with the dyes on the performance of DSSC, the liquid electrolyte systems containing various concentrations of LiI were used. Fig. 8 shows the

Table 1

Photovoltaic parameters of DSSCs with Ru-S dye containing various concentrations of LiI in the liquid electrolyte.

LiI (M)	η(%)	$V_{oc}\left(V\right)$	J_{sc} (mA cm ⁻²)	FF
0	6.25 ± 0.055	0.743 ± 0.005	11.99 ± 0.129	0.702 ± 0.008
0.05	$\textbf{7.39} \pm \textbf{0.056}$	0.739 ± 0.002	14.91 ± 0.083	0.671 ± 0.001
0.1	7.53 ± 0.040	0.740 ± 0.001	18.24 ± 0.040	0.558 ± 0.003
0.15	7.48 ± 0.069	0.722 ± 0.004	19.04 ± 0.183	0.544 ± 0.008
0.2	$\textbf{7.29} \pm \textbf{0.038}$	0.715 ± 0.002	16.71 ± 0.162	0.610 ± 0.001

Table 2

Photovoltaic parameters of DSSCs with Ru-S-cross-GPTA dye containing various concentrations of Lil in the liquid electrolyte.

LiI (M)	η (%)	$V_{oc}\left(V\right)$	J_{sc} (mA cm ⁻²)	FF
0	5.80 ± 0.11	0.742 ± 0.002	10.97 ± 0.15	0.71 ± 0.01
0.05	$\textbf{7.24} \pm \textbf{0.03}$	0.733 ± 0.005	14.25 ± 0.22	$\textbf{0.69} \pm \textbf{0.01}$
0.1	$\textbf{7.88} \pm \textbf{0.02}$	0.720 ± 0.001	18.73 ± 0.06	0.58 ± 0.01
0.15	$\textbf{7.69} \pm \textbf{0.06}$	0.713 ± 0.003	19.49 ± 0.08	0.55 ± 0.01
0.2	7.75 ± 0.08	0.704 ± 0.002	18.69 ± 0.06	$\textbf{0.59} \pm \textbf{0.02}$

photocurrent-voltage characteristics of DSSC with Ru-S and Ru-Scross-GPTA dyes, respectively containing various concentrations of Lil in the liquid electrolytes. Their related photovoltaic parameters such as V_{oc} , short circuit current density (I_{sc}), fill factor (ff), and power conversion efficiency (η) are listed in Tables 1 and 2. For the concentration of Lil lower than 100 mM, Voc of the DSSC with Ru-S dye was almost unchanged. Until the concentration of LiI was increased to 150 mM, V_{oc} began to drop from 743 to 722 mV. On the other hand, J_{sc} was steadily increased from 11.99 to 19.04 mA cm⁻² as the concentration of LiI was increased from 0 to 150 mM. The highest η of DSSC with Ru-S dye was 7.53 \pm 0.04%. The increase of I_{sc} with the presence of Li⁺ in the liquid electroltyte has been thoroughly studied by the transient absorbance decay kinetics of the K-51 dye and attributed to the higher dye regeneration rate compared to the absent of Li⁺ [21]. It has been suggested that because the surface of TiO₂ mesoporous film is negatively charged, Li⁺ would be adsorbed, which increased the local concentration of the iodide and hence increased the dye regeneration rate. However, if Lil is over supplied, it would increase the charge recombination rate and deteriorate the photovoltaic performance of DSSC. It explains why all the V_{oc} , J_{sc} and η decreased as the concentration of LiI increased to 200 mM for the DSSC with Ru-S dye.

For the DSSC with Ru-S-cross-GPTA and without containing LiI in the liquid electrolyte, the power conversion efficiency was only $5.80 \pm 0.11\%$, which is lower than that with Ru-S dye and without containing LiI. The crosslinked GPTA may retard the regeneration of Ru-S dye so that the power conversion efficiency was decreased. However, it steadily increased to $7.8 \pm 0.02\%$ as the concentration of LiI was increased to 100 mM. J_{sc} was also increased from 10.97 ± 0.15 to 19.49 ± 0.08 mA cm⁻², whereas V_{oc} was slightly decreased from 0.742 ± 0.002 to 0.720 ± 0.001 V. Further increase of LiI concentration decreased the photovoltaic performance of DSSC. Basically, the DSSC with Ru-S-cross-GPTA dye showed the similar trend of photovoltaic performance as that with Ru-S dye. The C–O–C linkages of Ru-S-cross-GPTA dye are likely to



Fig. 9. Photocurrent-voltage plots of Ru-S and Ru-S-cross-GPTA, respectively with the PMA-gelled electrolyte.



Fig. 10. Time-course changes of photovoltaic performance for PMA-gelled DSSCs with Ru-S and Ru-S-cross-GPTA dyes.

coordinate Li^+ preventing it from intercalation onto the surface of TiO₂ mesoporous layer.

3.3. Photovoltaic performance of PMA-gelled DSSCs with Ru-S and Ru-S-cross-GPTA dyes

Because the liquid electrolyte in DSSCs has problems of leakage and evaporation of solvent, polymers and their nanocomposites have been frequently used to gel the electrolyte systems [27,28,36]. It has been reported that by utilizing PMA with Tg of 6 °C to gel the electrolyte system, the power efficiency of fabricated DSSC is superior to that gelled by the polymers with higher Tg [28]. Therefore, in this study PMA was chosen to gel the electrolyte system of DSSCs with Ru-S and Ru-C-cross-GPTA dyes. Their typical photocurrent density-voltage characteristics were shown in Fig. 9. The average J_{sc} and V_{oc} of DSSCs with Ru-S were 15.83 \pm 0.02 mA cm⁻² and 0.723 \pm 0.001 V with a fill factor of 0.61 \pm 0.01, resulting the average $\eta = 6.96 \pm 0.02\%$. Whereas, the DSSC with Ru-S-cross-GPTA has $J_{sc} = 16.83 \pm 0.06$ mA cm⁻², $V_{oc} = 0.701 \pm 0.001$ V, fill factor of 0.64 \pm 0.01 and $\eta = 7.53 \pm 0.03\%$. The incorporation of GPTA to crosslink with Ru-S has brought higher J_{sc} and better fill factor, leading to higher power efficiency.

The PMA-gelled DSSCs with Ru-S and Ru-S-cross-GPTA dyes, respectively were then subjected to measure the long-term stability. All the samples were stored at ambient environment. At chosen time intervals, the samples were taken to measure the power efficiency at room temperature under AM 1.5 and 100 mW cm⁻² illumination. All the photovoltaic parameters such as power efficiency, photovoltage, photocurrent, and fill factors of samples at different storage time shown in Fig. 10 were normalized to their initial measured values. The results show that the power efficiences of all cells in the storge period fluctuated with time.

After 30 days of storage, the power efficiency of DSSC with Ru-S retained 99%, whereas that with Ru-S-cross-GPTA increased 1%. The V_{oc} for both of the devices with Ru-S and Ru-S-cross-GPTA dyes showed a little increase in the initial stage and stayed unchanged up to the end of storage time. The J_{sc} of the device with Ru-S dye showed an initial increase at first 10 days, and then slightly decreased. The increase of photocurrent in the initial storage of the DSSCs might be due to the excess penetration of gelled electrolytes into the pores of TiO₂ mesoporous layer [37]. After 30 days, J_{sc} decreased to 93% relative to the original value. The J_{sc} of the device with Ru-S-cross-GPTA dye also showed a similar trend. The fill factors of both devices were quite steady in the initial stage and then slightly increased when J_{sc} decreased. The increase of power efficiencey for the DSSCs with Ru-S-cross-GPTA dye was due to the increase of fill factor. V_{oc} barely changed.

4. Conclusion

A new crosslinkable Ru-S dye was synthesized and well characterized. Its capability of coordinating Li⁺ was verified by ART-FTIR spectroscopy. By crosslinking with GPTA to form a Ru-S-cross-GPTA layer on TiO₂ mesoporous film, it is almost insoluble in 0.1 N NaOH aqueous solution. By increasing the amount of LiI in the liquid electrolyte, the DSSCs with Ru-S and Ru-S-cross-GPTA both showed small drop of V_{oc} but significant increase of J_{sc} . The highest power conversion efficiency of 7.88% was achieved for the DSSC with Ru-Scross-GPTA dye containing 150 mM LiI in the liquid electrolyte. By using the PMA-gelled electrolyte system, the DSSC with Ru-S-cross-GPTA attained a power efficiency of 7.57%. For the time-course change test of power efficiency in storage, the DSSCs with Ru-S and Ru-S-cross-GPTA respectively showed an initial increase of power efficiencies and then stayed almost unchanged for a month.

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Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.05.035.

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