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Hybridized ruthenium(II) complexes with high molar extinction coefficient unit: Effect of energy band and adsorption on photovoltatic performances

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Abstract

Two hybridized Ru(II) complexes *cis*-Ru(dcbpy)$_2$(PNI-phen)(NCS)$_2$ and *cis*-Ru(dcbpy)$_2$(PERY-phen)(NCS)$_2$, coded as RuPBS and RuPPS containing naphthalimide or perylene imide unit, were synthesized and utilized in dye-sensitized TiO$_2$ solar cells (DSCs). Their absorption spectra, electrochemical and photovoltatic properties were studied. Both complexes, especially for RuPPS, have wide absorption bands with high molar extinction coefficient in the visible spectrum region. The effects of the energy band of the incorporated ligand and adsorption on TiO$_2$ were extensively discussed. The complexes are served to enhance our knowledge regarding manipulation of new sensitizers for DSCs, providing a powerful strategy for prediction of photovoltatic performances.

Keywords: Perylene imide; Naphthalimide; Ru(II) complexes; Sensitization; Solar cells

1. Introduction

Since the breakthrough work by Grätzel and co-workers, dye-sensitized solar cells (DSCs) in which the photoanode was prepared by sintering nanocrystalline TiO$_2$ on a conducting glass support have attracted considerable attention as organic/inorganic hybrids in the request of alternatives to silicon-based solar cells [1,2]. The photovoltatic performances of solar cells are critically dependent on sensitizers. By now, bipyridyl Ru(II) complexes are still the most efficient sensitizers. For instance, *cis*-dithiocyanato bis(4,4′-dicarboxy-2,2′-bipyridine)Ru(II) (called *N3* dye) can produce solar energy-to-electricity conversion efficiency (η) of up to 11% under 1.5 G irradiation [3]. Some metal-free organic dye sensitizers [4–7], porphyrin dyes [8–11], and cyanine dyes [12,13] have also been developed for DSCs giving respectable IPCE partly due to wide absorption spectrum and high molar extinction coefficient.

As well known, the region of visible light takes more than half of all solar radiation energy. The optimal sensitizer for DSCs should be panchromatic, that is, be capable of responding wide spectrum. Ideally, all photons below a threshold wavelength of about 920 nm should be harvested and converted to electric current [14]. It is reasonable to increase the response of visible spectrum region for the sake of enhancing the efficiency of solar cells. Recently, Yanagida's group has developed a new sensitizer HRS-1, which is composed of dcbpy, SCN and the bpy ligand conjugated with 2-thiophen-yl-vinyl units, can surprisingly gain very high solar light-to-electricity conversion efficiency compared to N719-based DSCs under their experimental conditions [15]. However, the molar extinction coefficients are still not very high, especially in visible spectrum region (1.87×10^4 M^{-1} cm^{-1}). In this paper, we designed two ligands for developing Ru(II) complexes RuPBS and RuPPS (Scheme 1), in which the chromophore of naphthalimide or perylene unit was incorporated. Dyes based on perylene imides have received much attention as sensitizers with their outstanding chemical, thermal and photochemical stability and high molar extinction coefficient in the visible to NIR [6a]. Our concept is to introduce a large π-conjugation chromophore unit into the

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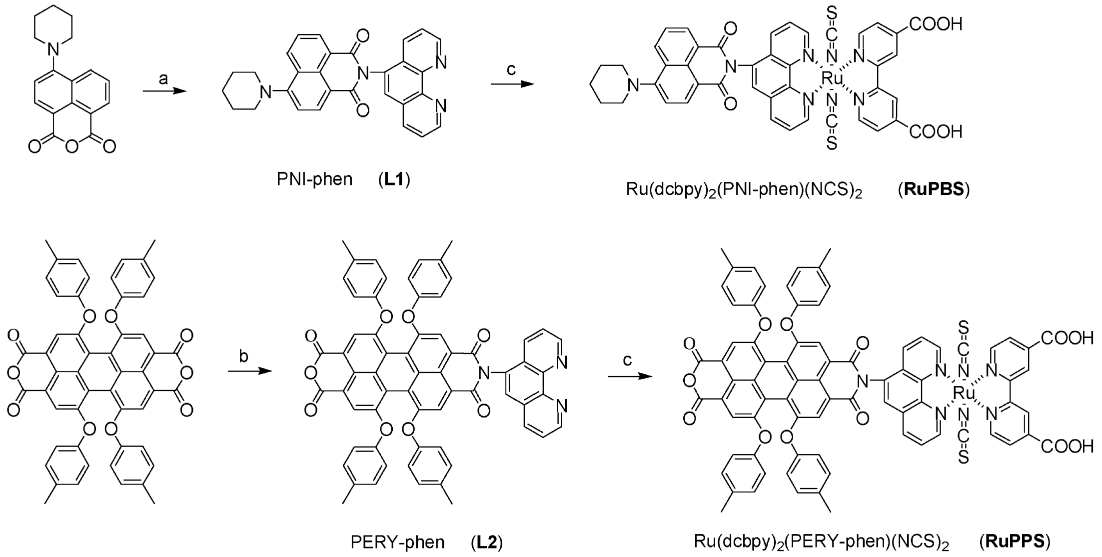


Scheme 1. Synthetic routes of target complexes: (a) 5-amino-1,10-phenanthroline, ethylene glycol monomethylether, reflux; (b) 5-amino-1,10-phenanthroline, $Zn(OAc)_2$, quinoline, 180 °C; (c) $RuCl_3\cdot 3H_2O$, H_2dcbpy, NH_4NCS, DMF, heat.

ligand for developing a novel kind of hybridized Ru(II) complexes with high molar extinction coefficient unit, thus take an effort in improving their photosensitizing properties with wide spectral response. The absorption spectra, electrochemical and photovoltatic properties of RuPBS and RuPPS were extensively studied. The effects of the energy band of the incorporated ligand and adsorption on TiO_2 on photovoltatic performances were discussed. The model complexes of RuPBS and RuPPS are served to enhance our knowledge regarding manipulation of new sensitizers for DSC, providing a powerful strategy for prediction of photovoltatic performances.

2. Experimental

2.1. Preparation of dye-sensitized solar cells (DSCs)

The preparation of TiO_2 colloidal dispersion (100–150 g L^{-1}), containing poly(ethylene glycol) (MW 20,000, 40 wt.%), was followed the reported procedure [1a] except the autoclaving was performed at 220 °C instead of 200 °C. Films of colloidal nanocrystalline TiO_2 on FTO were prepared by sliding a glass rod over the conductive side of the FTO. Sintering was carried out at 450 °C for 30 min. Before immersing in the dye solution, these films were soaked in 0.2 M aqueous $TiCl_4$ solution overnight in a closed chamber, which has been proved that can increase the short-circuit photo-current significantly [3a]. After being washed with deionized water and fully rinsed with ethanol, the nanoporous TiO_2 was heated again at 450 °C, then cooled to 80 °C and finally dipped into a 3×10^{-4} M solution of dyes in DMF for 12 h at room temperature. The DSCs were fabricated by following Ref. [16], except that the platinum sputtered FTO was used as counter electrode and the DSCs were sealed with HY-914 adhesives. The electrolyte of liquid-state DSCs was 0.3 M LiI and 0.03 M I_2 in acetonitrile and 3-methyl-2-oxazolidinone (9:1 v/v) solution.

2.2. Photoelectrochemical measurements

IPCE data were measured using a Model SR830 DSP Lock-In Amplifier and a Model SR540 Optical Chopper (Stanford Research Corp., USA) and photoelectric conversion system. Voltage–current characteristics were performed on Model 2400 Sourcemeter (Keithley Instruments Inc., USA) and a 500 W xenon lamp served as a white light source in conjunction with a GRB3 neutral filter. Here a GRB3 neutral filter was used to cut off infrared light to protect the electrode from heating. The active area of DSC is 0.5 cm^2. Notably, in the test of IPCE based on RuPPS, there was too much noise signal owing to the very low photo-current response. In order to cover up these noise signals, we took off the mask which limited the action area as 0.500 cm^2 of the cells and used the full scale (0.828 cm^2) as the action area.

2.3. Synthesis

^1H NMR spectra were measured with Bruker Avance at 500 MHz. Mass spectra were obtained with HP5989A, Mariner API time-of-flight (TOF, TIS ion source, PE Corp.) and API2000 (TIS, PE Corp.) spectrometers. Infrared spectra were obtained with NICOLET-380 FTIR spectrophotometer in compressed KBr pellets. UV–vis spectra were recorded on a Cary 100 absorption spectrometer.

5-Amino-1,10-phenanthroline and 4,4′-dicarboxy-2,2′-bipyridine were synthesized according to the published methods [17,18]. All other materials and solvents were analysis grade and purchased from Sinopharm Chemicals and used as received.

2.3.1. Synthesis of N-(1,10-phenanthroline)-4-piperdinyl-1,8-naphthalimide (L1)

4-Piperdinyl-1,8-naphthalic anhydride (0.68 g, 2.4 mmol) and 5-amino-1,10-phenanthroline (0.62 g, 3.2 mmol) were dissolved in 2-methoxyethanol (10 mL), followed by adding piperidine (1 mL) into the solution. After refluxed for 36 h under argon, the solution was cooled at room temperature and filtered off. The crude product was refluxed in ethanol (10 mL) for 1 h and cooled to give the corresponding ligand (L1, 0.48 g) with a yield of 44%. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.75 (m, 2H, $-CH_2$), 1.95 (m, 4H, $-CH_2$), 3.34 (t, J = 4.5 Hz, 4H, $-CH_2$), 7.30 (s, 1H, phenanthroline-H), 7.65 (m, 1H, naphthalene-H), 7.78 (t, J = 7.5 Hz, 2H, naphthalene-H, phenanthroline-H), 7.95 (s, 1H, phenanthroline-H), 8.15 (d, J = 8.0 Hz, 1H, phenanthroline-H), 8.38 (d, J = 7.8 Hz, 1H, phenanthroline-H), 8.53 (d, J = 7.7 Hz, 1H, naphthalene-H), 8.60 (d, J = 8.2 Hz, 1H, naphthalene-H), 8.68 (d, J = 7.3 Hz, 1H, naphthalene-H), 9.33 (d, J = 9.2 Hz, 2H, phenanthroline-H). MS-ESI *m/e*: 458.2 [M^+] (100%).

2.3.2. Synthesis of N-(1,10-phenanthroline)-1,6,7,12-tetrakis(4-methylphenoxy)perylene-3,4-dicarboxyli canhydride-9,10-dicarboximide (L2)

A mixture of 1,6,7,12-tetrakis(4-methylphenoxy)perylene-3,4;9,10-tetracarboxylic anhydride (0.4 g, 0.49 mmol), 5-amino-1,10-phenanthroline (0.2 g, 1.03 mmol), anhydrous zinc acetate (1.7 g) and freshly distilled quinoline (7 mL) was heated to 180 °C for 18 h under argon. After cooled to room temperature, the mixture was poured into HCl (1 M, 200 mL) with strongly stirring. The precipitate was filtered, washed with water and dried in a vacuum. The product was purified by column chromatography on silica gel eluting with CH_2Cl_2:triethylamine = 20:1 to give L2 as dark red solid (0.189 mg, yield 38.8%). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.32 (s, 12H, $-CH_3$), 6.85 (d, J = 7.8 Hz, 8H, phenyl-H), 7.11 (d, J = 7.8 Hz, 8H, phenyl-H), 7.54 (m, 1H, phenanthroline-H), 7.65 (m, 1H, phenanthroline-H), 7.78 (s, 1H, phenanthroline-H), 7.98 (d, J = 8.3 Hz, 1H, phenanthroline-H), 8.14 (m, 4H, perylene-H), 8.22 (d, J = 6.9 Hz, 1H, phenanthroline-H), 9.18 (d, J = 2.8 Hz, 1H, phenanthroline-H), 9.23 (d, J = 4.2 Hz, 1H, phenanthroline-H). MS-ESI *m/e*: 993.3 [M^+] (100%).

2.3.3. Synthesis of RuPBS and RuPPS

In a typical one-pot synthesis, a mixture of $RuCl_3 \cdot 3H_2O$ (21.04 mg, 0.08 mmol), L1 (36.7 mg, 0.08 mmol) or L2 (80 mg, 0.08 mmol) and DMF (25 mL) was heated to 80 °C for 4 h in the dark under argon. To this reaction flask, H_2dcbpy (19.25 mg, 0.08 mmol) was added and refluxed for further 4 h. Finally, an excess of NH_4NCS (500 mg, 6.57 mmol) was added to the solution and continued refluxing for another 4 h. After removed solvent by using a vacuum rotary-evaporator, deionized water (50 mL) was added to the flask, followed by sonification for 5 min. The crude product was obtained by filtration, and then recrystallized from DMF/ether to offer brown and dark purple solid, respectively.

RuPBS: 54 mg, yield 73%. IR (cm^{-1}, KBr): 3415.5, 2108.9, 1699.3, 1653.9, 1582.4, 1367.8, 1231.2. Anal. Calc. for $RuC_{43}H_{30}N_8O_6S_2$ (%): C 56.14, H 3.29, N 12.18; Found: C 55.79, H 3.42, N 11.93; MS-ESI *m/e*: 959.0 [M^+ + K] (41%).

RuPPS: 79 mg, yield 68%. IR (cm^{-1}, KBr): 3434.9, 2108.9, 1706.1, 1673.3, 1588.7, 1497.8, 1283.3. Anal. Calc. for $RuC_{78}H_{47}N_7O_{13}S_2$ (%): C 64.37, H 3.25, N 6.74; Found: C 64.05, H 3.73, N 6.28; MS-ESI *m/e*: 1494.4 [M^+ + K] (34%).

2.4. Electrochemical measurements

Electrochemical data were recorded by cyclic voltammetry at Versastat II electrochemical workstation (Princeton Applied Research) using a conventional three-electrode cell equipped with a glassy carbon working electrode, an Ag/AgCl reference electrode (0.22 V vs. NHE) and a platinum counter electrode. A scan speed of 25 mV/s was generally used. The cyclic voltammogram data of two complexes were measured in DMF containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte.

3. Results and discussion

3.1. Design and synthesis of RuPBS and RuPPS

Since the nanocrystalline electrode of bare TiO_2 is transparent and colorless, displaying the fundamental absorption in the UV region, so a solar cell with high efficiency needs efficient sensitization by a dye. It is necessary to increase the response of visible spectrum region to enhance the efficiency of solar cells. A simple approach is to utilize two or more different dyes by a coadsorption method, which shows strong absorption at a different wavelength and compensatory absorbency [19]. However, multilayer adsorption is not always helpful as the inner layer tends to act as an insulator with respect to the outer ones.

Another possible approach is to incorporate known chromophoric units into a molecule. Such multi-chromophoric dyes should have a wide absorptive region, whose photo-current could cover the whole visible region. Furthermore, it might be possible to avoid the complication of doping and to find a novel route to design appropriate solar cell sensitizers. Taking theses points into account, our strategy is to introduce the chromophore of naphthalimide or perylene unit with high molar extinction coefficient unit into the ligand of Ru(II) complexes. As shown in Scheme 1, the preparation of complexes RuPBS and RuPPS is straightforward. Two ligands (L1 and L2) were obtained by reaction of naphthalic anhydride and perylene dianhydride with 5-amino-1,10-phenanthroline, respectively. Through a typical one-pot process, followed by recrystallization from DMF/ether, the two target complexes were afford as *cis*-type. Their chemical structures were further confirmed by infrared spectra, element analysis, and mass spectra.

3.2. Absorption spectra and electrochemical studies

The general idea is to utilize naphthalimide or perylene imide unit for extending the π-conjugation and enhancing molar extinction coefficient. Exactly, the resulting RuPBS and RuPPS show wide absorption spectra and high molar extinction coefficient in visible region, especially for RuPPS. As shown in Fig. 1, the absorption spectra of RuPBS contain two bands located at 418 nm ($1.29 \times 10^4\ M^{-1}\ cm^{-1}$) and 511 nm ($0.46 \times 10^4\ M^{-1}\ cm^{-1}$), which are correspond-

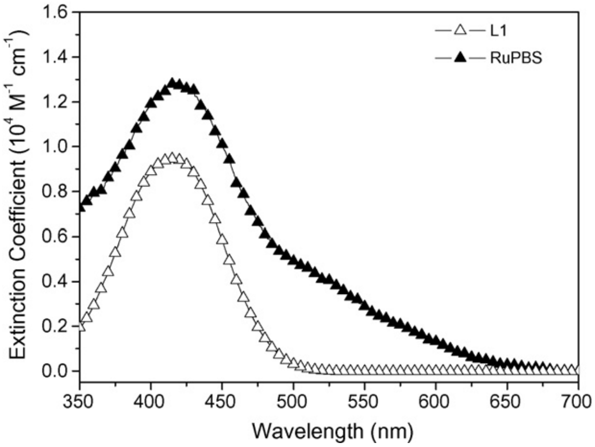


Fig. 1. Absorption spectra of L1 and RuPBS in DMF.

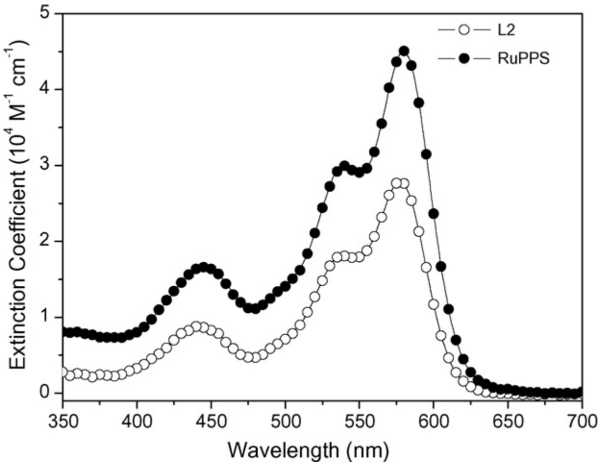


Fig. 2. Absorption spectra of L2 and RuPPS in DMF.

ing to the transitions of naphthalimide unit and MLCT band from Ru(II) complex unit. The characteristic MLCT transition indirectly reflects the successful incorporation of Ru(II) complex unit. RuPPS exhibits three bands located at 447 nm ($1.68 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$), 540 nm ($2.99 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) and 580 nm ($4.50 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) (Fig. 2), which are attributed to the transitions of perylene imide unit. Notably, the MLCT band from Ru(II) complex unit is overlapped with the ones of perylene imide unit, and cannot be clearly observed. The absorption spectra data of two complexes are listed in Table 1.

Compared with their ligands (L1 and L2), there is slightly red shift in Ru(II) complexes. As expected, the ligand characteristics of high molar extinction coefficient are predominated in absorption spectra of complexes RuPBS and RuPPS, indicating that there is no distinct interaction between the incorporated chromophore unit and the central Ru(II) in the ground state. Compared with *N3* [1d], which shows a MLCT band at 539 nm ($1.42 \times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$) in visible region, RuPPS contains broader absorption spectra and higher molar extinction coefficient. The higher molar extinction coefficient in visible region, the more efficient to capture solar radiation energy. Especially, absorption spectrum of complex RuPPS become much wider evidently when anchored on TiO_2 films (Fig. 3). Therefore, incorporating naphthalimide or perylene imide unit to Ru(II) complexes could be expected to enhance the harvest of solar radiation energy.

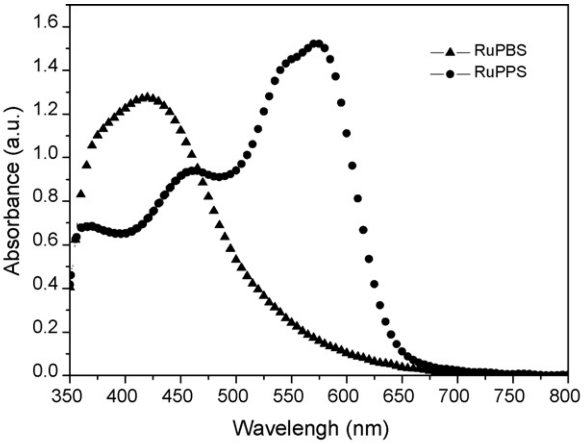


Fig. 3. Absorption spectra of RuPBS and RuPPS anchored on TiO_2 film.

Generally, suitable HOMO and LUMO levels of sensitizer are required to match the iodine redox potential and the conduction band edge level (E_{cb}) of TiO_2 electrode. That is, HOMO level must be more positive than the iodine redox potential to accept electrons, and the LUMO level must be more negative than the E_{cb} of TiO_2 electrode to inject electrons. Thus, the electrochemical properties of complexes RuPBS and RuPPS were studied to clarify their HUMO and LUMO levels. The band gap energies ($E_{(0–0)}$) of complexes were estimated from the onset of the absorption spectra of dyes adsorbed on TiO_2, which were 1.77 and 1.63 eV for RuPBS and RuPPS, respectively. As shown in Table 2, the E_{ox} corresponding to the HOMO levels of RuPBS and RuPPS obtained from cyclic voltammetry were 1.02 and 0.92 V (vs. NHE), respectively, which were sufficiently more positive than the iodine redox potential value (~0.4 V vs. NHE). Also, the LUMO levels of RuPBS and RuPPS were −0.75 and

Table 1
Absorption and electrochemical data of RuPBS and RuPPS

Compounds	Absorption maximum (nm), ε ($\times 10^4\ \mathrm{M^{-1}\,cm^{-1}}$)[a]		$E_{ox\,\mathrm{Ru(II/III)}}$[b] (V vs. NHE)
	π–π*	MLCT	
RuPBS	418 (1.29)	511 (0.46)	0.99
RuPPS	447 (1.68), 540 (2.99), 580 (4.50)	Overlapped	0.87

[a] Absorption spectra was measured in DMF at 298 K.

[b] Oxidation potential (E_{ox}) of dyes were measured in 0.1 M tetrabutylammonium hexafluorophosohate in DMF (working electrode, glassy carbon; reference electrode, Ag/AgCl KCl_{sat}; counter electrode, Pt).

Table 2
Electrochemical properties of dyes adsorbed on a TiO_2 film[a]

Dye	E_{ox} (V vs. NHE)	$E_{0\text{–}0}$[b] (eV)	$E_{ox} - E_{0\text{–}0}$ (V vs. NHE)
RuPBS	1.02	1.77	−0.75
RuPPS	0.92	1.63	−0.71

[a] Conditions: working electrode, a dye-coated TiO_2 electrode; reference electrode, Ag/AgCl KCl_{sat}; counter electrode, Pt electrode; electrolyte, 0.1 M tetrabutylammonium hexafluorophosohate in DMF.

[b] $E_{0\text{–}0}$ were estimated from the onset of absorption spectra of dyes adsorbed on TiO_2 film.

−0.71 V (vs. NHE), respectively, which were more negative than the E_{cb} of TiO_2 (∼−0.5 V vs. NHE) [20,21].

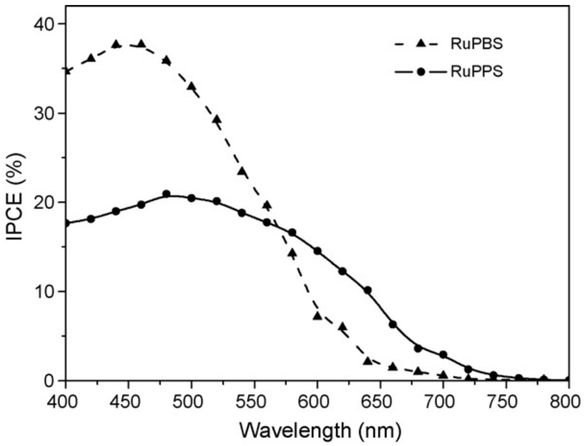


Fig. 4. Photo-current action spectrum based on RuPBS and RuPPS.

3.2.1. Photovoltatic measurements

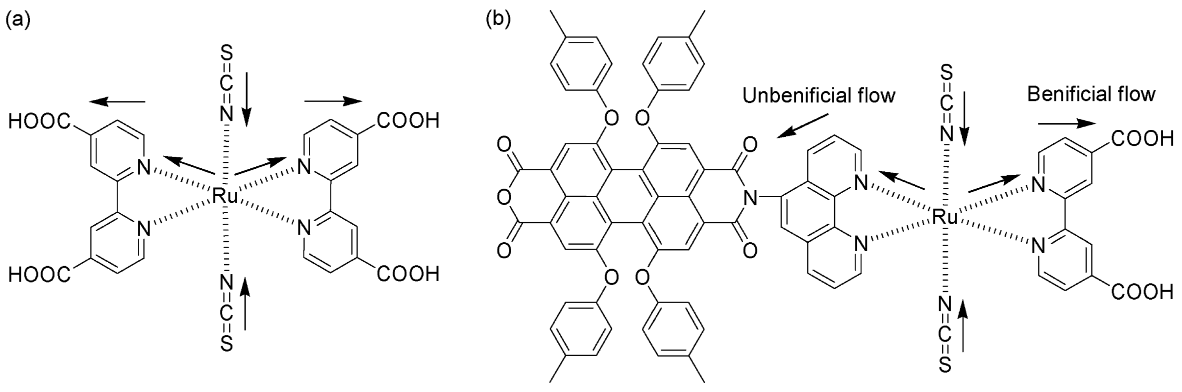
IPCEs of Grätzel cells based on RuPBS and RuPPS are shown in Fig. 4. IPCEs are calculated by the following equation:

$$\text{IPCE} = \frac{1240 J_{sc}}{\lambda \phi}$$

where J_{sc} is the short circuit photo-current density (mA cm^{-2}) for the monochromatic irradiation, λ the wavelength (nm) and ϕ is the incident radiative flux (W m^{-2}). The onset wavelength of the IPCE spectrum for DSC based on RuPBS is about 720 nm, and its IPCE has a maximum value of 39% at 458 nm. In the case of RuPPS, it has much wider photo-electronically responsive spectra with the onset wavelength of the IPCE spectrum reaching at about 780 nm, which is red shifted by 60 nm comparing that based on RuPBS. The IPCE of DSC based on RuPPS in plateau region is only about 19% with a maximum value of 21% at 490 nm. The maximum value of λ_{max} and IPCE cannot match relatively. Expressing the IPCE by the relation:

$$\text{IPCE}(\lambda) = \text{LHE}(\lambda) \times \text{APCE}$$

where LHE is the light harvesting efficiency (95% at 415 nm for RuPBS and 97% at 572 nm for RuPPS), calculated from Fig. 3, according to Ref. [3a] and APCE is the absorbed photon to current conversion efficiency (38% for RuPBS and 18% for RuPPS), which means that at least 38% of the injected electrons for RuPBS and 18% of the injected electrons for RuPPS are drawn of as a current, the remainder recombining with parent cations. Comparing with parent Ru(II) complexes [3], the incorporating chromophore unit does not increase the action spectrum of IPCE and photovoltatic performances. More than a half of excited electrons recombine with parent cations instead of flowing into the conduction band of TiO_2 at λ_{max}. This might be attributed to the strong electron-withdrawing ability of the imide group, which has effect on the polarity of the whole molecule and the transferring flow of photo-generated electrons. To keep in mind that perylene imide derivatives have a high electron affinity, the imide group possesses strong electron-withdrawing nature. As a case illustrated for RuPPS, the LUMO level of perylene imide unit (*Pery) is −0.6 V [22,23], which is more positive than that of bipyridine ligand (*Bipy, −0.7 V). Therefore, it is reasonable that a considerable part of excited electrons flow from Ru(II) to perylene imide group (Scheme 2b) instead of flowing from Ru(II) to the carboxylic groups which are anchored on nanoporous TiO_2 film. Since this part of electrons cannot be injected into the conduction band of TiO_2, it would be released through other ways [24] and does not bring about the contri-



N3 dye **RuPPS**

Scheme 2. Photo-generated electron transfer due to the energy band: (a) beneficial direction from Ru(II) to the carboxylic group, and then to the conduction band of TiO_2 in *N3* dye; (b) unbeneficial direction being a considerable part of excited electrons flow from Ru(II) to imide group instead of flowing from Ru(II) to the carboxylic group in RuPPS.

Table 3
Photovoltatic performance of DSCs based on different sensitizers (xenon lamp, 200 W m^{-2})

	V_{oc} (V)	J_{sc} (mA cm^{-2})	ff	η (%)	N (mol cm^{-2})	$J_{sc/mol}$ (mA cm^{-2} mol^{-1})
RuPBS	0.40	2.64	0.58	3.08	3.16×10^{-7}	8.35×10^{6}
RuPPS	0.42	1.35	0.62	1.75	5.12×10^{-8}	2.64×10^{7}

bution of photo-current. This suggested that the photovoltatic performance of Ru(II) complex is dependent on the energy level of the incorporated ligand. The high performance such as *N3* dye can keep the photo-generated electron transferring from Ru(II) to the carboxylic group, and then to the conduction band of TiO_2 (Scheme 2a) [25].

Fig. 5 compares the photo-current–voltage (*J*–*V*) curves of two DSCs based on RuPBS and RuPPS. Analysis of the *J*–*V* curves indicates that RuPBS yield higher photocurrents than RuPPS, whereas the V_{oc} is slightly lower. The overall conversion efficiencies of DSC based on RuPBS and RuPPS are 3.08 and 1.75%, respectively. The J_{sc} enhancement for RuPBS can be correlated with the increased amount of RuPBS adsorbed on the TiO_2 films. The amount of the adsorbed dye on TiO_2 is calculated by the changes of their UV–vis spectra absorbance. Photo-current performance of DSCs based on two sensitizers is given in Table 3. The amount of RuPBS adsorbed on the TiO_2 film was 3.16×10^{-7} mol cm^{-2}, which was 5 times higher than the amount of RuPPS (5.12×10^{-8} mol cm^{-2}). The lower adsorption on TiO_2 of RuPPS is thought to be due to the introduction of larger perylene imide unit, compared to smaller naphthalimide unit. This type of geometrical constraints of sensitized dyes to occupy sites on TiO_2 particles are explained in a recent report by Bandara and Weerasinghe [26]. This result suggests that less molecules of RuPPS adsorbed on TiO_2 have attended the process of photo-current conversion, which resulted in sharp decrease in the overall photo-current performance. However, considering the contribution of each molecule, RuPPS showed higher performance than that of RuPBS, that is, we observed a higher $J_{sc/mol}$ of 2.64×10^{7} mA cm^{-2} mol^{-1} with RuPPS compared to 8.35×10^{6} mA cm^{-2} mol^{-1} with RuPBS.

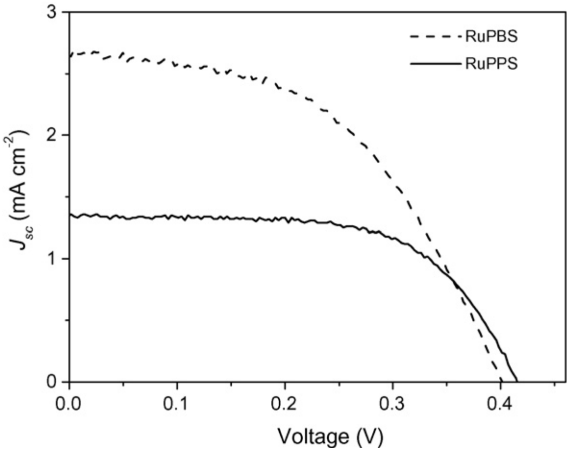


Fig. 5. Photovoltaic characteristics based on RuPBS and RuPPS. The active area of DSC is 0.5 cm^2.

4. Conclusions

Two novel hybridized Ru(II) complexes RuPBS and RuPPS containing large π-conjugation chromophore ligand were designed and synthesized. Our strategy is to introduce the chromophore of naphthalimide or perylene unit with high molar extinction coefficient unit into the ligand of Ru(II) complexes, thus greatly improving the ability of capturing solar light. Both of them, especially for RuPPS, possess wide absorption bands and high molar extinction coefficient. However, the imide group which contains strong electron-withdrawing nature has effect on the polarity of the whole molecule, resulting in the unbeneficially transferring direction of photo-generated electrons. In addition, the large π-planar unit of perylene ligand leads to low adsorption on TiO_2, which also decreases the overall photo-current performance. Our results strongly suggest that in order to design an effective sensitizer, both the energy level of the incorporated ligand and adsorption on nanoporous TiO_2 should be taken into consideration [1c,27].

Acknowledgments

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