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## Introduction

Dye-sensitized solar cells (DSSCs) have attracted vast attention due to their easy fabrication and high power conversion efficiency (PCE), feasible for commercial applications.<sup>1-17</sup> To pursue better photovoltaic performance, the photo-electrodes,<sup>3-5</sup> dyes,<sup>6-10</sup> electrolytes<sup>11-15</sup> and counter electrodes<sup>16,17</sup> in DSSCs have been investigated extensively over the past decades. For example, ruthenium dye with a bipyridyl ligand tethering triethylene oxide methyl ether functional groups capable of coordinating the lithium cation (Li<sup>+</sup>) in the electrolyte has been reported.18-20 It significantly enhanced the photocurrent of DSSCs by increasing the dye regeneration rate. Furthermore, to improve the long term stability, we have designed a cross-linkable dye, Ru(2,2'-bipyridine-4,4'-bicaracid)(4,4'-bis((4-vinyl-benzyloxy) methyl)-2,2'-bipyrboxylic idine)(NCS)2 (denoted as Ru-S) with the chemical structure shown below.21

## Ruthenium complex dye with designed ligand capable of chelating triiodide anion for dye-sensitized solar cellst

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Ru(4,4'-dicarboxyl-2,2'-bipyridine)[4,4'-bis(styrylaminocarbonyl)-2,2'-bipyridine](NCS)<sub>2</sub>, denoted as RuAS dye, was synthesized and well characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, heteronuclear single quantum coherence, UV-vis and ESI-MS spectra. Its capability of chelating triiodide anions with the 4,4'-bis(styrylaminocarbonyl)-2,2'-bipyridine ligand, which was revealed by ATR-FTIR and <sup>1</sup>H-NMR spectroscopies, reduced the charge recombination for dye-sensitized solar cells (DSSCs) by keeping the triiodide ions away from contact with the mesoporous TiO<sub>2</sub> layer. Therefore, the open-circuit photovoltage of the DSSC barely changed with the triiodide concentration in the electrolyte. Moreover, the electron-withdrawing ability of the amide groups in the ligand increased the molar extinction coefficient of the dye, leading to the increase of photocurrent for DSSCs. The enhanced photovoltaic performance was further examined by incident photon-to-current conversion efficiency spectra, electrochemical impedance spectroscopy and open-circuit potential decay transient measurements.



Ru-S dye is also capable of coordinating Li<sup>+</sup> with its ether groups. As Ru-S was cross-linked with triethyleneglycodimethacrylate, not only did the long term stability improve, but the PCE also increased to over 8%.<sup>22</sup>

On the other hand, the charge recombination rate at the interface between the  $TiO_2$  mesoporous layer and triiodide anions ( $I_3^-$ ) in the electrolyte responsible for the decrease of open circuit photovoltage ( $V_{oc}$ ) of DSSCs may be reduced if  $I_3^-$  can be kept away from contact with the  $TiO_2$  layer. Therefore, in this work we designed a novel  $I_3^-$ -chelating and cross-linkable ruthenium complex dye, Ru(4,4'-dicarboxyl-2,2'-bipyridine) [4,4'-bis(styryl-aminocarbonyl)-2,2'-bipyridine](NCS)<sub>2</sub>, denoted as RuAS with the chemical structure shown in Fig. 1. Two amide groups in the bipyridyl ligand of RuAS dye are able to chelate  $I_3^-$ , as revealed by ATR-FTIR and <sup>1</sup>H-NMR spectroscopies. Therefore, our discussion in this contribution will be focused on the synthesis, characterization and  $I_3^-$  chelating properties of RuAS in association with the photovoltaic performance of DSSCs.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: <sup>13</sup>C-NMR and HSQC spectra of RuAS; UV-vis absorption spectra of RuAS and Ru2A; <sup>1</sup>H-NMR spectra of bsacbpy and its mixtures with LiI<sub>3</sub> and LiI; *J*-*V* plots of DSSCs with RuAA containing various concentrations of I<sub>2</sub>; IPCE spectra of DSSCs with RuAS and Ru2A, respectively containing various concentrations of I<sub>2</sub>. See DOI: 10.1039/c3ta01567j



Fig. 1 Synthesis route of RuAS dye.

## Experiments

#### Materials

All chemicals were obtained from Alfa Lancaster, Acros and Aldrich. The solvents were dried over sodium or CaH<sub>2</sub> and distilled before use. RuAS dye was synthesized by the typical one-pot synthetic method developed for heteroleptic polypyridyl ruthenium complexes.<sup>23</sup> The synthesis procedure is schematically illustrated in Fig. 1 and described in detail below.

#### Synthesis of 4,4'-bis(styrylaminocarbonyl)-2,2'-bipyridine

4,4'-Bis(styrylaminocarbonyl)-2,2'-bipyridine (bsacbpy) prepared for the ligand of RuAS dye was synthesized from 4,4'-dicarboxy-2,2'-bipyridine (dcbpy), the preparation of which has been given elsewhere.23 A suspension of dcbpy (1 mmol) in 5 mL of thionyl chloride (SOCl<sub>2</sub>) was refluxed in argon overnight. The excess SOCl<sub>2</sub> was removed under vacuum and 4,4'-bis(chlorocarbonyl)-2,2'-bipyridine (bclbpy) in white solid form was obtained. A solution of 4-aminostyrene (2.2 mmol) and triethylamine (2.5 mmol) in 10 mL of dry THF was then added dropwise into the flask containing dclbpy. After stirring for 2 h, the solution was poured into ice-water to produce a light-yellow precipitate, which was then filtered and washed with water, dichloromethane and diethyl ether. After drying under vacuum, a white solid product was afforded in 60% yield. <sup>1</sup>H-NMR (500 MHz,  $d_6$ -DMSO):  $\delta$  5.24 (d, 1H), 5.82 (d, 1H), 6.76 (m, 1H), 7.52 (d, 2H), 7.78 (d, 2H), 8.00 (m, 1H), 8.92 (s, 1H), 8.97 (d, 1H), 10.76 (s, 1H).

#### Synthesis of RuAS dye

To a solution of  $[\operatorname{RuCl}_2(p\text{-cymene})]_2$  (0.5 mmol) in 50 mL of dry DMF was added bsacbpy (1.0 mmol) with stirring. After reaction at 80 °C under argon for 4 h at dark, dcbpy (1.0 mmol) was added. After refluxing at 160 °C for another 4 h, excess NH<sub>4</sub>NCS was added to the reaction mixture. The reaction proceeded at 130 °C for 5 h and then the solvent was removed using a rotary-evaporator under vacuum. Water was added to the resulting mixture to remove excess NH<sub>4</sub>NCS. The water-insoluble product was collected on a sintered glass crucible by suction filtration and washed with water, followed by diethyl ether and dried in air. The crude product was dissolved in methanol containing

tetrabutylammonium hydroxide and then passed through a Sephadex LH-20 column using methanol as the eluent. The main band was collected and concentrated. A few drops of 0.01 M HNO<sub>3</sub> aqueous solution were added to precipitate the product. <sup>1</sup>H-NMR (500 MHz,  $d_6$ -DMSO):  $\delta$  5.23 (dd, 2H), 5.80 (dd, 2H), 6.72 (m, 2H), 7.47-7.86 (m, 12H), 8.36 (d, 1H), 8.43 (d, 1H), 8.99 (s, 1H), 9.13 (s, 1H), 9.16 (s, 1H), 9.30 (s, 1H), 9.44 (d, 1H), 9.45 (d, 1H), 10.71 (s, 1H), 10.93 (s, 1H). <sup>13</sup>C-NMR (500 MHz, d<sub>6</sub>-DMSO): δ 113.26, 113.34, 120.26, 120.53, 121.23, 121.48, 121.94, 122.25, 124.18, 124.94, 125.22, 125.98, 126.46, 126.55, 133.19, 133.32, 133.77, 134.39, 135.96, 136.01, 137.96, 138.09, 141.05, 141.61, 151.47, 152.17, 152.74, 156.63, 157.31, 157.92, 158.62, 162.64, 162.83, 165.14, 165.63 (see ESI, Fig. S1<sup>+</sup>). ESI MS (m/z): 907.0. Elemental analysis: anal. calcd for C<sub>42</sub>H<sub>30</sub>N<sub>8</sub>O<sub>6</sub>RuS<sub>2</sub>: C, 55.56, H, 3.33, N, 12.34, S, 7.06, O, 10.57%, found: C, 52.55, H, 3.86, N, 12.17, S, 7.13, O, 12.73%.

#### Fabrication of DSSCs

Dye-sensitized solar cells were fabricated using fluorine-doped tin oxide (FTO, 15  $\Omega$  per square) and indium-doped tin oxide (ITO, 7  $\Omega$  per square) glasses as substrate for the photo-electrode and counter-electrode, respectively. The counter-electrode was fabricated by depositing a thin Pt layer with sputtering. For preparation of the photo-electrode, a mesoporous film of anatase TiO<sub>2</sub> coated on the FTO glass substrate was fabricated by a sol–gel process, according to the literature.<sup>24</sup>

An active area of  $0.16 \text{ cm}^2 \text{ TiO}_2$  was selected from the sintered electrode, immersed in a mixed solution of acetonitrile (ACN) and *tert*-butanol (1 : 1 by volume) containing 0.3 mM of RuAS dye for 24 h, rinsed with acetone and dried. The liquid electrolytes containing 0.6 M propylmethylimidazolium iodide (PMII), 0.1 M LiI, 0.1 M guanidine thiocyanate (GuNCS) and 0.5 M *tert*-butylpyridine (TBP) and various concentrations of iodine (I<sub>2</sub>) in methoxyproprionitrile (MPN) were prepared.

#### Analytical methods

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) and heteronuclear single quantum coherence (HSQC) spectra were recorded on a Bruker Avance-500 MHz spectrometer by utilizing deuterated dimethyl sulphoxide (d<sub>6</sub>-DMSO) as solvent. ATR Fourier-transform infrared (FTIR) spectra were recorded on a ThermoNicolet NEXUS470 FTIR spectrometer using dye-adsorbed TiO<sub>2</sub> films and a blank TiO<sub>2</sub> film for background correction. UV-vis spectra were recorded on a JASCO V-550 UV-vis spectrometer. The electrospray ionization mass (ESI-MS) spectra were recorded on an LCQ Advantage and MS spectrometer. Elemental analysis was conducted by a HERAEUS VarioEL EA, NCH elemental analysis instrument. Photovoltaic characterization of the DSSCs was carried out by illuminating the cell with a 1000 W ozone-free xenon lamp equipped with a waterbased IR filter and AM 1.5 filter (Sciencetech). Photocurrentvoltage characterization plots were recorded with a potentiostat/ galvanostat (PGSTAT 302N, Autolab, Eco-Chemie, the Netherlands). The monochromator was scanned through the UV-vis region to generate the IPCE plot as defined by IPCE =  $1240(J_{sc}/$  $\omega\lambda$ ), where  $J_{\rm sc}$  is the short-circuit photocurrent (mA cm<sup>-2</sup>),  $\omega$  is the incident irradiative flux (W cm<sup>-2</sup>), and  $\lambda$  is the wavelength. Electrochemical impedance spectra (EIS) were obtained on the above-mentioned potentiostat/galvanostat equipped with an FRA2 module under constant light illumination of 100 mW cm<sup>-2</sup> and in the dark. The frequency range employed was from 65 kHz to 0.07 Hz. The applied bias voltage was set at the open circuit voltage of the DSSCs under illumination and at -0.7 V in the dark. The ac amplitude for both was set at 10 mV. The measurements for open-circuit potential decay transients of the DSSC were carried out using the same potentiostat/galvanostat and a green light-emitting diode (LXHL-NM98, Luxeon, 530 nm) as light source, whose power from LEDs applied on the DSSC was 20 mW cm<sup>-2</sup>.

## **Results and discussion**

#### **Characterization of RuAS**

RuAS dye synthesized according to the route illustrated in Fig. 1 was characterized by <sup>1</sup>H, <sup>13</sup>C and HSQC NMR, UV-vis, FTIR and ESI-MS spectra. Its <sup>1</sup>H NMR spectrum shown in Fig. 2(a) reveals that the pyridyl ring protons in the bipyridine ligand which tethers two styrylaminocarbonyl side chains have two different resonance peaks electronically in different environments, indicating that the ligands are coordinated to the ruthenium center in *cis*-heteroleptic complex form.<sup>25</sup> Interestingly, the RuAS dimer was frequently formed by intermolecular interaction between dicarboxylic anions from one dye and amide hydrogen groups from another dye, as indicated in Fig. 2(b), if the content of carboxylic salts was not controlled properly during purification of RuAS.<sup>25,26</sup> Trace amount of dimers are still observable in Fig. 2(a) for purified RuAS. The <sup>13</sup>C NMR spectrum of RuAS shows two resonance peaks at 133.29 and 133.32 ppm assigned to the carbons of the *N*-coordinated NCS ligands besides the pyridine peaks (see ESI, Fig. S1<sup>†</sup>). All of the NMR peaks have been assigned and confirmed by HSQC NMR spectrum (see ESI, Fig. S2<sup>†</sup>).

UV-vis absorption spectra of RuAS dissolved in the co-solvent of ACN and *tert*-butanol (volume ratio of 1 : 1) at a concentration range of 1–100  $\mu$ M are shown in Fig. 3. The high energy absorption peaks at 254 and 308 nm are attributed to the  $\pi$ – $\pi$ \* transitions for bsacbpy and dcbpy ligands,<sup>27</sup> whereas the low energy peaks at 393 and 541 nm are attributed to the metal-toligand charge transfer transitions (MLCT), whose molar extinction coefficients ( $\varepsilon$ ) are 14 250 and 11 883 M<sup>-1</sup> cm<sup>-1</sup> estimated from Beer's law,  $A = \varepsilon lc$ , where A is the absorption intensity, l is the path length and c is the concentration.



**Fig. 3** UV-vis absorption spectra of RuAS dye at various concentrations of ACN/ *tert*-butanol (1 : 1 by volume) solutions.



Fig. 2 <sup>1</sup>H NMR spectra of (a) RuAS and (b) its dimer.

Compared with Ru(4,4'-dicarboxyl-2,2'-bipyridine)(4,4'-dimethyl-2,2'-bipyridine)(NCS)<sub>2</sub> (denoted as Ru2A) dye,<sup>28</sup> RuAS has higher  $\varepsilon$  due to the electron-withdrawing amide groups containing in the bsacbpy ligand (see ESI, Fig. S3<sup>†</sup>).

ATR-FTIR spectra of RuAS adsorbed on the mesoporous TiO<sub>2</sub> film after background correction for mesoporous TiO<sub>2</sub> film were shown in Fig. 4(a). The absorption band at 2106 cm<sup>-1</sup> was attributed to the stretching of the NCS ligand, those at 3300 and 1670 cm<sup>-1</sup> were attributed to  $\nu$ (N–H) and  $\nu$ (C=O) of the amide group, and those at 1599 and 1385 cm<sup>-1</sup> were attributed to the asymmetric and symmetric stretching bands of carboxylate groups.<sup>29</sup> According to Deacon and Phillips, the frequency difference,  $\Delta \nu = \nu_{asym.}$ (COO<sup>-</sup>) –  $\nu_{sym.}$ (COO<sup>-</sup>), can be used to determine the binding mode of the dye on the mesoporous TiO<sub>2</sub> surface.<sup>30,31</sup> The  $\Delta \nu$  value of 214 cm<sup>-1</sup> for RuAS suggests the dye has anchored onto the mesoporous TiO<sub>2</sub> surface using a bidentate chelating mode.

#### Chelating triiodide anion with amide groups of RuAS

ATR-FTIR spectroscopy was used to investigate the chelating  $I_3^-$  capability of RuAS which has been chemisorbed on the mesoporous TiO<sub>2</sub> film. First, a few drops of 0.2 M LiI mixed with 0.2 M I<sub>2</sub> in methyl ethyl ketone (MEK) were added onto the film

Fig. 4 (a) ATR-FTIR spectra of RuAS dye chemisorbed onto TiO<sub>2</sub> film, the same film after adding two drops of 0.2 M Lil mixed with 0.2 M I<sub>2</sub> in MEK and drying, and the same film after rinsing with acetone; and (b) similar to (a) but without adding I<sub>2</sub>.

and fully dried. The change of IR spectrum was monitored as shown in Fig. 4(a). The broad peaks at 3300 cm<sup>-1</sup>  $\nu$ (N–H) and 1657 cm<sup>-1</sup>  $\nu$ (C=O) corresponding to amide groups clearly shifted and increased in strength, indicating the chelating interactions of amide hydrogen groups with triiodide anions  $(NH\cdots I_3^{-})$ . Notably, barely any change was observed when  $I_2$ was not added to produce  $LiI_3$  (see Fig. 4(b)). As the film was rinsed with acetone to remove LiI<sub>3</sub> and dried, the affected peaks were restored to their original positions, as shown in Fig. 4(a). Apparently, the chelating process is reversible. Chelating evidence for  $I_3^-$  rather than  $I^-$  by bacoby ligand can also be found from the <sup>1</sup>H NMR spectra of bsacbpy mixed with LiI<sub>3</sub> and LiI, respectively, in  $d_6$ -DMSO (see ESI, Fig. S4<sup>+</sup>). Because the size of the  $I_3^-$  anion is large enough, it is chelated by both amide hydrogen groups of RuAS dye, the chelating structure of which was simulated by ChemBio3D software (see ESI, Fig. S5<sup>+</sup>).

#### Photocurrent-voltage characteristics

The photocurrent density-voltage (J-V) characteristic plots of the DSSCs with RuAS and liquid electrolyte containing 0.6 M PMII, 0.10 M LiI, 0.1 M GuNCS, 0.5 M TBP, and various concentrations of I<sub>2</sub> in MPN under AM 1.5 full sunlight (100 mW cm<sup>-2</sup> illumination) were shown in Fig. 5(a) with their photovoltaic properties listed in Table 1. I<sub>2</sub>, being added to the liquid electrolyte, will react with I<sup>-</sup> to form I<sub>3</sub><sup>-</sup>, as shown in the following equation:

$$I_2 + I^- \leftrightarrow I_3^- \tag{1}$$

Because the equilibrium constant is rather high in organic solvent and the total I<sup>-</sup> source (LiI plus PMII) is 0.7 M, I<sub>2</sub> nearly transformed into  $I_3^{-.3^2}$  As the concentration of I<sub>2</sub> in the liquid electrolyte increased from nil to 0.03 M, the short circuit current density ( $J_{sc}$ ) of the DSSC increased by 45% and then decreased as the concentration further increased to 0.2 M. Because the total concentration of I<sup>-</sup> was 0.7 M, as 0.03 M I<sub>2</sub> was added to consume I<sup>-</sup>, it would not noticeably affect the dye regeneration rate. However, at high concentration of I<sub>2</sub> (over 0.1 M), the concentration of I<sup>-</sup> would be reduced and delay the dye regeneration rate. On the other hand, I<sub>3</sub><sup>-</sup> is responsible for the reduction reaction in the counter electrode of the DSSC, as shown in the following equation:

$$I_3^- + 2e^- \rightarrow 3I^- \tag{2}$$

If  $I_2$  was not added to the electrolyte, the source of  $I_3^-$  would only come from the dye regeneration in the photoelectrode by performing the reverse reaction of eqn (2). Because only a small amount of  $I_3^-$  was obtained from dye regeneration, the photocurrent was significantly reduced, as shown in Fig. 5(a). In addition, the charge recombination rate at the mesoporous TiO<sub>2</sub>-electrolyte interface was also reduced, leading to the highest  $V_{oc}$ . Although the addition of a small amount of  $I_2$  to the electrolyte substantially decreased  $V_{oc}$ , further increase of  $I_2$ concentration from 0.01 to 0.2 M. barely changed  $V_{oc}$ , as shown in Fig. 5(a) and Table 1. It has been reported that  $V_{oc}$  of the DSSC





**Fig. 5** (a) Photocurrent–voltage characteristic plots of the DSSCs with RuAS and liquid electrolyte containing various  $I_2$  concentrations under AM 1.5 full sunlight, and (b) IPCE spectra of the DSSCs with RuAS and Ru2A dyes, respectively containing 0.05 M  $I_2$  in the liquid electrolyte.

with N3 dye and liquid electrolyte almost linearly decreased as the concentration of  $I_3^-$  was increased from 0.01 to 0.05 M in logarithmic scale.<sup>33</sup> Besides, the  $V_{oc}$  of DSSCs with Ru2A which contains the 4,4'-dimethyl-2,2'-bipyridine ligand<sup>28</sup> gradually decreased from 0.703 to 0.639 V as the concentration of  $I_2$  was increased from 0.01 to 0.2 M (see ESI, Fig. S6 and Table S1<sup>+</sup>).

Because RuAS dye is capable of chelating  $I_3^-$ , few  $I_3^-$  anions could make contact with the TiO<sub>2</sub> mesoporous layer. Therefore, even increasing the  $I_2$  concentration to 0.2 M did not noticeably affect  $V_{oc}$ . To investigate the electron-withdrawing effect of amide groups in the bsacbpy ligand of the RuAS dye on the photocurrent, we have compared the IPCE spectrum of RuAS dye in DSSCs with Ru2A dye. Both IPCE spectra shown in Fig. 5(b) are similar except that the DSSC with RuAS has a higher IPCE in the visible light region from 500 to 800 nm wavelength. The higher IPCE for RuAS dye is obviously attributed to its higher molar extinction coefficient related to the electronwithdrawing amide groups (see ESI, Fig. S3<sup>†</sup>). All IPCE spectra of DSSCs with RuAS compared to Ru2A with various concentrations of I<sub>2</sub> are also provided in the ESI (see Fig. S7<sup>†</sup>). After all, compared to Ru2A dye, RuAS dye not only has a higher  $J_{sc}$ , but  $V_{oc}$  is also enhanced since the amide groups are capable of chelating I<sub>3</sub><sup>-</sup>.

#### **EIS analysis**

The EIS technique is often used to characterize the kinetics of DSSCs by analysing the variation in impedance associated with the different interfaces of cells.<sup>34</sup> In this work, by varying I<sub>2</sub> concentrations in the liquid electrolyte, the Nyquist plots were measured at the  $V_{\rm oc}$  of the DSSCs under 1.5 AM full sunlight. By choosing an appropriate equivalent circuit model, shown in Fig. 6(a), the Nyquist plots of the DSSCs were fitted with Z-view software (see Fig. 6(b)) and the results are also listed in Table 1. Its main three semicircles, from low to high impedance, are related to the Pt-electrolyte interface with the resistance  $R_1$ , the dye-sensitized TiO<sub>2</sub> film-electrolyte interface with the resistance  $R_2$  and electrolyte diffusion with the resistance  $R_3$ . In the DSSCs with the  $I_2$  containing electrolyte, the  $R_2$  values are similar. However, R<sub>3</sub> reduced substantially with increasing concentration of I<sub>2</sub>. Notably, the increase of fill factor from  $0.55 \pm 0.01$  to  $0.65 \pm 0.01$  by increasing the concentration of I<sub>2</sub> from 0.05 to 0.1 M might be related to the faster charge transportation or smaller  $R_3$  in the electrolyte (see Table 1).

In the Bode phase plot, the second characteristic peak at the frequency (*f*), associated with the electron transfer rate at the TiO<sub>2</sub> and electrolyte interface, had shifted to higher frequency as 0.01 M I<sub>2</sub> was added to the liquid electrolyte. The electron lifetime ( $\tau_r$ ) calculated by the following equation,

$$\tau_{\rm r} = 1/2\pi f,\tag{3}$$

due to charge recombination was reduced from 20.75 to 12.32 ms. Further increase of  $I_2$  concentration from 0.01 to 0.05 M barely changed the charge recombination rate. It is noteworthy that the concentration of I<sup>-</sup> was much higher than that of  $I_3^-$  in this concentration range. However, as the  $I_2$  concentration was increased to 0.1 M,  $\tau_r$  decreased to 7.31 ms along with the decrease of  $J_{sc}$ . This implied that the competition between the charge recombination and dye regeneration rates had taken place simultaneously at the TiO<sub>2</sub>/dye/electrolyte interfaces. Because the number of injected charges in the TiO<sub>2</sub> layer was

Fable 1         Photovoltaic characteristics and EIS data of DSSCs with RuAS containing various I <sub>2</sub> concentrations in liquid electrolyte under 100 mW cm <sup>-2</sup> illumination											
$\left[ I_{2}\right] \left( M ight)$	PCE (%)	$J_{\rm sc}  ({ m mA}  { m cm}^{-2})$	$V_{\rm oc}$ (V)	ff	$R_{\rm s}\left(\Omega\right)$	$R_1\left(\Omega\right)$	$R_2(\Omega)$	$R_3(\Omega)$	$\tau_{\rm r}  ({\rm ms})$		
0	$5.74\pm0.22$	$11.29\pm0.35$	$0.736\pm0.001$	$0.69\pm0.01$	26.86	8.10	12.50	34.35	20.75		
0.01	$5.46 \pm 0.12$	$15.54\pm0.07$	$0.702\pm0.002$	$0.50\pm0.01$	27.70	10.10	9.40	12.76	12.32		
0.03	$6.36\pm0.07$	$16.38\pm0.06$	$0.699 \pm 0.001$	$0.56\pm0.01$	22.86	15.40	9.10	9.50	10.35		
0.05	$6.37 \pm 0.05$	$16.29\pm0.10$	$0.709 \pm 0.001$	$0.55\pm0.01$	23.44	12.20	9.90	8.70	10.35		
0.10	$6.86 \pm 0.12$	$14.86\pm0.30$	$0.706\pm0.011$	$0.65\pm0.01$	24.50	11.60	10.20	7.50	7.31		
0.20	$6.33\pm0.13$	$14.72\pm0.31$	$0.697\pm0.002$	$0.62\pm0.01$	25.30	11.87	9.34	7.47	6.14		



Fig. 6 (a) Equivalent circuit model, (b) Nyquist and (c) Bode plots of DSSCs with RuAS containing various  $I_2$  concentrations in liquid electrolyte under 100 mW cm<sup>-2</sup> illumination.

decreased by reducing the charge regeneration rate, the total number of recombined charges in the interface might not be affected as  $\tau_r$  decreased, which explains why  $V_{oc}$  was not affected as the I<sub>2</sub> concentration was increased to 0.1 M.

In dark conditions, we also measured the impedance spectra of the DSSC with RuAS dye using the Nyquist plots and Bode plots, as shown in Fig. 7, and the data obtained by the equivalent circuit model and eqn (3) are listed in Table 2.  $R'_2$  in the dark is more than ten times larger than  $R_2$  under illumination for all the DSSCs and decreased with the content of I<sub>2</sub> in the electrolyte, unless the concentration of  $I_2$  is higher than 0.1 M. Obviously, under high impedance the charge in the TiO<sub>2</sub> layer was able to perform the charge recombination, even if  $I_3^-$  was located far from TiO<sub>2</sub>. The electron lifetime,  $\tau'_r$ , due to charge recombination in the dark is also ten times longer than  $\tau_r$  under illumination for all the DSSCs and decreased with the content of I<sub>2</sub> in the electrolyte. Higher concentration of  $I_3^-$  in the vicinity of the TiO<sub>2</sub> layer indeed increased the charge recombination of the DSSC if time for recombination was long enough.



Fig. 7 (a) Nyquist and (b) Bode plots of DSSCs with RuAS and liquid electrolyte containing various  $I_2$  concentrations in the dark.

#### Open-circuit potential decay transient measurements

The measurement of open-circuit potential decay transients developed by Duffy and Hagfeldt *et al.*<sup>35-37</sup> was used to investigate the electron transport in the DSSCs. The DSSC was illuminated for 5 seconds at 20 mW cm<sup>-2</sup> under open-circuit conditions, and then the voltage ( $V_d$ ) was left to decay for a certain period of time ( $t_d$ ) in the dark. The measured  $V_d$  versus  $t_d$  plots for the DSSCs with RuAS and liquid electrolyte containing various I<sub>2</sub> concentrations in the liquid electrolyte are shown in Fig. 8.

The onset of  $V_d$  (*i.e.*,  $V_{d,o}$ ) appeared at 0.75 V for the DSSC without I<sub>2</sub> in the liquid electrolyte. As 0.01 M I<sub>2</sub> was added to the liquid electrolyte,  $V_{d,o}$  decreased to 0.72 V. With further increase

 Table 2
 EIS data of DSSCs with RuAS and liquid electrolyte containing various I<sub>2</sub> concentrations in the dark

$\left[ I_{2}\right] \left( M ight)$	$R_{ m s}^{\prime}\left(\Omega ight)$	$R_{1}^{\prime}\left(\Omega ight)$	$R_{2}^{\prime}\left( \Omega ight)$	$\tau_{ m r}^{\prime}({ m ms})$
0	28.63	127.70	902.40	299.94
0.01	27.80	156.30	374.10	167.34
0.03	22.37	81.35	206.60	118.17
0.05	25.21	92.72	199.60	118.17
0.10	22.80	56.20	137.00	70.13
0.20	25.75	77.86	158.00	58.93



Fig. 8 Voltage decay transient plots of the DSSC with RuAS containing various  $I_2$  concentrations in liquid electrolyte after illumination at 20 mW cm<sup>-2</sup> from LED for 5 seconds under open-circuit conditions.

of I<sub>2</sub> concentration to 0.2 M,  $V_{d,o}$  only decreased to 0.7 V. The change of  $V_{d,o}$  with increasing content of I<sub>2</sub> in the liquid electrolyte is similar to that of  $V_{oc}$  for the DSSCs illuminated at full sunlight, as shown in Table 1. However, as the content of I<sub>2</sub> in the liquid electrolyte increased,  $V_d$  decayed faster after 0.1 s in the dark (see Fig. 8). This indicated that although I<sub>3</sub><sup>-</sup> was chelated by RuAS, more free I<sub>3</sub><sup>-</sup> anions in the vicinity of the TiO<sub>2</sub> layer would have higher chance of charge recombination, resulting in a higher descending rate of  $V_d$  after 0.1 s.

## Conclusions

RuAS dye is capable of chelating  $I_3^-$  anions, which was confirmed by ART-FTIR and <sup>1</sup>H-NMR spectroscopies. With increasing  $I_2$  concentration in the liquid electrolyte,  $V_{oc}$  of the DSSC barely changed owing to the fact that the  $I_3^-$  anions in the liquid electrolyte were chelated by RuAS dye and free  $I_3^-$  anions located far from the mesoporous TiO<sub>2</sub> layer play a lesser role in the charge recombination reaction.

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### Notes and references

- 1 B. O'Regan and M. Grätzel, Nature, 1991, 353, 37.
- 2 M. Grätzel, Nature, 2001, 414, 338.
- 3 W. Q. Wu, J. Y. Liao, H. Y. Chen, X. Y. Yu, C. Y. Su and D. B. Kuang, *J. Mater. Chem.*, 2012, 22, 18057.
- 4 J. Zhao, B. Sun, L. Qiu, H. Caocen, Q. Li, X. Chen and F. Yan, *J. Mater. Chem.*, 2012, **22**, 18380.
- 5 J. T. Park, R. Patel, H. Jeon, D. J. Kim, J. S. Shin and J. H. Kim, *J. Mater. Chem.*, 2012, **22**, 6131.
- 6 C. Y. Chen, M. Wang, J. Y. Li, N. Pootrakulchote, L. Alibabaei, C. H. Ngoc-Le, J. D. Decoppet, J. H. Tsai, C. Grätzel, C. G. Wu, S. M. Zakeeruddin and M. Grätzel, *ACS Nano*, 2009, 3, 3103.

- 7 F. Gao, Y. Wang, D. Shi, J. Zhang, M. Wang, X. Jing,
  R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and
  M. Grätzel, *J. Am. Chem. Soc.*, 2008, 130, 10720.
- 8 D. Kuang, C. Klein, S. Ito, J. E. Moser, R. Humphry-Baker, S. M. Zakeeruddin and M. Grätzel, *Adv. Funct. Mater.*, 2007, 17, 154.
- 9 H. Y. Yang, Y. S. Yen, Y. C. Hsu, H. H. Chou and J. T. Lin, Org. Lett., 2010, 12, 16.
- 10 J. S. Ni, C. Y. Hung, K. Y. Liu, Y. H. Chang, K. C. Ho and K. F. Lin, J. Colloid Interface Sci., 2012, 386, 359.
- 11 Y. H. Chang, P. Y. Lin, S. R. Huang, K. Y. Liu and K. F. Lin, J. Mater. Chem., 2012, 22, 15592.
- 12 J. N. D. Freitas, A. F. Nogueira and M. A. D. Paoli, *J. Mater. Chem.*, 2009, **19**, 5279.
- 13 C. H. Lee, K. Y. Liu, S. H. Chang, K. J. Lin, J. J. Lin, K. C. Ho and K. F. Lin, *J. Colloid Interface Sci.*, 2011, **363**, 635.
- 14 C. W. Tu, K. Y. Liu, A. T. Chien, C. H. Lee, K. C. Ho and K. F. Lin, *Eur. Polym. J.*, 2008, 44, 608.
- 15 K. C. Huang, Y. H. Chang, C. Y. Chen, C. Y. Liu, L. Y. Lin, R. Vittal, C. G. Wu, K. F. Lin and K. C. Ho, *J. Mater. Chem.*, 2011, **21**, 18467.
- 16 K. C. Huang, C. W. Hu, C. Y. Tseng, C. Y. Liu, M. H. Yeh, H. Y. Wei, C. C. Wang, R. Vittal, C. W. Chu and K. C. Ho, *J. Mater. Chem.*, 2012, 22, 14727.
- 17 W. J. Hong, Y. X. Xu, G. W. Lu, C. Li and G. Q. Shi, *Electrochem. Commun.*, 2008, **10**, 1555.
- 18 D. Kuang, C. Klein, H. J. Snaith, J. E. Moser, R. Humphry-Baker, P. Comte, S. M. Zakeeruddin and M. Grätzel, *Nano Lett.*, 2006, 6, 769.
- 19 J. H. Yum, S. J. Moon, C. S. Karthikeyan, H. Wietasch, M. Thelakkat, S. M. Zakeeruddin, M. K. Nazeeruddin and M. Grätzel, *Nano Energy*, 2012, 1, 6.
- 20 N. Cho, C. W. Lee, D. W. Cho, S. O. Kang, J. Ko and M. K. Nazeeruddin, *Bull. Korean Chem. Soc.*, 2011, 32, 3031.
- 21 K. Y. Liu, C. Y. Ko, K. C. Ho and K. F. Lin, *Polymer*, 2011, 52, 3318.
- 22 K. Y. Liu, K. C. Ho and K. F. Lin, Prog. Photovolt: Res. Appl., 2012, DOI: 10.1002/pip.2329.
- 23 K. Y. Liu, C. L. Hsu, S. H. Chang, J. G. Chen, K. C. Ho and K. F. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 366.
- 24 C. J. Barbe, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover and M. Grätzel, J. Am. Ceram. Soc., 1997, 80, 3157.
- 25 D. Kuang, S. Ito, B. Wenger, C. Klein, J. E. Moser, R. Humphry-Baker, S. M. Zakeeruddin and M. Grätzel, J. Am. Chem. Soc., 2006, 128, 4146.
- 26 J. R. Jennings, Y. Liu, Q. Wang, S. M. Zakeeruddin and M. Grätzel, *Phys. Chem. Chem. Phys.*, 2011, 13, 6637.
- M. K. Nazeeruddin, S. M. Zakeeruddin, R. Humphry-Baker,
   M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover,
   C. H. Fischer and M. Grätzel, *Inorg. Chem.*, 1999, 38, 6298.
- 28 K. F. Lin, J. S. Ni, C. H. Tseng, C. Y. Hung and K. Y. Liu, J. Colloid Interface Sci., submitted.
- 29 Z. S. Wang, K. Hara, Y. Dan-Oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa and H. Sugihara, *J. Phys. Chem. B*, 2005, **109**, 3907.
- 30 G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, 33, 227.

- 31 H. N. Tian, X. C. Yang, R. K. Chen, R. Zhang, A. Hagfeldt and L. C. Sunt, *J. Phys. Chem. C*, 2008, **112**, 11023.
- 32 G. Boschloo and A. Hagfeldt, Acc. Chem. Res., 2009, 42, 1819.
- 33 S. Y. Huang, G. Schlichthörl, A. J. Nozik, M. Grätzel and A. J. Frank, *J. Phys. Chem. B*, 1997, **101**, 2576.
- 34 K. D. Benkstein, N. Kopidakis, J. van de Lagemaat and A. J. Frank, *J. Phys. Chem. B*, 2003, **107**, 7759.
- 35 N. W. Duffy, L. M. Peter, R. M. G. Rajapakse and K. G. U. Wijayantha, *Electrochem. Commun.*, 2000, 2, 658.
- 36 L. M. Peter, N. W. Duffy, R. L. Wang and K. G. U. Wijayantha, *J. Electroanal. Chem.*, 2002, **524–525**, 127.
- 37 G. Boschloo and A. Hagfeldt, J. Phys. Chem. B, 2005, 109, 12093.