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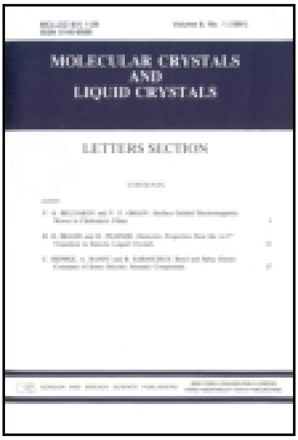

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Synthesis and Photovoltaic Performance of Ionic Dyes for Quasi-Solid State Dye-Sensitized Solar Cells

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We prepared the ionic dyes and investigated their electrochemical properties and photosensitizing performances in the quasi-solid state dye-sensitized solar cells (QS-DSSCs). The LUMO energy level of ionic dye with carbazole moiety is higher than that of the dyes with phenothiazine and triphenylamine chromophore, resulting in highest power conversion efficiency (PCE) in the QD-DSSC. Compared with Ru-complex sensitizer, the ionic dyes showed relatively low photovoltaic performance in the QS-DSSCs, originating in lower LUMO energy level. The effect of Li^+ ion in the quasi-solid state electrolyte on the photovoltaic characteristics of QS-DSSCs was investigated in order to confirm the correlation between the conduction band of TiO_2 electrode and LUMO energy level of photosensitizers. The conduction band of TiO_2 electrode could be reduced by adding the Li^+ ion in the electrolyte, attributing for the enlargement of PCE value in the QS-DSSC.

Keywords Ionic dyes; organic photosensitizers; photovoltaic performances; quasi-solid state dye-sensitized solar cells; semi-solid state electrolyte

Introduction

Dye-sensitized solar cells (DSSCs) have attracted much attention of many research groups on account of their benefits, which include a low-cost fabrication process with fairly high power conversion efficiency (PCE) compared to conventional p-n junction solar cells [1,2]. The structure of the DSSC was composed of a dye-adsorbed wide band gap semiconductor electrode, a liquid type of electrolyte containing I^-/I_3^- redox couples, and a Pt-coated counter electrode [3–5]. The mechanism of the DSSC is based on the injection of electrons from photosensitizers (mainly Ru-complex such as N3 and N719) into the conduction band

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of the electrode on which the photosensitizers are adsorbed. The oxidized photosensitizers are reduced by electron transfer from the electrolyte.

In spite of relatively lower photovoltaic performance in DSSCs, organic dyes have been employed as promising candidates for the photosensitizer because of their great advantages (e.g., high molar extinction coefficient, convenient synthetic process, customized molecular design), interesting photophysical and photochemical properties, and low-cost production [6–13].

On the other hand, the potential problems caused by liquid electrolytes such as the leakage and volatilization of solvents, desorption and photo-degradation of attached dyes and corrosion of the Pt counter electrode, have had the effect of limiting the long-term stability and practical application of DSSCs. In order to solve above mentioned problems, many studies have been made quasi-solid type of electrolytes composed of organic and inorganic hole-transport materials [14], polymer gels [15] and solid state type of electrolytes [16] to replace liquid electrolytes.

In this paper, a series of ionic structure of organic dye has been synthesized and applied to the quasi-solid state DSSCs (QS-DSSCs). The photovoltaic performances of QS-DSSCs composed of ionic dye systems were investigated in order to verify sensitizing properties of organic dyes containing different electron donor moiety in the chromophore. In detail, the electro-optical spectral properties, current density-voltage characteristics, and the incident photon-to-current conversion efficiencies were observed to explain the photovoltaic properties of ionic dye systems in QS-DSSCs.

Experimental

Synthesis

Materials: All commercially available starting materials and solvents were purchased from Aldrich, TCI, and ACROS Co. and used without further purification unless otherwise stated.

2,3,3-Trimethyl-3H-indole-5-carboxylic acid (1)

A mixture of 4-(2-(3-methylbutan-2-ylidene)hydrazinyl) benzoic acid (11.5 g, 52.2 mmol) and115 ml acetic acid were refluxed under nitrogen atmosphere for 24 hr.The solvent was removed, and the crude product was purified using column chromatography on a silica gel with methanol:chloroform (V/V ratio 1:9). The product was obtained as a yellow solid. (Yield: 73 %.) H NMR (300 MHz, DMSO-d_6): δ 7.98 (s, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 8.1 Hz,1H), 2.25 (s, 3H), 1.27 (s, 6H).

5-Carboxy-2,3,3-trimethyl-1-octyl-3H-indolium iodide (2)

2,3,3-Trimethyl-3H-indole-5-carboxylic acid (6.15 g, 30.0 mmol) and1-iodooctane (21.85 ml, 120 mmol) were dissolved in 100 mlofacetonitrile. The mixture was stirred at 90 °C for 30 hr under nitrogen atmosphere.The solvent was removed and the crude product was washed with Ethyl Ether. The product was obtained as yellow solid. (Yield: 61%). H NMR (300 MHz, DMSO-d_6): δ8.38 (s, 1H), 8.15 (d, J = 8.3 Hz, 1H), 8.07 (d, J = 8.3 Hz,1H), 4.45 (t, J = 7.5Hz, 2H), 2.87 (s, 3H), 1.57 (s, 6H), 1.45–1.10 (m, 12H), 0.83 (t, J = 5.5 Hz, 3H).

10-hexyl-10H-phenothiazine-3-carbaldehyde (3)

10-Hexyl-10H-phenothiazine (10 g, 35.3 mmol) was dissolved in 80 mL DMF. $POCl_3$ (27.06 g, 176.5 mmol) was added drop to drop to the mixture at 0 °C. As the temperature was increased to room temperature, the mixture was changed to a clear bright red solution. The reaction mixture was heated to 45 °C and then stirred for an additional 2 hr. The mixture was poured in an ice-bath and then neutralized with sodium bicarbonate. Recrystallization of resulting precipitates from ethanol afforded crystals of 10-hexyl-10H-phenothiazine-3-carbaldehyde. Pale white solids were collected by filtering. (Yield: 94%). H NMR (300MHz, DMSO-d_6):δ9.83 (s, 1H), 7.77 (d, J = 8.1Hz,1H), 7.64 (s, 1H), 7.28–7.02 (m, 5H), 4.02–3.97 (m, 2H), 1.76–1.71 (m, 2H), 1.43 (s, 2H), 1.30 (s, 4H), 0.87 (s, 3H).

4-(diphenylamino)benzaldehyde (4)

Compound (4) was prepared from 9-hexyl-9H-carbazole as a light yellow powder with the same method used for (3) (Yield: 90%). H NMR (300 MHz, $CDCl_3$): δ9.79 (s, 1H), 7.30–7.36 (t, 4H), 7.67 (d, 2H), 7.15–7.18 (m, 6H), 7.00 (d,2H).

9-hexyl-9H-carbazole-3-carbaldehyde (5)

Compound (5) was prepared from triphenylamine as a light yellow powder with the same method used for (3) (Yield: 90%). H NMR (300 MHz, DMSO-d_6): δ 10.21 (s, 1H), 8.91 (s, 1H), 8.44 (d, J = 8.1Hz, 1H), 8.14 (d, J = 8.7 Hz,1H), 7.93 (d, J = 8.4 Hz,1H), 7.85 (d, J = 8.1 Hz,1H), 7.72–7.67 (m, 1H), 4.64–4.591 (m, 2H), 1.94 (s, 2H), 1.41 (s, 6H), 0.95 (s, 3H).

(E)-5-carboxy-2-(2-(10-hexyl-10H-phenothiazin-3-yl)vinyl)-3,3-dimethyl-1-octyl-3H-indolium iodide (PTZ)

10-Hexyl-10H-phenothiazine-3-carbaldehyde (0.16g, 0.514 mmol) was dissolved in 35 ml methanol. 5-carboxy-2,3,3-trimethyl-1-octyl-3H-indolium iodide (0.23g, 0.514 mmol) was added drop to the mixture. The solution was refluxed and then stirred 12 hr. Recrystallization of resulting precipitates from ethyl acetate afforded crystals of (E)-5-carboxy-2-(2-(10-hexyl-10H-phenothiazin-3-yl)vinyl)-3,3-dimethyl-1-octyl-3H-indolium iodide (**PTZ**). Pale dark red solids were collected by filtering (0.19 g, 50%). H NMR (300 MHz, DMSO-d_6) : δ 8.59 (m, 2H), 8.32 (d, J = 8.4 Hz, 1H), 8.25 (s, 2H), 8.13 (s, 1H), 7.68 (d, J = 16.2Hz, 1H), 7.42–7.29 (m, 4H), 7.20 (t, 1H), 4.83 (s, 2H), 4.18 (s, 2H), 1.98–1.87 (m, 10H), 1.56–1.38 (m, 16H), 1.01 (s, 6H). H NMR (600 MHz, DMSO-d_6) : δ8.41 (d, J = 15.6Hz, 1H), 8.38 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 8.05 (m, 2H), 7.93 (d, J = 7.8 Hz, 1H), 7.50 (d, J = 16.2 Hz, 1H), 7.24 (t, 1H), 7.17 (d, J = 7.8 Hz, 2H), 7.12 (d, J = 8.4 Hz, 1H), 7.02 (t, 1H), 4.64 (t, 2H), 4.00 (t, 2H), 1.80 (s, 7H), 1.70 (t, 3H), 1.27–1.19 (m, 16H), 0.84 (t, 3H), 0.78 (t, 3H).

(E)-5-carboxy-2-(4-(diphenylamino)styryl)-3,3-dimethyl-1-octyl-3H-indolium (TPA)

(E)-5-Carboxy-2-(4-(diphenylamino)styryl)-3,3-dimethyl-1-octyl-3H-indolium (TPA) was prepared from (5) as a dark purple powder with the same method used for (CBZ) (Yield: 48%). H NMR (300 MHz, DMSO-d_6) : δ8.48 (d, J = 15.9Hz, 1H), 8.37 (s, 1H), 8.12 (t, J = 9.6Hz, 3H), 7.92 (t, J = 8.1Hz, 2H), 7.51–7.25 (m, 10H), 6.88 (d, J = 8.4Hz, 2H), 4.58 (s, 2H), 1.81 (s, 8H), 1.28–1.20 (m, 10H), 0.81 (s, 3H).H NMR (600 MHz, DMSO-d_6) :

δ8.46 (d, J = 15Hz, 1H), 8.35 (s, 1H), 8.12 (d, J = 8.4Hz, 1H), 8.08 (d, J = 9Hz, 2H), 7.89 (d, J = 9 Hz, 1H), 7.46 (t, 4H), 7.38 (d, J = 16.2 Hz, 1H), 7.38 (t, 2H), 7.25 (d, J = 7.8 Hz, 4H), 6.86 (s, J = 8.4 Hz, 2H), 4.56 (t, 2H), 1.79 (s, 8H), 1.27–1.89 (m, 10H), 0.78 (t, 3H).

(E)-5-carboxy-2-(2-(9-hexyl-9H-carbazol-3-yl)vinyl)-3,3-dimethyl-1-octyl-3H-indolium (CBZ)

9-Hexyl-9H-carbazole-3-carbaldehyde (0.1g, 0.358 mmol) was dissolved in 35 ml methanol. 5-carboxy-2,3,3-trimethyl-1-octyl-3H-indolium (0.16 g, 0.394 mmol) was added drop to the mixture. The solution was refluxed and then stirred 12 hr. Recrystallization of resulting precipitates from ethyl acetate afforded crystals of (E)-5-carboxy-2-(2-(9-hexyl-9H-carbazol-3-yl)vinyl)-3,3-dimethyl-1-octyl-3H-indolium (CBZ). Pale dark red solids were collected by filtering. (0.1 g, 50%). H NMR (300 MHz, DMSO-d_6) : δ9.11 (s, 1H), 8.64 (d, J = 16.2 Hz, 1H), 8.41 (s, 2H), 8.19 (q, 2H), 7.66 (d, J = 9 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.20 (t, 2H), 7.61 (t, J = 6.9 Hz, 1H), 7.37 (t, J = 6.9 Hz, 1H), 4.70 (s, 2H), 4.50 (s, 2H), 1.88 (s, 10H), 1.26–1.19 (m, 16H), 0.79 (q, 6H). H NMR (600 MHz, DMSO-d_6): δ9.09 (s, 1H), 8.77 (d, J = 16.2Hz, 1H), 8.39 (d, J = 92Hz, 2H), 8.21 (d, J = 7.8Hz, 1H), 8.15 (d, J = 7.8 Hz, 1H), 7.95 (d, J = 9 Hz, 1H), 7.83 (d, J = 9 Hz, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 16.8 Hz, 1H), 7.57 (t, 1H), 7.37 (t, 1H), 4.71 (t, 2H), 4.51 (t, 2H), 1.88 (s, 7H).1.79 (t, 3H), 1.27–1.18 (m, 16H), 0.77 (t, 3H), 0.74 (t, 3H).

Instrumental Analysis

All ^{1}H NMR spectra were recorded on a Varian Mercury NMR 300 MHz, 600 MHz spectrometer using $CDCl_3$ and DMSO-d_6 purchased from Cambridge Isotope Laboratories, Inc. The redox properties of three dyes were examined using cyclic voltammetry (Model: CV-BAS-Epsilon). The electrolyte solution was used with 0.10 M of tetrabutylammoniumhexafluorophosphate ($TBAPF_6$) in freshly dried dimethylformamide (DMF). Ag/AgCl and Pt wire (0.5 mm in diameter) electrodes were used as reference and counter electrodes, respectively. The scan rate was fixed at 100 mV/s. The active areas of the dye-adsorbed TiO_2 films were estimated using a digital microscope camera with image-analysis-software (Moticam 1000). The photovoltaic I-V characteristics of the prepared QS-DSSCs were measured under 1 sunlight intensity (100 mW/cm^2, AM 1.5) verified with an AIST-calibrated Si-solar cell (PEC-L11, Peccell Technologies, Inc.). The monochromatic IPCEs were plotted as a function of light wavelength using an IPCE measurement instrument (PEC-S20, Peccell Technologies, Inc.).

Assembly and Characterization of QS-DSSCs

The QS-DSSCs were fabricated as follows. The conducting glass substrate (FTO; TEC8, Pilkington, 8 Ω/cm^2, thickness of 2.3 mm) was cleaned in ethanol by ultrasonication. TiO_2 pastes (TiO_2 particles size: approximately 20–30 nm) were prepared using ethyl cellulose (Aldrich), lauric acid (Fluka), and terpineol (Aldrich). The prepared TiO_2 paste was coated on the pre-cleaned glass substrate using a doctor-blade, and sintered at 450 °C for 30 min. The thickness of the sintered TiO_2 layer (8 μm) was measured with an Alpha-step IQ surface profiler (KLA Tencor). The TiO_2 paste was re-coated over the sintered layer using roughly 250 nm TiO_2 particles as a scattering layer and sintered again at 450 °C for 30 min. The prepared TiO_2 film was dipped in 0.04 M of $TiCl_4$ aqueous solution at 70 °C for 30 min. For dye adsorption, the annealed TiO_2 electrodes were immersed in the ionic dye solutions

(0.1 mM with 10 mM concentrations of chenodeoxycholic acid (CDCA)in ethanol) and kept at room temperature for 24 h. The Pt counter electrodes were prepared by thermal reduction of a thin film formed from 7 mM of H_2PtCl_6 in 2-propanol at 400 °C for 20 min. The dye-adsorbed TiO_2 electrode and Pt counter electrode were assembled using 60 μm-thick Surlyn (Dupont 1702) as a bonding agent. A quasi-solid electrolyte was composed 10 wt% PMMA (MW: 120,000; 10 wt%) into the solvent (ethylene carbonate, propylene carbonate, and dimethyl carbonate mixture with the mass ratio of 4:2:1) and the solution was stirred and heated at 60 °C for 24 h to dissolve PMMA, followed by cooling down to room temperature to form a polymer gel. Finally, lithium iodide (0.5 M), and iodine (0.05 M) were added into the gel system, then sonicated in 60 minutes with stirring for 24 h.

Results and Discussion

Synthesis and Electro-optical Properties of Ionic Dyes for Photosensitizers

A series of ionic dye structures as the photosensitizer were synthesized in order to investigate the photovoltaic properties in the QS-DSSCs. The ionic dyes, **PTZ, TPA, and CBZ** were designed to have a different electron donating moiety in the chromophore which was connected with same electron accepting indolenium carbocation, respectively. The ionic dyes were synthesized in moderate yields using the four steps that are illustrated in Scheme 1 and experimental section.

UV-Vis absorption spectra of the synthesized ionic dyes in ethanol solution (a) and on the TiO_2 film state (b) are shown in Fig. 1. The electro-optical characteristics of the ionic dyes are summarized in Table 1. The HOMO and LUMO energies of ionic dyes were determined with cyclic voltammogram and absorption edge in UV-Vis spectra [17]. The maximum absorption wavelength (λ_{max}) of the ionic dyes were appeared in 514 nm ~ 570 nm in ethanol solution, and 520 nm ~ 575 nm on the TiO_2 film state. The relatively weak electron donating property of carbazole moiety in **CBZ** brought about low wavelength absorption band in solution state, due to the their lower HOMO energy level compared with those of phenothiazine or triphenylamine derivatives. Furthermore, the highest LUMO

Table 1. Electrochemical parameters of the organic dyes

Dyes	ε_{max} (M^{-1} $cm^{-1)}$	λ_{max} (nm) Soln.[a]	TiO_2[b]	$E_{0\text{–}0}$ (eV)[c](abs)	E_{ox}[d] (V vs NHE)	E_{ox}-$E_{0\text{–}0}$[e] (V vs NHE)	HOMO[f] (eV)	LUMO (eV)
PTZ	28800	570	575	1.81	1.023	−0.787	−5.37	−3.56
TPA	65900	552	560	1.98	0.983	−0.997	−5.32	−3.35
CBZ	50900	514	520	2.16	1.075	−1.085	−5.42	−3.27

[a]Maximum absorption and extinction coefficient at the maximum absorption of the dyes in the ethanol solution. [b]Maximum absorption of the dyes that were adsorbed onto the TiO_2 films. [c]$E_{0\text{–}0}$ (band gap) was determined from the intersection of the absorption and emission spectra in the DMF solution. [d]The oxidation potential (E_{HOMO}) of the dye was measured using the cyclic voltammogram in the DMF solution (containing 0.1M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte; working electrode: glassy carbon; reference electrode: Ag/Ag^+ calibrated with ferrocene/ferrocenium (Fc/Fc^+); counter electrode: Pt. [e]$E_{ox} - E_{0\text{–}0} = E_{LUMO}$. [f](HOMO (eV) = -4.8-($E_{onset}$ $- E_{Ferrocene}$)).

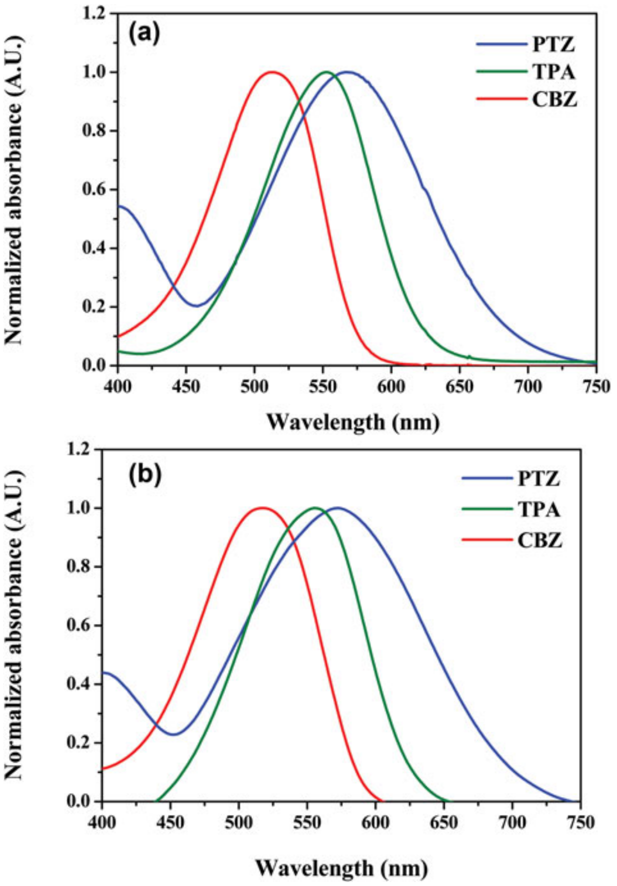

Figure 1. (a) Normalized absorption spectra of the organic dyes in the ethanol solution. (b) Normalized absorption spectra of the ionic dyes adsorbed onto the TiO_2 films.

energy level of ionic dye was found in **CBZ,** which can affect significantly the photovoltaic performance of the sensitizer in the QS-DSSC. We found that the absorption spectra of ionic dyes adsorbed on the TiO_2 film showed almost identical with those of solution state, as shown in Fig. 1.

Photovoltaic Performances of the QS-DSSCs with Ionic Dyes

CDCA has been widely employed in DSSCs as a co-adsorbent with sensitizers to suppress the loss of photon energy by disrupting the π-aggregates of photosensitizing dyes on the TiO_2 electrode [18–20]. We prepared the QS-DSSC devices which are containing ionic dyes with CDCA on the TiO_2 photoelectrode to investigate photovoltaic properties of ionic dyes. Figure 2 shows the photovoltaic characteristics (a) and incident photon-to-current (IPCE) efficiencies (b) of ionic dyes in QS-DSSC, and the corresponding results are summarized in Table 2.

The synthesized ionic dyes showed relatively low PCE in the QS-DSSC, due to the low electron mobility of quasi-solid state electrolyte and the relatively lower LUMO level

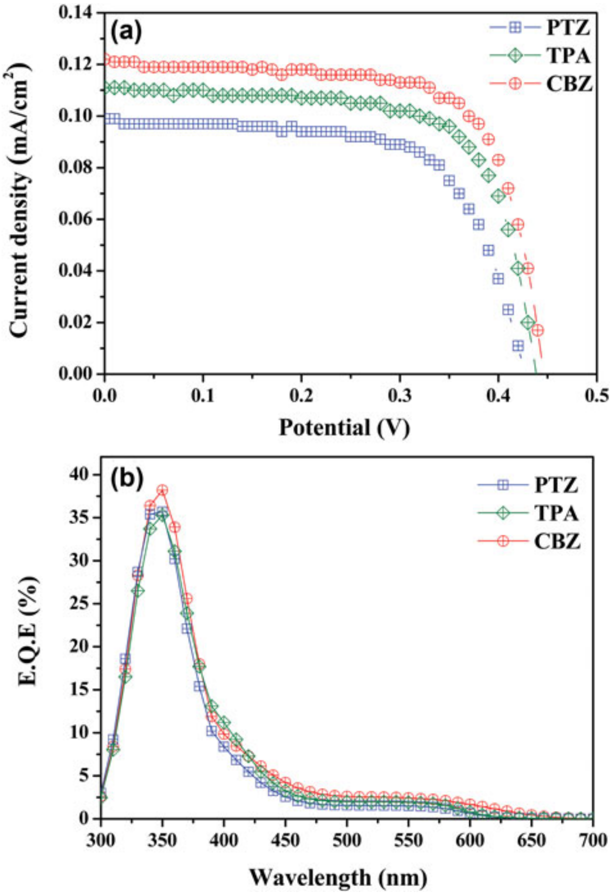

Figure 2. (a) Current density-voltage characteristics for QS-DSSCs with organic dyes under illumination of simulated solar light (AM 1.5, 100 mW/cm^2). (b) IPCE curves for QS-DSSCs with organic dyes. *Sample condition : Blocking layer, TiO_2 paste : B32, Organic Dye 0.1mM with 10mM CDCA in Ethanol, Electrolyte solution-PMMA (Mw: 120,000) 10 wt% : Mixture 90 wt% (EC, PC, and DMC with a mass ratio of 4:2:1), sodium iodide (0.6M), iodine (0.06M), 4- tertbutylpyridine (0.5M), Pt electrode solution (7 mM), 60 μm surlyn, Dr. blade (2T).

of ionic dyes. It is well known that LUMO level of dye molecules should be more negative than the conduction band edge of TiO_2 to ensure the effective electron injection from the excited dye molecules to the conduction band of TiO_2 electrode, and the HOMO level of the dye should be more positive than the redox potential of I^-/I_3^- redox couples to ensure the

Table 2. Photovoltaic performance of QS-DSSCs with organic dyes

Dyes	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)
PTZ	0.097	0.427	64.2	0.11
TPA	0.108	0.439	70.6	0.14
CBZ	0.118	0.446	71.6	0.16

regeneration of dye molecules [12(b)]. The **CBZ** showed higher photovoltaic performance than those of **PTZ** and **TPA**, resulting from the higher LUMO energy level of **CBZ**.

The correlation between LUMO energy level of sensitizer and conduction band of TiO_2 electrode could be confirmed with LiI concentration in electrolyte [21]. Small cations such as Li^+ could be easily adsorbed on the semiconductor surface which resulted in the downward shift of conduction band of the photoelectrode. Some studies have shown that the shift of TiO_2 conduction band edge can be attributed to an increase in the efficiency of electron injection from the exited sensitizer [21(b)]. Thus, we added Li^+ ion in electrolyte to reduce the energy level of conduction band of TiO_2 which could enhance the electron injection of dye molecules in QS-DSSC. The photovoltaic properties of QS-DSSC containing different amount of LiI in the electrolyte were shown in Fig. 3 and summarized in Table 3. The increase in the LiI concentration was found to the increase in PCE of QS-DSSC. Importantly, the V_{oc} value of the DSSC containing Li^+ ion in the electrolyte

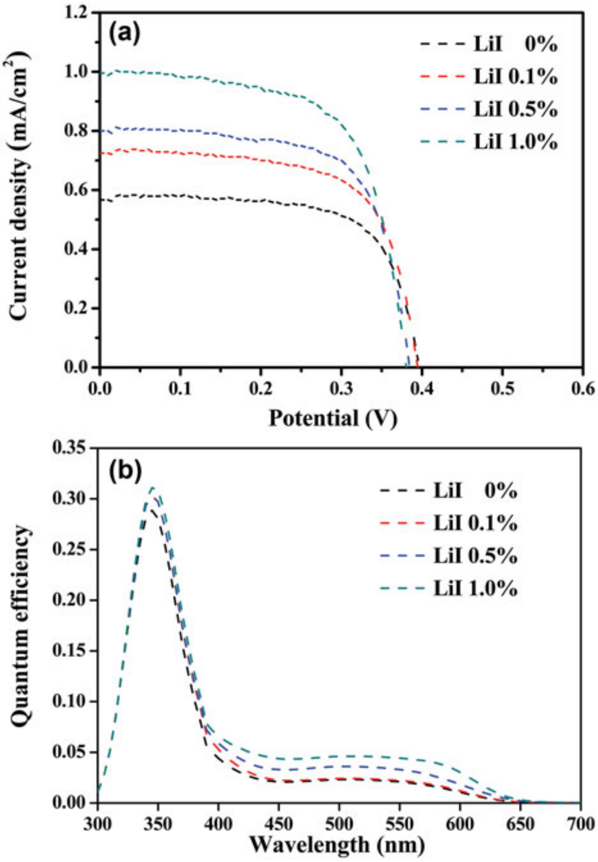

Figure 3. (a) Current density-voltage characteristics for QS-DSSCs with CBZ dye and different LiI concentration under illumination of simulated solar light (AM 1.5, 100 mW/cm^2). (b) IPCE curves for DSSCs with CBZ dye and different LiI concentration. *Sample condition : Blocking layer, TiO_2 paste : B32, Organic Dye 0.1mM with 10mM CDCA in Ethanol, Electrolyte solution-PMII(0.7 M) + LiI (0.2M)+ I_2 (0.05 M) + TBP (0.5 M) in ACN/VN = 85:15 added with various concentration of LiI (0wt%, 0.1wt%, 0.5wt%, 1wt%), Pt electrode solution (7 mM), 60 μm surlyn, Dr. blade (2T).

Table 3. Photovoltaic performance of QS-DSSCs with **CBZ** dye and different LiI content

Dyes	LiI content (%)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)
CBZ	0.0	0.57	0.398	69.1	0.16
CBZ	0.1	0.72	0.396	67.7	0.20
CBZ	0.5	0.79	0.386	68.6	0.21
CBZ	1.0	0.98	0.381	66.3	0.25

decreased from 0.398 mV to 0.366 mV, due to the reduced energy gap between the redox potential of $I^-/I_3{}^-$ redox couples and conduction band edge of TiO_2. However, the increase of Li^+ ion content becomes the enlargement of the driving force for electron injection, resulting in the enhancement of PCE of QS-DSSC.

Conclusions

We prepared a series of ionic dyes containing different electron donor moiety as an organic photosensitizer for the QS-DSSC. The QS-DSSC composed of ionic dyes showed the relatively low PCE due to the low electron mobilities in quasi-solid state electrolyte and lower LUMO energy level of ionic dye structure. The carbazole sensitizer showed higher LUMO energy level, compared with those of phenothiazine or triphenylamine chromophore, being enhanced PCE of QS-DSSC. We confirmed that the electron injection efficiency from the excited sensitizer to TiO_2 electrode could be increased by adding Li^+ ion in electrolyte. Although the V_{oc} value decreased in the DSSC containing Li^+ ion, the PCE enhanced by adding the LiI in electrolyte, due to lowering the conduction band edge of TiO_2.

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