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# Pyridine derivatives; new efficient additives in bromide/tribromide electrolyte for dye sensitized solar cells

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In this work, two new inexpensive pyridine derivatives, propyl isonicotinate (PIN) and isopropyl isonicotinate (IPIN), have been synthesized through a simple and low cost method and for the first time, they have been applied as effective additives in bromide/tribromide electrolyte in dye sensitized solar cells (DSSCs). Although the iodide/triiodide redox shuttle shows remarkable performance in DSSCs, but bromide/ tribromide couple has a more positive redox potential in comparison to this couple. Therefore, it is good idea to design dyes whose HOMO and LUMO levels match with the redox potential of bromide/ tribromide and the conduction band (CB) of TiO<sub>2</sub>, respectively. We have synthesized 3-(4-carbazole-9yl-phenyl)-2-cyano-acrylic acid (TC301) and 2-cyano-3-(4-(3,6-di-tert-butyl-9H-carbazole-9-yl)phenyl) acrylic acid (TC302) as two carbazole dyes and applied them with modified electrolyte in DSSCs. The influence of PIN and IPIN additives in bromide/tribromide redox electrolyte on the DSSC performances is investigated. In comparison to electrolyte without additive, adding 0.5 M of these additives to the electrolyte solution leads to an increase in the open circuit voltage ( $V_{oc}$ ) and short current density ( $J_{sc}$ ), consequently the energy conversion efficiency ( $\eta$ ) improves. Electrochemical impedance spectroscopy show that the enhancement in  $V_{\rm oc}$  is due to increasing electron density in the CB of TiO<sub>2</sub> so that a shift in the Fermi level ( $E_{\rm F}$ ) occurs. It leads to a suppression in electron recombination that has beneficial effect on the  $V_{\rm oc}$ . Furthermore, cyclic voltammetry results reveal that PIN and IPIN has similar effect mechanisms to 4-tert-butylpyridine (TBP) additive in the DSSCs. Our findings show that TBP can be replaced with PIN and IPIN in the DSSCs.

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## 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted lot of attention, since the breakthrough work by O'Regan and Gratzel in 1991, because of their potential of becoming a clean, unlimited, renewable energy source and low-cost photovoltaics.<sup>1</sup> The device is based on an optically transparent mesoporous film of semiconductor, usually titanium dioxide coated on a conductive glass. The dye is adsorbed on the semiconductor substrate. The sensitizer harvests light in the visible range and injects electrons in the semiconductor conduction band. The oxidized dye is then regenerated by electron donation from the electrolyte, which usually contains the iodide/triiodide redox couple.<sup>2</sup>

Not every dye can be a sensitizer; this depends on its physical and chemical properties which need to satisfy certain requirements in order to maximize electron injection when adsorbed on the semiconductor. Ruthenium polypyridine complexes are a class of compounds that have been widely studied in the past three decades is due to their chemical stability, redox properties (they have stable oxidized and reduced forms),<sup>3</sup> lifetime and reactivity of the excited state.4 Furthermore, photophysical properties such as absorption in the visible range made this class of compounds attractive for fundamental and practical science studies. There are two most problematic components of a dye sensitized solar cell. One of them is ruthenium based dye. Despite many advantages of ruthenium complexes as sensitizer, the idea of developing organic sensitizers originates from the need to find cheaper and easier ways to synthesize dyes compared to those based on the ruthenium. The main advantages of organic dyes can be summarized as follows: very high molar extinction coefficients, simple modelling and facile synthesis, absorption energies that can be easily tuned and low cost.5,6 Another problem is associated to iodide/triiodide electrolyte and they are numerous: it is corrosive, volatile and has high color. Probably the most critical drawback to iodide/ triiodide is its redox potential that is significantly more negative than thermodynamically necessary for cell operation. Consequently, the open circuit voltage  $(V_{oc})$  attainable from a DSSC containing iodide/triiodide electrolyte is less than is theoretically possible. Because the overall efficiency of a solar cell scales directly with  $V_{\rm oc}$ , this constitutes a significant limitation.7,8

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The bromide/tribromide couple has a more positive redox potential (about 1.1 V *vs.* NHE) in comparison to the iodide/ triiodide couple (about 0.35 V *vs.* NHE).<sup>9</sup> Thus, the electrolyte containing the bromide/tribromide redox system can improve greatly the photovoltage of the DSSCs if used together with well-designed dyes. The research results approved that the DSSCs with bromide/tribromide electrolyte had higher  $V_{\rm oc}$  values than that of the DSSCs with iodide/triiodide electrolyte for appointed dyes.<sup>10-15</sup>

Liquid electrolytes typically consist of a redox couple and additives dissolved in a liquid solvent. The photovoltaic properties of DSSCs can be optimized by employing additives.16 The redox couple potential, semiconductor surface state, shift of the conduction band edge, recombination kinetics, as well as the photovoltaic parameters of DSSCs can be improved by adding a small amount of additives.17,18 One class of the most commonly used additives in liquid electrolytes are nitrogencontaining heterocyclic compound. 4-tert-Butylpyridine (TBP) is the most famous used additive in DSSCs. The Lewis base trait of TBP is caused that it deprotonates the TiO<sub>2</sub> surface, therefore causing a negative shift of the CB of the TiO<sub>2</sub>. The effect of TBP has been extensively investigated in dye sensitized solar cell over the past several years, and several mechanisms have been put forward.19-22 It has been proposed that the dramatic increase of the  $V_{\rm oc}$  arising from the introduction of the TBP can be attributed to either the suppression of the dark current at TiO<sub>2</sub>/electrolyte interface or the negative shift of the CB in the TiO<sub>2</sub> film, or a combination of both. Despite wide use of TBP as additive in dye sensitized solar cell, it's price is so much and many investigations have been devoted to replace it with other pyridine derivatives.<sup>23-29</sup> Although pyridine derivatives have widely been used to modify iodide/triiodide electrolyte, but no example of their application as additive in bromide/tribromide electrolyte have not been reported. So, in this work, two inexpensive pyridine derivative (IPIN and PIN) were synthesized through a simple and low cost method with commercial and available materials. Beside, effects of propyl isonicotinate and isopropyl isonicotinate additives are investigated in the bromide/tribromide electrolyte on the DSSC performance. By means of the electrochemical impedance spectroscopy and cyclic voltammetry approach, we decided to study the performance of carbazole dyes sensitized solar cells based on redox couple bromide/tribromide that contain these new additives. The adsorption of PIN and IPIN on the semiconductor surface suppresses the electron recombination from the TiO<sub>2</sub> to the tribromide in the electrolyte effectively and finally enhances  $V_{\rm oc}, J_{\rm sc}$  and  $\eta$ . To the best of our research, for a DSSC containing bromide/tribromide electrolyte, PIN and IPIN are the first additives which have been replaced TBP.

### 2. Experimental

#### 2.1. Materials

All solvents and reagents were purchased from Merck and Aldrich Companies. Propanol and isopropanol were distilled under vacuum prior to the use. For preparation of dry acetonitrile in the electrolytes it was kept over 4 Å molecular sieves for 24 h. The fluorine doped tin oxide coated glass substrates (FTO) (transmission >90% in the visible, sheet resistance 8  $\Omega$  per square, 2.3 mm thickness) and surlyn spacer (30  $\mu$ m) were purchased from Dye sol (Australia). The detailed preparing processes for TiO<sub>2</sub> paste (P25, Degussa, Germany) were similar to our previous article.<sup>30</sup>

#### 2.2. Instrumentation

The FT-IR spectrum was recorded by using a Magna 550 Nicolet spectrometer using KBr pellets. <sup>1</sup>H NMR spectrum was recorded on Bruker DPX-400 MHz NMR spectrometer. Cyclic voltammetry (CV) was used to study the electrochemical properties of the electrolytes. The CV spectra were obtained with a Sama 500 potentiostat (Isfahan, Iran) using 0.1 M lithium perchlorate trihydrate in acetonitrile as a supporting electrolyte, a glassy carbon working electrode (2 mm diameter) and platinum wire counter electrode, an Ag/AgCl/KCl (sat) as a reference electrode were employed as electrodes. The electrochemical impedance spectroscopy (EIS) measurements of the cells were achieved under AM 1.5 G simulated light (Luzchem) using potantiostat/ galvanostat (PGSTAT 100, Autolab, Eco-Chemie), at an AC amplitude of 5 mV within the frequency range from 0.01 Hz to 100 kHz. The photocurrent-voltage (I-V) characteristics of the cells were measured using a Keithley model 2400 digital source meter (Keithley, USA). The obtained spectra from the EIS measurements were fitted by Z-view software (v2.9c, Scribner Associates Inc.).

#### 2.3. Synthesis of additives and dyes

#### 2.3.1. Additives

2.3.1.1. Propyl isonicotinate. Isonicotinic acid (20 g, 0.16 mol) was refluxed with excess thionyl chloride (40 mL, 0.55 mol) for 1 hour. Excess thionyl chloride was removed by evaporation in vacuum to leave the acid chloride. The crude product was washed with diethyl ether and dried in vacuum at 40 °C. Isonicotinoyl chloride hydrochloride were yielded as white crystals (27.6 g, yield 96%).31 Propanol (16.5 mL, 0.22 mol) was added in to the isonicotinoyl chloride hydrochloride (4 g, 0.022 mol) and reflux for 2 hours. Aqueous sodium bicarbonate solution (20 mL) was added, then the product extracted into dichloromethane (3  $\times$  15 mL), drying with MgSO<sub>4</sub>, and then evaporation to give propyl isonicotinate (2.52 g, yield 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.78 (2H, d, J = 6 Hz), 7.85 (2H, d, J = 6 Hz), 4.31 (2H, t, J = 4.8 Hz), 1.80 (2H, sext, J = 7 Hz), 1.02 (3H, t, J = 7.6 Hz). IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1729 (ester carbonyl group stretching), 1596 and 1405 (C=C stretching bands of the pyridine ring), 1282 and 1121 (C-O bands in the ester group), 2969 (C-H stretching band of the propyl group).

2.3.1.2. Isopropyl isonicotinate. Isopropyl isonicotinate was synthesized by similar method as described above by reacting isonicotinoyl chloride hydrochloride (4 g, 0.022 mol) and isopropanol (16.8 mL, 0.22 mol), (2.38 g, yield 64%) product was obtained after purification: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.64 (2H, d, J = 4.4 Hz), 7.71 (2H, d, J = 6 Hz), 5.14 (1H, m), 1.25 (6H, d, J = 6.4 Hz); IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1725 (ester carbonyl group stretching), 1596 and 1407 (C=C stretching bands of the

pyridine ring), 1283 and 1105 (C–O bands in the ester group), 2982 (C–H stretching band of the isopropyl group), 1327 and 1351 (C–H bending bands of the isopropyl group).

2.3.1.3. Allyl isonicotinate. Allyl isonicotinate was synthesized by similar method mentioned above by reacting isonicotinoyl chloride hydrochloride (4 g, 0.022 mol) and allyl alcohol (32.34 mL, 0.22 mol), (2.35 g, yield 64%) product was obtained after purification: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.67 (2H, d, J = 6 Hz), 7.70 (2H, d, J = 6 Hz), 5.93 (1H, m), 5.32 (1H, d, J = 17.2 Hz), 5.22 (1H, d, J = 10.4 Hz), 4.75 (2H, d, J = 4.8 Hz); IR (KBr),  $\nu$  (cm<sup>-1</sup>): 1648 (C=C stretching band of the allyl group), 1725 (ester carbonyl group stretching), 1596 and 1409 (C=C stretching bands of the pyridine ring), 1281 and 1122 (C–O bands in the ester group). Synthetic pathway of three additives is presented in Fig. 1.

2.3.2. Dyes (TC301 and TC302). 4-(9*H*-Carbazole-9-yl) benzaldehyde was synthesized according to the literature.<sup>32</sup> A mixture of 4-fluorobenzaldehyde (1.06 mL, 10 mmol), K<sub>2</sub>CO<sub>3</sub> (4.15 g, 30 mmol) and carbazole (1.67 g, 10 mmol) in DMF (15 mL) was refluxed for 12 h, cooled to room temperature and poured into ice water. The resulting precipitate was filtered and washed with water, methanol, ethanol, and *n*-hexane. A yellowish white solid was obtained after drying under vacuum (2.02 g, yield 75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 10.13 (1H, s), 8.13–8.17 (4H, m), 7.81 (2H, d, *J* = 8.4 Hz), 7.52 (2H, d, *J* = 7.6 Hz), 7.45 (2H, t, *J* = 6.8 Hz), 7.35 (2H, t, *J* = 7.2 Hz).

To prepare 3-(4-(9H-carbazole-9-yl)phenyl)-2-cyanoacrylicacid (TC301),<sup>11</sup> 4-(9H-carbazole-9-yl)benzaldehyde (136 mg, 0.50 mmol) was dissolved in 10 mL of acetonitrile in a threenecked flask. Then cyanoacetic acid (85 mg, 1 mmol) and a few drops of piperidine (63.98 mg, 0.75 mmol) was added and heated under reflux for 4 h at argon atmosphere. The reaction mixture was cooled to room temperature and the solvent was removed by rotary evaporation. The residue was extracted with dichloromethane and 0.1 M HCl solution. Organic phase was purified by silica gel column chromatography with dichloromethane: methanol (v/v, 10 : 1) as eluent to afford the dye TC301 as a yellow solid (123 mg, yield 70%). <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  (ppm) 8.25 (2H, d, J = 7.6 Hz), 8.18 (2H, d, J = 7.2 Hz), 8.11 (1H, s), 7.79 (2H, d, J = 7.2 Hz), 7.420–7.496 (4H, m), 7.30 (2H, t, J = 6.8 Hz).

To prepare 3,6-di-*tert*-butyl-9*H*-carbazole,<sup>11</sup> a mixture of carbazole (5.00 g, 0.03 mol) and anhydrous AlCl<sub>3</sub> (4.00 g, 0.03 mol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 mL). At 0 °C, a solution of *tert*-butyl chloride (6.6 mL, 0.06 mol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added slowly. The mixture was stirred for 24 h at room temperature. Then, the mixture was poured into water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL), and dried with MgSO<sub>4</sub>. Solvent was evaporated to afford the crude products, which were recrystallized three times from petroleum ether to give white crystals (4.25 g, yield 51%). <sup>1</sup>H NMR (400 MHz, acetone):  $\delta$  (ppm) 8.19 (2H, s), 7.46 (2H, d, *J* = 7.2 Hz), 7.40 (2H, d, *J* = 8.2 Hz), 1.43 (18H, s).

To synthesize 4-(3,6-di-*tert*-butyl-9*H*-carbazole-9-yl)benzaldehyde,<sup>11,32</sup> a mixture of 4-fluorobenzaldehyde (1.06 mL, 10 mmol), K<sub>2</sub>CO<sub>3</sub> (4.15 g, 30 mmol), and 3,6-di-*tert*-butyl-9*H*carbazole (2.79 g, 10 mmol) in DMF (15 mL) was refluxed for 12 h and cooled to room temperature. After poured into ice water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 40 mL). The organic phase was dried with Na<sub>2</sub>SO<sub>4</sub> and evaporated. Finally, the crude product was purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub>: petroleum ether (v/v, 1 : 1) as eluent affording a pale yellow solid (1.58 g, yield 42%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 9.90 (1H, s), 7.95 (2H, s), 7.92 (2H, d, *J* = 8 Hz), 7.79 (2H, d, *J* = 8 Hz), 7.278–7.309 (4H, m), 1.28 (18H, s).

2-Cyano-3-(4-(3,6-di-*tert*-butyl-9*H*-carbazole-9-yl)phenyl) acrylic acid (TC302) was synthesized by similar method for TC301,<sup>15</sup> but with 4-(3,6-di-*tert*-butyl-9*H*-carbazole-9-yl)benzaldehyde (192 mg, 0.50 mmol) instead of 4-(9*H*-carbazole-9-yl) benzaldehyde. The dye TC302 was obtained as yellow solid (167 mg, yield 72%). <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta$  (ppm) 8.28 (2H, s), 8.16 (2H, d, J = 8.4 Hz), 8.10 (1H, s), 7.76 (2H, d, J = 8Hz), 7.76 (2H, d, J = 8 Hz), 7.46 (2H, d, J = 6.8 Hz), 7.40 (2H, d, J = 8.4 Hz), 1.39 (18H, s). Synthetic pathway of two dyes is observed in Fig. 2.



Fig. 1 (a) SOCl<sub>2</sub>, reflux, 1 h (ref. 31) (b) isopropanol, reflux, 2 h (c) propanol, reflux, 2 h (d) allyl alcohol, reflux, 2 h.



Fig. 2 (a) 4-Fluorobenzaldehyde,  $K_2CO_3$ , DMF, reflux, 12 h (ref. 11 and 32) (b) 2-cyanoacetic acid, piperidine, acetonitrile, reflux, 4 h (ref. 15) (c) *t*-BuCl, AlCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, Rt, 24 h (ref. 11).

2.3.3. 1-Butyl-2,3-dimethylimidazolium bromide (BDMIBr). (BDMIBr) 1-Butyl-2,3-dimethylimidazolium bromide was synthesized according to ref. 33. Briefly, 1-bromobutane (7 mL, 6.4 mmol) was slowly added to a stirred solution of 1,2-dimethylimidazole (4 mL, 4.2 mmol) in ethyl acetate. The mixture was then reflux. Finally, two phases were formed. The top phase was discarded. The bottom phase was recrystallized four times in ethyl acetate: acetonitrile (v/v, 3:2). Residual solvents were removed under vacuum in the presence of P<sub>2</sub>O<sub>5</sub> (24 h). BDMIBr was obtained as a white hygroscopic solid. The structure of the resulting salt was confirmed by <sup>1</sup>H NMR spectroscopy (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.91 (3H, t, J = 7.2 Hz), 1.301–1.375 (2H, m), 1.724-1.798 (2H, m), 2.76 (3H, s), 3.99 (3H, s), 4.18 (2H, t, J = 7.2 Hz), 7.50 (1H, d, *J* = 2.1 Hz), 7.72 (1H, d, *J* = 2.1 Hz).

#### 2.4. Cell fabrication

To prepare transparent working electrodes, FTO glass were first cleaned with deionized water, acetone and ethanol in an ultrasonic bath. After cleaning the FTO, they were treated with a 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 min. Then a TiO<sub>2</sub> paste was spread onto the FTO substrate with a glass rod using Scotch tape as spacer (doctor blade deposition). In this study, two layers of TiO<sub>2</sub> particles were deposited onto FTO glass and used as photoelectrode. The TiO<sub>2</sub> films were then heated at 500 °C for 30 minutes. Afterwards, the electrodes were immersed into the TiCl<sub>4</sub> aqueous as described previously and then were calcined at 500 °C for 15 min. After the film was cooled to 40 °C, the prepared thin film electrodes were immersed into a 2  $\times$  $10^{-4}$  M dye bath in THF solution and maintained in the dark for 8 h. After dye loading, the TiO2 films were rinsed with THF and assembled with platinum counter electrodes that were prepared by thermal decomposition of H<sub>2</sub>PtCl<sub>6</sub> solution (2 mg in 1 mL of ethanol) and heating at 400 °C for 15 min. To prepare sealed cells, the two electrodes were sealed together with a hot-melt polymer film frame around the titanium dioxide area. Electrolyte was introduced via the hole drilled through the counter electrode by vacuum filling.

## 3. Results and discussion

#### 3.1. Spectral properties of dyes

In terms of molecular structure, organic dyes can be divided in three major parts; donors, linkers and acceptors.<sup>34</sup> Linkers are usually  $\pi$ -conjugated system that link by bridges electrondonating (D) and electron-accepting (A) groups; so-called D- $\pi$ -A sensitizers. Light absorption induces charge separation between the donor and the acceptor moieties of the chromophore where the photo-absorption properties involve intermolecular charge transfer (ICT) between A and D.<sup>35</sup> One of the most relevant features that researchers would like to improve in the design of a new organic sensitizer is its absorption in the red region of the visible spectra. This can be obtained by expanding the  $\pi$ -conjugation of the linkers and increasing the electrondonating and electron-accepting capability of donors and acceptors. In a DSSC using organic dyes, there is a factor which is generally thought influences negatively the electron injection from the dyes to the CB of TiO<sub>2</sub>. This is  $\pi$ -stacked aggregation of dye molecules on TiO<sub>2</sub> surface. Dye aggregation is usually considered a phenomenon that should be avoided although a controlled aggregation could be considered beneficial. One way to avoid this problem is incorporate long alkyl chains and aromatic groups into the dye structure to prevent aggregation.<sup>36</sup>

In our study, we have synthesized two carbazole dyes as simple and low cost dyes for applying in the DSSCs. To gain further insight into the electronic properties of the carbazole dyes, DFT (density functional theory) calculations were performed at the B3LYP/6-31+G (d) level. The frontier orbital plots of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the TC301 and TC302 dyes are shown in Table 1. In these dyes like other D- $\pi$ -A systems, HOMOs are delocalized over the  $\pi$ -conjugated system in configurations centering on the donor side while the LUMOs are mainly delocalized on the acceptor side. Absorption spectra of solutions of TC301 and TC302 in THF have been shown in Fig. 3. The results showed that the absorption maximum were at 340 nm for TC301 and 347 nm for TC302. The absorption maxima of TC302 dye has a red-shifted compared to TC301 dye and the HOMO-LUMO energy gap of TC301 was larger than that of TC302. Therefore, tert-butyl groups facilitate absorption at long wavelengths. Furthermore, in TPA based dyes it is confirmed that presence of tert-butyl group as an electron donor group can improve the photovoltaic performance.37

# 3.2. Photovoltaic performance and electrical impedance analysis

During the course of our study, four electrolytes were prepared for DSSCs consisted of 0.05 M  $Br_2$ , 0.6 M BDMIBr with 0.5 M different additives (TBP, IPIN, PIN and bare (electrolyte without additive)). The photovoltaic parameters of the DSSCs employing the TC301 and TC302 sensitizers and bromide/tribromide electrolyte with different additives under simulated sunlight

 Dye
 HOMO
 LUMO

 TC301
 Image: Comparison of the second s

Table 1 Frontier molecular orbitals of the HOMO and LUMO calculated with DFT at the B3LYP/6-31+G (d) level of TC301 and TC302 dyes



Fig. 3 Absorption spectra of solutions of the dyes in THF.

at 100 mW cm<sup>-2</sup> were compared in Table 2. Interestingly, the data for all of additives in the bromide/tribromide electrolyte indicate an increase in open circuit voltage and the short circuit current density compared to bare electrolyte. The photocurrent density-voltage (I-V) curves are shown in Fig. 4 and 5. To investigate the influence of additive in bromide/tribromide electrolyte on performance the cell, one of the dyes for example, TC302 was selected. The values of the  $J_{\rm sc}$ ,  $V_{\rm oc}$  and fill factor (FF) of the DSSCs based on the electrolyte without any additive were 3.33 mA cm<sup>-2</sup>, 0.80 V and 0.62, respectively, yielding a conversion efficiency ( $\eta$ ) of 1.65%. Overall, among the various additives in the redox shuttles, the best energy conversion efficiency of 3.76%, achieved for IPIN, is the highest reported for DSSCs constructed with our modified electrolyte based on TC302 dye. In this additive, compared to TBP, we observed even a 30% increase in  $J_{sc}$ , were explainable for the obtained efficiency increase from 2.99% to 3.76%. This cell vielded an improvement of an additional 26% in efficiency. However, other electrolyte containing PIN exhibits less enhancing in efficiency (11%) compared to TBP.

Furthermore, AIN was applied as an additive in the electrolyte solution. Our results showed that it is not suitable additive for bromide/tribromide electrolyte because bromine reacts with

Table 2 Photovoltaic performance of DSSCs based on TC301 and TC302 dyes in presence of various additives in bromide/tribromide electrolyte systems under AM 1.5 (100 mW cm<sup>-2</sup>) illumination with an active area of 0.18 cm<sup>2</sup>

Dye/additive	$J_{ m sc}  [ m mA \ cm^{-2}]$	$V_{\rm oc} \left[ V \right]$	FF	$\eta$ [%]
TC201/po additive	2.09	0.70	0.65	1 50
TC201/TPD	3.00	1.06	0.65	1.50
TC301/IPIN	4.93	0.95	0.70	2.08
TC301/PIN	4.47	0.92	0.68	2.81
TC302/no additive	3.33	0.80	0.62	1.65
TC302/TBP	4.37	1.00	0.68	2.99
TC302/IPIN	5.69	0.94	0.70	3.76
TC302/PIN	5.29	0.91	0.69	3.35



Fig. 4 Photocurrent voltage characteristic plots of the DSSCs based on TC301 dye in the presence of various additives in bromide/tribromide electrolyte systems under 100 mW cm<sup>-2</sup> illumination (AM 1.5 G).



Fig. 5 Photocurrent voltage characteristic plots of the DSSCs based on TC302 dye in the presence of various additives in bromide/tribromide electrolyte systems under 100 mW cm<sup>-2</sup> illumination (AM 1.5 G).

double bond of allyl group. This reaction leads to disappear of electrolyte solution color and the concentration of bromine decreases.

Based on the obtained photovoltaic results (Table 2), it is clear that performance of dye TC302 as a sensitizer is better than TC301 dye. As mentioned in Section 3.1, this is attributed to the presence of *tert*-butyl group in the structure of TC302 dye. This is confirmed by absorption spectra solutions of TC301 and TC302 in THF (Fig. 3). The results showed that *tert*-butyl groups facilitate absorption at long wavelengths and finally is caused a higher DSSC performance.<sup>36,37</sup>

The photoelectrochemical behavior of the DSSC based on TC302 dye containing different additives can be followed successfully using EIS spectroscopy. Fig. 6 shows the typical Nyquist plot of our devices. The semicircle profile of the Nyquist plot of a DSSC represents the charge transfer resistances at different interfaces. We observe the first semicircle corresponding to the charge transfer impedance at the counter electrode/electrolyte interface, the second semicircle is associated with the charge transfer impedance of the TiO<sub>2</sub> electrode and the electrolyte. The equivalent circuit used for fitting the impedance spectra of the DSSC is shown in the inset of Fig. 6. In

the equivalent circuit,  $R_s$ ,  $R_{CE}$  and  $R_{CT}$  represent series resistance, charge transfer resistance at the counter electrode/ electrolyte interface and electron recombination resistance at the TiO<sub>2</sub>/electrolyte interface, respectively. C and CPE1 are attributed to the chemical capacitance at the counter electrode/ electrolyte interface and the TiO<sub>2</sub>/electrolyte interface, respectively. <sup>38,39</sup> Table 3 was extracted by using an equivalent circuit to fit the Nyquist plot.

Electron lifetime in TiO<sub>2</sub> ( $\tau$ ) is one of the main parameters, which could be extracted from the highest frequency peak of the second arc ( $\omega_{max}$ ) in the Nyquist plot by using  $\tau = 1/\omega_{max}$ . It shows the electron recombination in TiO<sub>2</sub> film.<sup>40</sup>

Adding additives in to the electrolyte lead to an increases in the electron lifetime and charge transfer resistance at the TiO<sub>2</sub>/ electrolyte interface. Hence, charge recombination is inhibited upon adding pyridine derivatives into electrolyte and thus an increase in  $V_{oc}$  is obtained. Among these additives, TBP shows the highest  $V_{oc}$  in the DSSCs. In the molecule of TBP, the *tert*butyl group as an electron donating group increases the charge density of the nitrogen atom of the pyridine ring, which enhances the interaction between the nitrogen atoms and the Ti(nv) ions. It seems that for the pyridine based additives, there is a stronger interaction so that the more negative shift of the conduction band edge there will be.<sup>23</sup> The negative shift of the conduction band edge is beneficial to the increase of the  $V_{oc}$ . However, the negative shift is too much, the electron injection from the photoexcited dye into the conduction band of the TiO<sub>2</sub>



**Fig. 6** Nyquist plots from the EIS spectra for the DSSC based on TC302 dye in the presence of various additives in the bromide/tribromide electrolyte.

Table 3Electrochemical parameters obtained by fitting the EIS ofDSSCs with different additives using an equivalent circuit for TC302dye

Additive	$k_{\mathrm{eff}}\left(\mathrm{s}^{-1} ight)$	$R_{\rm CT}$ (ohm cm <sup>-2</sup> )	$R_{\rm CE}$ (ohm cm <sup>-2</sup> )	τ (ms)
TBP	11.12	42.85	13.50	90.09
IPIN	14.91 14.91	21.34 29.10	6.02	67.06 67.06

becomes difficult, which leads to a decrease in the photocurrent. Therefore, we expect to design two new pyridine-based additive to adjust the interaction between the N atom of pyridine ring and the Ti(IV) ions, making the negative shift of the conduction band edge of TiO2 moderately. This moderate negative shift of the conduction band edge can increase the open-circuit voltage and the short-circuit photocurrent. For a DSSC, the photocurrent is determined by the following two processes: (1) the photoexcited dye molecules inject electrons into the conduction band of the  $TiO_2$ . (2) The injected electrons are extracted from the nanocrystalline to the outer electrical circuit to form the photocurrent. It has been concluded that if the negative shift of the conduction band edge be small enough, the electron injection will not be hindered.41 Due to presence of ester group as electron withdrawing group on the structure of IPIN and PIN, the adsorption of these isonicotinate lead to a small shift of the conduction band edge and do not hamper the injection of the electrons. Thus, the process (2), *i.e.* the charge extraction efficiency of the injected electrons, is decisive to the photocurrent of the cell.

TBP showed the largest resistance at Pt/electrolyte interface. This means that in device based on TBP, the reduction of bromine is the slowest at the Pt counter electrode. This indicates that the catalytic performance of Pt can be deteriorated in the presence of TBP. The increased  $R_{\rm CE}$  were also reason for the lowered  $J_{\rm sc}$  in device based on TBP compared to IPIN and PIN.<sup>10,42</sup>

#### 3.3. Cyclic voltammetry analysis

CV is a powerful tool to analyze the reaction kinetics between the bromide and tribromide ions in the electrolyte solution. Cyclic voltammograms of bromide/tribromide electrolytes are shown in Fig. 7.

Four peaks are observed for redox process in the electrolyte in every curve, which are attributed to anodic peaks potential, reactions (1) and (2) and cathodic peaks potential, reactions (3) and (4).<sup>43</sup>



Fig. 7 Cyclic voltammograms for the bromide/tribromide electrolyte without any additive (bare) and the electrolytes in the presence of TBP, IPIN and PIN as additives.

$$3Br^- \rightleftharpoons Br_3^- + 2e^-$$

$$2Br_3^- \rightleftharpoons 3Br_2 + 2e^- \tag{2}$$

 $3Br_2 + 2e^- \rightleftharpoons 2Br_3^-$  (3)

$$Br_3^- + 2e^- \rightleftharpoons 3Br^-$$
 (4)

In comparison to bare electrolyte, it is observed that addition of additives into the electrolyte causes a shift of redox reaction peaks to more negative or positive positions. For example, both of the anodic peaks in all of additives are shifted toward more positive potential. The same electrochemical behavior of isonicotinate derivatives and TBP in the bromide/tribromide electrolyte can be good idea to replace TBP with IPIN and PIN.

It should be noted that  $Br_2$  is a strong electrophile and tends to undergo bromination reaction with unsaturated bonds especially in the presence of catalysis or light irradiation, and because of this, the device efficiency and long-term stability will be limited. However, to achieve long-term stable DSSCs, the knowledge of dye stability in the presence of  $Br^{-}/Br_{3}^{-}$  redox couple under light illumination is highly needed.<sup>10</sup>

Electrolytes containing the  $Br^{-}/Br_{3}^{-}$  redox system have been used based on carbazole dyes. Although very high open-circuit voltage with a good energy conversion efficiency was achieved, it is found that stability of DSSCs based on  $Br^{-}/Br_{3}^{-}$  electrolytes and the novel dyes TC301 and TC306 was not very good.<sup>11</sup> Based on mentioned results, we could not get good data from ageing experiment.

## 4. Conclusions

In this study, two inexpensive pyridine derivative (IPIN and PIN) have been synthesized through a simple and low cost method with commercial and available materials and have been applied in bromide/tribromide electrolyte. Electrolytes containing the bromide/tribromide redox system can improve remarkably the efficiency of the DSSCs if they use together with well-designed dyes. We have synthesized two organic dyes, TC301 and TC302, with relatively high HOMO levels for application in DSSCs based on the bromide/tribromide electrolyte containing two new additives. Performance mechanism of PIN and IPIN as additives in the bromide/tribromide electrolyte are same as TBP and it is established by cyclic voltammetry. The electrochemical impedance spectroscopy show that in the presence of IPIN and PIN in comparison to TBP, a high recombination rate constant,  $k_{\rm eff}$ , a lower recombination resistance,  $R_{\rm CT}$  and a lower resistance at Pt/electrolyte interface, R<sub>CE</sub> are observed. PIN and IPIN are connected to the TiO<sub>2</sub> surface and shifted the conduction band of the TiO<sub>2</sub> toward negative potentials. Due to presence of ester group as an electron withdrawing group on pyridine ring this shift is not so much as TBP. Thus slightly decreasing in  $V_{oc}$  was observed in the presence of these two additives, whereas an increase in  $J_{sc}$  was obtained due to better electron injection from LUMO levels of the dyes to conduction band of TiO2 and

finally enhance efficiency in comparison to electrolytes contain TBP.

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