

## Effect of Ionic Liquids with Different Cations in $I^-/I_3^-$ Redox Electrolyte on the Performance of Dye-sensitized Solar Cells

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The effect of the addition of ionic liquids with four different cations (imidazolium, pyrrolidinium, piperidinium and pyridinium) on the performance of dye-sensitized TiO<sub>2</sub> solar cells based on electrolytes containing a *t*-butylpyridine (TBP) in 3-methoxypropionitrile (MPN) was studied. A total of 18 ionic liquids with mono-, di- and tri-alkyl derivatives were used in the present study, and among them a pyridinium cation with a mono-alkyl group showed better cell efficiency than the others. The best photoelectric conversion efficiency, 7.213%, was obtained using 1-hexylpyridinium iodide with an open-circuit photovoltage ( $V_{oc}$ ) = 0.731 V, a short-circuit photocurrent density ( $J_{sc}$ ) = 16.175 mA/cm<sup>2</sup>, and a fill factor (ff) = 0.610 under AM1.5 and 100 mW/cm<sup>2</sup> illumination.

**Key Words :** Dye-sensitized solar cell, Ionic liquid, High performance, Photo-voltage enhancement, Photo-current enhancement

### Introduction

There has been growing interest in dye-sensitized solar cells (DSCs), which were originally developed by M. Grätzel<sup>1</sup> as an alternative to the conventional silicon-based solar cells, because of their high energy conversion efficiency, simple fabrication process, and potential for low cost production.<sup>2,3</sup> The studies initially used volatile organic electrolytes, including ions such as Li<sup>+</sup> and K<sup>+</sup>, which can be absorbed onto TiO<sub>2</sub> surface to lower the Fermi level of TiO<sub>2</sub>. Ionic liquids (ILs) were first used in DSCs in Grätzel's laboratory, with the primary aim of preventing voltage drop by the Li<sup>+</sup> and K<sup>+</sup> ions because the IL cations can replace the absorption sites on the TiO<sub>2</sub> surface.<sup>4-7</sup> The first IL tested in DSC was based on the imidazolium cation, and subsequently, ILs based on this family have been widely used in electrolytes for DSCs. Room temperature ionic liquids are important because of their special properties, such as good chemical and thermal stability, wide electrochemical window, negligible vapor pressure, non-flammability and high ionic conductivity.<sup>8,9</sup> Another advantage of using ILs is that the properties of the IL can be suitably controlled by modifying the IL cation and anion. Although most of the initial work was carried out with imidazolium-based ILs, recently ILs with many other cations, such as sulfonium, guanidinium, ammonium, phosphonium, etc., have also been explored and used as solvent-free electrolytes for DSCs.<sup>10</sup> The use of various ILs in DSCs was recently reviewed by other researcher,<sup>11-13</sup> and, hence, will not be discussed again here. The reader can refer to these reviews and their references for detailed, updated information. The performance of DSCs containing different ILs reportedly depends upon different factors: *viz.* viscosity, ionic conductivity, diffusion coefficient,

size of the cation ring, number, position and length of alkyl groups, melting point, *etc.* Therefore, a study of the relative performance of DSCs based on ILs with different cations is needed.

In the present work, the effect of the presence of ILs with four different cations and various alkyl groups on the performance of DSCs was studied, and the IL with the best relative performance was identified in the MPN-based electrolyte.

### Experimental

**Ionic Liquids.** The ionic liquids, except for the 1-alkylpyridinium iodides, were purchased from Iolitec. The purity of the purchased ionic liquids was  $\geq 98\%$ . 1-alkylpyridinium iodides (R=ethyl, butyl, hexyl, heptyl, octyl, nonyl, dodecyl) were synthesized by reflux of pyridine and *n*-alkyl iodide (R=ethyl, butyl, hexyl, heptyl, octyl, nonyl, dodecyl) in 1:1 molar ratio at 100 °C for 3 h, followed by washing at least 3 times with anhydrous ethanol to remove unreacted starting materials. The washed products were vacuum dried at 80 °C for 2 h. The syntheses were confirmed with nuclear magnetic resonance (NMR) and infrared spectroscopy.

**Preparation of TiO<sub>2</sub> Photoelectrode and Ru(II) Dye Coating.** A TiO<sub>2</sub> paste (Ti-nano oxide D, Solaronix) was deposited onto the conducting glass with a fluorine-doped stannic oxide layer (FTO, TEC 8/2.3 mm, 8 Ω/□, Pilkington) using the screen-printing method. The resulting layer was calcined for 2 h at 470 °C in a muffle furnace. This process was repeated 3 times, or until a thickness of 15 μm was obtained. The area of the prepared porous TiO<sub>2</sub> electrode was 25 mm<sup>2</sup> (5 mm × 5 mm). Dye absorption studies were carried out by dipping the TiO<sub>2</sub> electrode in a 4 × 10<sup>-4</sup> M

*t*-butanol/acetonitrile (Merck, 1:1) solution of standard ruthenium dye: N719 (Solaronix) for 48 h at 25 °C. The photoelectrode was then washed, dried, and immediately used to measure the performance of the solar cell.

**Fabrication of Dye-sensitized Solar Cell.** Transparent counter electrodes were prepared by placing a few drops of 10 mM hydrogen hexachloroplatinate (IV) hydrate (99.9%, Aldrich) and 2-propanol solution onto drilled FTO glass (TEC 8/2.3 mm, Pilkington). After calcination at 450 °C for 2 h, the counter electrodes were assembled with dye-absorbed TiO<sub>2</sub> photoelectrodes. The two electrodes were separated by 25 μm surlyn and sealed by heating. The internal space was filled with electrolyte and the drilled hole was sealed with surlyn and a coverglass.

**Photovoltaic Characterization.** The photoelectrochemical properties of the prepared DSCs were measured using a computer-controlled digital source meter (Potentiostat/Galvanostat Model 273A, EG & G) and a solar simulator (AM 1.5, 100 mW/cm<sup>2</sup>, Oriel) as a light source. Photovoltaic performance was characterized by the  $V_{oc}$ ,  $J_{sc}$ , FF, and overall efficiency of the  $J$ - $V$  curve.  $V_{oc}$  is the electrical potential between the photo-anode and the cathode of solar cells with no external load.  $J_{sc}$  is the measured current when the circuit between the photo-anode and the cathode has a least-resistance connection. FF is the ratio of maximum power performance to its ideal maximum power by  $V_{oc}$  and  $J_{sc}$ .  $\eta$  can be defined as ( $V_{oc} \cdot J_{sc} \cdot FF$ ) divided by  $P_s$ , where  $P_s$  is the intensity of the incident light.

## Results and Discussion

The 4 different types of ILs used in the present study and their chemical structures are listed in Table 1. ILs based on 4 different cations having 5-member (imidazolium and pyrrolidinium) and 6-member (piperidinium and pyridinium) rings were used in the present study. The complete list of 18 ILs used in the present study, with various alkyl groups based on the 4 cations, their abbreviations, and chemical structures are listed in Table 2. The iodide anion

**Table 1.** Various kinds of ionic liquids

No	Ionic liquids	Chemical structure
1	Imidazolium iodide derivatives	
2	Piperidinium iodide derivatives	
3	Pyrrolidinium iodide derivatives	
4	Pyridinium iodide derivatives	

was used in all the ILs. The electrolytes used in the present study have the general composition of 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M IL, and 0.5 M TBP in 3-methoxy propionitrile (MPN). The composition of the different electrolytes (E1-E18) used

**Table 2.** Ionic liquids (ILs) for the experiment and their abbreviations

No	Ionic liquids	Abbreviation	Chemical structure
1	1-Methyl-3-propyl-imidazolium iodide	MPII	
2	1-Hexyl-3-methyl-imidazolium iodide	HMII	
3	1-Ethyl-3-methyl-imidazolium iodide	EMII	
4	1,2-Dimethyl-3-propyl-imidazolium iodide	DMPPI	
5	1-Butyl-3-methyl-imidazolium iodide	BMII	
6	1-Dodecyl-3-methyl-imidazolium iodide	DMII	
7	1-Butyl-2,3-dimethyl-imidazolium iodide	BDMII	
8	1-Butyl-1-methyl-pyrrolidinium iodide	BMPyI	
9	1-Methyl-1-propyl-pyrrolidinium iodide	MPPyI	
10	1-Ethyl-1-methyl-pyrrolidinium iodide	EMPyI	
11	1-Butyl-1-methyl-piperidinium iodide	BMPiI	
12	1-Methyl-1-propyl-piperidinium iodide	MPPiI	
13	1-Ethylpyridinium iodide	EPI	
14	1-Butylpyridinium iodide	BPI	
15	1-Hexylpyridinium iodide	HPI	
16	1-Butyl-2-methyl-pyridinium iodide	B2-MPI	
17	1-Butyl-3-methyl-pyridinium iodide	B3-MPI	
18	1-Butyl-4-methyl-pyridinium iodide	B4-MPI	

**Table 3.** Composition of electrolytes

No.	Solvent	Redox couple	Ionic liquid / additive(s)
E1	3-Methoxy-propionitrile	0.1 M LiI + 0.05 M I <sub>2</sub>	0.6 M MPiI + 0.5 M TBP
E2	"	"	0.6 M HMiI + 0.5 M TBP
E3	"	"	0.6 M EMiI + 0.5 M TBP
E4	"	"	0.6 M DMPII + 0.5 M TBP
E5	"	"	0.6 M BMiI + 0.5 M TBP
E6	"	"	0.6 M DMiI + 0.5 M TBP
E7	"	"	0.6 M BDMiI + 0.5 M TBP
E8	"	"	0.6 M BMPyI + 0.5 M TBP
E9	"	"	0.6 M MPPyI + 0.5 M TBP
E10	"	"	0.6 M EMPyI + 0.5 M TBP
E11	"	"	0.6 M BMPiI + 0.5 M TBP
E12	"	"	0.6 M MPPiI + 0.5 M TBP
E13	"	"	0.6 M EPI + 0.5 M TBP
E14	"	"	0.6 M BPI + 0.5 M TBP
E15	"	"	0.6 M HPI + 0.5 M TBP
E16	"	"	0.6 M B2-MPI + 0.5 M TBP
E17	"	"	0.6 M B3-MPI + 0.5 M TBP
E18	"	"	0.6 M B4-MPI + 0.5 M TBP

in the present work and their nomenclature are also listed in Table 3. The different ILs were based on the mono-, di- and tri-alkyl derivatives of different cations.

The DSCs were fabricated by using electrolytes containing the different ILs (E1-E18) listed in Table 3, and the photovoltaic parameters (open-circuit photovoltage, short-current photocurrent density, fill factor and efficiency) of all the cells were measured at room temperature under identical conditions. The values of the different photovoltaic parameters are listed in Table 4. The photovoltaic parameters of the DSCs obtained with electrolytes containing ILs with different cations are discussed below.

**(a) ILs Based on a 5-Member Ring Imidazolium Cation (E1-E7):** From the photovoltaic parameters of DSCs obtained using ILs with imidazolium iodide derivatives (E1-E7), which contain di-alkyl (E1-E3, E5-E6) and tri-alkyl (E4 and E7) imidazolium derivatives, the electrolyte E5, containing 1-butyl-3-methylimidazolium iodide, showed maximum values of  $V_{oc}$  (0.708 V) and  $J_{sc}$  (16.121 mA/cm<sup>2</sup>). The fill factor for this electrolyte was lower (0.547), but the efficiency (6.243%) was very close to the maximum efficiency (6.249%) observed for cells based on 1-methyl-3-propylimidazolium iodide. The cells with electrolytes containing tri-alkyl imidazolium iodide derivatives showed lower values for different photovoltaic parameters, except for the fill factor, as compared with E5. The lower short-circuit photocurrent density obtained with tri-alkyl derivatives, compared with di-alkyl derivatives, is related to the higher viscosity of these ILs, which lowers ionic mobility as viscosity and mobility are inversely related. The higher viscosity hinders the diffusion of the conducting species in the electrolytes. A large cation volume reportedly causes greater hindrance of mass transport, and as a result, cell efficiency is reported to decrease with an increase in the volume of the IL

**Table 4.** Photovoltaic parameters of DSCs containing various ionic liquids

No.	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	ff	$\eta$ (%)
E1	0.693	14.783	0.610	6.249
E2	0.688	13.918	0.607	5.809
E3	0.627	14.416	0.627	6.192
E4	0.680	14.294	0.603	5.864
E5	0.708	16.121	0.547	6.243
E6	0.652	13.376	0.519	4.528
E7	0.679	14.774	0.580	5.823
E8	0.714	14.645	0.632	6.602
E9	0.707	14.712	0.641	6.668
E10	0.715	16.060	0.618	7.098
E11	0.674	13.711	0.561	5.184
E12	0.663	13.531	0.579	5.189
E13	0.674	14.128	0.623	5.934
E14	0.702	15.889	0.640	7.139
E15	0.731	16.175	0.610	7.213
E16	0.711	15.604	0.565	6.267
E17	0.708	16.198	0.609	6.982
E18	0.676	14.302	0.601	5.814

cation.<sup>14</sup> The results above show that di-alkyl derivatives are better suited for applications in DSCs based on imidazolium-based ILs.

**(b) ILs Based on a 5-Member Ring Pyrrolidinium Cation (E8-E10):** The present study used 3 ILs containing di-alkyl pyrrolidinium iodide derivatives in electrolytes for DSCs, and their photovoltaic parameters are given in Table 4. In all 3 ILs, one alkyl group was methyl, whereas the second alkyl group was either ethyl (E10), propyl (E9) or butyl (E8). Of the 3 ILs based on this cation, the DSC based on E10 showed the best cell performance, and the maximum values for  $V_{oc}$  (0.715 V),  $J_{sc}$  (16.060 mA/cm<sup>2</sup>) and efficiency (7.098%) were obtained for this cell. The maximum short-circuit photocurrent density obtained with E10 was due to the shorter alkyl chain length, which resulted in lower viscosity and, hence, fast diffusion of the conducting species. The IL used in E10, 1-ethyl-1-methyl pyrrolidinium iodide, had the shortest alkyl chain length, so the viscosity of the IL was lower compared with the two other ILs (E8 and E9). Secondly, in this group of ILs the two alkyl groups are at the same site of the ring, so their viscosity is lower than that of imidazolium-based ILs, in which the alkyl groups are at different sites, and as a result the efficiency observed for E8-E10 was higher than that of imidazolium-based electrolytes. This shows that, in addition to the nature of the cation, the positions and lengths of the alkyl groups attached to the ILs also play an important role in affecting the viscosity, and, hence, the mobility and ionic conductivity of these electrolytes, which in turn affect the performance of DSCs. The efficiency of DSCs based on these three ILs containing the pyrrolidinium cation was relatively higher than that observed for the imidazolium-based cells.

**(c) ILs Based on 6-Member Ring Piperidinium Cation (E11-E12):** The two di-alkyl piperidinium iodide-based

electrolytes (E11 and E12) used in the present study that contained cations with 6-member rings showed relatively lower values of different photovoltaic parameters, as compared with ILs based on other 5- and 6-member cations. Although both the alkyl groups are at the same site in this case as well, the short-circuit photocurrent density was very low, which may be related to the presence of the 6-member ring in the cation of the IL used. Thus, the piperidinium-based ILs containing di-alkyl groups at the same site resulted in DSCs with lower cell efficiency, and, hence, were not suitable for use in electrolytes for DSCs.

**(d) ILs Based on 6-Member Pyridinium Cation (E13-E18):** Out of the 6 ILs based on 6-member ring pyridinium (E13-E18), 3 were mono-alkyl and the remaining 3 were di-alkyl derivatives. The alkyl groups were attached at different sites on the ring. The performance of the DSC based on E15, i.e., based on the IL 1-hexylpyridinium iodide, showed the best performance in this group. The photovoltaic parameters obtained with this IL were as follows:  $V_{oc}$  (0.731 V),  $J_{sc}$  (16.175 mA/cm<sup>2</sup>), ff (0.610) and efficiency (7.213%). The DSC fabricated using this IL showed the maximum efficiency among all 18 ILs used in the present study. The  $V_{oc}$  value was the highest, and the  $J_{sc}$  value was very close to the highest value obtained for E17 (16.198 mA/cm<sup>2</sup>). Although this cation contains a 6-member ring and the alkyl groups are attached at different sites of the ring, the performance of

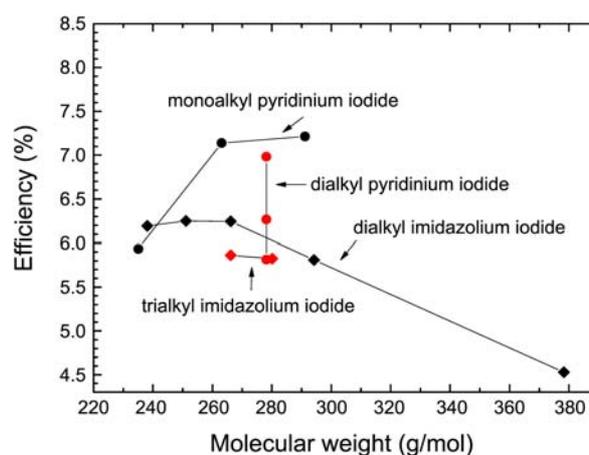


Figure 1. Efficiency of the ionic liquids vs. their molecular weight.

this IL (E15) was better than other ILs based on different cations with 5- and 6-member rings. Recent reports are that the 5-ring structure is helpful for electron exchange reaction at the electrode interface, and the 6-ring structure is useful for restraining dark current.<sup>15</sup>

**Effect of the Molecular Weight of IL.** The 18 ILs used in the present study are listed in Table 2, and can be classified on the basis of alkyl groups such as mono-alkyl pyridinium iodide, di-alkyl pyridinium iodide, di-alkyl imidazolium

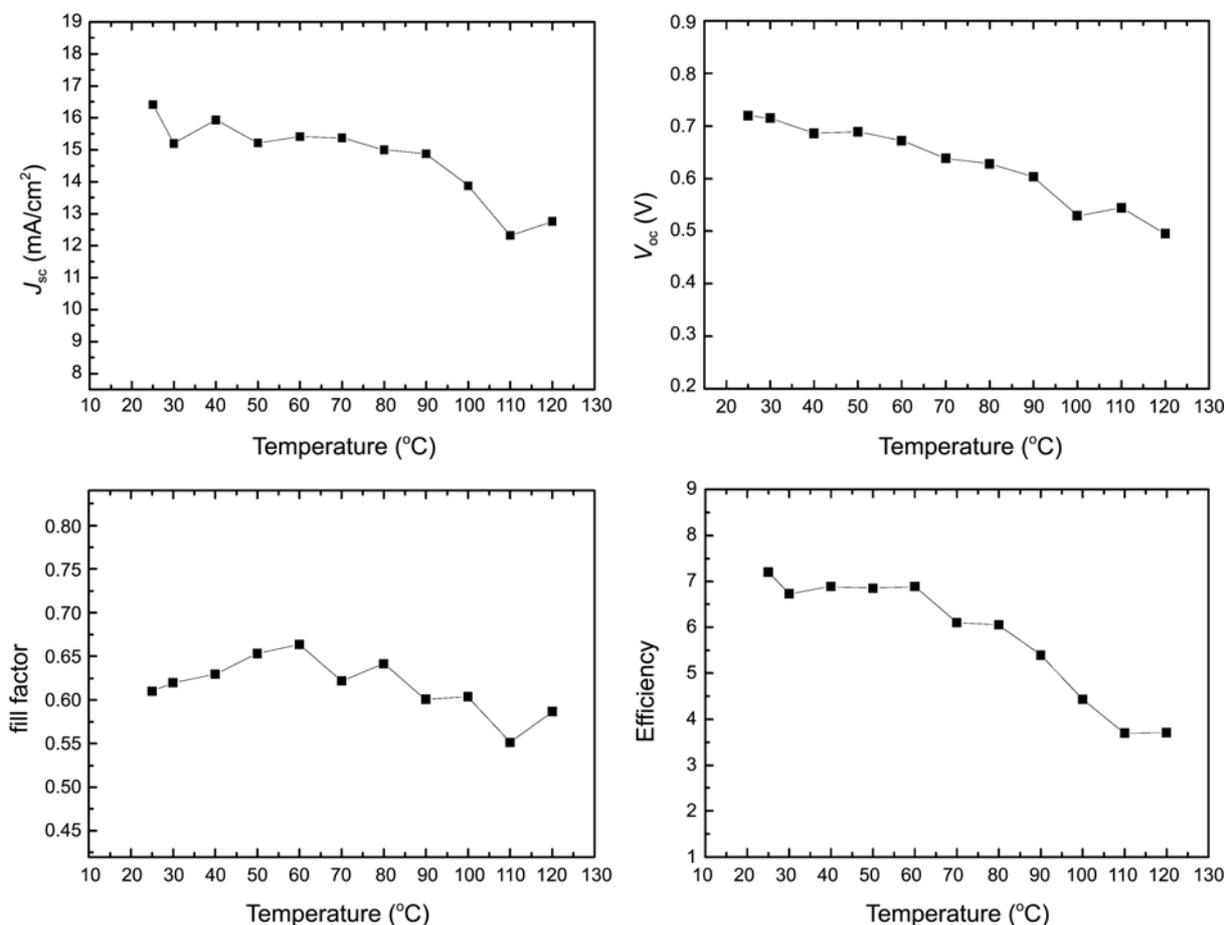


Figure 2. Temperature-dependent photovoltaic parameters of the DSCs prepared with E15. Light intensity: 100 mW/cm<sup>2</sup>.

iodide, di-alkyl piperidinium iodide, and tri-alkyl imidazolium iodide derivatives. As mentioned in the literature, the viscosity of the IL affects the performance of the DSC by affecting the mobility and ionic conductivity of the electrolyte. The viscosity of the IL depends upon the length of the alkyl chain group, so it should also depend upon the molecular weight of the IL. In order to check the effect of the molecular weight of the IL on the photovoltaic parameters of the cell, the efficiency of the DSCs based on different ILs used in the present study was plotted as a function of the molecular weight of the IL and the results are shown in Figure 1. The efficiency of the DSCs based on different ILs was found to depend upon the molecular weight of the ILs containing different cations (imidazolium and pyridinium). The dependence of photoelectric conversion efficiency on the molecular weight of the IL was found to be different for mono- and di-alkyl pyridinium and di- and tri-alkyl imidazolium iodide derivatives. Maximum efficiency was obtained for DSCs containing mono-alkyl pyridinium iodide (E14 and E15). The efficiency of cells containing di-alkyl pyridinium iodide (E16, E17, E18), which had the same molecular weight but contained methyl groups at different sites on the ring, increased as the methyl group changed position from 4- to 2- to 3-. The efficiency of DSCs containing di-alkyl imidazolium iodide, depended strongly on the molecular weight of the IL, and those containing hexyl and dodecyl alkyl groups showed much lower efficiency when compared with other ILs in the same group. The cells using tri-alkyl imidazolium iodide showed the lowest efficiency value. As shown in Figure 1, the cells containing mono-alkyl imidazolium iodides (E14 and E15) demonstrated the best cell performance and maximum efficiency.

The DSC containing electrolyte E15 showed the best cell efficiency, and the photovoltaic parameters for this cell were studied at different temperatures in the 20–120 °C range. The variation of different parameters with temperature is shown in Figure 2. The short-circuit photocurrent density did not change with temperature, remaining above 15 mA/cm<sup>2</sup> at temperatures up to 90 °C, and decreasing when the temperature was above 90 °C. The open-circuit photovoltage, however, decreased slowly and linearly as temperature increased. The fill factor increased with temperature up to 60 °C, then showed a small decrease at higher temperatures. The photoelectric conversion efficiency of the cell did not change with temperature up to 60 °C and remained near 7%, but it decreased at temperatures above 60 °C.

The results described above, related to the use of 18 different ILs based on 4 cations with mono-, di- and tri-alkyl derivatives, showed that cells containing ILs with mono-alkyl derivatives performed relatively better than cells containing ILs with di- and tri-alkyl derivatives. The positions

and lengths of the alkyl groups were observed to have more effect on cell performance than the nature of the 5- or 6-membered ring in the cation of the IL. Although most of the earlier work was done with ILs containing imidazolium cation, and recently some ILs based on other cations, the ILs based on pyridinium cation showed better cell performance and should be explored further for use in DSCs. The position and length of the alkyl groups can be modified to produce optimum properties. Detailed studies of DSCs containing ILs based on pyridinium cation can also help to improve the performance of DSCs, and can contribute to the development of cells with higher photoelectric conversion efficiency and better cell parameters.

### Conclusions

In the present study, 18 ILs based on four types of 5- and 6-member ring cations having different mono-, di- and tri-alkyl groups were used in electrolytes for dye-sensitized solar cells. The dye-sensitized solar cell containing 1-hexyl-pyridinium iodide was found to show the best overall cell conversion efficiency, 7.213%, and other photovoltaic parameters ( $V_{oc} = 0.731$  V,  $J_{sc} = 16.175$  mA/cm<sup>2</sup>,  $ff = 0.610$ ). The length and position of the alkyl groups of the ILs were observed to have more effect on the performance of the cell than the nature of the 5- or 6-membered ring of the IL cation.

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