

A Series of *N*-Alkylimidazolium Propylhexanamide Iodide for Dye-Sensitized Solar Cells

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We report a series of novel imidazolium iodides based ionic liquids (NMIPHI, NAIPHI, and NBIPHI) with different functional groups for the development of a quasi-solid type electrolyte for dye-sensitized solar cells (DSSCs). The diffusion coefficients of redox ions (I^- and I_3^-) are dependent on the molecular weight and it was higher for lighter salts. Among the three ionic liquids, NMIPHI showed highest efficiency of 4.18% when it was used in a liquid electrolyte of a DSSC with *ca.* 6 μm thick TiO_2 mesoporous film. Even though the efficiency was *ca.* 19% lower than that obtained from a liquid electrolyte composed of PMII. When NMIPHI was mixed with PMII with a molar ratio of 1:1 in a solvent free electrolyte, the efficiency of the DSSCs was enhanced compared to that based on pristine PMII.

Key Words : Imidazolium iodide, Electrolyte, Gel electrolyte, Binary ionic liquid, Dye-sensitized solar cells

Introduction

The dye-sensitized solar cells (DSSCs) have been considered as a promising technology for the next generation solar cells since it was first reported in 1991.¹ A DSSC comprising a ruthenium-based dyes adsorbed onto a mesoporous film of nanocrystalline TiO_2 , an iodide-triiodide based liquid electrolyte, and a Pt coated counter electrode showed efficiency as high as 11%.^{2,3} However, long-term stability of the cell has been a major concern due to the use of volatile organic solvent, which often causes leakage of the electrolyte and degradation of the cell at elevated temperature. To overcome this problem several research groups have introduced inorganic p-type semiconductors,^{4,5} organic hole transport materials,⁶ ionic liquids (IL's) based gel electrolytes,⁷⁻¹⁰ and solid state electrolytes.¹¹⁻¹³ Even though the DSSCs containing the above hole transport materials or redox mediators without any volatile organic solvent were thermally stable for long time, the cells still can suffer from the low efficiency because of the poor ionic conductivity and insufficient infiltration of the redox mediators through the mesoporous layer of nanocrystalline TiO_2 . Room-temperature ionic liquids (RTIL's), often act as the source of iodide as well as the solvent itself, are suitable candidate to replace the liquid electrolytes of DSSCs because of higher chemical and thermal stability with negligible vapor pressure in addition to their high ionic conductivity.^{10,14,15} Many gel electrolytes containing IL based imidazolium cations have been found to be comparable to their liquid counterpart when they were used in DSSCs.¹⁶ We report a series of novel *N*-alkylimidazolium propylhexanamide iodide with different functional groups for electrolytes of DSSCs.

Experimental

Synthesis and Characterization of *N*-Alkylimidazolium Propylhexanamide Iodide. All reagents and solvents were purchased from Aldrich unless otherwise mentioned.

***N*-(3-(1*H*-Imidazol-1-yl)propyl)-hexanamide (3).** All reagents and solvents were purchased from Aldrich unless otherwise mentioned. To a solution of 1-(3-aminopropyl)-imidazole (2.0 g, 16.0 mmol) and hexanoic acid (2.0 g, 17.6 mmol) in 50 mL of CH_2Cl_2 was added *N,N*-dicyclohexylcarbodiimide (4.0 g, 19.0 mmol). The mixture was stirred for 36 hr at 50 °C, and the reaction mixture was partitioned between CH_2Cl_2 and H_2O . The organic layer was separated, dried over Na_2SO_4 , and concentrated. The residue was subjected to column chromatography with CH_2Cl_2 -MeOH (10:1) as eluent to give 3.0 g (85%) of the desired product **3** as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, J = 6.8 Hz, 3H), 1.24-1.32 (m, 4H), 1.59 (quin, J = 7.6 Hz, 2H), 1.98 (quin, J = 6.8 Hz, 2H), 2.13 (t, J = 8.0 Hz, 2H), 3.24 (q, J = 6.4 Hz, 2H), 3.97 (t, J = 6.8 Hz, 2H), 5.84 (brs, 1H), 6.92 (s, 1H), 7.03 (s, 1H), 7.48 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 137.0, 129.5, 118.8, 44.7, 36.6, 36.5, 31.4, 31.2, 25.4, 22.4, 13.9.

***N*-(3-(1-Methylimidazolium)propyl)hexanamide Iodide (4) (NMIPHI).** In a sealed tube, a solution of hexanamide **3** (1.0 g, 4.5 mmol) and iodomethane (1.9 g, 13.4 mmol) in EtOAc (5 mL) was heated to 60 °C for 24 hr. Then, the precipitate was collected, washed with EtOAc several times, and dried under vacuum to give 1.3 g (78%) of the desired product **4** as a yellowish solid. ^1H NMR (400 MHz, CDCl_3) δ 0.79 (t, J = 6.8 Hz, 3H), 1.17-1.23 (m, 4H), 1.80 (s, 3H), 2.15 (q, J = 6.0 Hz, 2H), 2.22 (t, J = 8.0 Hz, 2H), 3.21 (q, J =

6.0 Hz, 2H), 3.98 (s, 3H), 4.35 (t, $J = 1.6$ Hz, 2H), 7.35 (s, 1H), 7.64 (s, 1H), 9.90 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.7, 136.7, 123.2, 123.1, 47.3, 36.9, 36.4, 35.0, 31.3, 30.2, 25.4, 22.3, 14.0.

***N*-(3-(1-Allylimidazolium)propyl)hexanamide Iodide (5) (NAIPHI).** A solution of hexanamide **3** (1.0 g, 4.5 mmol) and allyl iodide (1.5 g, 9.0 mmol) in EtOAc (15 mL) was heated to 40 °C for 5 hr. Then, the precipitate was collected, washed with EtOAc several times, and dried under vacuum to give 1.6 g (92%) of the desired product **6** as a yellowish solid. ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, $J = 7.2$ Hz, 3H), 1.29 (t, $J = 3.6$ Hz, 4H), 1.63 (t, $J = 7.6$ Hz, 4H), 2.20–2.30 (m, 3H), 3.23 (q, $J = 6.0$ Hz, 2H), 4.42 (t, $J = 6.0$ Hz, 2H), 4.90 (d, $J = 6.4$ Hz, 2H), 5.51 (t, $J = 9.6$ Hz, 2H), 5.98–6.08 (m, 1H), 7.52 (s, 1H), 7.60 (s, 1H), 10.22 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 136.2, 129.2, 123.2, 123.0, 121.7, 52.2, 47.5, 36.4, 35.1, 31.3, 30.2, 25.4, 22.3, 13.8.

***N*-(3-(1-Benzylimidazolium)propyl)hexanamide Iodide (6) (NBIPHI).** A solution of hexanamide **3** (1.0 g, 4.5 mmol) and benzyl iodide (1.5 g, 6.7 mmol) in EtOAc (15 mL) was heated to 60 °C for 24 hr. Then, the precipitate was collected, washed with EtOAc several times, and dried under vacuum to give 1.8 g (90%) of the desired product **5** as reddish oil. ^1H NMR (400 MHz, CDCl_3) δ 0.84 (d, $J = 6.4$ Hz, 3H), 1.27 (s, 4H), 1.58 (d, $J = 6.8$ Hz, 2H), 1.74 (s, 1H), 2.22–2.28 (m, 4H), 3.26 (d, $J = 5.6$ Hz, 2H), 4.39 (t, $J = 6.0$ Hz, 2H), 5.46 (s, 2H), 7.17 (s, 1H), 7.28–7.42 (m, 5H), 7.63 (s, 1H), 10.20 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 135.0, 131.8, 128.5, 128.0, 127.3, 122.3, 121.3, 52.3, 46.5, 35.4, 34.2, 30.4, 29.3, 24.5, 21.4, 13.0.

Preparation of Electrolyte. Liquid-type IL's based electrolytes for DSSC were prepared by dissolving each individual IL in 3-methoxypropionitrile (MPN) along with iodine and 4-tertbutylpyridine (TBP) as an additive. The concentration of the IL's, iodine, and TBP were 0.6, 0.03, and 0.5 M, respectively. 1-propyl-3-methylimidazolium iodide (PMII) is a very commonly used RTIL with a viscosity of *ca.* 900 cp.¹⁷ As a reference, a liquid electrolyte based on PMII was also prepared in the same way. For electrochemical characterization, the liquid type electrolytes were diluted in MPN containing 0.1 M tetrabutylammonium perchlorate (TBAP). Gel type composite electrolytes were prepared by dissolving NMIPHI in acetonitrile along with iodine and TBP at the same molar ratio as in liquid type while PMII (Solaronix SA) was added to the solution at five different molar ratio of NMIPHI. Finally, the solvent was evaporated completely in a vacuum oven at 40 °C under -0.1 MPa where TBP being high boiling point liquid eventually acted as both additive and solvent for PMII free gel electrolyte.

Fabrication of DSSCs. For photoelectrodes, nanocrystalline TiO_2 layer with an active area of 0.09 cm^2 were prepared by doctor-blading the TiO_2 pastes (TTP-20N, ENB Korea) with an average particle size of 15–20 nm on FTO glass (8 Ω/\square TEC8, Pilkington) substrates followed by sintering at 500 °C for 30 min in an electric muffle furnace.^{18–20} The TiO_2

electrodes were then kept in a 0.3 mM ethanolic solution of N719 dye for 24 hrs. Pt-counter electrodes were prepared by spin-coating an ethanolic solution of 50 mM chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) on FTO glass substrates and then sintered at 380 °C for 20 minutes. The TiO_2 photo-electrode and the platinized counter electrode were put together with 50 μm thick surllyn film as a spacer and sealing agent. Finally, a drop of the liquid electrolytes was directly injected into the cell through the drilled holes at the counter electrodes and the holes were sealed with scotch tape.^{21(a),(b),22} Gel type composite electrolyte was infiltrated into the cells in the same way but at 40 °C.

Measurements. The electrochemical characterization of the electrolytes, such as cyclic voltammetry and steady-state voltammetry were performed with electrochemical workstation, CHI430A (CHI instruments Inc., USA). A Pt disk with 3 mm in diameter and a *ca.* 5 μm radius Pt ultramicro-electrode (UME) were used as working electrode for cyclic voltammetry and steady-state voltammetry measurement, respectively. An Ag/AgCl wire and a Pt wire were used as a reference and a counter electrode, respectively. And the thermal analysis was performed by Thermogravimetric analysis (TGA, S-1000, Scinco).

Photovoltaic measurements of the DSSCs were performed at an illumination of 100 mWcm^{-2} (AM 1.5G) generated from a solar simulator (Polaronix K201, McScience, Korea) equipped with a 200 W Xenon lamp. The power of the simulated light was calibrated by a standard mono-Si solar cell, PVM-396 (PV Measurements Inc. USA). The standard cell was certified by National Renewable Energy Laboratory (NREL, USA). Current-voltage curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a photovoltaic power meter (Polaronix K101/LAB20, McScience, Korea). Thickness of the TiO_2 film was measured by a needle profiler (Surfcom 130A, ACCRETECH, Japan) and found to be 6 μm .

Results and Discussion

A series of imidazolium iodide salts *N*-propylhexanamide-alkylimidazolium iodides were synthesized as shown in the scheme of Figure 1. The reactions of hexanamide **3**, which was prepared using DCC coupling with amine **1** and acid **2**, with several iodides such as methyl iodide, allyl iodide, and benzyl iodide afforded the corresponding imidazolium iodide salts **4** (NMIPHI), **5** (NAIPHI), and **6** (NBIPHI), respectively, in good yields. The imidazolium iodide salts NMIPHI (M.W. 365.25 g/mol) and NAIPHI (M.W. 391.29 g/mol) are amorphous solid that is, solid at room temperature while NBIPHI is a room temperature ionic liquid, RTIL, having highest molecular weight (441.35 g/mol) among the three salts. All the ionic liquids have the same imidazolium cation *N*-(3-(1H-imidazol-1-yl)propyl)hexanamide (**3**). The only difference among them is the functional groups. Both NMIPHI and NAIPHI have smaller functional groups methyl and allyl, respectively while NBIPHI has benzyl group. Figure 2 shows the TGA plot of the IL's measured under nitrogen

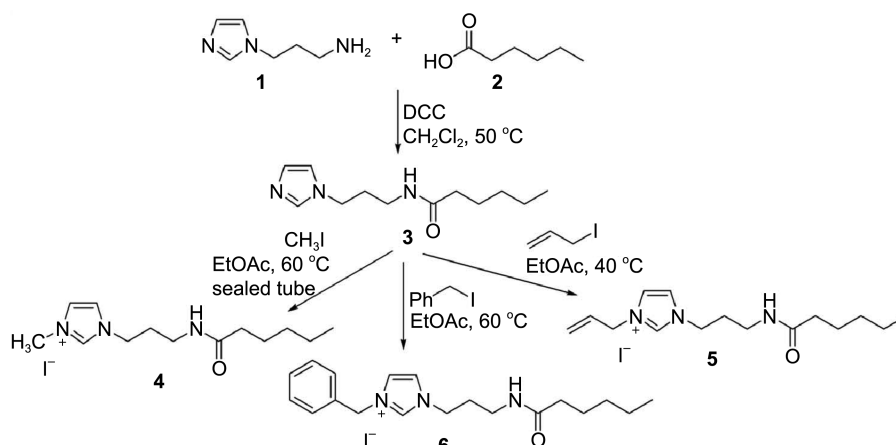


Figure 1. Synthesis scheme of the *N*-propylhexanamide-alkylimidazolium iodides.

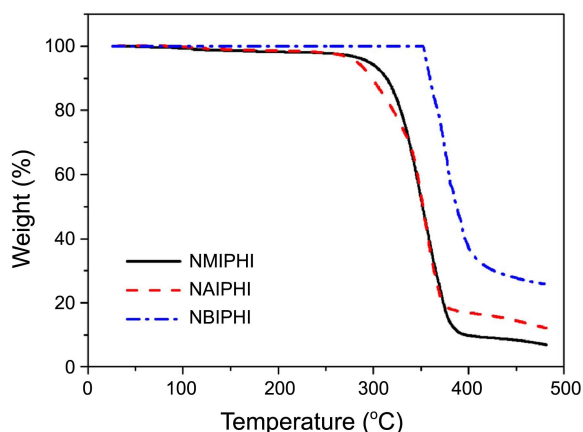


Figure 2. Thermo Gravimetric Analysis (TGA) of the *N*-propylhexanamide-alkylimidazolium iodides.

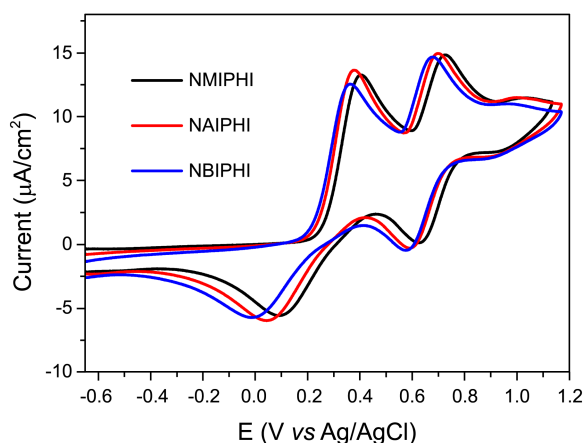


Figure 3. Cyclic voltammograms of the *N*-propylhexanamide-alkylimidazolium iodides dissolved in acetonitrile containing 0.1 M TBAP by Pt working electrode at a scan rate of 50 mV/s.

atmosphere. Among the three IL's, NBIPHI showed much better thermal stability due to higher molecular weight and the presence of benzyl group.

Figure 3 shows the cyclic voltammograms of the *N*-propylhexanamide-alkylimidazolium iodides. All the IL's showed two sequential redox reactions as $3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^-$

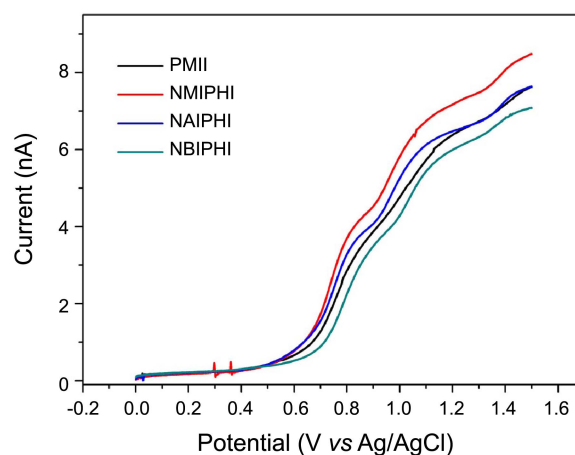


Figure 4. Steady-state voltammogram of the liquid type electrolytes based on the ionic liquids including PMII with Pt ultramicroelectrode (UME).

and $2\text{I}_3^- \rightarrow 3\text{I}_2 + 2\text{e}^-$. The apparent diffusion coefficient (D_{app}) of iodide and triiodide was determined from the steady-state current, i_{ss} , as shown in the Figure 4(a) by the expression²³ in Eq. (1).

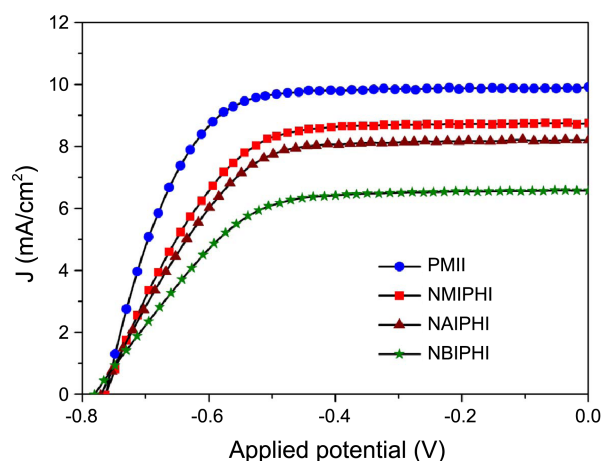
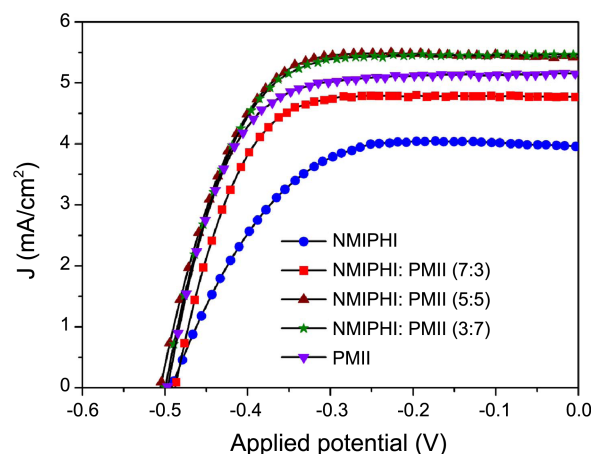
$$i_{ss} = 4n\alpha C^*FD_{app} \quad (1)$$

where n is the number of electron transferred, C^* is the bulk concentration of the electro active species, a is the radius of the UME used, and F is the Faraday's constant.

Table 1 summarizes the calculated values of apparent diffusion coefficients of iodide and triiodide in each liquid electrolyte solutions. NMIPHI, being the smallest among the three IL's, showed highest diffusion coefficients of both iodide ($4.36 \times 10^{-6} \text{ cm}^2/\text{s}$) and triiodide ($4.29 \times 10^{-6} \text{ cm}^2/\text{s}$) while NBIPHI showed lowest. It is consistent with the trends of the molecular weight of the salts used in this study. However, there is an exception for the case of PMII, the smallest among all the IL's, it showed unexpectedly lowest D_{app} of I^- and I_3^- . This trend is consistent with the current-voltage curves (Figure 5) of DSSCs when the IL's were used in liquid electrolytes. It was found that the photovoltaic performance including short-circuit current density (J_{sc}) and

Table 1. Apparent diffusion coefficients, D_{app} , of iodide, and triiodide in different liquid electrolytes; and photovoltaic parameters including open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and efficiency (η) of the DSSCs based on the liquid electrolytes

Liquid electrolytes	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)	$D_{app}(I^-) \times 10^{-6}$ cm ² /s	$D_{app}(I_3^-) \times 10^{-6}$ cm ² /s
PMII	0.76	9.91	68.3	5.17	3.62	3.59
NMIPHI	0.76	8.83	62.5	4.18	4.36	4.29
NAIPHI	0.77	8.24	60.8	3.85	3.94	3.89
NBIPHI	0.78	6.36	59.2	2.92	3.77	3.57

**Figure 5.** Current-voltage curves of the DSSCs based on liquid electrolytes PMII, NMIPHI, NAIPHI, and NBIPHI.**Figure 6.** Current-voltage curves of the DSSCs based on gel composite electrolytes.

fill-factor (FF) of the cell decreased with the increase of molecular weight of the imidazolium salts while open circuit voltage (V_{oc}) did not change much as summarized in Table 1. As a result, the electrolyte containing the smallest imidazolium salt NMIPHI showed highest efficiency (η) of 4.18%. It is to be noted here that PMII based liquid electrolyte showed the best photovoltaic performance even though it showed the lowest ionic diffusion coefficients. This superior performance of PMII compared to other three IL's could be attributed to the different energetics of photoelectrodes of the DSSCs in the presence of different IL's used in the electrolytes. However, this phenomenon is not clearly understood yet and it requires further investigation.

Using mixed ionic liquids (two or more) in solvent free electrolytes has been found to be a very effective way to control the electrochemical properties of the electrolytes for stable and high efficiency DSSCs.²⁴⁻²⁸ Recently, Cheng *et al.* showed remarkable enhancement of efficiency of DSSCs by using a binary ionic liquid composing imidazolium melt 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) and PMII (volume ratio of 50/50).²⁸ It was expected that addition of a highly viscous ionic liquid with high diffusion coefficient into a less viscous ionic liquid would provide sufficient flexibility and conductivity to make solvent free and gel type ionic liquid based electrolyte¹⁰ for highly efficient DSSCs. From this notion, gel type composite electrolytes were prepared by mixing NMIPHI and PMII at different molar ratio. The current-voltage curves of the

DSSCs based on these gel type electrolytes are shown in the Figure 6 and the corresponding photovoltaic parameters are summarized in Table 2. The photovoltaic performance of DSSCs based on these gel electrolytes improved significantly as the ratio of PMII increased while it decreased slowly when the content of PMII was higher than that of NMIPHI. The enhancement of the cell efficiency was almost up to 60%, which is comparable to the previous report,²⁸ when the molar ratio between NMIPHI and PMII was 1:1. J_{sc} and FF were generally improved while the open circuit voltage was not changed much upon addition of PMII. Even though the cell efficiency was decreased very slowly when the content of PMII kept increasing, it was still higher than that with the pure PMII as electrolyte. The enhanced performance of DSSCs upon addition of NMIPHI to PMII could be due to the improved diffusion coefficient of I^- and I_3^- in the binary system that mainly originated from NMIPHI

Table 2. Photovoltaic parameters including open circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and efficiency (η) of the DSSCs using gel electrolytes

NMIPHI:PMII (molar ratio)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
10:0	0.49	3.96	59.9	1.17
7:3	0.49	4.78	69.0	1.61
5:5	0.51	5.42	67.8	1.86
3:7	0.50	5.46	67.2	1.84
0:10	0.50	5.15	68.3	1.75

with highest diffusion coefficient. In addition, the cell efficiency (η) of all the cells was low because of the electrolyte composition and the TiO₂ photoelectrodes were not optimized for high efficiency condition, while the effect of the composition of binary ionic liquid system on the J - V performances of DSCCs was of main interests. However, the efficiency trend observed in this work is consistent with the previous reports.⁸⁻¹⁰

Conclusions

We have synthesized a series of new imidazolium-based iodide salts, NMIPHI, NAIPHI, and NBIPHI to develop a novel electrolyte for dye-sensitized solar cells (DSSCs). The efficiency (η), estimated for 6 μ m thick TiO₂ film, of the DSSC with the smallest ionic liquid NMIPHI reached up to 4.2% along with the fill factor (FF) of 62.5% at 1 sun condition. The overall efficiency and the fill factor decreased significantly when the size of the functional group of the imidazolium salts increased from methyl to benzyl. The ionic liquid NMIPHI was found to be suitable for developing solvent free gel type binary ionic liquids. The highest efficiency of 1.86% was obtained for the DSSCs based on a solvent free gel type binary ionic liquid NMIPHI/PMII (molar ratio of 50/50), with *ca.* 6% enhancement in comparison with pure PMII and *ca.* 58% enhancement in comparison with pure NMIPHI based DSSCs. The novel imidazolium salt introduced in the research can, therefore, be applied to develop solvent free gel type electrolyte for DSSCs.

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