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SYNTHESIS AND PROPERTIES OF *N*^{1}-(3-METHOXYPROPYL)-*N*^{3}-METHYLIMIDAZOLIUM SALTS

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Abstract – *N*^{1}-(3-Methoxypropyl)-*N*^{3}-methylimidazolium salts (**1c**–**1f**) were synthesized and characterized. The $N(SO_2CF_3)_2^-$ salt (**1c**) exhibited the lowest viscosity (51 cP) among the salts (**1c**–**1f**). The I^- salt (**1d**) was tested as an electrolyte solution to the dye-sensitized solar cells (DSSCs), and the devices worked as the DSSCs.

INTRODUCTION

Imidazolium-based molten salts known as ionic liquids (ILs) have been attracting current attention in many fields as a new class of non-flammable solvents with very low vapor pressure and/or as an electrolyte.[1,2] For these applications, however, their high viscosity, i.e., poor fluidity, are often problematic, since the ionic liquids in principal compose of only ions; the ionic bond is usually stronger than the Van der Waals forces between the ordinary molecule-based solvents. In order to develop ILs with low viscosity many efforts have been made, and recently several ILs with low viscosity (< 50 cP) have been reported.[3] A common structural feature in these ILs with low viscosity is to have alkyl group(s), which can weaken the intermolecular interaction. On the other hand, long alkyl groups often interact strongly via the hydrophobic interaction in the condensed phase, which is known as a fastener effect.[4] With these considerations, we are interested in ILs with an oxygen-containing alkyl group, rather than a simple alkyl group, since introduction of oxygen atom in alkyl group enhances flexibility and then

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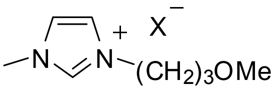
This paper is dedicated to Professor Dr. Albert Eschenmoser on the occasion of his 85th birthday.

weakens the fastener effect in the condensed phase. One of such ILs reported to date is *N*^{1}-(3-methoxypropyl)-*N*^{3}-methylimidazolium salts (counter anion, Cl^-, Br^-, and $N(SO_2CF_3)_2^-$ ions, **1a**–**1c**).[5,6] However, neither detail synthesis nor physical properties including viscosity has been reported, except for the aquatic toxicity.[5,6] In his paper, we report the synthesis and characterization of **1b**–**1f**, their properties including viscosity, thermal stability, and electrochemical properties. In addition, we also tested them as electrolyte and electrolyte solution in the dye-sensitized solar cells (DSSCs),[7] demonstrating the utility of these ILs as a solvent and/or an electrolyte.



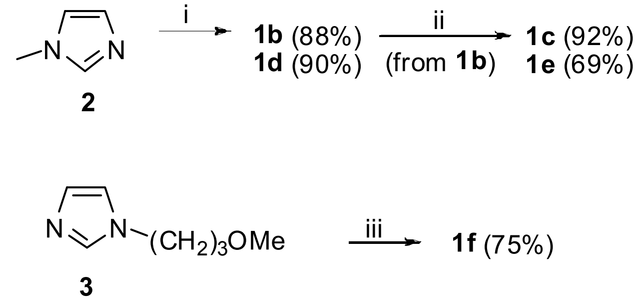
1a: X = Cl
1b: X = Br
1c: X = $N(SO_2CF_3)_2$
1d: X = I
1e: X = PF_6
1f: X = BF_4

Figure 1. Chemical structure of *N*^{1}-(3-methoxypropyl)-*N*^{3}-methylimidazolium salts

RESULTS AND DISCUSSION

Synthesis of **1b**–**1f** is shown in Scheme 1. As in the synthesis of ordinary imidazolium halide salts, **1b** and **1d** with Br^- or I^- anion were readily synthesized via a simple alkylation reaction of *N*-methylimidazole (**2**) with 1-bromo-3-methoxypropane or 1-iodo-3-methoxypropane, respectively. The bis(trifluoromethanesulfonyl)amide salt (**1c**) and hexafluorophosphate salt (**1e**) were also easily obtained via an anion exchange reaction of **1b** with lithium bis(trifluoromethanesulfonyl)amide ($LiN(SO_2CF_3)_2$) or aqueous hexafluorophosphonic acid (HPF_6) solution, respectively. On the other hand, similar anion exchange reactions of **1b** with potassium tetrafluoroborate (KBF_4) or aqueous tetrafluoroboric acid (HBF_4) solution did not gave pure **1f**, and the products of the reactions were always contaminated with **1b** owing to insufficient anion exchange. Alternatively, methylation of *N*-(3-methoxypropyl)imidazole (**3**)[8] with trimethyloxionium tetrafluoroborate ($(CH_3)_3OBF_4$) gave pure **1f**. All the newly synthesized salts (**1d**–**1f**) were liquid at room temperature as expected and fully characterized by spectroscopic and combustion elemental analyses.

Viscosity (η), thermal stability, and electrochemical stability of the present imidazolium salts (**1b**–**1f**) were summarized in Table 1. Their viscosities except for **1b** are low compared to ordinary alkyl-substituted imidazolium salts. For example, *N*^{1}-methyl-*N*^{3}-pentylimidazolium salts (Figure 2), which have the same number of atoms in the substituents, show relatively large viscosity: η = 59 cP for $N(SO_2CF_3)_2^-$ salt, η = 1362 cP for I^- salt, and η = 308 cP for PF_6^- salt.[9,10] These results indicate that introduction of oxygen atom in the alkyl side group of imidazolium salts is effective to reduce viscosity. In addition, among the present imidazolium salts, **1c** with $N(SO_2CF_3)_2^-$ anion shows very low viscosity (η = 51 cP), which is almost comparable to the state-of-the art ILs with viscosity of the lowest class.[2]



Scheme 1. Synthesis of **1b**–**1f**: Reagents and conditions: (i) $Br(CH_2)_3OMe$ or $I(CH_2)_3OMe$, THF, reflux; (ii) 10 eq 85% HPF_6 aq. or $LiN(SO_2CF_3)_2$, H_2O, rt; (iii) $(CH_3)_3OBF_4$, Et_2O, rt.

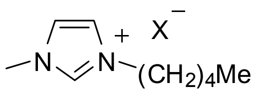


Figure 2. Chemical structure of N^1-methyl-N^3-pentylimidazolium salts

Thermal stability of the ILs was evaluated with thermogravimetric analysis (TGA), and thermal decomposition temperature (T_d) at 5% weight loss were tabulated in Table 1. The halide salts show lower T_d than the other salts, provably owing to thermally induced nucleophilic reaction of the halide anion on the side chain to liberate the imidazole moiety.[11] The other salts have very good thermal stability as ordinary imidazolium-based ILs have.

Electrochemical stability of **1b**–**1f** was also evaluated by means of cyclic voltammetry. In general, ILs are known to have very large electrochemical windows. However, the electrochemical behavior of the present salts depends very much on the anions: two halides (**1b** and **1d**) did not show clear current onset, and the most thermally stable **1c** has a very large electrochemical window than the other salts have. Such diverse behaviors often observed for other imidazolium-based ILs are explained by the electrochemical stability of the anions, but the imidazolium cation. In the present case also, it is rational to conclude that the present N^1-(3-methoxypropyl)-N^3-methylimidazolium cation has no significant electrochemical instability by itself.

Table 1. Physicochemical and thermal property of **1b**–**1f**

	1b (X = Br$^-$)	**1c** (X = N(SO$_2$CF$_3$)$_2$$^-$)	**1d** (X = I$^-$)	**1e** (X = PF$_6$$^-$)	**1f** (X = BF$_4$$^-$)
η / cP	4460	51	214	159	120
T_d/°C	265	380	234	418	327
E^{ox} (decomp)/V[1]	–[2]	+2.7	–[2]	+2.1	+1.5
E^{red} (decomp)/V[1]	–[2]	–2.4	–[2]	–2.1	–0.8

[1] Decomposition potentials (V) vs. Ag/AgCl, which were determined as on-set potentials of anodic (oxidation) or cathodic current (reduction). Scan rate: 100 mV/sec, working and counter electrode: Pt.
[2] No clear oxidation or reduction wave was observed.

Owing to relatively low viscosity (η), good thermal, and electrochemical stability, the present imidazolium salts (**1c**–**1f**) seem to be promising as a new solvent and/or an electrolyte. In order to evaluate their possible utilities, we tested them in the electrolyte solution of I/I$_3$ redox couple in the backside of the DSSCs (Figure 3a). Because one of the major drawbacks in the ordinary DSSC is associated with the liquid electrolyte consisting of volatile organic solvents (typically acetonitrile), DSSCs with the IL-based electrolyte solution in the backside are thought to be a potential solution for this drawback.[3,12]

The organic dye used in the present studies is an octithiophene-based cyanoacrylic acid derivative (Figure 3b), which was originally developed in our group,[13] and its standard DSSCs with the electrolyte solution in CH$_3$CN showed fairly good performances with open-circuit voltage (V_{oc}) = 710 mV, short-circuit current density (I_{sc}) = 11.9 mA, fill factor (FF) = 0.58, and power-conversion efficiency (η_p) = 4.9%. The I-V characteristics of the DSSCs with electrolyte solution based on **1c**–**1f** are depicted in Figure 4a, and the device parameters are summarized in Table 2. Although the device performances were rather poor compared to those of the standard device, η_p of the device with **1d** (device 1 in Table 2) is close to 1%. This performance is relatively good for organic solvent-free DSSC's electrolyte composed with single iodide based IL,[3,14] implying that **1d** can be a promising candidate as an electrolyte and/or iodide source in the DSSC application. To improve the performances, we applied combined electrolyte solution of **1d** with the ILs possessing lower viscosity (**1c**, **1e**, and **1f**): however, thus fabricated DSSCs (device 2–4 in Table 2) showed poor performances than the device 1 did. From these results, we can conclude that viscosity is not solely the key factor to determine the performances of DSSCs, and the anion species in the electrolyte may also play important role.

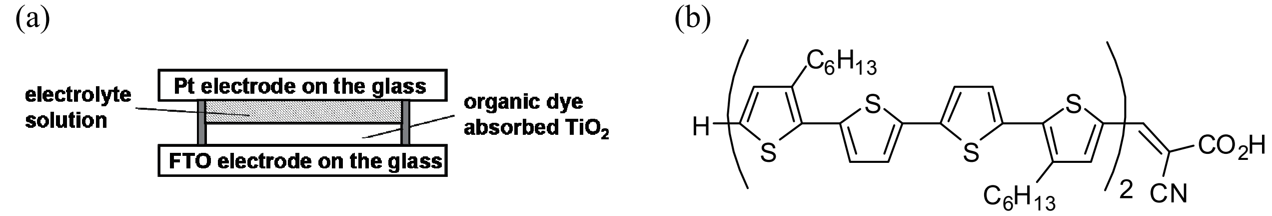


Figure 3. Schematic device structure of DSSCs (a) and the chemical structure of the dye used in the present study (b)

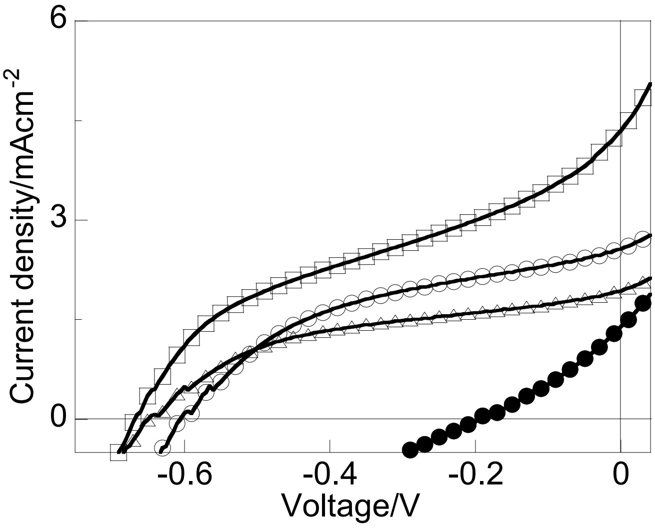


Figure 4. I-V characteristics of DSSCs with **1c**–**1f** as the electrolyte solution: **1c** (open circle), **1d** (open square), **1e** (open triangle), and **1f** (closed circle)

Table 2. Device characteristics of DSSCs with **1c**–**1f** as the electrolyte solution

Device	Electrolyte solution	V_{oc}/mV	I_{sc}/mA	FF	η_p/%
1	**1d** / 0.1 M I_2	670	4.3	0.33	0.95
2	**1c** / 0.8 M **1d** + 0.1 M I_2	610	2.6	0.42	0.66
3	**1e** / 0.8 M **1d** + 0.1 M I_2	650	1.9	0.45	0.56
4	**1f** / 0.8 M **1d** + 0.1 M I_2	200	1.4	0.20	0.05

In summary, we have synthesized and characterized a series of ILs with N^1-(3-methoxypropyl)-N^3-methylimidazolium cation. Physicochemical characterization of the ILs indicated that they are thermally and electrochemically stable materials with relatively low viscosity, and thus they can be applicable as a solvent and/or an electrolyte. In fact, preliminary application of the ILs as an electrolyte solution in DSSCs showed that the DSSCs with **1d** as an electrolyte solution gave a decent solar cell behavior with η_p close to 1%, although the device performances are still inferior to those of the corresponding DSSCs with ordinary organic solvent based electrolyte solution. Therefore, to develop ILs with rather lower viscosity as well as to improve the performances of DSSCs using the IL-based electrolyte solution are very interesting direction. Relevant experiments are now underway in our group.

EXPERIMENTAL

General. All reaction were carried out under a nitrogen atmosphere unless otherwise noted. All the reagents and solvents were used without further purification without following solvents. The following solvents were dried in parenthesis; THF (Na–benzophenon ketyl), Et_2O (Na–benzophenon ketyl), benzonitrile (P_4O_{10} and CaH_2).

^{1}H-NMR and ^{13}C-NMR spectra in deuterated chloroform were recorded on JEOL EX-270 and Varian 400-MR NMR spectrometer at room temperature, and the chemical shifts (δ) were referred to tetramethylsilane (TMS) or residual solvents as internal criteria. Electron ionization (EI) mass spectra were recorded at 70 eV on a Shimadzu GC/MS QP5050. TGA was carried out on SII EXSTAR 6000 TG/DTA6200 with increment of 10 $^{\circ}$C/min. Elemental analyses were performed at Graduate School of Engineering, Hiroshima University. Cyclic voltammetry (CV) measurements were carried out on a potentiostat and a function generator in the neat ionic solvent at a scan rate of 100 mV/s. Counter and working electrodes were made of Pt, and the reference electrode was Ag/AgCl. Viscosities of the samples were measured on a Stony Brook Scientific PDV-100 viscometer for **1b** and a Ostwald viscometer for **1c**–**1f** at room temperature (20 ºC).

***N*^{1}-(3-Methoxypropyl)-*N*^{3}-methylimidazolium bromide (1b)**[6]**:** *N*-Methylimidazole (**2**, 14.5 g, 176 mmol) was placed in a 200 mL three-neck flask, and dissolved with THF (124 mL). After 1-bromo-3-methoxypropane (27.0 g, 176 mmol) was added, the reaction mixture was refluxed for 5 h. The solvent was removed in vacuo, to give **1b** (36.6 g, 88%) as yellow oil. TLC $R_f = 0.25$ ($MeCN/Al_2O_3$); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 10.54 (1 H, s), 7.40 (1 H, s), 7.34 (1 H, s), 4.46 (2 H, t, $J = 7.4$ Hz), 4.14 (3 H, s), 3.44 (2 H, t, $J = 6.3$ Hz), 3.34 (3 H, s), 2.22 (2 H, q, $J = 6.3$ Hz).

***N*^{1}-(3-Methoxypropyl)-*N*^{3}-methylimidazolium iodide (1d):** Yellow oil (9.15 g, 90%) from **2** (7.23 g, 36.1 mmol) and 1-iodo-3-methoxypropane (7.23 g, 36.1 mmol). TLC $R_f = 0.18$ (CH_2Cl_2/SiO_2); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 10.25 (1 H, s), 7.27 (1 H, s), 7.26 (1H, s), 4.45 (2 H, t, $J = 6.8$ Hz), 4.12 (3 H, s), 3.46 (3 H, t, $J = 5.8$ Hz), 3.34 (3 H, s), 2.24 (2 H, q, $J = 5.7$ Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.6, 123.0, 121.9, 67.5, 58.0, 46.5, 36.4, 29.2. Anal. Calcd for $C_8H_{15}N_2OI$: C, 34.06; H, 5.36; N, 9.93%. Found: C, 34.07; H, 5.60; N, 9.92%.

***N*^{1}-Methyl-*N*^{3}-(3-methoxypropyl)imidazolium bis(trifluoromethanesulfonyl)amide (1c)**[5]**:** *N*^{1}-Methyl-

N^3-(3-methoxy)propylimidazolium bromide (**1b**, 7.0 g, 30 mmol) was placed in a plastic bottle, and dissolved with deionized water (30 mL). Lithium bis(trifluoromethanesulfonyl)amide (9.4 g, 33 mmol) was added, then the solution was stirred at room temperature overnight. To the reaction mixture, deionized water was added, and water layer was extracted with CH_2Cl_2 (20 mL x 3). Organic layer was washed with deionized water (20 mL x 3), dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo. The residue was dissolved with CH_2Cl_2, and activated carbon (a cup of spatula) was added and stirred for 2 h. The crude product was purified by column chromatography (SiO_2, 1:2 hexane–EtOAc as eluent), to give **1c** (11.9 g, 92%) as colorless liquid. TLC R_f = 0.3 (1:2 hexane–EtOAc/Al_2O_3); ^{1}H-MNR (270 MHz, $CDCl_3$, TMS) δ 8.68 (s, 1H), 7.22 (s, 1H), 7.20 (s, 1H), 4.23 (t, 2H, J = 7.0 Hz), 3.88 (s, 3H), 3.29 (t, 2H, J = 7.0 Hz), 3.24 (s, 3H), 2.04 (q, 2H, J = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) 136.6, 123.3, 122.6, 121.4, 118.2, 68.2, 58.7, 47.6, 36.5, 29.9; Anal. $C_{10}H_{15}N_3O_5F_6S_2$: C, 27.59; H, 3.47; N, 9.65. Found: C, 27.45; H, 3.47; N, 9.43%.

N^1-(3-Methoxypropyl)-N^3-methylimidazolium hexafluorophosphate (1e): N^1-(3-Methoxypropyl)-N^3-methylimidazolium bromide (**1b**, 21.4 g, 91.1 mmol) was placed in a 50 mL plastic bottle, and dissolved with deionized water (75 mL). After a 65% hexafluorophosphoric acid (1.66 g, 7.4 mmol) was added, the reaction mixture was stirred at room temperature overnight. To the reaction mixture, deionized water (20 mL) and CH_2Cl_2 (10 mL) were added. Water layer was extracted with CH_2Cl_2 (20 mL x 3). Organic layers were combined, washed with deionized water (20 mL x 3), and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo. Residue was dissolved in CH_2Cl_2 (300 mL), then activated carbon (a cup of spatula) was added. After stirring at room temperature for 2 h, the mixture was filtered. The crude product was purified by column chromatography (Al_2O_3, eluted in CH_2Cl_2 and EtOAc), to give **1e** (18.2 g, 69%) as pale yellow liquid. TLC R_f = 0.17 (2:1 CH_2Cl_2:EtOAc/Al_2O_3); ^{1}H-NMR (270 MHz, $CDCl_3$) δ 8.65 (1 H, s), 7.25 (1 H, t , J = 1.7 Hz), 7.22 (1 H, t, J = 1.7 Hz), 4.31 (2 H, t, J = 7.7 Hz), 3.96 (3 H, s), 3.42 (2 H, t, J = 6.8 Hz), 3.33 (3 H, s), 2.12 (2 H, q, J = 6.8 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.0, 123.5, 122.8, 68.5, 59.0, 47.9, 36.7, 30.1. Anal. Calcd for $C_8H_{15}N_2OPF_6$: C, 32.01; H, 5.04; N, 9.33%. Found: C, 31.95; H, 5.10; N, 9.33%.

N^1-(3-Methoxypropyl)-N^3-methylimidazolium tetrafluoroborate (1f): N^1-(3-Methoxypropyl)-imidazole[8] (**3**, 3.60 g, 25.7 mmol) was placed in a 100 mL three-neck flask, and dissolved with Et_2O (11 mL). Trimethyloxionium tetrafluoroborate (3.45 g, 23.3 mmol) was gradually added, and the reaction mixture was stirred at room temperature overnight. Organic layer was separated, washed with Et_2O (10 mL x 3), and dried in vacuo. After the residue was dissolved with MeCN, the solution was washed with hexane. Activated carbon (0.75 g) was added and stirred for 2 h. After filtration, the solvent was removed in vacuo, to give **1f** (4.23 g, 75%) as pale yellow oil. TLC R_f = 0.84 (MeCN/Al_2O_3); ^{1}H-NMR (270 MHz,

$CDCl_3$) δ 8.85 (1 H, s), 7.27 (2 H, s), 4.32 (2 H, t, J = 7.0 Hz), 3.95 (3 H, s), 3.42 (2 H, t, J = 5.6 Hz), 3.33 (3 H, s), 2.14 (2 H, q, J = 3.9 Hz). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.5, 123.4, 122.7, 68.6, 59.0, 47.9, 36.8, 30.2; Anal. Calcd for $C_8H_{15}N_2OBF_4$: C, 39.70; H, 6.25; N, 11.57%. Found: C, 39.59; H, 6.37; N, 11.49%.

Fabrication and Evaluation of the DSSCs: After cleaning the FTO-coated glass, nanocrystalline TiO_2 electrode (20 nm, CCIC:PST18NR, JGC-CCIC) was prepared on a glass substrate coated on F-doped SnO_2 (FTO) by the doctor blade technique. The substrate was sintered at 500 ºC in air for 1 h. The organic dye, octithiophene-based cyanoacrylic acid derivative,[13] was absorbed in $CHCl_3$ overnight. The size of the TiO_2 electrode was 0.25 cm^2 (0.5 x 0.5 cm). The electrolyte solution was deposited on the TiO_2 electrode using separator, and finally a Pt electrode on the glass substrate was sandwiched to give the DSSC cell. The DSSC was evaluated by using the Newport 96000 solar simulator under simulated AM 1.5G solar irradiation at 100 mW cm^{-2}. The irradiation power was calibrated by the Newport 1918-C optical power meter with the Newport 818P-001-12 thermopile detector. The I-V characteristics was recorded on the Keithley 2400 source meter.

ACKNOWLEDGEMENTS

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