DOI 10.5012/bkcs.2011.32.8.2795

Anion Effects on Structure and Properties of Bis(3-methylimidazolium-1-yl) Salts

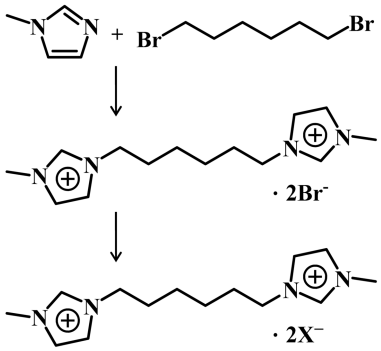
Tae Hwan Noh, Jungmin Ahn, Young Mee Na, and Ok-Sang Jung*

Department of Chemistry and Chemistry Institute of Functional Materials, Pusan National University, Pusan 609-735, Korea
**E-mail: oksjung@pusan.ac.kr*
Received June 13, 2011, Accepted June 20, 2011

Key Words : Anion effects, Bis(3-methylimidazolium-1-yl) salts, Conductivity, Crystal structures, Thermal properties

Research on diverse kinds of molten organic salts has been magnified as a green scientific field since the first room temperature ionic liquid, the mixture of *N*-ethylpyridinium bromide and metallic chlorides, was discovered in 1951.[1] Recently, various organic salts have been used as green solvents,[2-6] extraction liquids,[7,8] and electrolyte materials[9] owing to their task-specific properties such as high ionic conductivity, negligible vapor pressure, non-flammability, excellent thermal stability, and miscibility in both water and organic solvents. Thus, investigation on the chemical structures *vs* the unique physiochemical properties of organic salts is a hot issue. In particular, bis(imidazolium) salts have been considered as novel solvents and lubricants,[10] ultra-stable separation phases,[11,12] and the stationary phases in gas chromatography columns.[7] For some geminal dicationic ionic liquids, the wide range of cation and anion combinations allows various ionic salts.[13] In this context, in order to establish a relationship between the structure and the physiochemical properties of bis(imidazolium) salts, we describe the anion effects on single crystal structures and physiochemical properties of bis(3-methylimidazolium-1-yl) salts. The polyatomic counteranions play key roles in determining the molecular structures and behaviors since polyatomic anions have many characteristics such as negative charge, size, and geometry, and display variable differences, significant solvent effects, and pH dependence.[14-18] Recent developments in anion chemistry include exciting advances in anion template assembly, ion-pair recognition, the function of supramolecular materials,[19-23] environmental pollution, disease pathways, and biological processes.[24-26]

The reaction of 1,6-dibromohexane and 1-methylimidazole in an 1:2 molar ratio resulted in an ionic salt of bis(3-methylimidazolium-1-yl)hexane dibromide, $MIm_2C_6{\cdot}Br_2$, as shown in Scheme 1. Anion exchanges of $MIm_2C_6{\cdot}Br_2$ with NaX ($X^- = BF_4^-$, ClO_4^-, $CF_3SO_3^-$, PF_6^-) in acetone or with $AgNO_3$ in water, followed by recrystallization of the exchanged species, yielded single crystals of $MIm_2C_6{\cdot}(X)_2$ suitable for X-ray crystallography. The anion exchange of $MIm_2C_6{\cdot}Br_2$ with $AgNO_3$ was conducted in water owing to solubility problem. The products were confirmed by characteristic IR frequencies of each anion and ^{1}H NMR resonances (Supporting Information). IR stretching frequencies of BF_4^-, PF_6^-, $CF_3SO_3^-$, ClO_4^-, and NO_3^- were at 1036, 835, 1259, 1088, and 1363 cm^{-1}, respectively. ^{1}H NMR spectra in



Scheme 1. Synthetic procedure of bis(3-methylimidazolium-1-yl) salts. $X^- = BF_4^-$, ClO_4^-, $CF_3SO_3^-$, PF_6^-, NO_3^-.

CD_3OD showed that the chemical shifts of imidazolium ring of $MIm_2C_6{\cdot}Br_2$ (9.03, 7.69, 7.59 ppm) were deshielded relative to those of starting material, 1-methylimidazole (7.59, 7.07, 6.95 ppm). Elemental analyses data were consistent with the proposed structures. All the products are stable crystalline solids at room temperature. They are soluble in polar organic solvents such as water, methanol, ethanol, and acetonitrile, but are insoluble in tetrahydrofuran, chloroform, dioxane, benzene, diethyl ether, and *n*-hexane. All the products are soluble in acetone except for the product containing nitrate anions. The solubility in both some organic solvents and water can be attributed to the appropriate lipophilicity of the C_6 linkage chain. This is a good series of anions-containing ionic salts that can control desired characteristics.

The crystal structures of $MIm_2C_6{\cdot}(BF_4)_2$, $MIm_2C_6{\cdot}(CF_3SO_3)_2$, and $MIm_2C_6{\cdot}(ClO_4)_2$ were solved. They are centrosymmetric molecules as depicted in Figure 1. Two cationic 1-methylimidazolium rings were bound to the both sides of the typical linear *n*-hexyl group. The torsion angle of N(2)-C(5)-C(6)-C(7) of $MIm_2C_6{\cdot}(BF_4)_2$ is 174.9(2)° whereas that of $MIm_2C_6{\cdot}(CF_3SO_3)_2$ is 66.2(2)°, suggesting that bulky triflate (trifluoromethanesulfonate) anion has a strong influence on the conformation. The torsion angle of $MIm_2C_6{\cdot}(ClO_4)_2$ (174.9(2)°) is similar to that of $MIm_2C_6{\cdot}(BF_4)_2$. Thus, the packing structures of $MIm_2C_6{\cdot}(BF_4)_2$ and $MIm_2C_6{\cdot}(ClO_4)_2$ consisted of similar zigzag bands along the crystallographic *b*-axis in contrast to $MIm_2C_6{\cdot}(CF_3SO_3)_2$ (Figure 2). Those bands were formed by separated stacks of skeletal cations

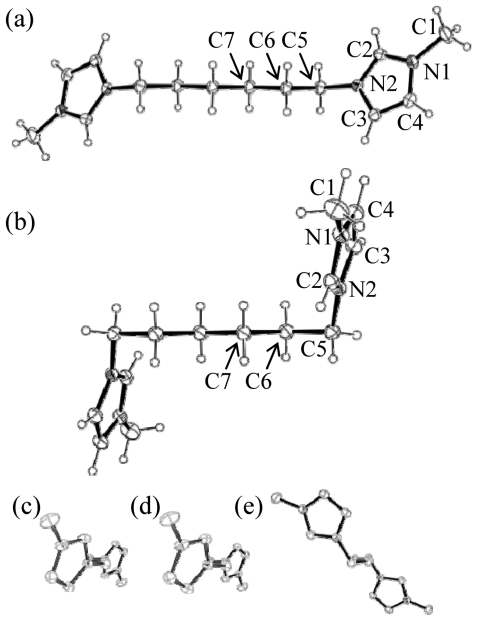


Figure 1. Front views of ORTEP drawing of $MIm_2C_6{\cdot}(BF_4)_2$ (a) and $MIm_2C_6{\cdot}(CF_3SO_3)_2$ (b), and side views of $MIm_2C_6{\cdot}(X)_2$ (c, BF_4^-; d, ClO_4^-; e, $CF_3SO_3^-$). Anions have been omitted for clarity.

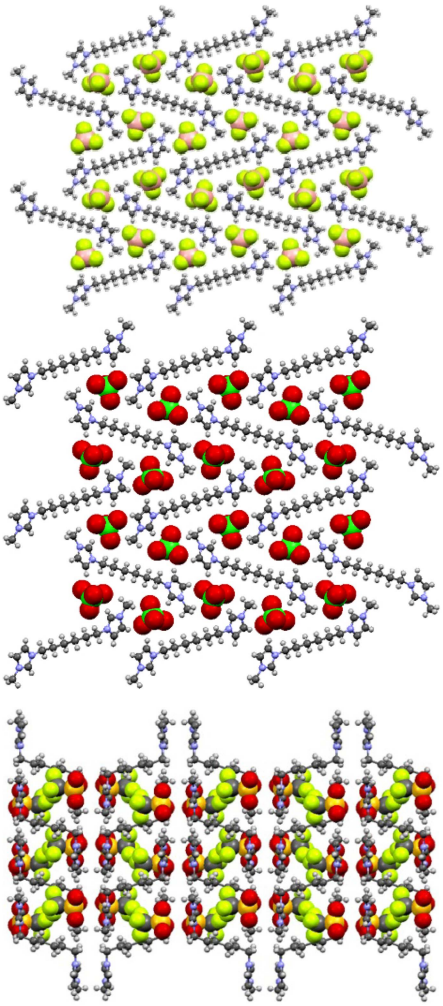


Figure 2. Packing diagrams of $MIm_2C_6{\cdot}(BF_4)_2$ (top), $MIm_2C_6{\cdot}(ClO_4)_2$ (middle), and $MIm_2C_6{\cdot}(CF_3SO_3)_2$ (bottom).

and polyatomic anions. It should be mentioned that the stacks are oriented along the short crystallographic *a*-axis (4.7485(1) Å for BF_4^- and 4.8975(6) Å for ClO_4^-). The polyatomic counteranions were placed near the imidazolium cations. For $MIm_2C_6{\cdot}(CF_3SO_3)_2$, one oxygen atom of $CF_3SO_3^-$ weakly interacted with the hydrogen atom attached to C(2) of the imidazolium plane (the shortest distance of C-H···OSO_2CF_3 = 2.20 Å) comparable to those of other anions (the shortest distances of C-H···FBF_3 = 2.42 Å and C-H···$OClO_3$ = 2.49 Å).

In order to elucidate the anion effect on thermal properties of the bis(3-methylimidazolium-1-yl) salts, differential scanning calorimetric analyses (DSC) and thermogravimetric analyses (TGA) were measured. The polyatomic anions played a significant role in determining the melting points: BF_4^- (125.9 °C) < PF_6^- (133.9 °C) < $CF_3SO_3^-$ (136.6 °C) < ClO_4^- (144.7 °C) < NO_3^- (174.2 °C) as depicted in Figure 3. Melting points of the organic salts are quite higher than the corresponding monocationic ionic liquids.[27] Furthermore, melting points of oxyanionic salts are higher than those of fluoroanionic salts, presumably owing to the difference of the ionic character.[28] The TGA and DSC curves indicate that the organic salts exist in liquid state in the range of 126-426 °C for BF_4^-, 134-391 °C for PF_6^-, 137-434 °C for $CF_3SO_3^-$,

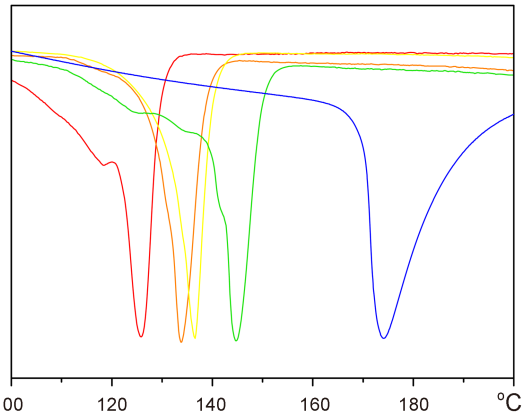


Figure 3. DSC endothermic curves showing the melting point of $MIm_2C_6{\cdot}(X)_2$ (X^- = BF_4^- (red), PF_6^- (orange), $CF_3SO_3^-$ (yellow), ClO_4^- (green), and NO_3^- (blue)).

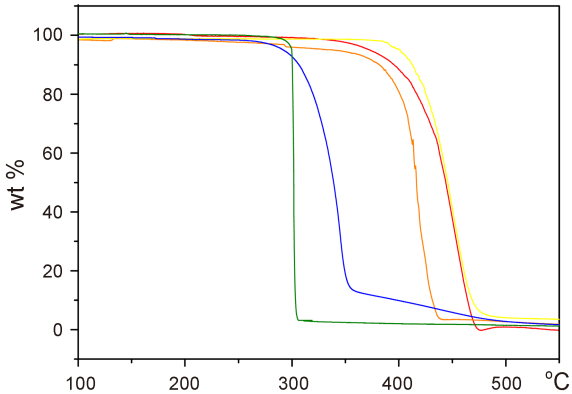


Figure 4. Thermogravimetric curves showing the decomposition of $MIm_2C_6{\cdot}(X)_2$ (X^- = BF_4^- (red), PF_6^- (orange), $CF_3SO_3^-$ (yellow), ClO_4^- (green), and NO_3^- (blue)).

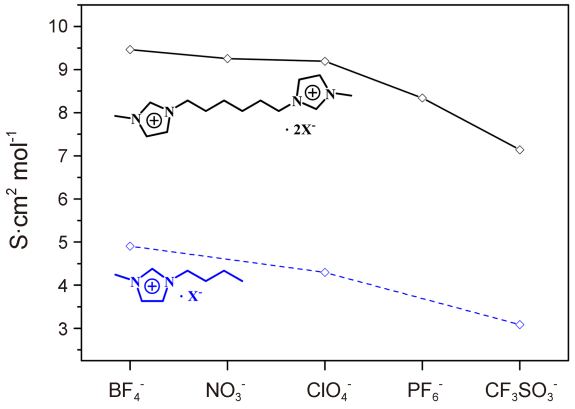


Figure 5. Molar conductivity (Λ_m) of $MIm_2C_6{\cdot}(X)_2$ (black) and BMIm·X (blue) in distilled water at room temperature.

145-301 °C for ClO_4^-, and 174-343 °C for NO_3^- counter-anions (Figure 4). This fact can be a crucial barrier to precisely calculating the lattice energy because solid-liquid transformation temperature depends on the energy of each crystal lattice. The energy of the crystal lattice mainly depends on the strength and the amount of interionic forces, molecular symmetry, and the conformational degrees of the freedom of the molecule.[29]

Molar conductivity ($S{\cdot}cm^2\ mol^{-1}$) of the present organic salts in distilled water at room temperature was measured to investigate the nature of polyatomic anions. The conductivity was in the order BF_4^- (9.46) > NO_3^- (9.25) > ClO_4^- (9.19) > PF_6^- (8.34) > $CF_3SO_3^-$ (7.14) (Figure 5). For comparison, the conductivity of mono(imidazolium) analogues, 1-butyl-3-methylimidazolium salts (BMIm·X, X^- = BF_4^-, ClO_4^-, and $CF_3SO_3^-$),[27] was measured under the same condition: BF_4^- (4.91) > ClO_4^- (4.30) > $CF_3SO_3^-$ (3.09). The conductivity of $MIm_2C_6{\cdot}(X)_2$ was higher than that of the corresponding BMIm·X salts, but the conductivity-order of $MIm_2C_6{\cdot}(X)_2$ was consistent with that of momo(imidazolium) salts. The low conductivity of triflate salts may be indebted to its different conformational structure. That is, the conductivity was significantly affected by the anions. The conductivity of the distilled water as a reference was 0.0749 at the same temperature.

In conclusion, for bis(3-methylimidazolium-1-yl) salts containing a series of polyatomic anions, the detailed anion effects were observed. The polyatomic anions played a crucial role in tuning of physiochemical properties of bis(3-methylimidazolium-1-yl) salts. Their thermal stabilities and conductivities are greater than those of the corresponding mono(imidazolium) salts. These results imply that the organic salts are promising ionic liquids at high temperature.

Experimental

Materials and Measurements. Commercially available chemicals including 1,6-dibromohexane and 1-methylimidazole were purchased from Aldrich and used without further purification. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Varian Mercury Plus 300. Elemental analyses were performed on crystalline samples using a Vario-EL III at Pusan center, KBSI. Conductivities were measured in distilled water using a Sartorius Professional Meter PP-50. Thermogravimetric analyses (TGA) and differential scanning calorimetric analyses (DSC) were carried out under a dinitrogen atmosphere at a scan rate of 10 °C/min using a Labsys TG/DSC 1600. 1,6-Bis(3-methylimidazolium-1-yl)hexane dibromide ($MIm_2C_6{\cdot}Br_2$), 1,6-bis(3-methylimidazolium-1-yl)hexane tetrafluoroborate ($MIm_2C_6{\cdot}(BF_4)_2$), and 1,6-bis(3-methylimidazolium-1-yl)-hexane hexafluorophosphate ($MIm_2C_6{\cdot}(PF_6)_2$) were prepared according to the procedures outlined in the literature.[13]

1,6-Bis(3-methylimidazolium-1-yl)hexane Triflate ($MIm_2C_6{\cdot}(CF_3SO_3)_2$). To a suspended solution of $MIm_2C_6{\cdot}Br_2$ (6 mmol, 2.449 g) in 100 mL of anhydrous acetone was added an equivalent of sodium triflate (6 mmol, 1.032 g), the mixture was stirred for 6 h at ambient temperature. Subsequently, an equivalent of sodium triflate (6 mmol, 1.032 g) was additionally added to the reaction mixture and stirred for 12 h. After the precipitated NaBr was filtered off, the filtrate was dried using rotary evaporator to yield white crystalline product. The single crystals suitable for X-ray crystallography were obtained *via* recrystallization in a mixture of ethanol/dioxane. Yield, 89% (2.919 g). mp 136.6 °C. Anal. Calcd for $C_{16}H_{24}N_4O_6F_6S_2$: C, 35.16; H, 4.43; N, 10.25. Found: C, 35.14; H, 4.43; N, 10.19. IR (KBr pellet, cm^{-1}): 3159, 3120, 2949, 1578, 1259 ($CF_3SO_3^-$), 1155, 1036, 642, 517. ^1H NMR (D_2O, Me_4Si, ppm): 8.63 (s, 2H), 7.40 (s, 2H), 7.37 (s, 2H), 4.12 (t, J = 7.2 Hz, 4H), 3.82 (s, 6H), 1.81 (m, 4H), 1.28 (s, 4H). ^{13}C NMR (D_2O, Me_4Si, ppm): 178.88, 135.92, 123.64, 122.27, 49.49, 35.68, 29.15, 24.94.

1,6-Bis(3-methylimidazolium-1-yl)hexane Perchlorate ($MIm_2C_6{\cdot}(ClO_4)_2$). The same procedure was used as $MIm_2C_6{\cdot}(CF_3SO_3)_2$ using sodium perchlorate instead of sodium triflate. The single crystals suitable for X-ray crystallography were obtained *via* recrystallization in a mixture of acetone/dioxane. Yield, 81% (2.169 g). mp 144.7 °C. Anal. Calcd for $C_{14}H_{24}N_4O_8Cl_2$: C, 37.60; H, 5.41; N, 12.53. Found: C, 37.61; H, 5.42; N, 12.51. IR (KBr pellet, cm^{-1}): 3431, 3157, 3095, 2937, 1578, 1178, 1088 (ClO_4^-), 856, 768, 623 (ClO_4^-). ^1H NMR (D_2O, Me_4Si, ppm): 8.63 (s, 2H), 7.39 (s, 2H), 7.36 (s, 2H), 4.12 (t, J = 6.9 Hz, 4H), 3.82 (s, 6H), 1.80 (m, 4H), 1.27 (s, 4H). ^{13}C NMR (D_2O, Me_4Si, ppm): 135.96, 123.58, 122.21, 49.42, 35.64, 29.14, 24.93.

1,6-Bis(3-methylimidazolium-1-yl)hexane Nitrate ($MIm_2C_6{\cdot}(NO_3)_2$). Under vigorous stirring, an aqueous solution of silver nitrate (12 mmol, 2.039 g) was added dropwise over 1 h to an aqueous solution (50 mL) of $MIm_2C_6{\cdot}Br_2$ (6 mmol, 2.449 g), and the reaction mixture was stirred further 3 h. After the precipitated AgBr was filtered off, the filtrate was dried using rotary evaporator to yield white product. The product can be recrystallized as colorless needles in a mixture of ethanol/dioxane solution in a 92% (2.051 g). mp 174.2 °C. Anal. Calcd for $C_{14}H_{24}N_6O_6$: C, 45.15; H, 6.50; N, 22.57. Found: C, 45.10; H, 6.54; N, 22.56. IR (KBr pellet, cm^{-1}): 3422, 3055, 2943, 1576, 1385

Table 1. Crystal Data and Structure Refinements for $MIm_2C_6{\cdot}(X)_2$

	$X^- = BF_4^-$	$CF_3SO_3^-$	ClO_4^-
Empirical formula	$C_{14}H_{24}B_2N_4F_8$	$C_{16}H_{24}N_4O_6F_6S_2$	$C_{14}H_{24}N_4O_8Cl_2$
Formula weight	421.99	546.51	447.27
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/n$
a, Å	4.7485(1)	10.1390(2)	4.8975(6)
b, Å	15.1509(2)	12.5742(3)	15.365(2)
c, Å	13.5716(2)	18.5242(4)	13.577(2)
β, °	99.508(1)	-	100.39(1)
V, Å^3	962.98(3)	2361.65(9)	1004.9(2)
Z	2	4	2
d_{cal}, gcm^{-3}	1.455	1.537	1.478
μ, mm^{-1}	0.141	0.313	0.372
R_{int}	0.0475	0.0391	0.0231
Completeness, %	99.8 (θ = 28.30°)	99.1 (θ = 28.24°)	99.4 (θ = 26.50°)
GOF on F^2	1.141	0.945	1.078
Final R indices $[I > 2\sigma(I)]^a$	0.0527	0.0374	0.0399
R indices (all data)^b	0.1890	0.1081	0.1217

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2 = (\Sigma(F_o^2-F_c^2)^2/\Sigma wF_o^2)^{1/2}$

(NO_3^-), 1173, 669, 625. ^{1}H NMR (D_2O, Me_4Si, ppm): 8.64 (s, 2H), 7.40 (s, 2H), 7.36 (s, 2H), 4.12 (t, J = 7.2 Hz, 4H), 3.82 (s, 6H), 1.79 (m, 4H), 1.26 (s, 4H). ^{13}C NMR (D_2O, Me_4Si, ppm): similar to $MIm_2C_6{\cdot}(ClO_4)_2$.

Crystallographic Structure Determinations. All X-ray data were collected on a Bruker SMART automatic diffractometer with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a CCD detector at 170 K. Thirty-six frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the multi-scan method (SADABS). The structures were solved by the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).[30] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions and refined using a riding model. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1 and the relevant bond lengths and angles are listed in Table 2. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-829088 for $MIm_2C_6{\cdot}(BF_4)_2$, CCDC-829089 for $MIm_2C_6{\cdot}(CF_3SO_3)_2$, and CCDC-829090 for $MIm_2C_6{\cdot}(ClO_4)_2$. The data can be obtained free of charge *via http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Relevant Bond Lengths (Å) and Angles (°) for $MIm_2C_6{\cdot}(X)_2$

	$X^- = BF_4^-$	$CF_3SO_3^-$	ClO_4^-
N(1)-C(1)	1.462(3)	1.472(2)	1.469(3)
N(1)-C(2)	1.324(3)	1.324(2)	1.322(3)
N(1)-C(4)	1.372(3)	1.372(2)	1.377(3)
N(2)-C(2)	1.324(2)	1.330(2)	1.327(3)
N(2)-C(3)	1.377(2)	1.372(2)	1.376(2)
N(2)-C(5)	1.467(2)	1.471(2)	1.471(2)
C(1)-N(1)-C(2)	125.2(2)	125.4(2)	125.0(2)
C(1)-N(1)-C(4)	125.9(2)	125.9(2)	126.2(2)
N(1)-C(2)-N(2)	108.6(2)	108.6(2)	108.6(2)

Acknowledgments. This work was supported by a 2 year Pusan National University Research Grant.

Supporting Information. IR and ^{1}H NMR spectra of $MIm_2C_6{\cdot}(X)_2$ are available on request from the correspondence author.

References

1. Hurley, F. H.; Wier, T. P. *J. Electrochem. Soc.* **1951**, *98*, 203.
2. Plechkova, N. V.; Seddon, K. R.; Tundo, P.; Perosa, A.; Zecchini, F. *Methods and Reagents for Green Chemistry*; Wiley: New York; 2007; pp 103-130.
3. Toma, Š.; Meèiarová, M.; Šebesta, R. *Eur. J. Org. Chem.* **2009**, 321.
4. Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, *37*, 123.
5. Welton, T. *Coord. Chem. Rev.* **2004**, *248*, 2459.
6. Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2000**, *39*, 3772.
7. Han, X.; Armstrong, D. W. *Acc. Chem. Res.* **2007**, *40*, 1079.
8. Huddleston, J. G.; Rogers, R. D. *Chem. Commun.* **1998**, 1765.
9. MacFarlane, D.; Forsyth, M. *The Handbook of Ionic Liquids: Electrochemistry*; Wiley-VCH: Weinheim, 2008.
10. Jin, C.; Ye, C.; Phillips, B. S.; Zabinski, J. S.; Liu, X.; Liu, W.; Shreeve, J. M. *J. Mater. Chem.* **2006**, *16*, 1529.
11. Anderson, J. L.; Armstrong, D. W. *Anal. Chem.* **2005**, *77*, 6453.
12. Lambertus, G. R.; Crank, J. A.; McGuigan, M. E.; Kendler, S.; Armstrong, D. W.; Sacks, R. D. *J. Chromatogr. A* **2006**, *1135*, 230.
13. Anderson, J. L.; Ding, R.; Ellern, A.; Armstrong, D. W. *J. Am. Chem. Soc.* **2005**, *127*, 593.
14. Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79.
15. Jung, O.-S.; Kim, Y. J.; Lee, Y.-A.; Park, K.-M.; Lee, S. S. *Inorg. Chem*. **2003**, *42*, 844.
16. Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327.
17. Lee, J. W.; Kim, E. A.; Kim, Y. J.; Lee, Y.-A.; Pak, Y.; Jung, O.-S. *Inorg. Chem.* **2005**, *44*, 3151.
18. Janiak, C.; Uehlin, L.; Wu, H.-P.; Klufers, P.; Piotrowski, H.; Scharmann, T. G. *J. Chem. Soc., Dalton Trans*. **1999**, 3121.
19. Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.
20. Campos-Fernandez, C. S.; Clerac, R.; Dunbar, K. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 3477.
21. Turner, B.; Shterenberg, A.; Kapon, M.; Suwinska, K.; Eichen, Y. *Chem. Commun.* **2001**, 13.
22. Sharma, C. V. K.; Griffin, S. T.; Rogers, R. D. *Chem. Commun.* **1998**, 215.
23. Lee, B. S.; Chi, Y. S.; Lee, J. K.; Choi, I. S.; Song, C. E.; Namgoong, S. K.; Lee, S.-G. *J. Am. Chem. Soc.* **2004**, *126*, 480.
24. Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609.
25. Beer, P. D. *Acc. Chem. Res.* **1998**, *31*, 71.
26. Beer, P. D.; Smith, D. K. *Prog. Inorg. Chem.* **1997**, *46*, 1.
27. Bonhôte, P.; Dias, A.-P.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem.* **2006**, *35*, 1168.
28. Siegel, E. J. *Phys. Status Solidi A* **1972**, *11*, 45.
29. Dearden, J. C. *Sci. Total Environ.* **1991**, *59*, 109.
30. Sheldrick, G. M. SHELXS-97: A Program for Structure Determination; University of Göttingen, Germany, 1997; Sheldrick, G. M. SHELXL-97: A Program for Structure Refinement; University of Göttingen, Germany, 1997.