Inorg. Chem. **2006**, *45*, 1585–1590

Inorganic Chemistry

Article

Influence of Ionic Liquids Bearing Functional Groups in Dye-Sensitized Solar Cells

Fellicien Mazille,[†,‡] Zhaofu Fei,[‡] Daibin Kuang,[†] Dongbin Zhao,[‡] Shaik M. Zakeeruddin,*[,†] Michael Grätzel,[†] and Paul J. Dyson*[,‡]

Laboratory for Photonics and Interfaces and Institute of Chemical Sciences and Engineering,
Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Received October 10, 2005

Ionic liquids containing the nitrile and vinyl functional groups attached to imidazolium cations combined with various anions, e.g., iodide, bis[(trifluoromethyl)sulfonyl]imide ([TFSI]$^-$), or dicyanamide ([N(CN)$_2$]$^-$), have been prepared and characterized. These ionic liquids have been successfully used as electrolytes for dye-sensitized solar cells based on nanocrystalline TiO$_2$ with the amphiphilic ruthenium sensitizer [ruthenium (4,4′-dicarboxylic acid-2,2′-bipyridine)(4,4′-bis(*p*-hexyloxystyryl)-2,2′-bipyridine)][NCS]$_2$ (coded K-19). The iodide salt was used in 3-methoxypropionitrile-based electrolytes, and the performances of both types of devices were evaluated on the basis of their photocurrent density–voltage characteristics and dark current measurements, demonstrating that the functional groups do not exert a detrimental effect on the performance. The solid-state structure of the nitrile-functionalized salt [C$_1$C$_3$CN(im)]I has also been established by single-crystal X-ray diffraction, revealing extensive hydrogen bonding between the cation protons and the iodide.

Introduction

Following the discovery of dye-sensitized solar cells (DSCs), intensive research has been undertaken in developing semiconductor materials, dyes, and electrolytes to enhance device performance.[1–5] Alternative redox couples to I$^-$/I$_3^-$ have also been developed and successfully applied in DSCs;[6] however, I$^-$/I$_3^-$ has proven to be the most efficient redox couple for high efficiency. Although a highly efficient DSC with an 11% photovoltaic performance has been obtained based on an I$^-$/I$_3^-$ redox electrolyte in an acetonitrile solvent, the long-term stability of the cells at elevated temperatures still remains a major challenge.[7] Electrolytes based on volatile organic solvents may cause practical problems for encapsulation of the electrolyte and are unstable at high temperatures. Recently, some efforts have been made to replace the organic solvent electrolytes with p-type inorganic semiconductors,[8] polymer electrolytes,[9] and organic hole-transport materials, but their efficiencies are relatively low.[10] Ionic liquid based electrolytes are promising as alternative electrolytes for DSCs because of their intriguing properties such as negligible vapor pressure and nonflammability.[11] Ionic liquids have been widely accepted as “greener” alternatives to classical organic

---

* To whom correspondence should be addressed. E-mail: shaik.zakeer@epfl.ch (S.M.Z.), paul.dyson@epfl.ch (P.J.D.).

[†] Laboratory for Photonics and Interfaces.

[‡] Institute of Chemical Sciences and Engineering.

(1) O’Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

(2) Benkstein, K. D.; Kopidakis, N.; van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2003**, *107*, 7759.

(3) Benkö, G.; Skårman, B.; Wallenberg, R.; Hagfeldt, A.; Sundström, V.; Yartsev, A. P. *J. Phys. Chem. B* **2003**, *107*, 1370.

(4) Nakade, S.; Saito, Y.; Kubo, W.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2003**, *107*, 8607.

(5) (a) Nazeeruddin, M. K.; Pechy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc*. **2001**, *123*, 1613. (b) Thomasa, K. R. J.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. *Chem. Commun*. **2005**, 4098. (c) Velusamy, M.; Thomas, K. R. J.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. *Org. Lett.* **2005**, *7*, 1899.

(6) (a) Wang, P.; Zakeeruddin, S. M.; Moser, J.-E.; Humphry-Baker, R.; Grätzel, M. *J. Am. Chem. Soc*. **2004**, *126*, 7164. (b) Nusbaumer, H.; Moser, J.-E.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Graetzel, M.; Nusbaumer, H.; Zakeeruddin, S. M.; Moser, J.-E. *Chem.—Eur. J.* **2003**, *9*, 3756. (c) Nusbaumer, H.; Moser, J.-E.; Zakeeruddin, S. M.; Nazeeruddinm, M. k.; Graetzel, M. *J. Phys. Chem. B* **2001**, *105*, 10461. (d) Sapp, S. A.; Elliot, M.; Contado, C.; Caramori, S.; Bignozzi, C. A. *J. Am. Chem. Soc*. **2002**, *124*, 11215.

(7) Grätzel, M. *J. Photochem. Photobiol.* **2004**, *164*, 3.

(8) (a) O’Regan, B.; Lenzmann, F.; Muis, R.; Wienke, J. *Chem. Mater*. **2002**, *14*, 5023. (b) Kumara, G. R. A.; Kaneko, S.; Okuya, M.; Tennakone, K. *Langmuir* **2002**, *18*, 10493.

(9) (a) Nogueira, A. F.; Durrant, J. R.; DePaoli, M. A. *Adv. Mater*. **2001**, *13*, 826. (b) Stergiopoulos, T.; Arabatzis, I. M.; Katsaros, G.; Falaras, P. *Nano Lett.* **2002**, *2*, 1259.

(10) Bach, U.; Lupo, D.; Comte, P.; Moser, J.-E.; Weissortel, F.; Salbeck, J.; Spreitzer, H.; Grätzel, M. *Nature* **1998**, *395*, 583.

(11) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2002.

10.1021/ic051751a CCC: $33.50

solvents. Recently, ionic liquids have been widely used in organic synthesis/catalysis,[11−13] DSCs,[14] the synthesis of nanomaterials,[15] and many other applications.[16]

To have a better understanding of the solvent properties of ionic liquids, a series of new ionic liquids have been designed and their use in DSCs has been explored. Room-temperature ionic liquids containing 1,3-dialkylimidazolium cations are particularly attractive because of their ability to solvate ionic and molecular species despite being miscible with organic solvents as well as with other ionic liquids. Various functionalities are introduced on the alkyl side chains of imidazolium cations to produce what has been termed task-specific ionic liquids,[16a] and the influence of the functional group on the physicochemical properties of ionic liquids has been studied.[17]

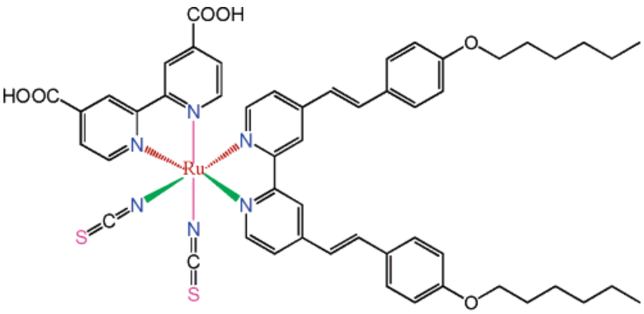
In this study, we introduce the nitrile and vinyl functionalities into the imidazolium cation and combine the resulting cations with various anions, including iodide. The properties of the corresponding ionic liquids in DSCs were studied and compared to simple alkyl-chain congeners.

Experimental Section

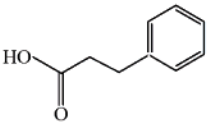
Reagents and Electrolytes. *N*-Methylbenzimidazole (NMBI) was purchased from Aldrich and recrystallized from diethyl ether before use. 3-Methoxypropionitrile (MPN) was obtained from Fluka and distilled before use. [Ruthenium (4,4′-dicarboxylic acid-2,2′-bipyridine)(4,4′-bis(*p*-hexyloxystyryl)-2,2′-bipyridine)][NCS]$_2$(K-19) was synthesized as reported in our earlier publication;[18] for its structure, see Chart 1. 1-Methyl-3-propylimidazolium iodide (PMII)[19] and 1-methyl-3-propylimidazolium bis[(trifluoromethyl)sulfonyl]imide ($[C_1C_3(im)][TFSI]$)[20] were prepared according to the literature methods, and 400-nm-sized TiO_2 particles were received as a gift from CCIC (Japan).

Synthesis and Characterization. 1-Methyl-3-(3-cyanopropyl)imidazolium chloride ($[C_1C_3CN(im)]Cl$) was prepared according to a literature method.[21] IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400, using $SiMe_4$ for ^1H and ^{13}C NMR as an external standard at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument on a sample diluted in methanol based on a literature protocol.[22] Elemental analysis was carried out at the Institute of Molecular and Biological Chemistry at the EPFL. Viscosities were measured with a Brookfield DV-II+ viscometer on 0.50 mL of sample. The temperature of the samples was maintained at 20 ± 1 °C by means of an external temperature controller. The measurements were performed in duplicate.

Chart 1



K-19



PPA

Synthesis of 1-Methyl-3-(3-cyanopropyl)imidazolium Iodide, $[C_1C_3CN(im)]I$. A mixture of $[C_1C_3CN(im)]Cl$ (1.86 g, 0.01 mol) and NaI (1.80 g, 0.012 mol) in acetone (100 mL) was stirred at room temperature for 48 h. After filtration and removal of the solvents, the resulting solid was washed with tetrahydrofuran (3 × 20 mL) and diethyl ether (3 × 20 mL) and dried under vacuum for 24 h. The solid was recrystallized from acetone and diethyl ether (5:1) to give the product. Yield: 2.24 g, 81%. Mp: 69 °C. ESI-MS (CH_3OH): positive ion, 150 ($[C_1C_3CN(im)]^+$); negative ion, 127 ($[I]^-$). ^1H NMR (D_2O): δ 9.30 (s, 1H), 8.20 (s, 1H), 8.15 (s, 1H), 4.96 (t, *J*(HH) = 6.8 Hz, 2H), 4.54 (s, 3H), 3.20 (t, *J*(HH) = 6.9 Hz, 2H), 2.85 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 135.0, 131.2, 120.7, 116.7, 44.7, 33.8, 22.0, 10.1. IR (cm^{-1}): 3089, 3005 (ν_{C-H} aromatic), 2918 (ν_{C-H} aliphatic), 2243 ($\nu_{C\equiv N}$), 1733, 1628, 1574, 1564 ($\nu_{C=N}$). Anal. Calcd for $C_8H_{12}IN_3$ (%): C, 34.68; H, 4.36; N, 15.16. Found: C, 34.58; H, 4.43; N, 15.20.

Synthesis of 1-Methyl-3-(3-cyanopropyl)imidazolium Bis[(trifluoromethyl)sulfonyl]imide, $[C_1C_3CN(im)][TFSI]$. $[C_1C_3CN(im)]Cl$ (18.5 g, 0.1 mol) was dissolved in water (50 mL), and Li[TFSI] (28.7 g, 0.10 mol) was added at room temperature. The resulting solution was stirred for 30 min. The resulting colorless hydrophobic liquid was separated and washed with water (3 × 30 mL). The product was dried under vacuum for 24 h. Yield: 32.3 g, 75%. ESI-MS (H_2O, *m*/*z*): positive ion, 150 ($[ClC_3CNmim]^+$); negative ion, 280 ($[TFSI]^-$). ^1H NMR (acetone-d_6): δ 8.99 (s, 1H), 7.48 (s, 1H), 7.38 (s, 1H), 4.25 (t, *J*(HH) = 6.83 Hz, 2H), 3.81 (s, 3H), 2.55 (t, *J*(HH) = 6.83 Hz, 2H), 2.25 (t, *J*(HH) = 6.83 Hz, 2H). ^{13}C NMR (acetone-d_6): δ 136.8, 122.5, 121.6, 118.5, 48.2, 35.8, 25.8, 13.5. IR (cm^{-1}): 3097, 3007 (ν_{C-H} aromatic), 2912 (ν_{C-H} aliphatic), 2250 ($\nu_{C\equiv N}$), 1739, 1577 ($\nu_{C=N}$). Anal. Calcd for

---

(12) Antonietti, M.; Kuang, D.; Smarsly, B.; Zhou, Y. *Angew. Chem., Int. Ed*. **2004**, *43*, 4988.

(13) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev*. **2002**, *102*, 3667.

(14) (a) Kubo, W.; Kitamura, T.; Hanabusa, K.; Wada, Y.; Yanagida, S. *Chem. Commun*. **2002**, 374. (b) Wang, P.; Wenger, B.; Humphry-Baker, R.; Moser, J.-E.; Teuscher, J.; Kantlehner, W.; Mezger, J.; Stoyanov, E. V.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc*. **2005**, *127*, 6850. (c) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Exnar, I.; Grätzel, M. *J. Am. Chem. Soc*. **2003**, *125*, 1166. (d) Wang, P.; Zakeeruddin, S. M.; Moser, J. E.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 13280.

(15) (a) Fei, Z.; Geldbach, T. J.; Zhao, D.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem*. **2005**, *44*, 5200. (b) Fei, Z.; Zhao, D.; Geldbach, T. J.; Scopelliti, R.; Dyson, P. J.; Antonijevic, S.; Bodenhausen, G. *Angew. Chem., Int. Ed*. **2005**, *44*, 5720.

(16) (a) Davis, J. H., Jr. *Chem. Lett*. **2004**, *33*, 1072. (b) Fei, Z.; Geldbach, T. J.; Zhao, D.; Dyson, P. J. *Chem.—Eur. J*. **2005**, published on the Web.

(17) (a) Pernak, J.; Sobaszkiewicz, K.; Foksowicz-Flaczyk, J. *Chem.—Eur. J*. **2004**, *10*, 3479. (b) Zhou, Z.-B.; Matsumoto, H.; Tatsumi, K. *Chem.—Eur. J*. **2005**, *11*, 752. (c) Zhao, D.; Fei, Z.; Ohlin, C. A.; Laurenczy, G.; Dyson, P. J. *Chem. Commun*. **2004**, 2500.

(18) Wang, P.; Klein, C.; Humphry-Baker, R.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc*. **2005**, *127*, 808.

(19) Bonhôte, P.; Dias, A. P.; Armand, M.; Papageorgiou, N.; Kalyanasundaram, K.; Grätzel, M. *Inorg. Chem*. **1996**, *35*, 1168.

(20) Kitaoka, S.; Nobuoka, K.; Ishikawa, Y. *Tetrahedron* **2005**, *61*, 7678.

(21) Zhao, D.; Fei, Z.; Scopelliti, R.; Dyson, P. J. *Inorg. Chem*. **2004**, *43*, 2197.

(22) Dyson, P. J.; McIndoe, J. S. *Inorg. Chim. Acta* **2003**, *354*, 68.

$C_{10}H_{12}F_6N_4O_4S_2$ (%): C, 27.91; H, 2.81; N, 13.02. Found: C, 28.92; H, 2.85; N, 13.10.

Synthesis of 1-Methyl-3-(3-cyanopropyl)imidazolium Dicyanamide, [C_1C_3CN(im)][N(CN)$_2$]. [C_1C_3CN(im)]Cl (18.5 g, 0.1 mol) and Na[N(CN)$_2$] were mixed in acetone (30 mL) and stirred at room temperature for 48 h. The resulting solution was filtered and evaporated under vacuum, and the colorless liquid obtained was washed with diethyl ether (3 × 30 mL). Yield: 78%. ESI-MS (CH_3OH): positive ion, 150 ([ClC$_3$CNmim]$^+$); 82 ([mim]); negative ion, 66 ([N(CN)$_2$]), 282 ([anion−cation−anion]). ^{1}H NMR (CD_3CN): δ 8.64 (s, 1H), 7.44 (s, 1H), 7.40 (s, 1H), 4.20 (t, 2H, NCH_2, $J = 7.08$ Hz), 3.83 (s, 3H, NCH_3), 2.48 (t, 2H, CH_2CN, $J = 7.12$ Hz), 2.17 (m, 2H, CH_2). ^{13}C NMR (CD_3CN): δ 137.32, 124.75, 123.21, 120.42, 119.85, 48.87, 36.78, 26.44, 14.59. IR (cm^{-1}): 3153, 3107 (ν_{C-H} aromatic) 2233, 2197, 2139 ($\nu_{C\equiv N}$). Anal. Calcd for $C_{10}H_{12}N_6$ (%): C, 55.54; H, 5.59; N, 38.86. Found: C, 55.38; H, 5.62; N, 39.01.

Synthesis of 1-Methyl-3-vinylimidazolium Iodide, [$C_1C{=}C$(im)]I. The preparation is similar to that reported previously,[23] essentially using considerably less methyl iodide. To freshly distilled 1-vinylimidazole (9.41 g, 0.10 mol) was added methyl iodide (15.60 g, 0.11 mol) at 0 °C. The reaction mixture was stirred for 1 h and then brought to room temperature overnight, during which time colorless crystals formed. The mixture was washed three times with anhydrous diethyl ether. Yield: >99%. Mp: 78 °C.

Synthesis of 1-Methyl-3-vinylimidazolium Bis[(trifluoromethyl)sulfonyl]imide, [$C_1C{=}C$(im)][TFSI]. To a solution of [$C_1C{=}C$(im)]I (23.6 g, 0.10 mol) in water (50 mL) was added Li[TFSI] (28.7 g, 0.10 mol) at room temperature, and the reaction mixture was strirred for 30 min. The resulting colorless hydrophobic liquid was washed with water (3 × 30 mL). The product was dried in a vacuum for 24 h. Yield: 28.00 g, 72%. ESI-MS (dichloromethane, m/z): positive ion, 109 ([$C_1C{=}C$(im)]$^+$); negative ion, 280 ([TFSI]$^-$). ^{1}H NMR (acetone-d_6): δ 7.68 (s, 1H), 7.11 (s, 1H), 7.04 (s, 1H), 6.91 (m, 1H), 5.42 (m, 1H), 4.99 (m, 1H), 3.88 (s, 3H). ^{13}C NMR (acetonitrile-d_6): δ 135.1, 128.2, 124.8, 115.5, 109.1, 36.0. IR (cm^{-1}): 3159, 3113 (ν_{C-H} aromatic), 2947 (ν_{C-H} aliphatic), 1660 ($\nu_{C=C}$). Anal. Calcd for $C_8H_9F_6N_3O_4S_2$ (%): C, 24.68; H, 2.33; N, 10.79. Found: C, 25.02; H, 2.35; N, 10.80.

Crystallography. Data collection for the X-ray structure determination was performed on a KUMA CCD diffractometer system using graphite-monochromated Mo Kα radiation (0.710 70 Å) and a low-temperature device [$T = 140(2)$ K]. Crystals suitable for X-ray diffraction studies were obtained from slow diffusion of diethyl ether into an acetone solution. Data reduction was performed by CrysAlis RED,[24] and structure solution and refinement were carried out using the *SHELX97* software package.[25] The structure was solved by Patterson methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically, and the contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. An empirical absorption correction (DELABS)[26] was applied. Relevant crystallographic data are compiled in Table 1.

Preparation of Double-Layer TiO$_2$ Electrodes. Fluorine-doped SnO_2 conducting glass was first cleaned in Triton-100 (aqueous solution), washed with ethanol, and treated with a 50 mmol L^{-1} $TiCl_4$ aqueous solution at 70 °C for 30 min to facilitate a good mechanical contact between the following printed TiO_2 layer and the conducting glass matrix. Next, a 10-μm-thick film of 20-nm-sized TiO_2 particles was printed on the treated conducting glass and further coated by a 4-μm-thick second layer of 400-nm light-scattering anatase particles (CCIC, Japan). For the second layer, the screen-printing paste was composed of 10 g of 400-nm-sized TiO_2 scattering particles and 2 g of 15-nm-sized TiO_2 fine particles to obtain a mechanically tough layer. The screen-printed layer was gradually heated to 500 °C under oxygen and subsequently left for 10 min for sintering. The layer thickness was determined by an Alpha-step 200 surface profilometer (Tencor Instruments, San Jose, CA). After further treatment with 40 mmol L^{-1} $TiCl_4$, the layer was rinsed with water and ethanol.

Table 1. Crystallographic Data for [C_1C_3CN(im)]I

formula	$C_8H_{12}IN_3$
M	277.11
T [K]	140(2)
cryst syst	triclinic
space group	$P\bar{1}$
a [Å]	7.8633(8)
b [Å]	7.9248(8)
c [Å]	9.0394(6)
α [deg]	87.382(7)
β [deg]	86.872(8)
γ [deg]	75.985(9)
V [Å^3]	545.40(9)
Z	2
density [Mg m^{-3}]	1.687
μ [mm^{-1}]	2.893
2θ range [deg]	$3.28 \leq 2\theta \leq 25.00$
reflns collected	3224
independent reflns	1688 [R(int) = 0.0355]
GOF on F^2	1.043
final R1, wR2 [$I > 2\sigma(I)$]	0.0215, 0.0539

Device Fabrication. After sintering at 500 °C and cooling to 80 °C, the double-layer-structured TiO_2 electrode was dye-coated by immersion into a 0.3 mM solution of K-19 in acetonitrile and *tert*-butyl alcohol (volume ratio 1:1) [the solution consisted of 300 μM K-19 dye and 75 μM 3-phenylpropionic acid as a coadsorbent in acetonitrile and *tert*-butyl alcohol; volume ratio 1:1], at room temperature for 12 h and was then assembled with thermally platinized conducting glass electrodes. The electrodes were separated by a 35-μm-thick Bynel hot-melt ring (DuPont, Wilmington, DE). The sealing was done by heating the counter electrode to 150 °C on a hot ring for a few seconds to reduce the effect of overheating on the photoanode side. The internal space was filled with electrolytes using a vacuum pump. The electrolyte-injecting hole made with a sand-ejecting drill on the counter electrode glass substrate was sealed with a Bynel sheet and a thin glass cover with heating. Electrolyte A contained 0.8 M 1-methyl-3-propylnitrile-imidazolium iodide, 0.15 M I_2, 0.1 M guanidinium thiocyanate, and 0.5 M NMBI in a MPN solvent. The electrolytes B−E contained 0.2 M iodine and 0.5 M NMBI in a mixture of PMII and [C_1C_3CN(im)][TFSI], PMI[TFSI], [C_1C_3CN(im)][N(CN)$_2$], or [$C_1C{=}C$(im)][TFSI] ionic liquids (13:7, v/v), respectively. The corresponding DSC devices A−E were fabricated using electrolytes A−E, respectively.

Photoelectrochemical Measurements. A 450-W xenon light source (Oriel from Newport Instruments, Mountain View, CA) was used to give 100 mW cm^{-2} (the equivalent of 1.0 sun at AM 1.5) at the surface of the solar cells. The spectral output of the lamp was matched in the region of 350−750 nm with the aid of a Schott KG-5 sunlight filter (Präzisions Glas & Optik GmbH, Iserlohn, Germany) so as to reduce the mismatch between the simulated and

---

(23) Salamone, J. C.; Israel, S. C.; Taylor, P.; Snidert, B. *Polymer* **1974**, *13*, 639.

(24) Oxford Diffraction Ltd., M.P., Abingdon OX14 4 RX, U.K., 2003.

(25) Sheldrick, G. M. *SHELX-97, Structure Solution and Refinement Package*; Universität Göttingen: Göttingen, Germany, 1997.

(26) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

true solar spectra to less than 2%. Various incident light intensities were regulated with neutral wire mesh attenuators. The photocurrent density−voltage characteristics of the cell under these conditions were obtained by an external potential bias to the cell, measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, Cleveland, OH). This process was fully automated using Wavemetrics software (http://www.wavemetrics.com). A similar data acquisition system was used to control the incident photon-to-current conversion efficiency (IPCE) measurement. Under full computer control, light from a 300-W xenon lamp (ILC Technology, Sunnyvale, CA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., Middlesex, U.K.) onto the photovoltaic cell under evaluation. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined in the following:

$$\mathrm{IPCE}\ (\lambda) = 1240(J_{\mathrm{SC}}/\lambda\phi) \qquad (1)$$

where λ is the wavelength, J_{SC} is the short-circuit current photocurrent (mA cm^{-2}), and ϕ is the incident radiative flux (W m^{-2}). This curve can be derived from the measured absorption spectrum of the adsorbed photosensitizer for comparison.

Device Stability. Hermetically sealed cells were used to check the long-term stability at thermal stress (60 °C) and visible light soaking. The cells were covered with a polymer film of 50-μm thickness (Preservation Equipment Ltd., Norfolk, U.K.), which has a UV cutoff filter (up to 400 nm), and were illuminated at open circuit under a Suntest CPS lamp (ATLAS GmbH, Rodgau, Germnay; 100 mV cm^{-2}, 60 °C). The cells were taken out, and the photocurrent density−voltage curve was measured once a week for 1000 h.

Results and Discussion

The nitrile-functionalized salt [C_1C_3CN(im)]I was prepared from the chloride salt by reaction with a slight excess of NaI in acetone. The ^{1}H and ^{13}C NMR spectra of the iodide [C_1C_3CN(im)]I were essentially the same as that of the chloride salt, reported previously.[21] In the IR spectrum of [C_1C_3CN(im)]I, the C≡N group absorption is observed at 2243 cm^{-1}, the same as that observed in the chloride salt; however, the absorptions between 2850 and 2900 cm^{-1} were slightly weaker compared to those observed in the chloride, presumably because of weaker hydrogen bonding between the imidazolium protons with the iodide (C−H···I) compared to the chloride (C−H···Cl).[21] The TFSI and dicyanamide salts of the 1-methyl-3-(3-cyanopropyl)imidazolium cation were also prepared via anion exchange, affording liquids at room temperature. The vinyl-functionalized salt [C_1C=C(im)][TFSI] was prepared from the iodide salt according to a slight modification to the literature procedure (see the Experimental Section).[23]

The cation−anion combination of the ionic liquids has significant effects on their viscosities, a critical parameter related to the efficiency of DSCs. In Figure 1, the ionic liquids used in this study are depicted together with their viscosities.

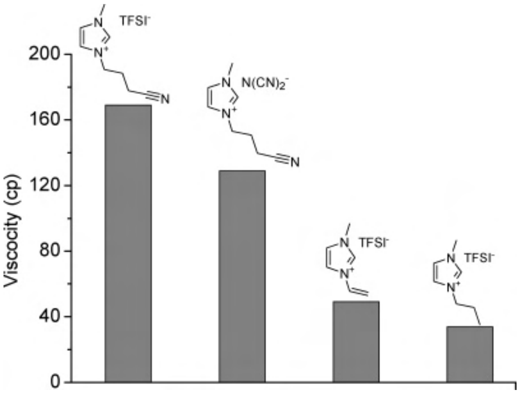


Figure 1. Ionic liquids used in this study with corresponding viscosity data (the iodide salt of the [C_1C_3CN(im)] cation is omitted because it is a solid at room temperature).

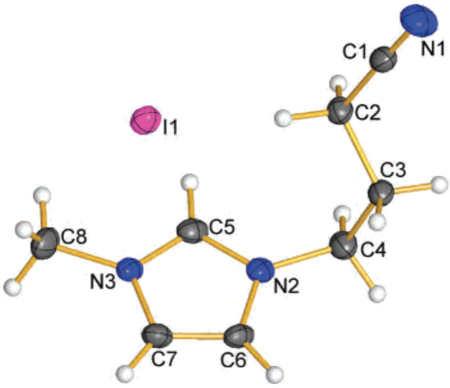


Figure 2. Crystal structure of [C_1C_3CN(im)]I. Bond lengths (Å) and angles (deg): N1−C1 1.146(4), N2−C5 1.341(4), N2−C6 1.379(4), N2−C4 1.467(4), N3−C5, 1.324(4), N3−C7 1.376(4), N3−C8 1.464(4), C1−C2 1.459(4), C2−C3, 1.526(4); C5−N2−C6 108.1(2), C5−N2−C4 125.6(3), C6−N2−C4 126.2(2), C5−N3−C7 109.1(3), C5−N3−C8 124.6(3), C7−N3−C8 126.3(3), N1−C1−C2 178.2(3), C1−C2−C3 110.8(2).

Crystals of [C_1C_3CN(im)]I suitable for single-crystal X-ray diffraction were grown by slow diffusion of diethyl ether into an acetone solution containing the compound. The structure is shown in Figure 2, and key bond parameters are listed in the caption. The [C_1C_3CN(im)]I salt crystallized in the triclinic system rather than in the orthorhombic system of the chloride [C_1C_3CN(im)]I, and further crystallographic details are listed in Table 1. Nevertheless, their bonding parameters are very similar: the C1−N1 (C≡N bond) and the C6−C7 (C=C bond) distances are 1.146 (4) and 1.349 (5) Å, respectively, both comparable with the chloride distances [cf. 1.139(5) and 1.349(3) Å, respectively]. The N2−C5−N3 angle is 108.5(3)°, essentially the same as that observed in [C_1C_3CN(im)]Cl [cf. 108.19(15)°].[21]

The salt [C_1C_3CN(im)]I (electrolyte A) used as an electrolyte in combination with the K-19 dye in a DSC gives an IPCE that reaches a maximum efficiency of 80% at 540 nm. Typical photocurrent density−voltage curves for these cells under AM 1.5 sunlight illuminations are shown in Figure 3. The short-circuit photocurrent density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) are 14.82 mA cm^{-2}, 740 mV, and 0.66, respectively, yielding an overall energy conversion efficiency (η) of 7.20%. The overall conversion efficiency is 8% in low-light irradiations (see Table 2).

Device A showed an excellent light-soaking stability when subjected to the accelerated experiment in the solar simulator at 60 °C when covered by an ultraviolet-absorbing polymer film. Following 1000 h of light soaking under these conditions, there is a marginal decrease in the device efficiency

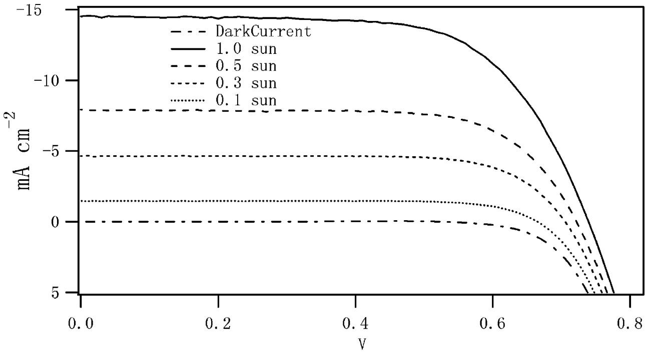


Figure 3. Current density−voltage characteristic of DSC device A under AM 1.5 simulated full sunlight (100 mW cm^{-2}) illumination. Cell active area: 0.158 cm^2.

Table 2. Detailed Photovoltaic Parameters of DSC Device A at Different Light Intensities[a]

	0.1 sun	0.5 sun	1.0 sun
J_{sc} (mA cm^{-2})	1.50	8.34	14.82
V_{oc} (mV)	665	722	740
FF	0.76	0.70	0.66
η (%)	7.90	7.94	7.20

[a] The spectral distribution of the xenon lamp simulates air mass 1.5 solar light. 1.0 sun corresponds to 100 mW cm^{-2}.

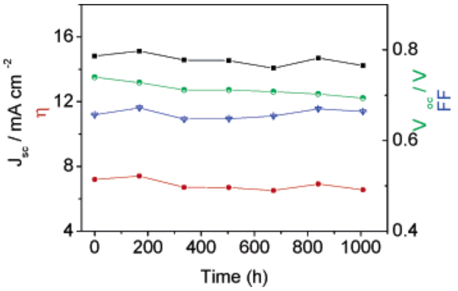


Figure 4. Evolution of the photovoltaic parameter (AM 1.5 full sunlight) of device A during continued 1.0-sun visible-light soaking at 60 °C.

(Figure 4) as compared to the initial values. With nearly constant FF values (changes of less than 2% were observed), the extraordinary stability is mainly due to the fact that the decrease in V_{oc} was well compensated for by the initial increase in J_{sc}.

The viscosity of dialkylimidazolium iodide ionic liquids and the inherently high iodide concentration in such electrolytes create an electron-deactivating channel through reductive quenching of the exited state of the sensitizer, which hampers the performance of the device.[14b] These limitations can be overcome using binary ionic liquid electrolytes for DSCs, not only reducing the viscosity of the electrolyte but also reducing the reductive quenching. Four new binary ionic liquid electrolytes were prepared by mixing PMII with [C_1C_3CN(im)][TFSI] (B), [PMI][TFSI] (C), [C_1C_2(im)][N(CN)$_2$] (D), or [C_1C═C(im)][TFSI] (E) (volume ratio 13:7, v/v) with a fixed concentration of iodine (0.2 M) and NMB base (0.5 M). The photovoltaic parameters of the corresponding devices B−E with the binary ionic liquid electrolytes are collected in Table 3. A comparison of the photovoltaic performance of devices B and C indicates that the introduction of the nitrile functionality on the alkyl chain has a marginal influence on the device performance. Even though these ionic liquids have different viscosities at room temperature, the overall photovoltaic conversion efficiencies of all of these devices are in the same range, with the efficiencies being measured at 60 °C.

Table 3. DSC Device Efficiencies at Different Incident Light Intensities[a]

	electrolyte			
	B	C	D	E
J_{sc} (mA cm^{-2})	11.04	12.51	12.9	10.78
V_{oc} (mV)	634	629	668	648
FF	0.706	0.69	0.69	0.743
η (%)	5.4	5.8	5.9	5.6

[a] The spectral distribution of the xenon lamp simulates air mass 1.5 solar light. 1.0 sun corresponds to 100 mW cm^{-2} measured at 60 °C.

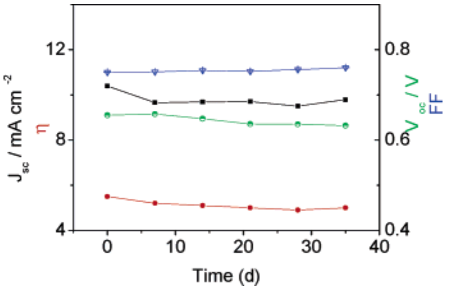


Figure 5. Evolution of the photovoltaic parameter (AM 1.5 full sunlight) of device E during continued 1.0-sun visible-light soaking at 60 °C.

The DSC device E exhibited excellent photostability when submitted to an accelerated test in a solar simulator at 100 mW cm^{-2}. The cells were covered with a 50-μm-thick layer of polyester film used as a UV cutoff filter (up to 400 nm). During light-soaking stability, there is a small drop in the short-circuit current density (0.55 mA cm^{-2}) and open-circuit voltage (20 mV) with an improvement in the FF (5%). As shown in Figure 5, the device photovoltaic conversion efficiency retained more than 90% stability of the initial value, even after 35 days under light soaking at 60 °C.

Conclusions

In this paper, we have explored the potential of using ionic liquids based on functionalized imidazolium cations as electrolytes or in binary systems in DSCs. Excellent energy conversion efficiencies have been observed, ca. 8% in low-light irradiations with a low-vapor-pressure organic solvent. Furthermore, excellent light-soaking stability was observed during 1000 h of aging, indicating quite an extraordinary stability. These nascent studies indicate that there could be considerable potential in systematically studying functionalized ionic liquids as electrolytes (or electrolyte components) in DSCs, and further studies are in progress.

Acknowledgment. We are grateful to P. Comte for the mesoporous TiO_2 film fabrication, to T. Koyanagi (CCIC, Japan) for donation of the 400-nm-sized light-scattering anatase particles, and to Rosario Scopelliti and Tilmann J. Geldbach for the data collection, solution, and refinement of the crystal structure reported herein. We thank the Swiss National Science Foundation for financial support.

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051751A