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A Supercooled Imidazolium Iodide Ionic Liquid as a Low-Viscosity Electrolyte for Dye-Sensitized Solar Cells

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A series of allyl-functionalized imidazolium salts are reported, including 1-allyl-3-ethylimidazolium iodide and 1-allyl-3-propylimidazolium iodide, which have melting points close to room temperature and show typical properties of supercooled fluids if heated above their melting points. Their viscosities in the liquid state are considerably lower than the benchmark ionic liquid used in solar cells, viz., 1-propyl-3-methylimidazolium iodide. Electrolytes containing these new liquids provide excellent efficiencies and good stability in dye-sensitized solar cells when subjected to an accelerated-light soaking test at 60 °C. The structures of three of the new salts have been established in the solid state by single-crystal X-ray analysis.

Dye-sensitized solar cells (DSCs) are among the most extensively investigated devices that provide a high light-to-electric energy conversion yield.[1] One of the critical components of DSCs is the electrolyte containing a I_3^-/I^- redox couple that meditates the dye regeneration process. Alkylimidazolium iodides are frequently employed as the electrolyte because they can improve the photovoltaic performance of such devices.[2] Notably, 1-propyl-3-methylimidazolium iodide (PMII), a liquid at room temperature with a viscosity of 880 cP, is by far the most commonly used. Recently, many imidazolium salts with functional groups have been reported, but seldom do they contain iodide as the anion,[3] although some functionalized imidazolium iodide salts have been evaluated as electrolytes in DSCs with some success.[4]

Herein, we report the synthesis of a series of 1-allyl-3-alkylimidazolium iodides in which 1-allyl-3-ethylimidazolium iodide is a supercooled fluid with the lowest viscosity observed for imidazolium-based iodides. Many ionic liquids are, in fact, supercooled fluids;[5] however, as far as we are aware, the application of such salts in the supercooled state, i.e., employed as liquids below their melting point, has not been reported. We also describe the application of the allyl-functionalized imidazolium-based ionic liquids in electrolytes in combination with the high molar extinction ion coordination sensitizer **K-60**, recently shown to demonstrate excellent photovoltaic performance in DSCs.[6]

The synthesis of the allyl-functionalized imidazolium iodides **1a**−**3a** (Chart 1) follows a literature method,[7] and their characterization is described in the Supporting Information. Compound **1a** has been reported before,[8] but its characterization was incomplete. In brief, the iodide salt **1a** solidified upon formation, whereas **2a** and **3a** were obtained as liquids after removal of an excess of iodoethane or iodopropane at 60 °C and did not solidify even upon storage at −20 °C for 2 months. If liquids **2a** and **3a** are cooled to −78 °C and then maintained at −20 °C for 24 h, they solidify and do not melt on warming to room temperature but do melt on warming to ca. 30 °C. Such behavior is characteristic of supercooled fluids.[9] In the liquid state, **2a** and **3a** exhibit

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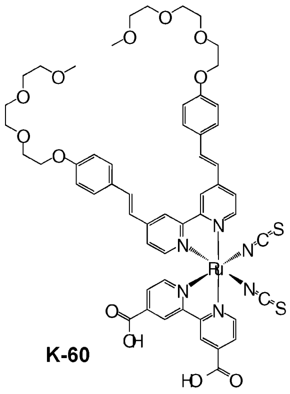
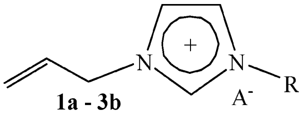
Chart 1. Dye **K-60** and the Ionic Liquids Described in This Study



K-60



1a - 3b

No.	R	Anion
1a	CH_3	I^-
2a	CH_2CH_3	I^-
3a	$CH_2CH_2CH_3$	I^-
1b	CH_3	$TFSI^-$
2b	CH_2CH_3	$TFSI^-$
3b	$CH_2CH_2CH_3$	$TFSI^-$

viscosities significantly lower than that of PMII (**2a** has 350 cP and **3a** has 360 cP versus 880 cP for PMII at 21 °C). In addition, a glass transition (T_g) is detected at −55 °C in both **2a** and **3a**, although the transition from the glass state to the crystal (T_c) is only observed for compound **2a** (heating process at −23 °C).

The ^1H and ^{13}C NMR and IR spectra of the allyl-functionalized iodides are of routine nature comparable with the corresponding bromides.[10]

Crystals of **1a**−**3a** suitable for X-ray diffraction analysis were grown by slowly cooling the liquid (**1a** involves cooling from ca. 80 °C to room temperature, whereas **2a** and **3a** require cooling from room temperature to −78 °C). For compounds **2a** and **3a**, the heating/cooling process had to be repeated several times before crystals suitable for X-ray diffraction analysis were obtained. The structure of **2a** is shown in Figure 1, and those of **1a** and **3a** are shown in the Supporting Information.

The main structural characteristics of the cations in **1a**−**3a** are similar (see the Supporting Information, Table S1, for a comparison of key bond lengths and angles). The imidazolium rings are essentially flat, with bond lengths between 1.319(11) and 1.391(13) Å. Despite modest structural differences, the crystal packings of the three compounds are distinct. For **1a** and **2a**, there are intermolecular $\pi-\pi$ stacking interactions between the allyl groups and imidazolium rings, at average centroid-to-centroid distances of 3.77 and 3.47 Å, respectively. No $\pi-\pi$ stacking interactions between the imidazolium rings are observed. In contrast, the lattice of **3a** is characterized by extensive $\pi-\pi$ stacking between the imidazolium rings, at an average centroid-to-centroid distance of 3.97 Å, and is devoid of $\pi-\pi$ stacking interactions between the allyl groups and imidazolium rings. On the basis of comparison with the structures of other ionic liquids, the low viscosities of **2a** and **3a** could be due to increased $\pi-\pi$ interactions, by virtue of the presence of the allyl group, at the expense of H-bonding interactions. We are currently trying to quantify this hypothesis at a theoretical level. In addition, the asymmetric unit of **3a** comprises two different molecules of the same imidazolium iodide salt. While there are slight differences in the bond lengths, the dispositions of the pendent allyl and alkyl groups with respect to the imidazolium ring are different. The presence of two crystallographically distinct forms of the same molecule is unusual and could be attributable to the presence of the flexible propyl group. In comparison, the methyl and ethyl groups in **1a** and **2a** are more rigid and less prone to disordered arrangements.

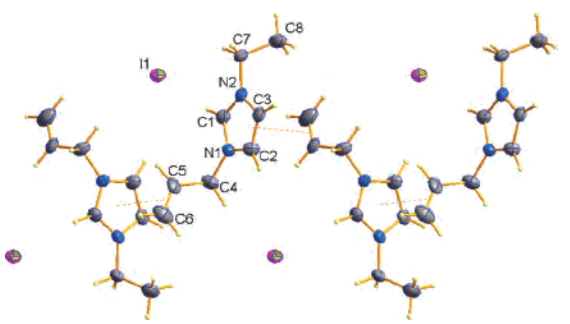


Figure 1. ORTEP representation of **2a** showing key intermolecular interactions. Atoms are represented by ellipsoids at 50% probability levels. Key bond parameters are given in the Supporting Information. Intermolecular π-stacking interactions are denoted by dotted lines.

Table 1. Detailed Device Parameters Based on a (7 + 4)-μm TiO_2 Double-Layer Film and Electrolytes **A**−**C** Simulated in AM 1.5 Full Sunlight Illumination[a]

electrolyte	J_{sc} (mA/cm^2)	V_{oc} (mV)	ff	η (%)
A	12.29	687	0.710	6.0
B	13.54	700	0.717	6.8
C	16.56	728	0.65	7.8

[a] J_{sc} = short-circuit photocurrent density, V_{oc} = open-circuit photovoltage, ff = fill factor, and η = total power conversion efficiency. Cell active area tested with mask: 0.158 cm^{-2}. The spectral distribution of the lamp (incident light source) simulates AM 1.5 solar light.

The iodide salts **1a**−**3a** were converted to "conventional" room-temperature ionic liquids (**1b**−**3b** in Chart 1) by reaction with an excess of LiTFSI (see the Supporting Information); the viscosity of **2b** is 29 cP, comparable with that of [PMI][TFSI]. Spectroscopic data of **1b**−**3b** related to the cationic component are comparable with those of **1a**−**3a**.

Because the efficiency of DSCs is intimately linked to the viscosity of the ionic liquid electrolyte, **2a** and **2b** were evaluated in this application (see the Supporting Information for full details). Here we used a dye-sensitized (7 + 4)-μm double-layer TiO_2 film as the photoanode according to previous optimizations for ionic liquid electrolyte based DSCs.[11] Three different electrolytes were prepared, electrolyte **A** containing 0.2 M iodine, 0.5 M *N*-methylbenzimidazole (NMBI), and 0.1 M guanidinium thiocyanate (GuNCS) in **2a**, electrolyte **B** containing 0.2 M iodine, 0.5 M NMBI, and 0.1 M GuNCS in a mixture of **2a** and **2b** (13:7 volume ratio), and electrolyte **C** containing 0.8 M **1a**, 0.15 M iodine, 0.1 M GuNCS, and 0.5 M NMBI in 3-methoxypropionitrile.

The detailed parameters (J_{sc}, V_{oc}, ff, and η) of the devices employing electrolytes **A**−**C** under simulated 1 sun illumination are shown in Table 1. The photovoltaic performances of devices based on electrolyte **B** are higher than those of

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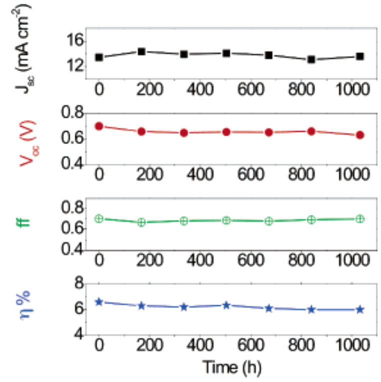

Figure 2. Photovoltaic parameter (J_{sc}, V_{oc}, ff, and η) variations with aging time for the device based on a (7 + 4)-μm film and electrolyte **B** during successive 1-sun visible-light soaking at 60 °C.

electrolyte **A** because of the addition of the low-viscosity ionic liquid **2b** to the pure iodide ionic liquid **2a**. The increase in the photocurrent and efficiency for device containing **B** compared with the device containing **A** may be directly attributed to the lower viscosity of the former electrolyte. The open-circuit photovoltage (V_{oc}), short-circuit photocurrent density (J_{sc}), and fill factor (ff) of the device **B** are 700 mV, 13.54 mA cm^{-2}, and 0.717, respectively, yielding an overall efficiency (η) of 6.8%. It is worth noting that the photoelectric conversion efficiency reached as high as 8.0% under irradiance of 30 mW cm^{-2}. For device **C**, containing 3-methoxypropionitrile, the corresponding photovoltaic parameters (J_{sc}, V_{oc}, ff, and η) are 16.56 mA cm^{-2}, 728 mV, 0.65, and 7.8%, respectively.

These devices based on binary ionic liquids electrolyte (**B**) and organic solvent electrolyte (**C**) exhibit good long-term stability when subjected to an accelerated-light soaking test at 60 °C. Figure 2 presents the stability data of the device containing **K-60** dye in combination with electrolyte **B** that retains 91% of the initial performance after 1000 h of light soaking. During 1000 h, there is a decrease of 70 mV in V_{oc} and a slight increase in the short-circuit current density. In the case of devices with electrolyte **C**, the drop in the efficiency during 1000 h of aging time is less than 5% (Figure S6 in the Supporting information).

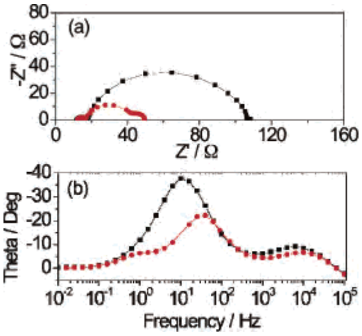

Figure 3. Impedance spectra of DSC devices based on electrolyte **C** for fresh and aged cells after 1000 h of light soaking at 60 °C, measured in the dark under −0.70 bias: (a) Nyquist plots; (b) Bode phase plots. Black: new cell. Red: aged cell.

The variations in the photovoltaic parameters of device **C** during light soaking at 60 °C were monitored by electrochemical impedance spectroscopy. A new cell and an aged device (at 60 °C under visible light soaking for 1000 h) with electrolyte **C** were measured under −0.7 V bias in the dark. In the Bode phase plots (Figure 3b), the characteristic peak (1−10^3 Hz) shifted to a higher value after aging for 1000 h, revealing a decrease in the electron recombination time (τ) from 47.2 to 11.9 ms, which was fitted using an appropriated EIS model.[12] This implies that the photovoltage should decrease, which is consistent with the above photovoltaic data. The high-frequency (10^3−10^5 Hz) peak corresponding to electron transfer at the counter electrode ($I_3^- + 2e = 3I^-$) also shifts to a higher frequency for the aged cell. This reveals that the increase in the fill factor arises from faster electron transfer at the counter electrode. Thus, the shift of the two characteristic frequency peaks rationalizes the drop in the photovoltage (∼60 mV) and the increase (∼4%) in ff.

In conclusion, we have prepared some allyl-functionalized imidazolium iodides, two of which are supercooled fluids, with low viscosities at ambient temperatures. These salts were evaluated as electrolytes in solar cells and were found to provide high efficiencies and good stabilities.

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Supporting Information Available: Synthesis, NMR spectra, differential scanning calorimetry measurement, X-ray crystallographic data (PDF and CIF), and experimental details of solar cell studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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