Stable, High-Efficiency Ionic-Liquid-Based Mesoscopic Dye-Sensitized Solar Cells

Daibin Kuang, Cedric Klein, Zhipan Zhang, Seigo Ito, Jacques-E. Moser, Shaik. M. Zakeeruddin,* and Michael Grätzel*

Efficient and stable mesoscopic dye-sensitized solar cells (DSCs) introducing a low-viscosity binary ionic liquid (1-propyl-3-methyl-imidazolium iodide (PMII) and 1-ethyl-3-methyl-imidazolium tetraycanoborate (EMIB(CN)₄)) electrolyte in combination with a new high-molar-extinction-coefficient ruthenium complex, Ru(2,2'-bipyridine-4,4'-dicarboxylic acid)(4,4'-bis(2-(4-tert-butyloxy-phenyl)ethenyl)-2,2'-bipyridine)₂(NCS), are demonstrated. The dependence of photovoltaic performance, charge transport and electron lifetime on the composition of the binary ionic-liquid electrolyte with different ratios of PMII/EMIB(CN)₄ were investigated by electrochemical impedance and photovoltage transient techniques. A photovoltaic conversion efficiency of 7.6% was obtained under simulated full sunlight illumination, which is a record for solvent-free DSCs. These devices exhibit excellent stability at 80 °C in the dark or under visible-light soaking at 60 °C during 1000 h of accelerated tests.

Keywords:
- dyes
- ionic liquids
- nanocrystals
- solar cells

1. Introduction

Mesoscopic dye-sensitized solar cells (DSCs) have attracted intense interest owing to the prospect of cheap, efficient light-to-electricity power conversion.¹⁻³ For high performance, fast electron injection from the excited state of the dye into the TiO₂ film, rapid dye regeneration, slow electron recombination at the TiO₂-electrolyte interface as well as efficient charge-carrier collection by fast electron diffusion in the mesoscopic TiO₂ film and transport of the redox mediator in the electrolyte are crucial.⁴⁻⁶ Record efficiencies exceeding 11 % under standard AM 1.5 solar illumination have been reached with volatile electrolytes⁶⁴⁻⁷⁸ having a boiling point near 100 °C. However, due to their high vapour pressure, they are difficult to use outdoors in warm climates; hermetic sealing requirements pose a challenge for practical application. In the last decade, much attention has therefore been paid to the development of nonvolatile electrolytes meeting the stability requirements for outdoor applications.⁹ In parallel, a series of high-molar-extinction-coefficient ruthenium complexes containing π-conjugated ligand systems have been successfully introduced and have shown excellent photovoltaic performance and stability.⁶⁻¹⁰ Employing these new sensitizers in conjunction with a nonvolatile electrolyte has recently culminated in the realization of a > 9 % efficient DSC exhibiting excellent stability under light soaking and thermal stress.⁶¹¹ However, this electrolyte still contains an organic solvent, that is, methoxypropionitrile (MPN), which precludes important applications for lightweight and flexible photovoltaic (PV) devices due to MPN permeation across the plastic current collector. The ultimate redox electrolyte for universal employment in the DSC should be solvent free.
Ionic liquids (ILs) represent a new and attractive class of solvent-free electrolytes, having some characteristics of molten salts. Recently synthesized compounds are moisture, air, and temperature stable. They have a high conductivity and a very wide (>-4 V) electrochemical stability window. Their melting points are distinctly below room temperature. Importantly, they have no detectable vapour pressure even at the elevated operating temperatures of PV cells, presenting a huge practical advantage over all organic-solvent electrolytes including the nonvolatile “super robust” formulation introduced recently.[6] A number of ILs have already been examined for DSCs.[6a,11–15] However, till recently their performance lagged so far behind that of the organic solvent-based systems that the realm of applications was believed to be restricted to indoor applications where low light levels prevail.[16]

Until now ILs using imidazolium cations have fared the best for the DSC, but if iodide and triiodide are the only counter ions present, their viscosity becomes several hundred mPas, imposing severe mass-transfer limitations on the photocurrent in full sunlight. The very high concentration (ca 5.8 m) of I- present in the pure imidazolium iodide melts entails two other disadvantages, the first being a reduction of the open circuit voltage (Voc) of the cell due to the lowering of the Nernst potential of the counter-electrode and the second the occurrence of reductive quenching of the ruthenium sensitizer competing with electron injection from the excited state and decreasing the short-circuit photocurrent density (Jsc) of the cell.[17] These problems are alleviated by adding a low-viscosity IL having an inert anion to the iodide-containing IL. A variety of such binary ILs containing different anions have been explored, such as bis(trifluoromethylsulfonyl) imide (Tf2N-), thiocyanate (NCS-), tricyanomethanide ([CN]3-) and tetracyanoborate (B(CN)4-) of EMITFSI, the decay of the absorption signal recorded at 546 nm is of 19.4 x 10^4 m/s/cm, which is 1.5 times higher than that of the conventional Z907 dye.

Since the photovoltaic performance of the dye-sensitized solar cells is largely dependent on the kinetic competition between back-electron transfer of the injected electrons from the conduction band of the semiconductor electrode to the oxidized dye cations (S+) and the interception of the oxidized sensitizer by the redox mediator (dye regeneration), nanosecond time-resolved laser transient absorbance measurements were performed to scrutinize the kinetics of these two charge-transfer processes for the K77 dye in the presence of an inert IL or the I-/I3- ionic redox couple. Great care was taken to keep the excitation laser pulse intensity as low as possible (fluence <20 µJ/cm^2) in order to ensure that, at most, one electron was injected during one pulse per TiO2 nanoparticle. The probe light intensity was also reduced to a minimum by use of filters and a monochromator placed before the sample in order to avoid light biasing of the sensitized TiO2 films. In the electrochemically inert ionic liquid EMITFSI, the decay of the absorption signal recorded at λ=680 nm reflects the dynamics of the recombination of injected electrons with the oxidized dye (S+). At the low laser-light intensities employed, the reaction involves only one geminate electron per S+ pair occupying the same TiO2 particle, hence it should follow first-order kinetics if the interfacial electron-transfer step and not the transport within the TiO2 is rate determining.[18] This appears to be the case here as the rate data in the inert IL
could be fitted by a single exponential with a typical half-life \( \tau_{1/2} = 250 \mu s \) yielding a rate constant of \( k_r = 1.6 \times 10^5 \text{s}^{-1} \) (Figure 2). This value is 2.3 times smaller than the recombination rate constant of \( 3.7 \times 10^5 \text{s}^{-1} \) measured in the MPN solvent.\[6d\] The Marcus model for nonadiabatic electron-transfer reactions is normally employed to analyze the re-capture dynamics of TiO₂ conduction-band electrons by the oxidized sensitizer.\[19\] Due to their large driving force and small reorganization energy these reactions fall in the inverted Marcus region. The recombination rate was found to be independent of electrolyte composition.\[20\] The agreement between the two \( k_r \) values is fortuitous as the IL has a 3.5 times higher iodide concentration than the MPN-based organic electrolyte. The increased I⁻ concentration appears to compensate slower mass transport in the IL, resulting in very similar interception rates. Thus for both electrolytes the dye-regeneration efficiency is close to unity.

The volume ratio of PMII/EMIB(CN)₄ in the binary IL electrolytes was optimized, maintaining 0.1 M Guanidinium thiocyanate (GuNCS), 0.2 M I⁻ and 0.5 M N-methyl-benzimidazole (NMB) concentration in the IL mixtures containing different volume ratios of PMII and EMIB(CN)₄. The short-circuit current density (\( J_{sc} \)) and power-conversion efficiency (\( \eta \)) increases first when the PMII fraction is raised from 20% to 65%, as shown in Figure 3. Further increase in the PMII concentration reduces the \( J_{sc} \) and \( \eta \) values. A complete set of photovoltaic parameters for the different volume ratios is shown in Table 1.

The short-circuit current densities under AM 1.5 sun illumination for PMII volume percentages of 20, 65, and 100% are 9.5, 14.56, and 13.42 mA cm⁻², respectively. The corresponding photovoltaic efficiencies are 4.98%, 7.2%, and 6.4%, respectively, the changes in the open-circuit voltage (\( V_{oc} \)) and the fill factor (FF) being only a few percent.
The best results are obtained using a PMII/EMIB(CN)4 of 65%/35%.

Figure 4 shows the photocurrent dynamics for various volume percentages of PMII and different light intensity. The short-circuit photocurrent is shown in response to a light on–off sequence produced by opening and closing a mechanical shutter that blocks the light beam. Under low light levels (\(< 100 \text{ Wm}^{-2}\)), the photocurrent signal raises vertically to remain constant on a time scale of seconds while for all PMII concentrations a decay is noted when the light intensity passes 300 Wm\(^{-2}\). The relative decay in the photocurrent depends on the IL composition and increases with increasing light intensity, indicating control of the photocurrent by mass transfer under these conditions. For DSCs based on low-viscosity organic-solvent electrolytes such as acetonitrile or the recently described MPN-based formulation,\(^{[6d]}\) no current decay is observed even under full sunlight illumination as there is no mass-transport limitation. Note that the IL containing 20% PMII showed the largest photocurrent transient even though it has the lowest viscosity. This is attributed to a lack of dye regeneration due to the I\(^{-}\)/C\(_0\) depletion in the pores. However, for 100% PMII (5.8 m of I\(^{-}\)), a linear decay of photocurrent was observed due to the mass-transport limitation because of the high viscosity of electrolyte. Figure 4 shows that DSCs based on the binary IL electrolyte containing 65% PMII in volume percent have only 8% photocurrent decay at full sun irradiation, the smallest fraction for all examined compositions. The mass-transport limitation of the \(J_{sc}\) in full sunlight accounts for the remaining relatively small difference in the conversion efficiency (7–8%) achieved with the new IL-based DSC and that of the MPN based organic electrolyte (8–9%).\(^{[6d]}\) The present results are very encouraging pointing at future opportunities to further enhance the performance of this very important solvent-free DSC system.

For further analysis the diffusion coefficients of I\(^{-}\)/C\(_0\) and I\(_3^-\)/C\(_0\) were measured (Table 2) at various concentrations of PMII in the binary ILs. The diffusion coefficients of I\(^{-}\)/C\(_0\) and I\(_3^-\)/C\(_0\) were obtained from the anodic and cathodic steady-state currents \(I_{ss}\) according to the equation \(I_{ss} = 4ncaFD_{app}\), where \(a\) is the microelectrode radius, \(n\) is the number of electrons transferred in the electrochemical step, \(F\) is the Faraday constant and \(c\) is the bulk concentration of electroactive species. The diffusion coefficients of I\(^{-}\) and I\(_3^-\) decreased from 6.03 \(\times 10^{-7}\) to 3.93 \(\times 10^{-7}\) cm\(^2\) s\(^{-1}\) and 7.18 \(\times 10^{-7}\) to 2.03 \(\times 10^{-7}\) cm\(^2\) s\(^{-1}\), respectively, with PMII concentration increasing from 20% to 100%.

### Table 1: Complete set of photovoltaic parameters for DSCs based on K77 sensitizer and the binary IL electrolyte with various PMII volume percent measured under AM 1.5 full sunlight (100 mWcm\(^{-2}\)) irradiation.\(^{[a]}\)

<table>
<thead>
<tr>
<th>PMII%</th>
<th>(J_{sc}) [mAcm(^{-2})]</th>
<th>(V_{oc}) [mV]</th>
<th>FF</th>
<th>(H) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>13.42</td>
<td>0.700</td>
<td>0.677</td>
<td>6.4</td>
</tr>
<tr>
<td>80</td>
<td>14.07</td>
<td>0.709</td>
<td>0.698</td>
<td>7</td>
</tr>
<tr>
<td>65</td>
<td>14.56</td>
<td>0.709</td>
<td>0.697</td>
<td>7.2</td>
</tr>
<tr>
<td>50</td>
<td>14.18</td>
<td>0.713</td>
<td>0.693</td>
<td>7.01</td>
</tr>
<tr>
<td>35</td>
<td>12.44</td>
<td>0.714</td>
<td>0.723</td>
<td>6.42</td>
</tr>
<tr>
<td>20</td>
<td>9.5</td>
<td>0.707</td>
<td>0.725</td>
<td>4.98</td>
</tr>
</tbody>
</table>

\([a]\) The spectral distribution of the xenon lamp simulates AM 1.5 solar light. The active area of the devices with a metal mask is 0.158 cm\(^2\).

### Table 2: Diffusion coefficients of iodide and triiodide for ILs based on different volume percentages of PMII.

<table>
<thead>
<tr>
<th>PMII% (vol)</th>
<th>(D_{I^-}) ([10^{-7} \text{ cm}^2 \text{s}^{-1}]^{[a]})</th>
<th>(D_{I_3^-}) ([10^{-7} \text{ cm}^2 \text{s}^{-1}]^{[b]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>20%</td>
<td>6.03</td>
<td>7.18</td>
</tr>
<tr>
<td>35%</td>
<td>5.75</td>
<td>5.86</td>
</tr>
<tr>
<td>50%</td>
<td>5.04</td>
<td>4.64</td>
</tr>
<tr>
<td>65%</td>
<td>4.3</td>
<td>3.51</td>
</tr>
<tr>
<td>80%</td>
<td>4.4</td>
<td>2.65</td>
</tr>
<tr>
<td>100%</td>
<td>3.93</td>
<td>2.03</td>
</tr>
</tbody>
</table>

\([a]\) Calculated from microelectrode measurements and \([b]\) obtained from the EIS measurements.
DSC devices fabricated by K77 dye in the presence of 3-phenylpropionic acid (PPA) as co-adsorbent, using the binary IL containing 65% of PMII and 35% of EMIB(CN)₄, resulted in the highest efficiency of 7.6% under full sunlight illumination. Figure 5a presents the photocurrent-density–voltage curves of the DSC measured under various light-intensity irradiations. The short-circuit current density (Jₛ𝑐), open-circuit voltage (Vₒ𝑐), and fill factor (FF) under simulated AM 1.5 illumination were 15.1 mA cm⁻², 702 mV, and 0.714, respectively. It is interesting to note that 8.6% power-conversion efficiency was obtained under one third of a sun (300 Wm⁻²). The incident photon-to-current conversion efficiency (IPCE) defined as the number of generated electrons divided by the number of incident photons is shown in Figure 5b. The IPCE spectrum reveals that the maximal efficiency was over 80% at 546 nm and exceeds 70% in spectral range between 480 nm and 650 nm.

Electrochemical impedance spectroscopy (EIS) is a powerful technique for characterization of electronic or ionic transport process in DSCs. The different volume ratios of PMII/EMIB(CN)₄ were therefore subjected to EIS investigation. Figure 6 shows the impedance data measured in darkness under −0.70 V applied bias. a) Bode phase plots, b) Nyquist plots.

Figure 5. a) I–V curves of DSCs based on K77 sensitizer with PPA co-adsorbant and the binary IL electrolyte using the optimal volume ratio of PMII/EMIB(CN)₄, namely 65% of PMII and 35% of EMIB(CN)₄, measured under different light-intensity irradiations. b) Photocurrent action spectrum of the above device. The active area of the device with a metal mask is 0.158 cm².

Figure 6. Impedance spectra of DSCs based on K77 sensitizer and the binary IL electrolytes with different volume percentage of PMII, measured in darkness under −0.70 V applied bias. a) Bode phase plots, b) Nyquist plots.
Electron lifetimes of the devices based on K77 sensitizer and IL with different volume ratio of PMII/EMIB(CN)$_4$ at open-circuit voltage under varying light bias. Dot curve: PMII/EMIB(CN)$_4$ is 20:80, square: PMII/EMIB(CN)$_4$ is 65:35, triangle: 100% PMII.

Figure 8. Time dependence of photovoltaic parameters ($J_{sc}$, $V_{oc}$, FF, and η) of DSCs based on K77 sensitizer and the binary IL electrolyte varied with the time during the accelerated tests at 80 °C in darkness.

Figure 9. Impedance spectra of DSCs based on K77 and the binary IL electrolyte (Z655) for the fresh and aged cell following the accelerated testing time (1000 h) at 80 °C in darkness, measured as −0.7 V bias. a) Bode phase plots, b) Nyquist plots.

Characterization of Dye-Sensitized Solar Cells

at different open-circuit potentials ($V_{oc}$) are shown in Figure 7. The $V_{oc}$ was adjusted by varying the light bias level. The electron lifetime decreases with the PMII volume fraction, values at 20%, 65% and 100% being 7.2 ms, 5.8 ms and 5.3 ms under one sun illumination, respectively. The same tendency was observed in the EIS measurements. Clearly, the presence of tetracyanoborate instead of iodide at the interface retards the recapture of conduction-band electrons by triiodide ions. A likely reason for this effect is the coordination of surface titanium ions by cyanide groups reducing the density of states that act as recombination center. The earlier observation that binary ILs containing dicyanoamide and tricyanomethide counter ions show higher $V_{oc}$ values than the pure iodide melts supports this interpretation.

It was noted that the absolute values of the electron lifetimes observed from photovoltage transient measurements at a specific concentration of PMII were smaller than those derived from the EIS measurements. This behaviour can be rationalized in terms of different local I$_3^-$ concentrations present in the pores of the nanocrystalline titania film. During the photovoltage transient decay studies the DSC is illuminated leading to a higher I$_3^-$ concentration than in the EIS experiments that were conducted in the dark.

Accelerated aging tests were performed to scrutinize the photo and thermal stability of the new solvent-free DSC system employing the EMIB(CN)$_4$-based binary IL along with the K77 sensitizer. The Z655 electrolyte contained 0.1 M GuNCS, 0.2 M I$_3^-$ and 0.5 M NBB in a 65/35 v/v% mixture of PMII/EMIB(CN)$_4$. Figure 8 presents the photovoltaic data of the DSC during aging at 80 °C in the dark. The performance was remarkably stable over this period a 30 mV $V_{oc}$ decay and 0.7 mA cm$^{-2}$ decrease of $J_{sc}$ being compensated by an increase in FF (5%). Hence, 91% of the initial photovoltaic performance was retained even after a continuous 1000 h accelerated test under 80 °C in darkness. Indications of photovoltage and efficiency decrease can be seen since the middle frequency peak shifts to a slightly higher frequency in the Bode phase plots, which means that the electron lifetime decreased for the aged cell. The calculated values of the electron lifetime.
tron lifetime according to the appropriate equivalent circuit are 20.9 ms and 9.6 ms for fresh cell and aged cell, respectively. Interestingly, this decrease is smaller than that observed with the MPN-based electrolyte where the electron lifetime decreased from 62.5 to 15.2 ms during thermal aging. Further studies are under way to elucidate this observation.

The high-frequency peak also shifts to larger values, implying faster electron transfer at the counter electrode for the aged cell, which will result in an improved fill factor in agreement with the photovoltaic data. The increase in the radius of the low-frequency hemicycle in the Nyquist plot shows that the diffusion resistance augments during aging probably due to a decrease in the triiodide concentration caused by reaction with impurities. Interestingly, this decrease is smaller than that observed for the photovoltage and photovoltaic performance measurements, which is probably due to different measurement conditions. EIS results reveal that the I$_3^-$ transport in the electrolyte and charge transfer at the counter electrode become slower with the increasing PMII concentration due to the increase in viscosity of the binary IL electrolyte. Both EIS and photovoltage transient measurements show that the electron lifetime of DSCs decreases after a 1000 h accelerated test at 80°C in darkness. The present results are very encouraging pointing at future opportunities to further enhance the performance of this very important solvent-free DSC system.

3. Conclusions

For the first time, a 7.6% photon-to-electricity conversion efficiency was reached with a solvent-free DSC using the PMII/EMIB(CN)$_4$ binary IL in conjunction with the new high-molar-extinction-coefficient sensitizer (K77). The effects of volume ratio on the photovoltaic performance were investigated and the optimal volume ratio was 65%:35%. The photovoltaic parameters ($J_{sc}$, $V_{oc}$, FF, and $\eta$) with various PMII fractions were evaluated by electrochemical impedance spectroscopy and photovoltage transient techniques. EIS results reveal that the I$_3^-$ transport in the electrolyte and charge transfer at the counter electrode become slower with the increasing PMII concentration due to the increase in viscosity of the binary IL electrolyte. Both EIS and photovoltage transient measurements show that the electron lifetime of DSCs decreases after a 1000 h accelerated test at 80°C in darkness. The present results are very encouraging pointing at future opportunities to further enhance the performance of this very important solvent-free DSC system.

4. Experimental Section

Reagents: The high-molar-extinction-coefficient sensitizer K77, Ru(2,2'-bipyridine-4,4'-dicarboxylic acid)(4,4'-bis(2-(4-tert-butoxyphenyl)ethenyl)-2,2'-bipyridine) (NCS), and 1-butyl-1H-benzimidazole (NBB) were synthesized as reported earlier. The ILs 1-propyl-3-methylimidazolium iodide (PMII), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), and 1-ethyl-3-methyl-imidazolium tetracyanoborate (EMIB(CN)$_4$) were synthesized according to the literature methods and the purity was confirmed by 1H NMR analysis. 3-phenylpropionic acid (PPA) and guanidinium thiocyanate (GuNCS) was purchased from Aldrich. N-methylbenzimidazole (NMB, from Aldrich) was recrystallized from diethyl ether before use. N-buty1-benzimidazole (NBB) was synthesized according to the literature method.

EIS: Impedance spectra of DSCs were measured in the dark at −0.7 V forward bias using a potentiostat (EG&G, M273) equipped with a frequency-response analyzer (EG&G, M1025). The spectra were scanned in a frequency range of 0.005 Hz to 100 kHz at room temperature with modulation amplitude set at 10 mV. The obtained impedance spectra were fitted with ZView software (v2.8b, Scribner Associates Inc.) to the appropriate equivalent circuits.

Diffusion coefficient measurements: A two-electrode electrochemical cell, consisting of a 5.0-μm-radius Pt ultramicroelectrode as working electrode and a Pt foil as counter electrode, was used to measure the iodide and triiodide diffusion coefficient. The radius of the Pt microelectrode was determined by using standard solutions.

Photovoltage transient decay: Photovoltage transients were measured using a pump pulse generated by a ring of red LEDs controlled by a fast solid-state switch. Pulse widths of 200 ms were used. The pulse was incident on the photoanode side of the cell and its intensity was controlled to keep the increment of the voltage below 10 mV. A white bias light, also incident on the same side of the cell, was supplied by light-emitting diodes. Usually, transients were measured at different white-light bias intensities ranging from 150% to 0.1% sun regulated by the applied voltage on the diodes.
Preparation of mesoscopic TiO₂ films and fabrication of DSCs: The mesoscopic TiO₂ films used as photoanodes consisted of double layers of TiO₂ (6-μm thick transparent layer of 20-nm TiO₂ anatase nanoparticles and 4 μm thick scattering layer of 400 nm anatase TiO₂ particles). The detailed method of TiO₂ film preparation, device fabrication, and the photocurrent–voltage measurements was reported in our earlier publications.[14, 27] The double-layer films were heated to 520 °C and sintered for 30 min, then cooled to ≈80 °C and immersed into the dye (K77) solution containing 300 μM of K77 in acetonitrile and tertbutyl alcohol (volume ratio: 1:1) at room temperature for 16 h. If desired, 300 μM PPA co-adsorbent was introduced into the above dye solution. Dye-coated double-layer films were assembled and sealed with 35-μm-thick Bynel hot-melt rings (DuPont) to the counter electrodes. The latter employed FTO glass with a small hole that was subsequently sealed with a Bynel sheet and a thin electrode space from the counter electrode side through a predrilled acid solution in isopropyl alcohol and subsequent heating at 400 °C for 15 min. The electrolyte was injected into the interelectrode space from the counter electrode side through a predrilled hole that was subsequently sealed with a Bynel sheet and a thin glass slide cover by heating. The IL electrolyte contained 0.2 M iodine, 0.1 M GuNCS, and 0.5 M NMB and a mixture of PMII and EMI(BCN). For the stability testing, an electrolyte coded Z655 was employed containing 0.2 M iodine, 0.1 M GuNCS, and 0.5 M NNB the PMII/EMI(BCN) volume ratio being 65/35.

Photocurrent–voltage measurements: The light source for the photocurrent–voltage (I–V) measurement was a 450 W xenon lamp (Oriel, USA), simulating AM 1.5 solar light. The incident light intensity was calibrated with a standard Si solar cell. The spectral output of the lamp was matched precisely to the iodine, 0.1 M dye solution. Dye-coated double-layer films were assembled and sintered, 300 μM amount of Pt catalyst deposited from 0.005 M counter electrodes. The latter employed FTO glass with a small hole that was subsequently sealed with a Bynel sheet and a thin electrode space from the counter electrode side through a predrilled acid solution in isopropyl alcohol and subsequent heating at 400 °C and sintered for 19 min. The electrolyte was injected into the interelectrode space through a predrilled hole that was subsequently sealed with a Bynel sheet and a thin glass slide cover by heating. The IL electrolyte contained 0.2 M iodine, 0.1 M GuNCS, and 0.5 M NMB and a mixture of PMII and EMI(BCN). For the stability testing, an electrolyte coded Z655 was employed containing 0.2 M iodine, 0.1 M GuNCS, and 0.5 M NNB the PMII/EMI(BCN) volume ratio being 65/35.

Stability test: Hermetically sealed cells were used to check the long-term stability at 80 °C in darkness or under visible-light soaking at 60 °C. The light-soaking experiments employed a monochromator (Jobin Yvon Ltd., UK) onto the cell under test. The incident light from a 300 W xenon lamp (Oriel, USA), simulating AM 1.5 solar light. The incident light intensity was calibrated with a standard Si solar cell. Various sunlight filter (Prk:LLJzisions Glas & Optik GmbH, Germany). Various standard global AM 1.5 solar spectrum in the region of 350–800 nm-thick Bynel hot-melt rings (DuPont) to the sample of the 400-nm light-scattering particles, and the long-term stability at 80 °C.

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