Electrolyte Tuning in Iron(II)-Based Dye-Sensitized Solar Cells: Different Ionic Liquids and I₂ Concentrations

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Abstract: The effects of different I₂ concentrations and different ionic liquids (ILs) in the electrolyte on the performances of dye-sensitized solar cells (DSCs) containing an iron(II) N-heterocyclic carbene dye and containing the I⁻/I₃⁻ redox shuttle have been investigated. Either no I₂ was added to the electrolyte, or the initial I₂ concentrations were 0.02, 0.05, 0.10, and 0.20 M. The short-circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), and the fill factor ($ff$) were influenced by changes in the I₂ concentration for all the ILs. For 1-hexyl-3-methylimidazole iodide (HMII), low $V_{OC}$ and low $ff$ values led to poor DSC performances. Electrochemical impedance spectroscopy (EIS) showed the causes to be increased electrolyte diffusion resistance and charge transfer resistance at the counter electrode. DSCs containing 1,3-dimethylimidazole iodide (DMII) and 1-ethyl-3-methylimidazole iodide (EMII) showed the highest $J_{SC}$ values when 0.10 M I₂ was present initially. Short alkyl substituents (Me and Et) were more beneficial than longer chains. The lowest values of the transport resistance in the photoanode semiconductor were found for DMII, EMII, and 1-propyl-2,3-dimethylimidazole iodide (PDMI) when no I₂ was added to the initial electrolyte, or when I₂ was less than 0.05 M. Higher I₂ led to decreases in the transport resistance in the electrolyte and the counter electrode resistance. The electron lifetime and diffusion length depended upon the I₂. Overall, DMII was the most beneficial IL. A combination of DMII and 0.1 M I₂ in the electrolyte produced the best performing DSCs with an average maximum photoconversion efficiency of 0.65% for a series of fully-masked cells.

Keywords: N-heterocyclic carbene; iron(II); dye-sensitized solar cell; ionic liquid; iodine

1. Introduction

Sustainable approaches to energy generation are of critical societal importance and are one of the United Nations Sustainable Development Goals (SDG7) [1]. The conversion of solar to electrical energy is a critical sustainable goal, and an alternative strategy to the well-established silicon photovoltaics is seen in the development of dye-sensitized solar cells (DSCs) [2]. An n-type DSC (Figure 1) employs a wide-bandgap n-type semiconductor, typically TiO₂ (anatase), with a sensitizer adsorbed on the surface to extend the absorption of light into the visible region [3–6]. Sensitizers in DSCs are typically metal-free (organic) or ruthenium(II)-based dyes. Although state-of-the-art ruthenium dyes reach up to ca. 12% photoconversion efficiency (PCE or $\eta$) [7], the use of metals with low natural abundances does not address the problem of sustainability [8,9]. Thus, investigations of coordination compounds of Earth abundant metals, such as copper [10–14] and iron [14–18], as sensitizers in DSCs are of prime interest.

The first DSCs based on $[\text{Fe(dcbpy)}_2\text{(CN)}_2]$ (dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid) were disappointing and produced only a very low short-circuit current density ($J_{SC}$) and open-circuit voltage ($V_{OC}$) [19]. In order to successfully utilize iron(II) complexes as sensitizers, one must overcome the problem of fast deactivation from a metal-to-ligand charge transfer (MLCT) state to a metal-centred (MC) state [16]. This deactivation leads to inefficient electron injection into the semiconductor and, therefore, low $J_{SC}$ values. Tuning the
electrolyte has been highly beneficial in enhancing the performance of [Fe(dcbpy)\(_2\)(CN)\(_2\)], and Jakubikova, McCusker and coworkers systematically increased values of \(J_{SC}\) from 0.10 to 1.46 mA cm\(^{-2}\) and \(\eta\) from 0.024\% to 0.35\% for masked DSCs by the addition of different salts and pyridine derivatives [20]. Cyclometallated iron(II) complexes have been suggested as one means of accessing more efficient iron-based photosensitizers [21]. However, a move to N-heterocyclic carbene (NHC) ligands proved to be the critical turning point in utilizing iron(II)-based dyes. After a report by Wärnmark and coworkers that the iron(II) NHC complex 1 (Scheme 1) exhibited a long 3MLCT lifetime of 9 ps [22], the group of Gros demonstrated that 1 performed in n-type DSCs with \(\eta = 0.13\%\) [23]. Until very recently, complex 1 continued to be one of the most promising iron(II)-based sensitizers [15,24], and tuning the composition of the electrolyte has been crucial in improving the performance of DSCs sensitized by 1 [25,26]. Gros reported in 2020 that the presence of both Mg\(^{2+}\) ions and guanidium thiocyanate in the electrolyte with an I\(^-\)/I\(_3^-\) redox shuttle resulted in a high \(J_{SC}\) of 3.3 mA cm\(^{-2}\) and \(\eta\) of 1\%. A critical factor to the improvement in DSC performance was the presence of an additional blocking underlayer on the electrodes [26]. While our own investigations for the current work were in progress, Gros and coworkers reported a series of heteroleptic iron(II) NHC dyes and achieved a value of \(\eta = 1.44\%\) for masked devices, thereby setting a new record for Fe(II)-based DSCs [27]. Manipulation of the electrolyte composition (specifically, the addition of Mg\(^{2+}\) ions and Bu\(_4\)NI), the use of poly(3,4-ethylenedioxythiophene (PEDOT) coated counter electrodes, and the application of a blocking underlayer on the electrodes proved to be important factors.

Figure 1. Schematic diagram of an n-type DSC. \(S\) and \(S^*\) = ground and excited states of the dye; \(V_{OC}\) = open-circuit voltage; \(E_{CB}\) = energy of conduction band of the semiconductor; \(E_F\) = Fermi level; \(E_{redox}\) = redox potential of the redox shuttle.

Scheme 1. The structure of the iron(II)-NHC dye 1.
The $\Gamma^-/I_3^-$ redox couple has been used for all investigations of iron(II)-NHC dyes reported to date. For DSCs containing other sensitizers, it has been established that additional $I_n^-$ species are formed in the electrolyte at high $I_2$ concentrations but that they are not of importance in the device [28]. The operation of a DSC is based on effective dye regeneration after electron injection into conduction band of the semiconductor, and this is a multistep process. After dye excitation, the dye is formally in its oxidized state $(D^+)$, and this is reduced by $I^-$ ion from the redox shuttle after initial formation of a dye-iodide complex, $D^+:I^-$. The formation of this complex has been studied for $[\text{Ru}($dcbpy$)_2X_2]$, and is considered to be key for dye regeneration [29]. The addition of a second iodide ion results in complex dissociation and formation of the radical anion $I_2^-$ and the dye molecule in its ground state (Equation (1)). After this, two radicals undergo disproportionation as shown in Equation (2)) [28].

$$[D^+:I^-] + I^- \rightarrow D + I_2 \quad (1)$$
$$2I_2^- \rightarrow I^- + I_3^- \quad (2)$$

Dye regeneration therefore depends upon the presence of $I^-$ ions in the electrolyte solution, and it has been established that an increase in $I^-$ concentration can be beneficial for DSC performance [30]. Wang et al. have demonstrated that for solvent-free electrolytes with ionic liquids (ILs) as media, a high $I^-$ concentration is essential for efficient dye regeneration [31]. On the other hand, a high concentration of $I^-$ may lead to undesired quenching of the excited-state dye, $D^*$ (Equation (3)) [31].

$$D^* + 2I^- \rightarrow D^- + I_2^- \quad (3)$$

The concentration of $I_3^-$ ions is of importance for well-performing DSCs and directly affects the value of $V_{OC}$ due to changes in the potential of the redox couple [33]. The formation constant for triiodide (equilibrium 4) is usually high in organic solvents; in MeCN, $\log K = 6.76$ at 298 K [34]. At the same time, the concentration of $I^-$ ions in the electrolyte is typically much higher than that of $I_2$ [28]. We have previously shown that an electrolyte composed of LiI (0.18 M), $I_2$ (0.05 M), and the IL 1-propyl-2,3-dimethylimidazolium iodide (PDMI, Scheme 1, 0.60 M) in methoxypropionitrile (MPN) led to a photoconversion efficiency of up to 0.66% for fully masked DSCs [25]. At the time of publication [25], this was the highest observed overall efficiency for an iron(II)-NHC sensitizer. In the latter electrolyte, the total concentration of $I^-$ is 0.78 M (LiI 0.18 M in combination with PDMI 0.60 M), while the starting concentration of $I_2$ is only 0.05 M.

$$I_2 + I^- \leftrightharpoons I_3^- \quad (4)$$

Using the ruthenium(II) dye N719, it has been demonstrated that an increase in $I_2$ concentration has a direct influence on $J_{SC}$ [35]. The optimal $I_2$ concentration for the electrolyte in acetonitrile was 0.03 M. The remaining electrolyte components were 1-propyl-3-methylimidazolium iodide (PMII, Scheme 2, 1.00 M), guanidinium thiocyanate (0.10 M), and 1-methylbenzimidazole (MBI, 0.50 M). Upon going from lower to higher $I_2$ concentrations (0.03 M to 0.20 M to 0.50 M), a positive shift of the redox potential was observed. Despite this shift, the $V_{OC}$ values were not affected by different $I_2$ concentrations. Interestingly, the use of the IL 1-ethyl-3-methylimidazolium tetracyanoborate (EMIBCN) as the solvent led to a different trend and 0.20 M $I_2$ was the most beneficial concentration. It was also shown that the effective diffusion coefficient for $I_3^-$ was in a good agreement with the literature for the IL electrolyte, while for MeCN media, it was one order of magnitude lower than expected [35].
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Scheme 2. The structures of the ionic liquids (ILs) 1,3-dimethylimidazole iodide (DMII), 1-ethyl-3-methylimidazole iodide (EMII), 1-propyl-3-methylimidazole iodide (PMII), 1-propyl-2,3-dimethylimidazole iodide (PDMII), 1-butyl-3-methylimidazole iodide (BMII), 1-butyl-2,3-dimethylimidazole iodide (BDMII), 1-hexyl-3-methylimidazole iodide (HMII), and 1-hexyl-2,3-dimethylimidazole iodide (HDMI).

Significant differences between acetonitrile and EMIBCN lie in their density and viscosity, with the latter having a noteworthy influence on ion diffusion in the electrolyte. Table 1 gives the densities and viscosities of MeCN, EMIBCN, and MPN. The $I_3^-$ diffusion capability directly contributes to the DSC efficiency. Since the viscosity of electrolyte directly influences the transport of the components of the redox shuttle, more viscous solvents retard ion diffusion, and higher $[I_3^-]$ concentrations can help to overcome this limitation [35]. At the same time, a greater number of recombination processes involving the redox shuttle can occur. Hence, it is essential that the $I_2$ concentration is optimized to provide the best possible electrolyte composition to enhance DSC performance.

Table 1. Solvent densities and viscosities at room temperature [36–38].

| Solvent                                      | Density at 298 K/g mL$^{-1}$ | Viscosity /mPa s$^{-1}$ |
|----------------------------------------------|------------------------------|-------------------------|
| Acetonitrile                                 | 0.786                        | 0.37 (298 K)            |
| 1-Ethyl-3-methylimidazolium tetracyanoborate (EMIBCN) | 1.294                        | 19.8 (293 K)            |
| 3-Methoxypropionitrile (MPN)                 | 0.937                        | 2.5 (298 K)             |

$^1$ 1 cP = 1 mPa s.

In previous investigations, we have shown that the structure of the IL strongly influences the photoconversion efficiency of DSCs sensitized with the iron(II) dye 1 [25]. Here, we complement these results with a study of the effects on DSC performance of different $I_2$ concentrations in the presence of different ILs with MPN as the electrolyte solvent. The dye throughout the investigation is 1 [25] (Scheme 2).

2. Materials and Methods

2.1. DSC Fabrication

Commercial FTO/TiO$_2$ electrodes (Solaronix Test Cell Titania Electrodes, Solaronix SA, Aubonne, Switzerland) were rinsed with water, EtOH and dried on a heating plate at 450 °C for 30 min. Afterwards, the electrodes were cooled to 60 °C and immersed in the dye bath. For 1, the dye bath consisted of 1 (0.50 mM) and chenodeoxycholic acid (cheno, 0.10 mM) in MeCN and the dipping time was ca. 15 h. For the reference dye N719 (Solaronix SA, Aubonne, Switzerland), the dye bath was a solution of N719 (0.30 mM) in EtOH and the dipping time was ca. 15 h. The electrodes were removed from the dye baths and were rinsed with the solvent used in the dye bath and dried under a flow of N$_2$. Counter electrodes (Solaronix Test Cell Platinum Electrodes, Solaronix SA, Aubonne, Switzerland) were rinsed with EtOH and then heated at 450 °C for 30 min to remove volatile organic impurities.

The working and counter electrodes were combined with a thermoplas...
pressing them together while heating. Afterwards, the electrolyte was introduced into the space between the electrodes through a pre-drilled hole in the counter electrode by vacuum backfilling. The composition of the electrolytes varied as described in Section 3. The hole was sealed with hot-melt sealing foil and a cover glass (Solaronix Test Cell Sealing and Solaronix Test Cell Caps, Solaronix SA, Aubonne, Switzerland). Finally, silver paint (SPI Supplies, West Chester, PA 19381-0656, USA) was applied on the edges of each electrode from the FTO side.

2.2. DSC, External Quantum Efficiency (EQE) and Electrochemical Impedance Spectroscopy (EIS) Measurements

Current density-voltage (J–V) measurements were made by irradiating from the photoanode side with a LOT Quantum Design LS0811 instrument (LOT-QuantumDesign GmbH, Darmstadt, Germany, 100 mW cm\(^{-2}\) = 1 sun at AM 1.5) and the simulated light power was calibrated with a silicon reference cell.

For the EIS measurements, a ModuLab®XM PhotoEchem photoelectrochemical measurement system (Solartron Metrology Ltd., Leicester, UK) was used. The impedance was measured in galvanostatic mode at the open-circuit potential of the cell at a light intensity of 22 mW cm\(^{-2}\) (590 nm) in the frequency range 0.05 Hz to 100 kHz with an amplitude of 10 mV. The impedance data were analyzed and fitted using ZView® software (Scribner Associates Inc., Southern Pines, NC, USA).

3. Results and discussion

3.1. Comparison of Electrolytes Containing 0.05 M and 0.10 M \(I_2\)

In the first part of the investigation, DSCs sensitized with \(I\) in the presence of the co-adsorbant cheno were fabricated with electrolytes that differed in the ionic liquid present. The ILs shown in Scheme 1 were chosen as ionic liquid components, and the general composition was \(\text{LiI} (0.18 \text{ M}), \text{I}_2 (0.10 \text{ or } 0.05 \text{ M}), \text{IL} (0.60 \text{ M}) \text{ in MPN}\). An additional electrolyte, \(\text{PDMII}_a\), was made which contained the additive MBI; its composition was \(\text{LiI} (0.18 \text{ M}), \text{I}_2 (0.10 \text{ M}), \text{MBI} (0.50 \text{ M}), \text{and IL} (0.60 \text{ M}) \text{ in MPN}\). We recently published statistical data to evaluate the reproducibility of DSCs, and demonstrated the need to measure data for multiple devices, and the legitimacy of using average values for the parameters [39]. In the following discussion, the average values of \(J_{SC}\), \(V_{OC}\), fill-factor (ff), and \(\eta\) are considered for appropriate comparison of DSCs sets between each other. DSC parameters extracted from J–V curves for all DSCs are given in Supplementary Table S1, and average values are presented in Table 2. The ruthenium(II) dye N719 was used as a reference.

Table 2. Average values of DSC parameters for sets of multiple DSCs using electrolytes with different ionic liquids. The electrolyte composition for DMII, EMII, PMII, BMII, PDMII and BDMII was \(\text{LiI} (0.18 \text{ M}), \text{I}_2 (0.10 \text{ M}), \text{IL} (0.60 \text{ M}) \text{ in MPN}\); for \(\text{PDMII}_a\), the composition was \(\text{LiI} (0.18 \text{ M}), \text{I}_2 (0.10 \text{ M}), \text{PDMII} (0.60 \text{ M}), \text{MBI} (0.50 \text{ M}) \text{ in MPN}\); for \(\text{BDMII}_a\) and \(\text{HDMII}_a\), the composition was \(\text{LiI} (0.18 \text{ M}), \text{I}_2 (0.05 \text{ M}), \text{PDMII} (0.60 \text{ M}) \text{ in MPN}\). Electrolytes are labelled according to the IL present.

| Electrolyte Name | \(J_{SC}/\text{mA cm}^{-2}\) | \(V_{OC}/\text{mV}\) | ff\% | \(\eta\)% | Rel. \(\eta\)% \(^1\) |
|-----------------|----------------|----------------|------|--------|-----------------|
| DMII            | 3.82           | 285            | 60   | 0.65   | 10.5            |
| EMII            | 3.86           | 201            | 42   | 0.34   | 5.5             |
| PMII            | 2.48           | 297            | 63   | 0.47   | 7.6             |
| BMII            | 2.42           | 269            | 64   | 0.42   | 6.7             |
| HMII            | 2.60           | 146            | 31   | 0.12   | 1.9             |
| PDMII           | 3.50           | 156            | 43   | 0.24   | 3.8             |
| BDMII           | 2.55           | 272            | 60   | 0.42   | 6.8             |
| HDMII           | 2.58           | 242            | 55   | 0.35   | 5.6             |
| PDMII\(_a\)     | 0.07           | 282            | 51   | 0.01   | 0.2             |
| BDMII\(_a\)     | 3.48           | 290            | 60   | 0.60   | 10.7            |
| HDMII\(_a\)     | 2.99           | 285            | 62   | 0.53   | 9.4             |

\(^1\) Relative an N719-sensitized DSC efficiency of 6.19% (average of three cells with \(\eta = 6.22, 6.21\) and 6.14%).
Firstly, we consider the 1-alkyl-3-methylimidazolium iodide-based electrolytes. Values of \( J_{SC} \) are remarkably similar for DSCs containing the electrolytes DMII and EMII with 3.82 and 3.86 mA cm\(^{-2} \), respectively (Table 2). Then, a decrease in \( J_{SC} \) is observed for the electrolytes with PMII (2.48 mA cm\(^{-2} \)) and BMII (2.42 mA cm\(^{-2} \)), and a comparable \( J_{SC} \) value of 2.60 mA cm\(^{-2} \) is observed for the DSCs with electrolyte HMII. Values of \( V_{OC} \) lie in the same range (297–269 mV) for DSCs with electrolytes DMII, PMII, and BMII, but are considerably lower for EMII and HMII (201 and 146 mV, respectively). Significantly, the \( ff \) values for all DSCs containing EMII and HMII are low (Supplementary Table S1) and low average values of \( ff \) in Table 1 are appropriately representative. The data for the devices with 1-alkyl-3-methylimidazolium iodide-based electrolytes reveal that the highest average \( \eta \) value of 0.65% corresponds to the IL with the shortest alkyl chain (DMII). We note that all four DSCs with this IL perform well, with values of \( \eta \) in the range 0.62–0.67%, which represents 10.0–10.8% of the photoconversion efficiency observed for DSCs sensitized by N719 (Supplementary Table S1).

Upon going from ILs with a 1-alkyl-3-methylimidazolium cation to ILs containing 1-alkyl-2,3-dimethylimidazolium cations (Scheme 1), noticeable changes in performance are observed. For example, DSCs with PDMII as the IL have higher \( J_{SC} \) values than those with PMII (Table 2 and Supplementary Table S1). The average value increases from 2.48 to 3.50 mA cm\(^{-2} \). At the same time, the decrease in \( V_{OC} \) and \( ff \) resulted in lower overall photoconversion efficiencies. A comparison of DSCs with electrolytes BDMII or BMII reveals no significant changes, and both average \( \eta \) values are 0.42% (Table 2). In the case of HDMI, the trends in parameters are different. While \( J_{SC} \) remains approximately constant on going from HMII to HDMII, values of \( V_{OC} \) and \( ff \) increase, and this leads to enhanced values of \( \eta \) (Table 2 and Supplementary Table S1).

A comparison of the results from the current investigation with those reported earlier [25] are summarized in Figure 2. DSCs with electrolytes based on BDMII and HDMII ILs in the presence of 0.05 M I\(_2\) were not previously published, and their performance parameters are shown in Table 2 and Supplementary Table S1 (electrolytes BDMII\(_a\) and HDMII\(_a\)). At an I\(_2\) concentration of 0.05 M, the optimal IL was PDMII [25], but with 0.10 M I\(_2\), DMII gave the highest DSC performance. Cells with PDMII suffered from low values of \( V_{OC} \) and \( ff \) (Table 2 and Figure 2). Since values of \( J_{SC} \) were promising (average 3.50 mA cm\(^{-2} \), Table 2), it was decided to add MBI to the electrolyte since it has been established that MBI can improve \( V_{OC} \) [40,41]. However, although an increase in \( V_{OC} \) from 156 to 282 mV was observed (Table 2), it was accompanied by a dramatic reduction in \( J_{SC} \), and correspondingly low values of \( \eta \). However, although an increase in \( V_{OC} \) from 156 to 282 mV was observed (Table 2), it was accompanied by a dramatic reduction in \( J_{SC} \), and correspondingly low values of \( \eta \).

The open circuit voltage is the difference between the Fermi level of a semiconductor and the redox potential of electrolyte. From the Nernst equation, an increase in the concentration of I\(^{-}\) results in a negative shift in redox potential for the I\(^{-}\)/I\(_3^{-}\) couple [33], consequently decreasing \( V_{OC} \) [33], and higher I\(_2\) concentrations lead to increased \( V_{OC} \). However, we observed (Figure 2b) that an increase in the concentration of I\(_2\) from 0.05 M to 0.10 M resulted in lower values of \( V_{OC} \) for all ILs. This suggests that, in these DSCs, the effect of the increase in I\(_2\) concentration on \( V_{OC} \) values has more to do with recombination processes [28] than the change in the redox potential of the I\(^{-}/I_{3}^{-}\) shuttle.

Considering \( J_{SC} \), higher values were obtained with an increased concentration of I\(_2\) only for DSCs containing DMII and EMII ILs. With PDMII, there was almost no change in \( J_{SC} \) (Figure 2) at different I\(_2\) concentrations. In the case of DSCs containing HMII or HDMII, the change in \( J_{SC} \) is less than 0.5 mA cm\(^{-2} \) (Figure 2a). The trend in \( \eta \) (irrespective of the IL with the exception of DMII) is for a lower electrolyte concentration of I\(_2\) to lead to higher performances (Figure 2c).
Figure 2. Average (a) $J_{SC}$, (b) $V_{OC}$ and (c) $\eta_{\text{relative}}$ values ($\eta_{\text{relative}}$ is with respect to N719) and (d) $ff$ values for DSCs based on electrolytes with 0.05 or 0.10 M I$_2$ and 1-alkyl-3-methylimidazolium or 1-alkyl-2,3-dimethylimidazolium iodide to illustrate the influence of iodine concentration and IL structure. Average values for 0.10 M I$_2$ and for BDMII and HDMII ILs with 0.05 M I$_2$ are from Table 2, and for other cells with 0.05 M I$_2$, average values are calculated from the data in reference [25].

3.2. EIS Measurements

In order to rationalize the observations discussed in Section 3.1, we performed EIS measurements on the DSCs. Fitted parameters for multiple DSCs are presented in Supplementary Table S2, and average values [39] are given in Table 3. Only the average values will be used for data comparison in the following discussion. For fitting experimental EIS data, the electric circuit model shown in Supplementary Figure S1 was used. The model includes transmission line impedance and Nernst diffusion impedance represented by a Warburg impedance. EIS data give insight into interfacial electronic processes. The electron lifetime ($\tau_e$), transport time ($\tau_t$), and diffusion length ($L_d$) indicate the efficiency of electron collection on the back-side of the photoanode and contribute to the values of $J_{SC}$. Diffusion resistance ($R_d$) in the electrolyte is correlated to the mass transport of the redox species.

As expected, the series resistance, $R_S$, stays constant for all the DSCs. The resistance ($R_{Pt}$) and capacitance ($C_{Pt}$) of the counter electrodes are also invariant, except for cells which have HMII and HDMII ILs. These DSCs have the highest $R_{Pt}$ values (12 and 9 $\Omega$, respectively), and this can also be seen in the Bode plots (Figure 3, high frequency region). The differences in $R_{Pt}$ may be a result of different interfacial contact between the platinum layer and the electrolyte. The variation in $ff$ values (Table 2) may have a similar origin [42]. The process of catalytic I$_3^-$ reduction at the counter electrode is associated with a voltage loss due to overpotential, and this can cause a decrease in the fill-factor [43].
| Electrolyte Name | $R_{\text{rec}}/\Omega$ | $C_\mu/\mu\text{F}$ | $R_\mu/\Omega$ | $\tau/\text{ms}$ | $\tau/\text{ms}$ | $L_d/\mu\text{m}$ | $R_d/\Omega$ | $R_S/\Omega$ | $R_{\text{Pt}}/\Omega$ | $C_{\text{Pt}}/\mu\text{F}$ |
|-----------------|-------------------------|----------------------|----------------|----------------|----------------|-----------------|---------------|-------------|-----------------|----------------|
| DMII            | 113                     | 413                  | 26             | 47             | 10             | 26              | 15            | 10          | 4              | 6             |
| EMII            | 202                     | 1531                 | 2              | 319            | 3              | 137             | 28            | 11          | 6              | 6             |
| PMII            | 229                     | 350                  | 22             | 80             | 8              | 39              | 60            | 11          | 4              | 6             |
| BMII            | 186                     | 350                  | 27             | 66             | 8              | 36              | 47            | 13          | 6              | 5             |
| HMII            | 397                     | 2678                 | 1              | 3991           | 3              | 240             | 80            | 11          | 12             | 6             |
| BDMII           | 240                     | 1166                 | 2              | 282            | 3              | 124             | 20            | 12          | 6              | 5             |
| PDMII           | 230                     | 450                  | 9              | 103            | 4              | 60              | 49            | 13          | 7              | 5             |
| BDMII           | 240                     | 352                  | 25             | 85             | 9              | 37              | 26            | 12          | 9              | 6             |

1 $R_{\text{rec}}$ = recombination resistance; $C_\mu$ = chemical capacitance; $R_\mu$ = transport resistance; $R_S$ = series resistance; $R_{\text{Pt}}$ = resistance of the counter electrode; $C_{\text{Pt}}$ = capacitance of the counter electrode; $R_d$ = diffusion resistance; $L_d$ = diffusion length; $\tau_1$ = transport time; $\tau$ = electron lifetime.

Table 3. Average EIS parameters for DSCs with 0.10 M I$_2$ in electrolytes. See Table S2 for all data.

The transport of the components of the redox shuttle through the electrolyte medium is diffusion-driven and of key importance for efficient DSC performance [44]. High I$^-$ concentrations are required for rapid dye regeneration. As the I$^-$ concentration is always significantly greater than I$_3^-$, the I$_3^-$ concentration becomes rate limiting for mass transport in DSCs [35,43]. However, and in contrast to this, an excess of I$_3^-$ may lead to an increase in recombination processes at the photoanode. In addition to these effects, the I$_3^-$ ion has an absorption maximum around 360–380 nm in MPN [45], and leads to increased light absorption, but no electron injection [43]. In the Nyquist plots in Figure 4, the electrolyte contribution is observed in the low frequency region, and the counter electrode contribution in the high frequency region (expansion inset in Figure 4). The diffusion resistance $R_d$ in the electrolyte allows us to probe the electron transfer at the counter electrode and should be considered together with the charge transfer resistance $R_{\text{Pt}}$. The overall trend can be described as longer alkyl chains introduced into the IL correspond to higher $R_d$ values (15 $\Omega$ for DMII compared to 80 $\Omega$ for HMII, Table 3). The exception is BMII, the average $R_d$ value for which falls between those of EMII and PMII. The highest diffusion resistance corresponds to the highest $R_{\text{Pt}}$ value for the HMII electrolyte (Table 3). For ILs with an additional methyl group (PDMII, BDMII, and HDMMII), the average $R_d$ values are in the range of 20–49 $\Omega$ (Table 3), with the highest diffusion resistance corresponding to the BDMII electrolyte. Interestingly, this did not affect $R_{\text{Pt}}$, the value of which is comparable to other sets of DSC.
Another important parameter, which varies between cells, is the electron lifetime, $\tau$. The longest $\tau$ values are observed for DSCs containing HMII in the electrolyte, and the shortest for the DMII electrolyte (Table 3 and Supplementary Table S2). The tendency for changes in $\tau$ is illustrated in the low frequency region of the Bode plots in Figure 3, since $\tau$ is inversely related to the maximum frequency [43,46]. The trends in electron lifetime are in agreement with the transport time, $\tau_\text{tr}$, which must be lower than $\tau$ in order to ensure that there is effective transport of electrons through the TiO$_2$ semiconductor [44]. The diffusion length, $L_d$, is another crucial parameter for efficient electron transport in the semiconductor and should be longer than the active layer thickness [47]. For all electrolytes, $L_d$ is longer than the TiO$_2$ layer thickness ($\approx 12 \mu$m) and follows the trend in $\tau$ for all electrolytes.

A trend similar to that for $\tau$ is observed for both the chemical capacitance, $C_{\mu}$, and the recombination resistance, $R_{\text{rec}}$. These trends are as expected, because $\tau$ is directly related to $C_{\mu}$ and $R_{\text{rec}}$ [43]. The increase in $R_{\text{rec}}$ (Table 2) upon going from DMII (113 $\Omega$) to HMII (397 $\Omega$) is observed in both the Bode and Nyquist plots (Figures 3 and 4). The variation in the average values of $R_{\text{rec}}$ for the other ILs is not significant [39] and has no meaningful impact on the performance of the DSCs (Table 2).

The values of the chemical capacitance, $C_{\mu}$, are comparable for all DSCs, except for devices containing EMII, HMII and PDMII (Table 3 and Supplementary Table S2). Use of EMII and PDMII leads to remarkably high $J_{\text{SC}}$ values (~3.50 mA cm$^{-2}$), but all three sets have rather low values of $V_{\text{OC}}$ (146–201 mV) in agreement with the chemical capacitance data. Overall, this results in low photoconversion. Interestingly, these cells also have low values of transport resistance $R_d$. For the other electrolytes, $R_d$ is in the range of 22–27 $\Omega$ except for BDMII, which has an average value of 9 $\Omega$.

The increase in I$_2$ concentration in the electrolyte from 0.05 M to 0.10 M resulted in different impedance responses as seen by comparing the entries in Tables 3 and 4. While $R_{\text{Pt}}$ and $C_{\text{Pt}}$ stay constant, the diffusion resistance showed significant differences for all ILs as the I$_2$ concentration increased. The decrease in $R_{\text{rec}}$ for DMII and EMII brought a beneficial impact to $J_{\text{SC}}$ (Figure 2). For the EMII electrolyte, the large increase in chemical capacitance as well as a decrease in $R_{\text{tr}}$ are responsible for the higher $J_{\text{SC}}$. Unfortunately, the beneficial changes in $C_{\mu}$ typically resulted in a decrease in $V_{\text{OC}}$. In the case of electrolytes with PMII and BMII, an increase in the I$_2$ concentration resulted in increased values of $R_{\text{rec}}$, and therefore lower $J_{\text{SC}}$ (Figure 2). For the BMII electrolyte, a slight increase in $ff$ is observed. However, the increase in chemical capacitance for HMII from 311 $\mu$F (Table 4) to 2678 $\mu$F (Table 3) is followed by an increase in $R_{\text{rec}}$. The values of $ff$ decreased by a factor of two [25]. At the same time, a significant increase in $R_d$ from 18 to 80 $\Omega$ is seen.
Table 4. EIS parameters for DSCs containing electrolytes with 0.05 M $I_2$ 1.

| Electrolyte Name | $R_{rec}/\Omega$ | $C_{\mu}/\mu F$ | $R_{tr}/\Omega$ | $\tau_f/\mu m$ | $L_d/\mu m$ | $R_d/\Omega$ | $R_s/\Omega$ | $R_{Pd}/\Omega$ | $C_{Pt}/\mu F$ |
|------------------|------------------|-----------------|----------------|----------------|-------------|-------------|-------------|----------------|-------------|
| DMII             | 313              | 508             | 16             | 164            | 7           | 67          | 43          | 12             | 5           |
| EMII             | 315              | 468             | 16             | 148            | 8           | 55          | 36          | 12             | 7           |
| PMII             | 316              | 323             | 18             | 44             | 5           | 36          | 10          | 13             | 9           |
| BMII             | 152              | 358             | 12             | 55             | 4           | 46          | 10          | 14             | 9           |
| HMII             | 169              | 311             | 40             | 53             | 12          | 26          | 18          | 13             | 11          |

1 Average values have been calculated from data in reference [25].

Overall, the increase in $I_2$ concentration led to noteworthy changes, not only in the $I-V$ plots for all ILs (see Supplementary Figures S2 and S3), but also in the impedance. The most beneficial changes were observed for DMII. Interesting trends were seen for electrolytes containing EMII, HMII, and PDMII ILs with a radical increase in chemical capacitance values. Moreover, it was noticed that the structure of the IL had an impact on the electrolyte/counter electrode interface, what results in different trends in $R_{Pt}$.

3.3. Further Iodine Concentration Investigations for Electrolytes With DMII, EMII and PDMII ILs

Based on the results described above, three ILs (DMII, EMII and PDMII) were selected for an in-depth investigation of the effects of different $I_2$ concentrations. As well as 0.02 and 0.20 M $I_2$, we included electrolytes in which no $I_2$ was added to the initial electrolyte. These electrolytes were colorless when they were introduced to the DSC. Each electrolyte in Table 5 contains an excess of $I^-$ from a combination of the imidazolium iodide salts and LiI. Regeneration of the dye from its oxidized form by reaction with $I^-$ converts $I^-$ to $I_3^-$ (Equations (1) and (2) in the Introduction), and therefore the DSC is expected to operate without explicit addition of $I_2$ [48]. Sets of multiple DSCs were fabricated with electrolytes having the compositions shown in Table 5. The parameters for fully-masked DSCs are given in Supplementary Table S3, and average values are presented in Table 6.

Table 5. Electrolyte compositions with different $I_2$ concentrations and DMII, EMII or PDMII IL. The solvent was MPN in all electrolytes.

| Electrolyte Name | Concentration of IL/M | LiI/M | $I_2$/M |
|------------------|----------------------|-------|---------|
| DMII_b           | 0.60                 | 0.18  | none added |
| DMII_c           | 0.60                 | 0.18  | 0.02    |
| DMII_d           | 0.60                 | 0.18  | 0.20    |
| EMII_b           | 0.60                 | 0.18  | none added |
| EMII_c           | 0.60                 | 0.18  | 0.02    |
| EMII_d           | 0.60                 | 0.18  | 0.20    |
| PDMII_b          | 0.60                 | 0.18  | none added |
| PDMII_c          | 0.60                 | 0.18  | 0.02    |
| PDMII_d          | 0.60                 | 0.18  | 0.20    |

Table 6. Average values of the parameters for fully-masked DSCs using electrolytes with the compositions detailed in Table 5. See Table S3 in the Supporting Materials for all data.

| Electrolyte Name | $J_{SC}/mA cm^{-2}$ | $V_{OC}/mV$ | $\eta/%$ | Rel.$\eta/%$ 1 |
|------------------|----------------------|-------------|----------|---------------|
| DMII_b           | 3.13                 | 297         | 51       | 0.47          | 7.4           |
| DMII_c           | 3.17                 | 300         | 55       | 0.52          | 8.2           |
| DMII_d           | 2.76                 | 278         | 60       | 0.46          | 7.2           |
| EMII_b           | 3.32                 | 286         | 50       | 0.48          | 7.4           |
| EMII_c           | 3.10                 | 290         | 56       | 0.50          | 7.9           |
| EMII_d           | 2.56                 | 272         | 64       | 0.45          | 7.0           |
| PDMII_b          | 3.56                 | 317         | 43       | 0.49          | 7.7           |
| PDMII_c          | 3.22                 | 277         | 58       | 0.52          | 8.1           |
| PDMII_d          | 2.59                 | 278         | 64       | 0.46          | 7.2           |

1 Relative to an N719-sensitized DSC efficiency of 6.41% (average of two cells each with $\eta = 6.41\%$).
Irrespective of the IL, the same trend in $\eta$ is observed upon going from electrolytes without $I_2$ to 0.02 M and to 0.20 M $I_2$. For electrolytes without iodine, the lowest fill factor values were measured. Higher $I_2$ concentration led to an increase in $\eta$ values. The most significant changes occurred in the PDMII systems. An overall picture is gained from inspection of Figure 5 which combines data from Tables 2 and 6, and average values calculated from data in reference [25] for 0.05 M $I_2$.

Figure 5. Values of the average fill factor values for fully-masked DSCs with different ILs in the electrolyte and different concentrations of $I_2$.

Supplementary Figure S4 summarizes the variation in average values of $J_{SC}$, $V_{OC}$ and photoconversion efficiencies relative to the reference DSCs with N719, for $I_2$ concentrations from 0 to 0.20 M (Tables 2 and 6, and averages calculated from our previous study [25]). The trends are not clear cut, but we conclude that too high an $I_2$ concentration (0.20 M) is detrimental to performance, while 0.10 M $I_2$ leads to high $J_{SC}$, irrespective of IL, but to low $V_{OC}$ when the IL is EMII or PDMII. The greatest efficiency difference is observed for 0.05 and 0.10 M $I_2$ in PDMII based electrolytes with $\eta = 0.65\%$ (11.6 % relative to N719) and $\eta = 0.25\%$ (3.8% relative to N719), respectively. Figure 6 illustrates the $J-V$ curves for all cells with the PDMII_b, PDMII_c, and PDMII_d electrolytes, demonstrating the reproducibility of the trends in performance.

Figure 6. $J-V$ curves for multiple, masked DSCs with electrolytes PDMII_b (no added $I_2$), PDMII_c (0.02 M $I_2$) and PDMII_d (0.20 M $I_2$).

3.4. EIS Measurements of DSCs With 0.20 M, 0.02 M and No $I_2$ in the Electrolytes

EIS measurements were conducted for DSCs in which the electrolytes contained the ILs DMII, EMII, or PDMII with either no added $I_2$, or 0.02, or 0.20 M $I_2$ (for complete electrolyte compositions, see Table 5). The impedance was measured for multiple DSCs and the fitted parameters are given in Supplementary Table S4. Average values are given in Table 7 and these will be used in the following discussion.

The series resistance, $R_S$, remains constant for all the DSCs, as do values of $C_{Pt}$ for the platinum counter electrode. Independent of the structure of the IL, the DSCs without iodine have the greatest $R_P$ and $R_d$ values that increase upon going from DMII to EMII to PDMII ILs. This can be illustrated with the Nyquist plots as the changes along the real ($Z'$) axis indicate the changes in the diffusion resistance (Supplementary Figures S5–S7). With the addition of 0.02 M $I_2$, a decrease is observed for both parameters. A further increase of $I_2$
concentration to 0.20 M is followed by a decrease in the values of $R_{Pt}$ and $R_d$. The trend in resistance at the counter electrode is inversely proportional to the trend in the fill factor, and the lowest values of $ff$ (Table 6) correspond to electrolytes without added I$_2$. The variation in $R_{Pt}$ can be illustrated with the help of a Bode plot (Figure 7). The shift of the right-hand peak in each of Figure 7a–c from lower to higher frequencies upon going from 0.00 to 0.20 M I$_2$ is attributed to a decrease in the charge transfer time [49], and is observed for each of the ILs. The structure of the IL also influences the EIS response for the DSCs. Thus, DSCs with an electrolyte with no added I$_2$ and with methyl substituents in the IL (DMII) has a lower $R_d$ than cells containing the electrolyte EMII_b (120 and 138 $\Omega$, respectively, Table 7). Increasing the length of the substituent chain from EMII_b to PDMII_b increases $R_d$ further to 256 $\Omega$. On the other hand, DSCs with the electrolytes PDMII_d and EMII_d (0.20 M I$_2$) show lower $R_d$ values of 10 $\Omega$ compared to 24 $\Omega$ for DMII_d (Table 7).

Table 7. Average values of the EIS parameters for DSCs with 0.00, 0.02 and 0.20 M I$_2$ in the electrolytes. The electrolyte compositions are defined in Table 5.

| Electrolyte Name | $R_{rec}/\Omega$ | $C_v/\mu F$ | $R_0/\Omega$ | $\tau/\mu s$ | $\tau_f/\mu s$ | $L_d/\mu m$ | $R_d/\Omega$ | $R_g/\Omega$ | $R_{Pt}/\Omega$ | $C_{Pt}/\mu F$ |
|------------------|------------------|-------------|--------------|--------------|--------------|-------------|--------------|--------------|----------------|---------------|
| DMII_b           | 243              | 517         | 7            | 127          | 3            | 72          | 120          | 13           | 24             | 7             |
| DMII_c           | 269              | 626         | 7            | 168          | 5            | 83          | 40           | 12           | 19             | 6             |
| DMII_d           | 149              | 357         | 12           | 53           | 4            | 43          | 24           | 11           | 4              | 6             |
| EMII_b           | 192              | 697         | 10           | 133          | 7            | 55          | 138          | 12           | 33             | 8             |
| EMII_c           | 237              | 618         | 7            | 147          | 4            | 73          | 32           | 13           | 12             | 6             |
| EMII_d           | 109              | 189         | 60           | 21           | 11           | 16          | 10           | 12           | 3              | 8             |
| PDMII_b          | 233              | 1294        | 11           | 300          | 14           | 57          | 256          | 13           | 44             | 8             |
| PDMII_c          | 168              | 340         | 24           | 57           | 8            | 32          | 21           | 11           | 20             | 6             |
| PDMII_d          | 121              | 193         | 62           | 23           | 12           | 17          | 10           | 11           | 5              | 7             |

Figure 7. EIS Bode plots for DSCs with (a) electrolytes with DMII IL, (b) electrolytes with EMII, and (c) electrolytes with PDMII. Solid lines represent fitted curves, and circle represent experimental data. The yellow colour corresponds to electrolytes with no added I$_2$, dark blue to electrolytes with 0.02 M I$_2$, and purple to 0.20 M I$_2$.

The diffusion length $L_d$ was also affected by changes in the electrolyte compositions. In the case of the DMII family, DSCs containing electrolytes without added I$_2$ or with 0.02 M I$_2$ (DMII_b and DMII_c in Table 7) have a higher $L_d$, at least by a factor of six, than the active layer thickness $d$ ($d \approx 12 \mu m$). For DMII_d, a significant decrease was observed,
but still, the diffusion length is almost four times longer than the thickness of the TiO₂ layer. In the case of cells containing EMII, the highest diffusion lengths are again observed for electrolyte with no added I₂ or 0.02 M I₂ (Table 7). Increasing the I₂ concentration to 0.2 M resulted in a short L_d of 17 µm, which is comparable to the semiconductor thickness. This trend is also seen for DSCs in which the electrolyte contained the IL PDMII (Table 7). However, when L_d becomes shorter than the active layer thickness, the so-called Gerischer impedance (Z_C) overtakes the diffusion-recombination impedance model [47]. Typically, when a large recombination rate is observed, the diffusion–recombination impedance needs to be changed to the Gerischer impedance [30]. In this case, the transport resistance R_tr becomes significantly larger than the recombination resistance R_rec and the recombination time is shorter than the diffusion time through the active layer [30,51]. Practically, R_rec, R_tr, and C_µ parameters cannot be extracted in the presence of Z_C (L_d ≈ d) and L_d of ≈ 0.5d is the limit to obtain them. Thus, the diffusion-recombination impedance model used in this study is suitable for EIS fitting despite comparable values of L_d and d for EMII_d and PDMII_d electrolytes. At the same time, the shapes of the experimental curves for EMII_d and PDMII_d also change in the Z_C direction (Figures 8 and 7b,c). The effect is particularly seen for the EMII_d electrolyte (Figure 7b, EMII_d).

![Figure 8. The Nyquist plot with high frequency region expansion of the DSCs with DMII_d, EMII_d and PDMII_d electrolytes to demonstrate the change in spectra profile depending on IL structure.](image)

For all DSC sets, the electron lifetime significantly decreased from the electrolyte with no added I₂ to 0.20 M I₂. This trend can be seen in the Bode plots with the shift of the left-hand peaks to higher frequencies (Figure 7) and this is particularly noticeable for the DSCs containing PDMII (Figure 7c). Nevertheless, τ is considerably larger than τ_i for all electrolytes. The transport resistance, R_tr, increases for all electrolyte families upon going from no added I₂ to 0.20 M I₂. Interestingly, the lowest R_tr for electrolytes containing 0.20 M I₂ is observed for DMII (12 Ω, Table 7), indicating an efficient transport compared to that in ILs EMII and PDMII (60 Ω, Table 7).

The lowest values of chemical capacitance as well as recombination resistance are observed for all electrolytes when the I₂ concentration is 0.20 M (Table 7). The remarkably high C_µ for PDMII_b is consistent with the observed high values of J_SC (Table 6 and Supplementary Table S4). The dramatic fall in C_µ upon going from electrolyte PDMII_c to PDMII_d (Table 7) has a response in lower J_SC for this electrolyte. The recombination resistance follows the C_µ trend and supports the observed changes in values of J_SC. From EMII_b to EMII_c, the fluctuation in C_µ is not substantial, but in combination with an increase in R_rec results to lower J_SC. Upon going to EMII_d with 0.20 M I₂, R_rec and C_µ both decrease and lead to a consistent drop in J_SC. In the case of the DMII series, a drop in both R_rec and C_µ is observed as the concentration of I₂ is increased and this is consistent with a decrease in J_SC values (Tables 6 and 7, respectively).
Overall, changes in the I$_2$ concentration significantly influence most of the electronic processes in the DSCs, irrespective of the ionic liquid. The main trends were observed for resistance in the electrolyte, counter electrode resistance, transport resistance, and electron diffusion length in the semiconductor.

4. Conclusions

We have investigated the effect of changing the I$_2$ concentration in the electrolyte in DSCs sensitized with the Fe(II)-NHC dye 1 and containing the I$^-$/I$_3^-$ redox shuttle and different ILs. Either no I$_2$ was added to the initial electrolyte, or the initial concentrations were 0.02, 0.10, and 0.20 M. The study complements our earlier investigations where the electrolyte composition was LiI (0.18 M), I$_2$ (0.05 M), and PDMII (0.60 M) in MPN as solvent [25]. In the operating DSC, the IL has an influence on the TiO$_2$/electrolyte and electrolyte/counter-electrode interfaces. According to the EIS and J-V measurements, it was shown that the structure of the IL influences various parameters including the diffusion resistance in the electrolyte, resistance at the counter electrode and the charge diffusion in the semiconductor. Values of $J_{SC}$, $V_{OC}$, and the fill factor were influenced by changes in the I$_2$ concentration for all ILs used in this study. The most dramatic changes were observed when the IL was HMII, and the poor performances of these DSCs arose from low $V_{OC}$ and low fill factors. The limiting processes correlated to increased electrolyte diffusion resistance and charge transfer resistance at the platinum counter electrode. Interestingly, DSCs containing the ILs with the shortest alkyl-chains (DMII and EMII) showed an increase in $J_{SC}$ upon going from 0.05 to 0.10 M I$_2$ compared to ILs with longer side chains.

In the case of the ILs DMII, EMII, and PDMII, it was shown that cells in which there was no added I$_2$ or a concentration of I$_2$ lower than 0.05 M I$_2$ exhibited the lowest values of the transport resistance in the photoanode semiconductor. At the same time, higher I$_2$ concentrations led to a decrease in diffusion resistance in the electrolyte as well as in the platinum counter electrode resistance. The electron lifetime and diffusion length were also affected by the I$_2$ concentration, and the values decreased upon going from no added I$_2$ to 0.20 M I$_2$. A similar trend is observed in $J_{SC}$ for DMII, EMII and PDMII ILs. Considering all aspects in this study, DMII was the best performing IL, not only in terms of $\eta$, but it also had the most promising impedance profile. A combination of DMII and 0.1 M I$_2$ in the electrolyte produced the best performing DSCs with $\eta$ values in the range 0.62–0.67%, which correspond to 10.0–10.8% of the photoconversion efficiency observed for DSCs sensitized by N719. Despite the high values of $J_{SC}$ and $V_{OC}$ in DSCs with DMII where no I$_2$ was added to the initial electrolyte, these cells, as anticipated, suffered from low ff values, and consequently low $\eta$.

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/ma14113053/s1, Table S1: Parameters for sets of multiple, fully-masked DSCs using electrolytes with different ionic liquids, and electrolyte composition of LiI (0.18 M), I$_2$ (0.10 M), IL (0.60 M) in MPN; for PDMII$_a$: LiI (0.18 M), I$_2$ (0.10 M), PDMII (0.60 M). Table S2: EIS parameters for all DSCs with 0.10 M I$_2$ in the electrolytes; Table S3: Parameters for sets of multiple, fully-masked DSCs using electrolytes with the compositions detailed in Table S5; Table S4: EIS parameters for DSCs with 0.00, 0.02 and 0.20 M I$_2$ in the electrolytes. The electrolyte compositions are defined in Table S5; Figure S1: The equivalent circuit model used in the EIS study. This includes a series resistance ($R_s$), a resistance ($R_{ohm}$) and a constant phase element (CPE1) to model a counter electrode, an extended distributed element (DX1) to represent the mesoporous TiO$_2$/electrolyte interface as a transmission line model, and a Warburg element (Ws1), which represents the diffusion of the electrolyte; Figure S2: $J$-$V$ curves for DSCs containing electrolytes with different ionic liquids (see Scheme 2 for abbreviations) and 0.05 M I$_2$ in the initial electrolyte; Figure S3: $J$-$V$ curves for DSCs containing electrolytes with different ionic liquids (see Scheme 2 for abbreviations) and 0.10 M I$_2$ in the initial electrolyte; Figure S4: Average values of (a) $J_{SC}$, (b) $V_{OC}$ and (c) $\eta$ (relative to N719) for masked DSCs with different ILs and I$_2$ concentrations in the electrolytes; Figure S5: EIS Nyquist plots for DSCs with electrolytes with DMII IL. Solid lines represent fitted curves, and circle represent...
experimental data. The yellow colour corresponds to electrolytes with no added I$_2$, dark blue to electrolytes with 0.02 M I$_2$, and purple to 0.20 M I$_2$; Figure S6: EIS Nyquist plots for DSCs with electrolytes with EMII IL. Solid lines represent fitted curves, and circle represent experimental data. The yellow colour corresponds to electrolytes with no added I$_2$, dark blue to electrolytes with 0.02 M I$_2$, and purple to 0.20 M I$_2$; Figure S7: EIS Nyquist plots for DSCs with electrolytes with PDMII IL. Solid lines represent fitted curves, and circle represent experimental data. The yellow colour corresponds to electrolytes with no added I$_2$, dark blue to electrolytes with 0.02 M I$_2$, and purple to 0.20 M I$_2$

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