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Low Toxicity Functionalised Imidazolium Salts for Task Specific Ionic Liquid Electrolytes in Dye-Sensitised Solar Cells: A Step Towards Less Hazardous Energy Production.

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Abstract:

Novel solvent free Task Specific Ionic Liquid (TSIL) electrolytes for dye sensitised solar cells (DSSC) were synthesised and tested. Of great concern is the replacement of low-moderate toxicity second generation ILs, with high toxicity third generation TSILs. As most 1-Butyl-3-methylimidazolium (Bmim) and especially 1-Ethyl-3-methylimidazolium (Emim) based ILs have low toxicity, the designing of replacement TSILs of comparable toxicity is a challenge. Structural features of TSIL investigated herein were incorporation of heteroatoms into the side chain of imidazolium cations (i.e. ether, ester and amide) and anion (bromide, iodide, and triflimide [NTf_2]). Preliminary toxicity screening against 20 microorganisms (8 bacteria and 12 fungi) found that all ILs, imidazolium salts, *N*-butylbenzimidazole (NBB) and guanadinium thiocyanate (GNCS) do not exhibit high antimicrobial toxicity. However NBB and a pentyl ester substituted IL displayed moderate toxicity to several strains of bacteria and fungi. Further toxicity testing to establish IC_{50} values shows several novel TSIL compounds and imidazolium salts are in fact less toxic to microorganisms (e.g. bacteria) than commonly used 1-ethyl-3-methylimidazolium iodide (EmimI) and 1,3-Dimethylimidazolium iodide (DmimI). We have demonstrated that the presence of ether and either ester or amide groups in the structure of the cation of the TSIL and imidazolium salts reduces antimicrobial toxicity, which is consistent with the lowering of the lipophilicity of ILs. Iodide and bromide analogues have lower toxicity than the NTf_2 examples in this study. The DSSC performance using these "greener" ILs in place of the standard EmimI compare quite favourably. Two low antibacterial toxicity iodide examples exhibit photocurrents of 9.27 mA/cm^2 and 8.85 mA/cm^2, respectively, achieving promising efficiencies of 3.39 % and 3.31 %, respectively (EmimI = 4.94 %). DSSC performance is further improved by 15 % minimum to 66 % maximum, depending on IL chosen, by the presence of small amounts of moisture and DSSCs employing a low antibacterial toxicity iodide TSIL or imidazolium salt can surpass the performance of dry EmimI. Of note the DSSC containing TSIL NTf_2 examples, performed poorly compared to the halide analogues, with the outcome that the most toxic TSILs under investigation are also the least preferred based on performance.

Introduction

Over the last decade, Ionic Liquids (ILs) have been extensively investigated as potential replacements for volatile organic compounds (VOCs) for use as (*inter alia*) as tuneable reaction media.[1] Much of this interest has been focussed on the development of ILs as alternative, 'green' materials; with applications in processes as diverse as ionic compressors, the BASIL™ process and electroplating.[1q] Immense interest in the environmental impact of ILs[2] has led to a plethora of papers dealing with three assays: 1) their toxicity[3] (for example antibacterial and antifungal),[4] 2) the importance of biodegradation studies[5] (something only recognised since 2002),[6] and recently 3) bioaccumulation and metabolite identification studies.[7]

The design of a 'green' compound, be it as a solvent,[1] reagent or catalyst[8] should ideally address issues such as low toxicity and ready biodegradability without the generation of toxic, persistent metabolites. *Of equal importance is the functional performance of the environmentally benign material*. The decision to replace a 'toxic' chemical with a 'greener' alternative is easier if a performance benefit is also attained. The role of a green chemist (in our view) is to make this decision as easy as possible and to avoid the 'gray area' where environmental protection comes at a performance cost. One application of ILs is a solvent in electrolytes for dye sensitised solar cells (DSSC).[1s, 1t]

A typical DSSC consists of a TiO_2 layer electrode chemisorbed with a monolayer of dye molecules absorbing the visible light spectrum. Up on absorbing light the excited dye injects electrons into the conduction band of the TiO_2, which are then routed through an external circuit and a counter electrode into an electrolyte containing a suitable redox species (typically, iodide/tri-iodide couple). The electrolyte is an essential component, performing charge transport between the two electrodes. Iodide/triiodide electrolytes are the best performing examples utilising volatile solvents (e.g. >11 % power conversion efficiency achieved in acetonitrile/valeronitrile)[9,10], with the current DSSC record of 12.3 % efficiency which involves a $Co^{(II/III)}$tris(bipyridyl) tetracyanoborate complex as the redox couple in acetonitrile.[11] A significant problem of DSSC sealant failure occurs facilely due to the volatile organic solvent's large vapour pressures. Electrolytes with very low vapour pressures can be envisaged from ILs or eutectic melts of ionic compounds. These classes of salts solve this problem, to a significant extent, and show excellent stability under light soaking at 60°C for up to 1000 h.[12, 13] Record efficiencies of 8.2 %[13] and 7.6 %[12] are achieved with DmimI

/EmimI/EMITCB/I_2/NBB/GNCS eutectic melt and PMII/EMITCB/I_2/NBB/GNCS, respectively.

The design of ILs has progressed through three generations.[1] The first generation included examples with reactive and/or water sensitive cations? (e.g. $AlCl_4^-$ salts). Stability was improved in the second generation (e.g. $BMIMBF_4$ and BMIMOAc), while TSILs (Task Specific Ionic Liquids) are the third generation. When conventional electrolyte media were replaced with second generation ILs, discussion about IL toxicity, ecotoxicity and biodegradation was often lacking. This is more apparent with third generation TSILs and their role in DSSCs, where toxicity data for novel 'tailored' ILs is often not reported as a part of the green chemistry assessment. As ILs are considered as a 'greener' alternative to conventional solvents, it is important to investigate the toxicity and ecotoxicity of these chemicals on ecological systems and the fate of ILs due to potential accidental release or other exposures to environment.[14] Of great concern is the replacement of low-moderate toxicity second generation ILs, with high toxicity third generation TSILs. As most Bmim and especially Emim based ILs have low toxicity, the challenge of designing replacement TSILs of comparable toxicity is great. Antimicrobial toxicity studies have been previously proposed by several groups (including Gathergood[4,6,15] and Stephens[16]) as the starting point for screening ILs, due to the high toxicity of many analogous Quarternary Ammonium Compounds (QACs), especially surfactants.[3c,17,18] Antibacterial and antifungal toxicity studies of novel ILs are a rapid and convenient approach to investigate the IL effect on microorganisms important to our natural environment.

In this study, we have designed novel ester and amide based ILs with two aims 1) efficient synthesis of third generation TSILs containing functional groups known to reduce antimicrobial toxicity;[4,6,15,16] and 2) study the effect on DSSC properties of replacing a second generation IL with a low antimicrobial toxicity third generation TSIL. The attempts to eliminate liquid or gel electrolytes completely from high performance and stable DSSC is not yet successful. Therefore, first generation commercial DSSC, which requires good stability, will rely mostly on IL based electrolytes and hence its toxicity and environmental acceptance assumes utmost importance. As the introduction of heteroatoms into the IL structure is fundamental to lowering antimicrobial toxicity, we can assess the effect due to the presence of these H-bond donor/acceptor groups on DSSC performance.

Experimental

IL Synthesis

All starting chemicals were purchased from Sigma Aldrich, with the exceptions of lithium *bis*(trifluoromethanesulfonyl) imide ($LiNTf_2$) which was obtained from Solvionic. Methanol, hexane and triethylamine were dried over molecular sieves, diethyl ether was dried over sodium metal wire, Dichloromethane (DCM) was dried over calcium hydride. All dry solvents were distilled before use. Riedel de Haën silica gel was used for flash and thin layer chromatography. Sodium carbonate, ammonium chloride, calcium chloride anhydrous were obtained from Riedel de Haën and magnesium sulphate heptahydrate from Fluka.

ILs: 1,3-Dimethylimidazolium iodide (**1**, DmimI), 1-ethyl-3-methylimidazolium iodide (**2**, EmimI), 1-ethyl-3-methylimidazolium tetracyanoborate (**3**, EMTCB), and *N*-butylbenzimidazole (**4**, NBB) were purchased from Merck as Solarpur grade (>99.5 % by HPLC). Guanadinium thiocyanate (**5**, GNCS) and I_2 were purchased from Sigma-Aldrich.

Eleven ester and amide based imidazolium salts were synthesized according to procedures developed by Gathergood *et al* .[4,15i,19] (Fig. 1, **6-9a**; **6b, 8-9b**, **6-9c**). (See ESI for experimental procedure)

KARL Fischer analysis

Mettler Toledo V20 Compact Volumetric KF Titrator using Hydranal 5 titrant was employed for water content estimation. For each sample, a water content value was obtained by Karl Fischer titration according to the general procedure outlined below:

Solid Samples: 100 mg of the sample to be analysed was weighed on an analytical balance in a weighing boat. The sample was transferred to the automatic titrator's reaction vessel from the weighing boat without the aid of any solvents or spatula to avoid introduction of additional moisture or accidental sample loss *via* the spatula. The weight of the boat after the transfer was recorded to get the exact sample mass used for the analysis. The moisture content results from titration were expressed in %w/w.

Liquid samples: 0.1 mL of the sample to be analysed was drawn into a 1ml syringe and weighed on an analytical balance. The sample was transferred from the syringe to the automatic titrators reaction vessel. The weight of the syringe after the transfer gave the exact sample mass being analysed. The water content results were expressed in %w/w.

Antibacterial Toxicity Screening Procedure (Broad Spectrum):[20]

Three CCM strains (**SA**: *Staphylococcus aureus* CCM 4516, **EC**: *Escherichia coli* CCM 4517, **PA**: *Pseudomonas aeruginosa* CCM 1961) and five clinical isolates (**MRSA**: *Staphylococcus aureus* MRSA H 5996/08, **SE**: *Staphylococcus epidermidis* H 6966/08, **EF**: *Enterococcus sp*. J 14365/08, **KP-E**: *Klebsiella pneumoniae* ESBL J 14368/08, **KP**: *Klebsiella pneumoniae* D 11750/08) were studied from the collection of bacterial strains cultured at the Department of Biological and Medical Sciences, Faculty of Pharmacy, Charles University, Hradec Kralove, Czech Republic. The aforementioned CCM strains also served as the quality control strains.

All the isolates were maintained on Mueller-Hinton dextrose agar prior to being tested. Dimethyl sulfoxide (100 %) served as a diluent for all compounds with the final concentration never exceeding 2 %. Mueller-Hinton agar (MH, HiMedia, adersky-Envitek, Czech Republic) buffered to pH 7.4 (±0.2) was used as the test medium. The wells of the micro-dilution tray contained 200 µL of the Mueller-Hinton medium with 2-fold serial dilutions of the compounds (2000 or 1000 to 0.48 µmol/l) and 10 µL of inoculum suspension. Inoculum in MH medium was prepared to give a final concentration of 0.5 McFarland scale (1.5×10^8 cfu.mL^{-1}). The trays were incubated at 36°C and Minimum inhibitory concentrations (MICs) were read visually after 24 h and 48 h. The MICs were defined as 95 % inhibition of the growth of control. MICs were determined twice and in duplicate. The deviations from the usually obtained values were no higher than the nearest concentration value up and down the dilution scale.

Antifungal Toxicity Screening Procedure (Broad Spectrum):

Four ATCC strains (**CA1**: *Candida albicans* ATCC 44859, **CA2**: *Candida albicans* ATCC 90028, **CP**: *Candida parapsilosis* ATCC 22019, **CK1**: *Candida krusei* ATCC 6258) and eight clinical isolates of yeasts (**CK2**: *Candida krusei* E28, **CT**: *Candida tropicalis* 156, **CG**: *Candida glabrata* 20/I, **CL**: *Candida lusitaniae* 2446/I, **TA**: *Trichosporon asahii* 1188) and filamentous fungi (**AF**: *Aspergillus fumigatus* 231, **AC**: *Absidia corymbifera* 272, **TM**: *Trichophyton mentagrophytes* 445) were studied from the collection of fungal strains cultured at the Department of Biological and Medical Sciences, Faculty of Pharmacy, Charles University, Hradec Králové, Czech Republic. Three of the above ATCC strains (*C. albicans* ATCC 90028, *C. parapsilosis* ATCC 22019, *C. krusei* ATCC 6258) also served as the quality control strains.

All the isolates were maintained on Sabouraud dextrose agar prior to being tested. MICs were determined by the microdilution format of the NCCLS M27-A guidelines.[20] Dimethyl sulfoxide (100 %) served as a diluent for all compounds; the final concentration did not exceed 2 %. RPMI 1640 (Sevapharma, Prague) medium supplemented with L-glutamine and buffered with 0.165 M morpholinepropanesulfonic acid (Serva) to pH 7.0 by 10 N NaOH was used as the test medium. The wells of the microdilution tray contained 100 μL of the RPMI 1640 medium with 2-fold serial dilutions of the compounds (2000 or 1000 to 0.48 μmol/L) and 100 μL of inoculum suspension. Fungal inoculum in RPMI 1640 was prepared to give a final concentration of $5 \times 10^3 \pm 0.2$ cfu.mL^{-1}. The trays were incubated at 35°C and MICs were read visually for filamentous fungi and photometrically for yeasts as an absorbance at 540 nm after 24 h and 48 h. The MIC/IC_{50} values for the dermatophytic strain (*T. mentagrophytes*) were determined after 72 h and 120 h and for *A. fumigatus*, *A. corymbifera* after 24 and 48 h. For all other strains MIC/IC_{80} values were evaluated. The MICs were defined as 50 % or 80 % inhibition of the growth of control. MICs were determined twice and in duplicate. The deviations from the usually obtained values were no higher than the nearest concentration value up and down the dilution scale.

Antibacterial Toxicity Screening method (IC_{50} determination, 5 Strains):

Mueller-Hinton broth was purchased from Oxoid. Five bacteria strains were used in this study: the Gram-positive bacterium *Bacillus subtilis* DSMZ 10 (*B. subtilis*) and the Gram-negative bacteria *Escherichia coli* DSMZ 498 *(E. coli)*, *Pseudomonas fluorescens* DSMZ 270 50090 (*P. fluorescence)*, *Pseudomonas putida* CP1 (*P. putida* CP1) and *Pseudomonas putida* KT2440 (*P. putida* KT2440). All strains were purchased at DSMZ (German Collection of Microorganisms and Cell Cultures).

IC_{50} values for the compounds were determined using a modification of the broth microdilution method described by Amsterdam.[21] Strains were grown in nutrient broth overnight, washed with 0.01 M sodium phosphate buffer (pH 7) and the cell number adjusted to give an optical density reading of 0.07 at 660 nm. The antimicrobial activity of the ILs was tested in 96 well round bottom microplates. 180 μL of Mueller-Hinton broth was pipetted into column 1 of the wells and 100 μL into the other wells. 20 μL of the chemical solution was transferred into column 1 giving a concentration of 200 mM. 100 μL of the solution from

column 1 was then transferred to the next column and mixed. The procedure was repeated to give a series of two-fold dilutions. Each well was inoculated with 5 μL of bacterial culture. Wells containing medium only were used as blanks and wells containing medium and culture only were used as positive controls. All the toxicity tests were carried out in triplicate. The microplates were incubated overnight at 30°C. The presence or absence of growth was determined by measuring the optical density of the wells at a wavelength of 405 nm using a plate reader. The IC_{50} values were determined as the concentration or range of concentrations that caused a 50 % reduction in growth.

Fabrication of DSSC:

Full DSSC fabrication and measurement details are available in Supporting Information (ESI). Briefly, DSSC working electrodes[22,23] (WE) consisted of a compact blocking layer of TiO_2, seven layers of a transparent TiO_2 paste and two layers of a TiO_2 scattering paste followed by a compact TiO_2 over-layer yielding a total TiO_2 thickness of 15 micron, after sintering, with an active area of 0.28 cm^2. The WEs were placed in a dye bath of N719 overnight in order to sensitise the TiO_2 surface. A platinum counter electrode was then sandwiched together with the WE and heat sealed using a Bynel® polymer gasket (50 micron thick). The specified electrolyte was then filled into the space between the two electrodes through a hole in the counter electrode *via* vacuum back filling. The back hole was sealed with a thin piece of glass heat sealed with Bynel®.

Electrolyte Fabrication:

All ILs and imidazolium salts were dried for 24 h under high vacuum (0.05 mBar) and water content determined by Karl Fischer analyses. The electrolyte composition DmimI /X/EMITCB/I_2/NBB/GNCS was prepared in the molar ratio 12/12/16/1.67/3.33/0.67 as a homogenous mixture using the following procedure. Initially, DmimI (**1**) was dissolved in EMITCB (**3**) at 60°C on a hot plate while stirring. After approximately 1 h a clear yellow solution was obtained. Then the respective novel ILs (X = **2**, **6a**-**c** to **9a**-**c**) were added. After 30 min NBB (**4**), GNCS (**5**) and I_2 were added successively when dissolved. A dark red homogenous solution of low viscosity was obtained. All preparation steps were performed under argon atmosphere, since most of the compounds are highly hygroscopic.

Results and discussion

Imidazolium derived ionic liquids were selected for study: 1) due to outstanding performance of this class as electrolytes in DSSC[12,13], and 2) a plethora of toxicity data of imidazolium ILs,[14-18] including known high toxicity for some long alkyl chain examples,[3a,25] thus assisting a 'benign by design' ideal.

Considering the toxicity results of previously reported ILs from our group[4,15i] and Boethling's rules of thumb,[24] we designed ILs herein (Figure 1) which incorporate ester and amide functionalities and additional heteroatoms (e.g. ether groups) in the structure. Long hydrocarbon side chains were avoided as Pernak *et.al.*[3a] and Kanjilal *et. al.*[25] have disclosed that compounds with high antimicrobial toxicity include this structural motif.

7a-**c** was chosen to enable study of the inclusion of an ester group into the alkyl imidazolium substituent, while **6a**-**c** has in addition 2 ether functional groups. ILs **8a**-**c** are amide derivatives with 2 ether groups, and **9a**-**c** incorporate an amide and single ether , conformationally restricted due to 6 membered ring). Iodides (**6c**-**9c**) were selected, so study of the effect of the imidazolium cation (cf Emim Iodide, in high performing DSSC) was possible, while bromide derivatives (**6a**-**9a**) were also prepared as this is a frequently studied alternative in this field of work. NTf_2 examples (**6b**-**9b**) were selected due to the low viscosity observed for this class of ILs and stability in the presence of the iodide/triiodide redox couple, a fundamental component of the DSSC.

The designed ILs (**6a**-**c** to **8a**-**c and 9b**) and imidazolium salts (**9a** and **9c**) were synthesized according to our reported procedures with moderate overall yields (i.e. **6a**-**c** = 47 %, **7a**-**c** = 42 %, **8a**-**c** = 35 %, **9a**-**c** = 39 %).[4,15i,19]

Synthesis of ILs **6a**, **7a** and **8a** were successfully completed according to methods reported in our previous papers[4,15i] whereas novel NTf_2 ILs **6b**, and **8b** were prepared according to other patented procedures.[19] ILs **6a**-**8b** were synthesized in two or three steps: (i) preparation of ester or amide alkylating agent (**10**, 98%;**11** 64%; **12**, 76%) (Fig. 2); (ii) synthesis of bromide IL (**6a**, 90%; **7a** 97%; **8a**, 83%) and (iii) halide anion exchange on reaction with $LiNTf_2$. (**6b**, 80%; **8b**, 74%). (See ESI for experimental procedure)

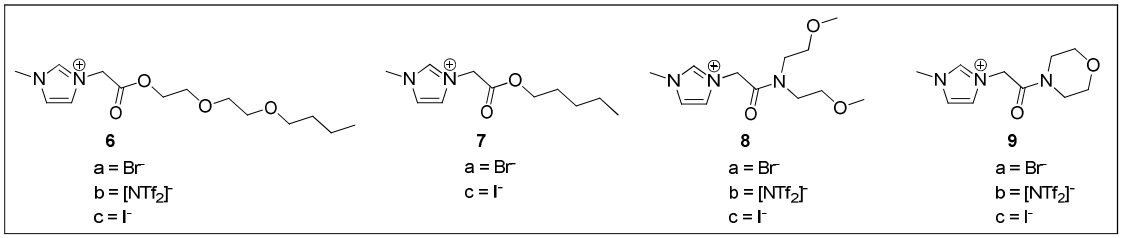


Figure 1: Ester and amide based ILs used for screening in DSSC.

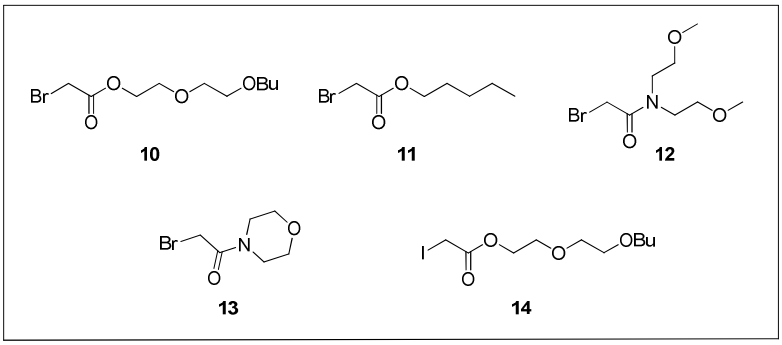
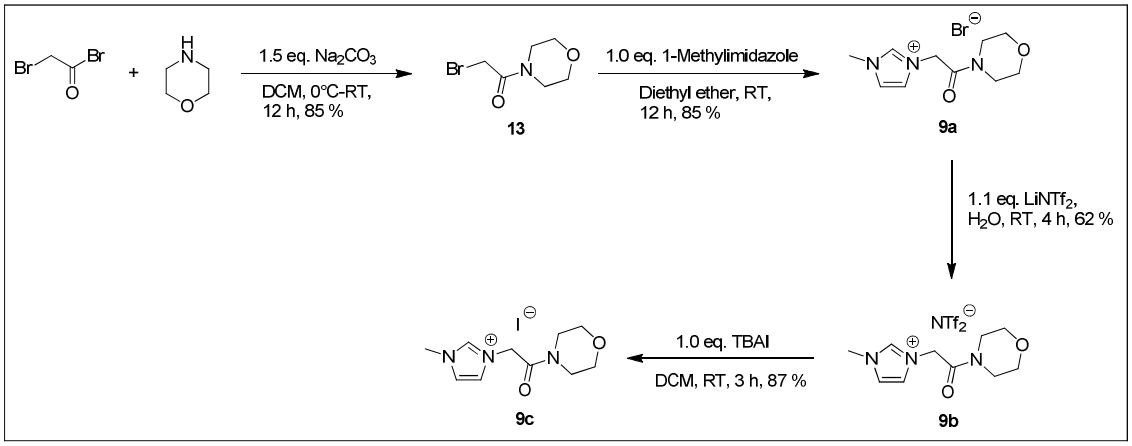


Figure 2: α-Bromoester, α-bromoamide and α-iodoester halide IL precursors.



Scheme 1: Synthesis of IL **9c** from morpholine.

Scheme 1 shows a representative synthesis of the bromide and iodide imidazolium salts and NTf_2 IL, starting with morpholine. α-Bromoamide **13** was formed in good yield (85%) via a condensation reaction of morpholine with bromo acetyl bromide. Synthesis of bromide **9a**, a 100% atom economy[26] addition reaction of methylimidazole and **13**, is achieved in 85% yield. Counterion metathesis with $LiNTf_2$ in water gave the NTf_2 based IL **9b** in 62% yield.

Iodides **6c, 8c** and **9c** were prepared by anion exchange of corresponding [NTf_2] salts (i.e **6b, 8b** and **9b**) respectively on treatment with tetrabutylammonium iodide (TBAI). For the morpholino based imidazolium salt **9c**, the procedure involves addition of a solution of TBAI in dichloromethane to a dichloromethane solution of the [NTf_2] salt **9b**.[27] After stirring the reaction mixture for 3 h at room temperature the product was extracted into an aqueous layer. Removal of water affords the corresponding iodide **9c** in 87 % yield (39 % yield, from α-bromoamide **13**). This procedure has an unsatisfactory high E-factor,[28] therefore, an alternative greener procedure was also developed where the iodide based alkylating agent (**14**) was synthesized from 2-iodoacetyl chloride (yield 68 %), and in the final step the target iodide IL **6c** was prepared from **14**, in 82 % yield.[4] IL synthesis was also demonstrated on a large scale with 155 g (ca 0.2 Mol) of **6b** prepared in 40 % overall yield from the alcohol starting material *via* the alkylating agent **10** = 68 %, Br IL **6a**= 73 %, and NTf_2 IL **6b**= 80 % yield. During the work up, ILs were warmed to 60°C under high vacuum (0.05 mBar) to reduce moisture content.

Karl Fischer analysis:

The lowest water content after drying for 24 h under high vacuum (0.05 mBar) was attained with the commercially available iodides EmimI (**2**) and DmimI (**1**) (200 and 700 ppm, respectively) (Table S1). NBB (**4**) under the same conditions had a water content of 5100 ppm. Novel ILs and imidazolium salts **6-9c** water content after drying was between 1500-6000 ppm, except for **9a** (10700 ppm). Increasing the drying time for **9a** did not further reduce the water content.

No thermal degradation was observed by NMR under these drying conditions. Seo *et. al.* reported the use of peptide based TSILs which were stable up to 200°C in DSSCs.[29] Also no degradation was observed when ester based imidazolium TSILs were screened in DSSCs by Wang *et. al.*[30] By analogy we do not expect significant thermal degradation of ester and amide based TSIL and imidazolium salts (Figure 1) under the test conditions, however, the eutectic mixture may behave differently at elevated temperature in the cell.

3.1 Toxicity:

In our study of DSSCs, we have replaced the 2° generation low-moderate toxicity ILs with 3° generation TSILs which have a comparatively high molecular weight. This is a potential 'catch 22' situation – many TSIL tailored properties are due to the presence of

function group(s) in the side chain, which are either an integral part of the side chain (i.e. amino acid sequence,[15k] or function groups appended to a hydrocarbon chain. If one assumes Emim (or even Bmim) as the model compound for IL studies, addition of functional groups to convert them into TSILs will increase MW. The toxicity of ILs analogues with a long hydrocarbon side chain (i.e. without heteroatoms) were found to exhibit high antimicrobial activity due to high lipophilicity.[3c,18] Hence, by the introduction of heteroatoms into the hydrocarbon alkyl chain, the lipophilicity of ILs is reduced (with expected decrease in antimicrobial toxicity).[4] Our hypothesis was supported by the recent work of Samori *et. al.*[31] , Gathergood and Costa Gomez *et. al.*[5e] who state that 'the lipophilicity of ILs decreases when the alkyl side-chain contain oxygen functionalities, and simultaneously reduces the toxicity of ILs'. **6b** and **7b** were two of the ILs under investigation.[5e] Over the previous decade the link between antimicrobial toxicity and side chain length of imidazolium ILs has been extensively reported.[3c,4,15i,18,32] However, as this is related to the lipophilicity of the IL, introduction of heteroatoms would be expected to reduce antimicrobial toxicity via this mode of action. Every TSIL is unique (and often complex compared to DmimI) and toxicity to microorganisms via a different mode of action is feasible. Therefore, antimicrobial screening of all ILs utilised in this project was performed.

Furthermore, the authors proposed that the introduction of oxygen-functionalised side chains (ester) can increase the biodegradability of ILs via hydrolysis.[5e] This offers a potential advantage when future ecological and environmental impact studies of TSILs are performed.

Antibacterial Toxicity Preliminary Screen

In the DSSC screening, we have utilised eleven amide and ester based ILs and imidazolium salts (Figure 1) and three commercially available ILs. Eight strains of bacteria were selected for the study to represent a wide range of different classes of bacteria. *In vitro* antibacterial activities[20] (IC_{95}) of ILs and additives NBB (**4**) and GNCS (**5**) were evaluated.

Table 1: Antibacterial toxicity study results for ILs, imidazolium salts, **4** and **5**.

Strains[a]	Time (h)	MIC IC_{95} (mM)			
		1-3, **5**, **6a**, **6c**, **7a**, **8a-c**,**9a-c**	**4**	**6b**	**7c**
SA	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
MRSA	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
SE	24	> 2	**2**	**0.5**	> 2
	48	> 2	**2**	> 1	> 2
EF	24	> 2	**1**	> 1	**2**
	48	> 2	**2**	> 1	> 2
EC	24	> 2	> 2	> 1	> 2
	48	> 2	> 2	> 1	> 2
KP	24	> 2	> 2	**1**	> 2
	48	> 2	> 2	> 1	> 2
KP-E	24	> 2	> 2	> 1	> 2
	48	> 2	> 2	> 1	> 2
PA	24	> 2	> 2	> 1	> 2
	48	> 2	> 2	> 1	> 2

[a] **SA**: *Staphylococcus aureus* CCM 4516, **EC**: *Escherichia coli* CCM 4517, **PA**: *Pseudomonas aeruginosa* CCM 1961) and five clinical isolates (**MRSA**: *Staphylococcus aureus* MRSA H 5996/08, **SE**: *Staphylococcus epidermidis* H 6966/08, **EF**: *Enterococcus sp*. J 14365/08, **KP-E**: *Klebsiella pneumoniae* ESBL J 14368/08, **KP**: *Klebsiella pneumoniae* D 11750/08

Table 1 shows that eleven ILs (**1**-**3**, **6a**, **6c**, **7a**, **7c**, **8a**-**c** and **9b**) and two imidazolium salts (**9a** and **9c**) were found to not have high antibacterial toxicity, up to the maximum test concentration validated (2 mM). IL **7c** was moderately toxic to one of the eight bacteria strains screened (*Enterococcus sp*.). IL **6b** was tested at 1 mmol due to limited solubility in the broth. **6b** does not have high toxicity (>1 mM) except for *S. epidermidis. N*-butylbenzimidazole (**4**, NBB) and guanadinium thiocyanate (**5**, GNCS) are used as additives in the electrolyte. NBB shows moderate toxicity for all four Gram-positive bacteria (IC_{95} 2mM) while not exhibiting high toxicity to Gram-negative strains (IC_{95} > 2 mM). This is a

lipophilic compound and can cross the membrane of cell, leading to enhanced biological activity.[33] Overall, Table 2 shows that the ILs and imidazolium salts utilised for the DSSC screening are not highly toxic to a wide range of strains of bacteria.

Antifungal Toxicity Preliminary Screen

Fungi belongs to a large group of eukaryotic micro-organisms and are distinguished among this group due to their chitin containing cell wall. Fungi toxicity is often assessed in tandem with bacteria toxicity to investigate compounds antimicrobial biological effect.[5]

The antifungal toxicity results (Table 2) indicate that ten ILs (**1**, **2**, **3**, **6a**, **6c**, **7a**, **8a**-**c** and **9b**), two imidazolium salts (**9a** and **9c**) and **5** do not exhibit high toxicity to the twelve strains of fungi, up to maximum validated test concentration limit (2 mM). **6b** was tested up to 1 mM concentration due to limited solubility in RPMI 1640 broth. **6b** has antifungal activity towards *T. asahii* (IC_{80} 0.5 mM), and moderate activity towards *C. albicans*, *C. tropicalis* (IC_{80} 1 mM). Table 3 also shows NBB (**4**) exhibits moderate activity to all strains of fungi. Although, the cell wall of fungi is different (composed of chitin) to bacteria, we submit that as NBB is a lipophilic neutral compound, it can penetrate this barrier more easily than the ILs (Figure 1).

ILs and imidazolium salts selected for DSSC screening (Fig. 1), including **1**, **2** and **3** do not show high antimicrobial toxicity (Table 1 and 2). However, these preliminary results do not establish the toxicity limit for ILs, hence the toxicity study was expanded to higher concentrations i.e. 200 mM, solubility limits withstanding. All compounds were screened against five bacteria strains: Gram-positive (*Bacillus subtilis*) and Gram-negative (*Escherichia coli*, *Pseudomonas fluorescence*, *Pseudomonas putida* CP1, *Pseudomonas putida* KT2440). Compound toxicity determination was based on bacterial growth inhibition in a 24 hour assay and was expressed as IC_{50} value range. The maximum test concentration for ILs (**1**, **2**, **3**, **6a**, **6c**, **7a**, **7c**, **8a, 8c** and **9b**) and imidazolium salts (**9a** and **9c**) was 200 mM whereas ILs (**6b** and **8b**) were tested at 50 mM. The lower test concentration for (**6b** and **8b**) was necessary due to the limited solubility of ILs in the broth. The IC_{50} value ranges are presented in Table 3.

Table 2: Antifungal toxicity study results for ILs, imidazolium salts, **4** and **5**.

Strains[a]	Time (h)	MIC IC_{80}/IC_{50} (mM)[b]			
		1-3, **5**, **6a**, **6c**, **7a**, **8a-c**, **9a-c**	**4**	**6b**	**7c**
CA1	24	> 2	**2**	**1**	> 2
	48	> 2	**2**	> 1	> 2
CA2	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
CP	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
CK1	24	> 2	**2**	> 1	**2**
	48	> 2	**2**	> 1	> 2
CK2	24	> 2	**1**	> 1	**2**
	48	> 2	**2**	> 1	> 2
CT	24	> 2	**2**	**1**	> 2
	48	> 2	**2**	> 1	> 2
CG	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
CL	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
TA	24	> 2	**1**	**0.5**	> 2
	48	> 2	**1**	> 1	> 2
AF	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
AC	24	> 2	**2**	> 1	> 2
	48	> 2	**2**	> 1	> 2
TM	72	> 2	**2**	> 1	> 2
	120	> 2	**2**	> 1	> 2

[a] (**CA1**: *Candida albicans* ATCC 44859, **CA2**: *Candida albicans* ATCC 90028, **CP**: *Candida parapsilosis* ATCC 22019, **CK1**: *Candida krusei* ATCC 6258) and eight clinical isolates of yeasts (**CK2**: *Candida krusei* E28, **CT**: *Candida tropicalis* 156, **CG**: *Candida glabrata* 20/I, **CL**: *Candida lusitaniae* 2446/I, **TA**: *Trichosporon asahii* 1188) and filamentous fungi (**AF**: *Aspergillus fumigatus* 231, **AC**: *Absidia corymbifera* 272, **TM**: *Trichophyton mentagrophytes* 445).[b] IC_{50} values were assessed for AF, AC and TM. For all other fungi strains IC_{80} values were evaluated.

Table 3: Antibacterial toxicity study at higher concentrations. IC_{50} values.

Compound	IC_{50} value (mM)				
	E. coli	**B. subtilis**	**P. fluorescens**	**P. putida (CP1)**	**P. putida (KT2440)**
1	100-200	50-100	50-100	50-100	100-200
2	100-200	50-100	50-100	50-100	50-100
3	12.5-25.0	6.25-12.5	6.25-12.5	12.5-25	12.5-25
4	0.78-1.56	1.56-3.12	1.56-3.12	6.25-12.5	6.25-12.5
5	50-100	> 200	50-100	50-100	50-100
6a	50-100	50-100	50-100	50-100	100-200
6b	25-50	25-50	25-50	25-50	> 50
6c	25-50	50-100	50-100	50-100	50-100
7a	25-50	25-50	25-50	25-50	25-50
7c	25-50	6.25-12.5	6.25-12.5	25-50	50-100
8a	> 200	> 200	> 200	> 200	> 200
8b	12.5-25	25.50	6.25-12.5	> 50	> 50
8c	> 200	> 200	100-200	> 200	> 200
9a	> 200	> 200	> 200	> 200	> 200
9b	6.25-12.5	6.25-12.5	6.25-12.5	6.25-12.5	12.5-25
9c	> 200	> 200	100-200	> 200	100-200

Table 3 shows that of the commercially available ILs **(1-3)** and electrolyte additives (**4** and **5**), **4** has the highest toxicity to Gram positive and Gram negative bacteria. These results are consistent with the preliminary antibacterial toxicity study (Table 2). The iodide based ILs **1** and **2** have IC_{50} values in the ranges 50-100 or 100-200 mM depending on the bacteria strains. EMTCB (**3**) has moderate toxicity (IC_{50} values 6.25-25 mM) to the 5 bacteria strains. GNCS (**5**) shows low activity towards Gram negative bacteria in the range 50-100 mM, while even lower toxicity >200 mM for the Gram positive bacteria strain *Bacillus subtilis* was found.

A general trend is the iodide series **6c**-**9c** is more toxic to bacteria than the bromides **6a**-**9a**, although the difference is marginal (only for 1 out of 5 strains screened) for **8c** and **9c**. Significantly, the bromides (**8a** and **9a**) and iodides (**8c** and **9c**) have lower antibacterial toxicity than commercially available widely applied ILs **1** and **2**. TSIL **6a** exhibits similar antibacterial toxicity to **1** and **2**.

The $[NTf_2]^-$ series **6b**, **8b** and **9b** is more toxic to the 5 bacteria strains than the bromide analogues, with the increase in toxicity more prominent for the amide TSIL **8b** and **9b** than ester **6b**. While the amide examples **8a,c** and **9a,c** have very low antibacterial toxicity (IC50

values > 200mM), exchanging the halide for the $[NTf_2]^-$ lead to ILs with the greatest toxicity to bacterial, within the scope of this study (Figure 1 and Table 4). This demonstrates the importance of toxicity screening of individual compounds, as the increase in antibacterial toxicity of the ester TSIL **6a** to the **6b** is only slight (i.e. no clear trend when comparing the effect of anion on toxicity for the ester TSILs to the amide TSILs series). However results in Table 4, from an intelligent design perspective, highlight lipophilic ILs (NTf_2 examples and alkyl ester TSILs) in general are more toxic to bacteria than the hydrophilic ILs (halide examples and incorporating ether function groups into sidechain).

DSSC performance (dry):

The low toxicity of some the TSILs and imidazolium salts prepared (particularly **6a**, **8a**, **8c**, **9a** and **9c**) compared to standard **2** suggested they would be more suitable, greener and safer for use as DSSC electrolytes. We fabricated DSSC with the best reported IL combination[13] [**1**/**2**/**3**/I_2/**4**/**5** in molar ratio 12/12/16/1.67/3.33/0.67] electrolyte to act as a standard comparison for the new IL electrolyte materials tested here.

We achieve an efficiency of 4.94 % with this standard EmimI (**2**) combination, which is lower than the 8.2 % reported for similar electrolytes and it is due to the use of different TiO_2 paste, dye and fabrication procedures employed here. However, within this study it can act as a benchmark for comparing the performance of the new electrolytes. The performance results of DSSC fabricated with either our new ILs or imidazolium salts replacing **2** are given in Table 4and Fig. 3.

All iodide salts (**6c** to **9c**) achieve current densities greater than 8 mA/cm^2. The only bromide or triflimide salt that reaches above 8 mA/cm^2 is **7a** with a value of 8.83 mA/cm^2. The two best performing ILs achieve efficiencies of 3.92 % and 3.76 % for **7c** and **7a** respectively. **7c** and **7a** compare well to the efficiency achieved with the EmimI (**2**) standard. **7a** exhibits a J_{sc} of 8.83 mA/cm^2 which is much lower than the EmimI (**2**) value of 11.5 mA/cm^2 but its power conversion efficiency is aided by a relatively better fill factor (FF). **7c** yields a notably high current density of 10.4 mA/cm^2 which is comparable to **2** as displayed in Fig. 4. Slightly lower power conversion efficiency is mostly due to the lower FF value compared to **2** (64 vs 56). Both involve the long chain alkyl cation suggesting this cation structure performs best of the four tested here, although these are also two of the more toxic TSILs. Two of the other novel imidazolium derived compoundsalso exhibit noteworthy performance, the lower antibacterial toxicity iodide TSIL **8c** showed 3.39% and imidazolium

salt **9c** gave 3.31% power conversion efficiencies. **9c** exhibits a high photocurrent of 9.27 mA/cm^2, which is the second highest J_{sc} value of the new TSILs and imidazolium salts tested (Figure 4) suggesting this structure may be the key towards TSIL for electrolytes with high current and low toxicity. **8c** exhibits a lower J_{sc} value of 8.85 mA/cm^2 but coupled with a good FF results in a similar power conversion efficiency as **9c**. The J-V curves of these best performing ILs are compared to **2** in Fig. 4 (left). Clearly, **7c** is the best, it achieves 80 % the performance of **2** with similar voltage and comparable current density values. **8c** and **9c** achieve almost 70 % the performance of EmimI (**2**), but with much lower toxicity.

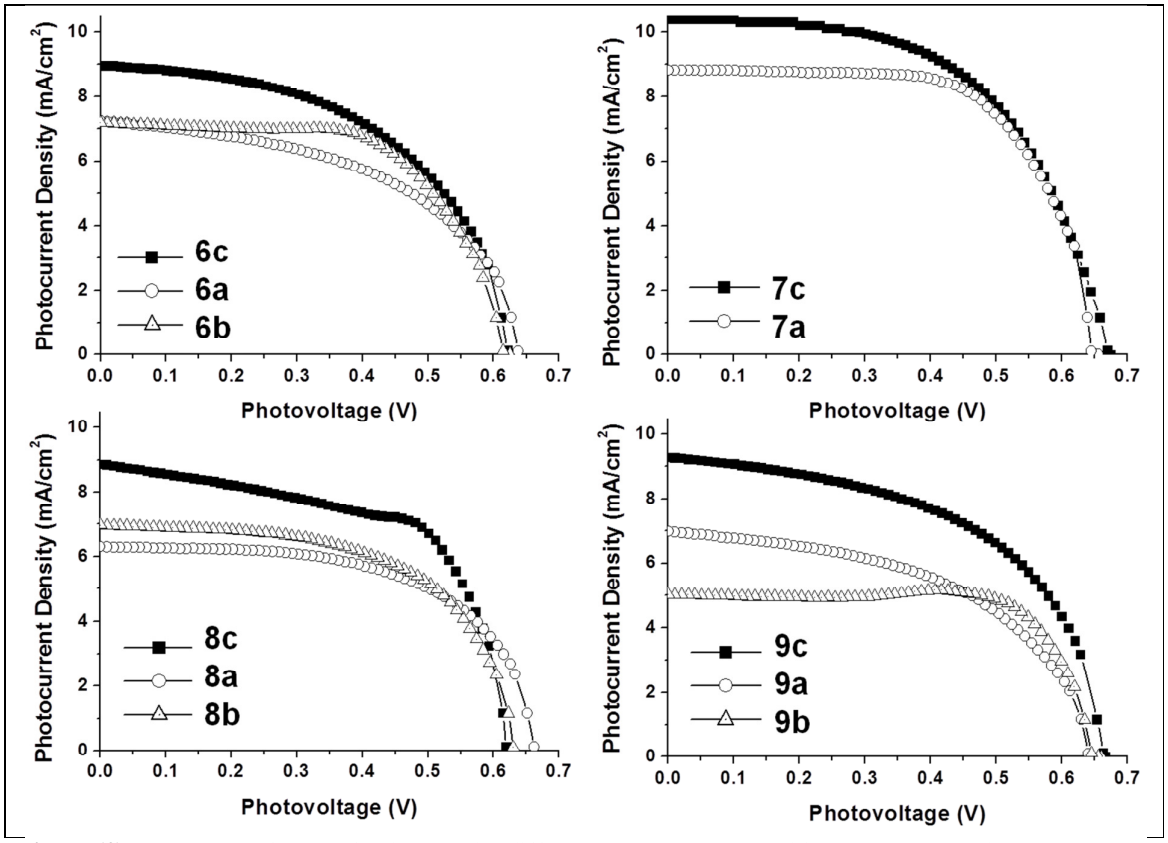


Figure (3): J-V curves of DSSC fabricated with different electrolyte compositions measured under standard AM1.5 (1000 W/m^2) simulated solar light conditions. Electrolyte compositions consisted of dried DmimI /X/EmimTCB/I_2/NBB/GNCS in the molar ratio 12/12/16/1.67/3.33/0.67 (X = **6a-c** to **9a-c**).

We also compared the effect of different counter-ions on the performance. In all cases the iodide salts (**6c**-**9c**) yield superior performance, as can be observed in Table 4. Iodide TSILs better performance is due to significantly higher currents than the corresponding bromide or triflimide (NTf_2^-) salts. Cross couple redox systems such as these are complicated. Interhalogen redox systems based on the IBr_2^- and the I_2Br^- anions are difficult to characterize

due to the complex equilibrium between various interhalogen anions in the electrolyte solution.[34]

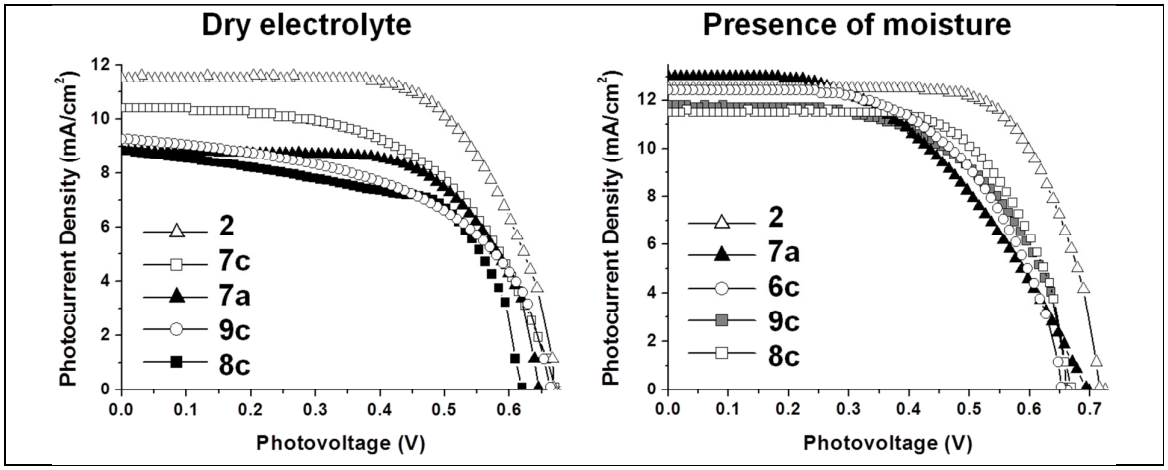


Figure (4): *left)* J-V curves of DSSC using the best performing novel IL electrolytes compared with the standard EmimI based electrolyte measured under AM1.5, 1000 W/m^2 simulated solar light conditions. *Right)* The best performing novel ILs compared to electrolyte containing the standard EmimI (**2**) in the presence of small amounts of moisture.

Furthermore, the triflimide anion is considerably more bulky than I^- and Br^- and shows high resonance-stability resulting in low Lewis basicity. The formation of the iodide-triflimide and iodide-bromide cross couples is complicated and much slower than tri-iodide formation which occurs more readily in the iodide ILs. Thus the higher iodide ILs cell currents may be rationalised by their enhanced tri-iodide diffusion via a Grotthus-like bond exchange. It may be expected that in general the NTf_2^- anion is not as involved in cross couple formation, compared to Br^-, which could lead to lower photocurrents and lower charge transfer resistances at the counter electrode.

Improved performance by presence of water

It is known that the performance of IL electrolytes in DSSC can be improved by presence of small amounts of moisture.[35] Improvements are brought about by enhancements of J_{sc}, FF and V_{oc} which are associated with a decrease in charge transfer resistances at the counter electrode and increases in ionic conductivities and an increase in the difference between redox potentials of I^-/I_3^- and the Fermi level of TiO_2.[35] ILs consist entirely of ion pairs, which differ in degrees of dissociation, on a case by case basis. As a consequence, formation of aggregates occurs. With the presence of water, ions can be separated by the neutral solvent molecules, the number of mobile charge carriers increases, resulting in an increase of conductivity.[36] In this study we opened the back seal of our DSSCs and stored in ambient conditions for a period of up to one month to allow moisture ingress from the atmosphere and

observed considerable improvement in cell performance. The standard EmimI (**2**) electrolyte improved from 4.94 % to 6.33 % with improved FF, J_{sc} and V_{oc} (Table 5). For all compounds tested here, the presence of a small amount of moisture causes significant increase in J_{sc} with values approaching or exceeding 10 mA/cm^2 observed and efficiencies greater than 3.5 % in all cases. Seven of the eleven TSILs and imidazolium salts (Fig 1) now show efficiencies greater than 4 %. (Table 4 and Fig. 5).

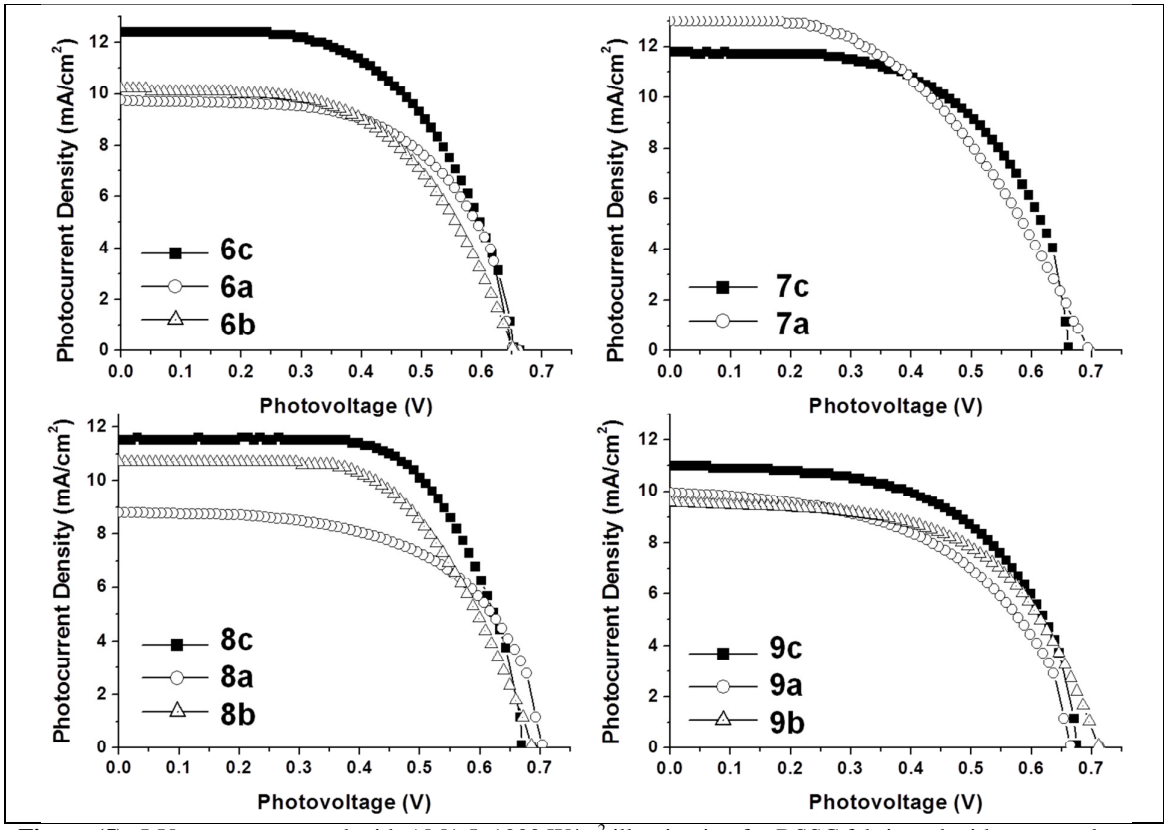


Figure (5): J-V curves measured with AM1.5, 1000 W/m^2 illumination for DSSC fabricated with our novel electrolytes in the presence of small amounts of moisture.

The percentage increase in cell parameters in the presence of moisture is given in Table S2. For the iodide salts a slight increase in FF (less than 10 %) is observed in each case. This is coupled with considerable increase in short circuit currents with values increasing by 13.5 % up to 38.5 %. These resulted in improved performance efficiencies of up to 60 % compared to their initial dry analogue. The bromides also all showed improved J_{sc} upon presence of moisture with increases of 35 % to 47 % observed. This is coupled with small increases in V_{oc} values. In some cases FF improved (**6a** and **9a**) but with (**7a** and **8a**) FF decreased. The improved J_{sc} and V_{oc} increases cell performance efficiencies in all cases by amounts of 15 % to 63 %. For the triflimide salts, decreased cell FF is observed but large

increases in cell short circuit currents (42 % to 85 %) lead to higher power conversion efficiencies with the presence of moisture.

Table 4: Photovoltaic parameters of the DSSC devices made with DmimI/X/EmimTCB/I_2/NBB/GNCS electrolyte measured at 1 sun (1000 Wm^{-2}) incident intensity of AM1.5 solar light. Their performance when freshly made and after one month exposed to ambient ie following moisture ingress, are listed.

	As fabricated (dry)					After one month back seal open to allow moisture entry			
Compound (X)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)		J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η (%)
2	11.5	669	64	4.94		12.5	725	70	6.33
6c	8.95	622	53	2.92		12.4	663	57	4.71
6a	7.23	638	52	2.38		9.74	661	60	3.87
6b	7.19	625	62	2.79		10.2	656	55	3.69
7c	10.4	675	56	3.92		11.8	661	60	4.63
7a	8.83	655	65	3.76		13.0	698	48	4.33
8c	8.85	620	62	3.39		11.6	669	66	5.08
8a	6.30	662	60	2.51		8.80	703	59	3.67
8b	6.97	630	60	2.61		10.7	689	59	4.34
9c	9.27	667	53	3.31		11.0	675	58	4.34
9a	6.97	640	52	2.30		9.95	665	53	3.53
9b	5.15	660	72	2.46		9.56	716	57	3.90

One might suggest that the improved performance is caused by the IL cation being attacked by water molecules, degrading the IL cation. For example, hydrolysis of the ester group of **6** and **7** would produce imidazolium carboxylate by-products which may be the cause of improved performance. However, if this imidazolium carboxylate was the source of increased performance then similar improvements for both **6** and **7** would be expected, due to comparable rates of hydrolysis for the ester groups. This however is not the case. For example **7c** increases in current by 1.4 mA/cm^2 but for **6c** it is dramatically different, increasing by more than twice as much, 3.5 mA/cm^2.

Recent studies[37] reported that water molecules seemed to interact mainly with trifluoromethane-sulfonyl-imide anion ($TFSI^-$) and Emim and with other water molecules, but not with I^- or I_3^- implying ILs containing bulky anions such as NTf_2^- should show a higher anion-moisture interaction compared to our I^- and Br^- TSILs. This higher interaction with moisture could result in higher charge transfer resistances at the counter electrode and thus the observed decreased FF for the NTf_2^- ILs tested here. Small amounts of water were found to increase the entropy and mobility[37] of Emim and since I^- and I_3^- are coordinated by several Emim, it leads to higher local fluctuation which should increase the rate of Grotthus-like

electron transfer which is diffusion-controlled and can lead to an improving performance of the DSSC. Therefore, we expect the crucial factor determining the amount of atmospheric moisture absorbed and improved DSSC performance relates to the hydrophilic or hydrophobic nature of the cation. Molecular interaction with the cation can include hydrogen bonding of the acidic proton of the imidazolium ring to the oxygen atom of water as well as interactions with the substituent on the 1-position of the imidazolium ring, since atoms with high electro-negativity (oxygen and nitrogen) are present. Increasing the number of oxygen and nitrogen atoms, increases the hydrophilicity of the IL via enhanced hydrogen bonding interactions with water molecules. The tendency of the performance of the ILs and imidazolium salts in relation to their hydrophilicity increases in the order **7**, **9**, **8**, **6**. The more oxygen atoms that are incorporated into the chemical structure of the TSIL cation (and thus more hydrophilic), the greater the increase of the performance of the DSSC after exposure to air. Of the ILs and imidazolium salts in this study, **7a** and **7c** show the smallest performance improvement of 15 % and 18 % respectively (Fig. 4) which can be related to their greater hydrophobic nature (due to pentyl ester side chain) as longer alkyl chains are known to lead to increased hydrophobicity[38]. The standard EmimI (**2**) with slightly shorter ethyl side chain shows a greater improvement in performance of 28 %. The most hydrophilic TSIL cation (**6c** and **6a**) containing four oxygen atoms in the side chain shows the greatest increases in performance (61 % and 63 % respectively).

This trend applies to the I^- and Br^- containing ILs and imidazolium salts, but for NTf_2^- the trend is not so clear cut. We propose this is due to NTf_2^- interactions with moisture,[34] likely leading to increased Lewis basicity, due to decreased resonance-stability, which can cause large increases in current between the dry and moisture enriched analogues e.g., up to 85 % for **9b**.

Two TSILs of noteworthy performance are **6c** and **7c** which show efficiencies of 4.71 % and 4.63 % respectively. Both exhibit similar V_{oc} and FF values, with **6c** displaying a slightly higher J_{sc} as outlined in Fig. 4 (right). **7a** exhibits a large photocurrent value of 13.0 mA/cm^2 which is higher than **2** (12.5 mA/cm^2) and would be expected to give an outstanding power conversion efficiency except for its poor FF value of 48 % but offers no advantage in terms of toxicity. The best performing TSIL is the low toxicity iodide salt **8c,** which exhibits a performance of 5.08 % which compares favourably to the 6.33 % value achieved with **2** and surpasses the performance of the dry EmimI (**2**) analogue.

Conclusion

As most second generation Bmim and especially Emim based ILs have low toxicity, the challenge of designing replacement third generation TSILs of comparable toxicity is great. Structural features of TSIL investigated herein (which are known to reduce antimicrobial toxicity compared to alkyl derivatives) were incorporation of heteroatoms into the sidechain of imidazolium cations (i.e. ether, ester and amide) and anion (bromide, iodide, and NTf_2).

Preliminary toxicity screening against 20 microorganisms (8 bacteria and 12 fungi) found that all ILs, imidazolium salts and additives NBB (**4**) and GNCS (**5**) do not exhibit high antimicrobial toxicity. However NBB (**4**) and **6b** displayed moderate toxicity to several strains of bacteria and fungi. Further toxicity testing to establish IC_{50} values shows several novel TSIL and imidazolium salts are less toxic to microorganisms (e.g. bacteria) than commonly used EmimI and DmimI. We have demonstrated that the presence of ether and either ester or amide groups in the structure of the substituted imidazolium cation reduces antimicrobial toxicity, which is consistent with the lowering of the lipophilicity of ILs. Iodide and bromide TSILs and imidazolium salts have lower toxicity than the NTf_2 examples in this study.

Furthermore, we report the toxicity limits against five bacteria strains of common DSSC electrolyte components namely: EmimI, DmimI, 1-ethyl-3-methylimidazolium tetracyanoborate (EmimTCB) and additives *N*-butylbenzimidazole (NBB) and guanadinium thiocyanate (GNCS). NBB has the highest toxicity of all compounds in the study with IC_{50} values in the range 0.78-1.56 mM observed. This significant finding identifies the additive NBB as the compound of concern based on the scope of the toxicity assessment of ILs, imidazolium salts and additives screened in this study.

In addition, while none of the novel TSILs herein, lead to exceptional improvement in DSSC performance, they compare favorably with EmimI, without a significant increase in antimicrobial toxicity. In dry conditions the novel TSIL **8c** and imidazolium salt **9c** show promise due to their lower toxicity compared to EmimI (**2**) and good performance in terms of J_{sc} and FF respectively. Upon the addition of moisture to the electrolyte system, low toxicity **8c** continues to show promise exhibiting the highest efficiency of the 11 TSIL and imidazolium salts investigated. This is again due to its excellent FF suggesting future TSIL with improved performance should be based on these low toxicity cation structures (**8** and **9**).

In both dry and moisture containing forms, 70-80 % the performance of EmimI (**2**) standard is possible but with much lower toxicity. These results show how IL structure influences toxicity and performance in DSSC. Also of note, the DSSC containing TSIL NTf_2 examples, performed poorly compared to the halide analogues, with the outcome that some of the most toxic TSILs under investigation are also the least preferred based on performance.

The attempts to eliminate liquid or gel electrolytes completely from high performance and stable DSSC is not yet successful. Therefore, first generation commercial DSSC, which requires good stability, will rely mostly on IL based electrolytes and hence its toxicity and environmental acceptance assumes utmost importance.

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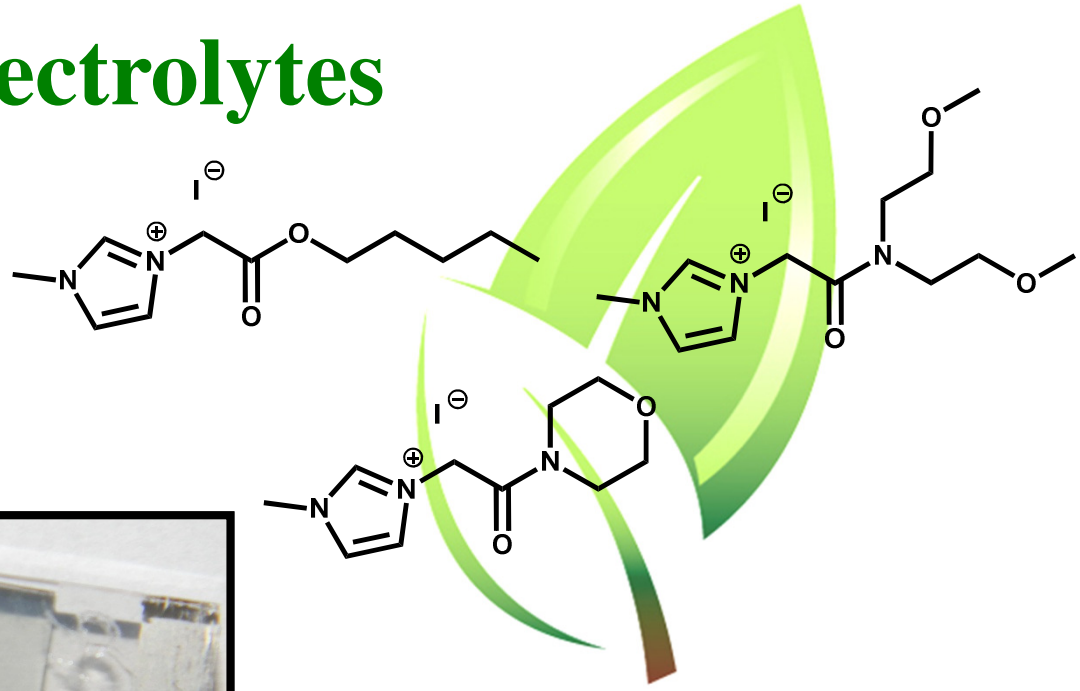
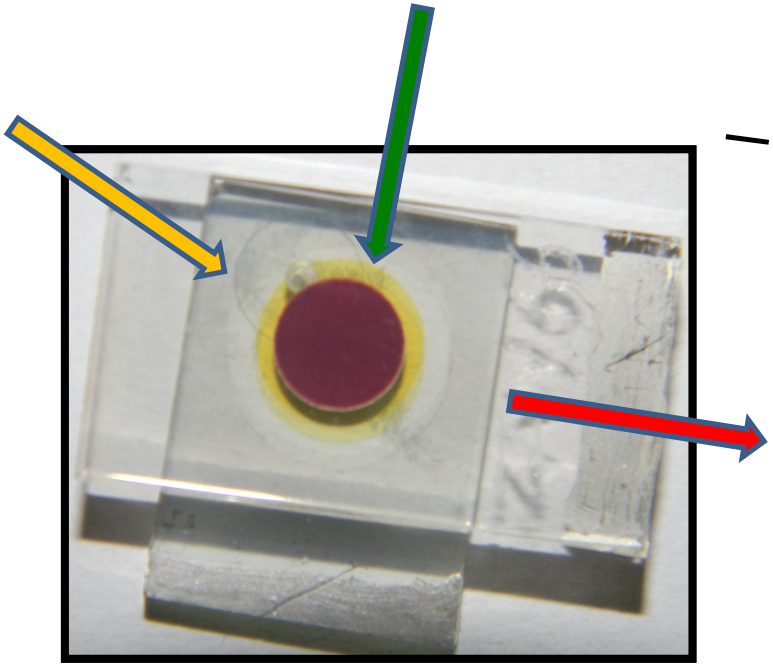
Toxicity Evaluation of Electrolytes





Less Hazardous Energy from Dye Sensitised Solar Cells

Graphical Abstract Text.

Tandem evaluation of ionic liquids and imidazolium salts toxicity and performance in Dye Sensitised Solar Cells is presented.