Highly Selective and Near-Quantitative Conversion of Fructose to 5‑Hydroxymethylfurfural Using Mildly Acidic Ionic Liquids

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Keywords

Abstract

The room temperature ionic liquid, $[C_4C_1im][HSO_4]$ provides a multi-faceted medium in which to convert fructose to the versatile chemical building block, 5-hydroxymethylfurfural (HMF). A range of metal salts have been investigated in order to establish some of the properties required for the optimization of this process. This has led to almost quantitative conversion of fructose to 5-HMF in a system which is both selective for the desired product, less energy intensive and more environmentally benign than the commercial process.

Introduction

Conversion of biomass to useful platform chemicals is a vital aspect in the replacement of petroleum-based feedstocks with sustainable alternatives.[1,2] It is likely that lignocellulosic biomass will be heavily used as a feedstock for future large-scale biorefineries as lignocellulose is distributed widely and can be grown on a billion ton scale. This offers opportunities for reducing the carbon footprint and diversifying fuel and material supplies. A major driving force behind this is the fact that the fuels and materials derived from such biomass are potentially 'carbon neutral', however, the current production of lignocellulosic biomass requires extensive, costly and environmentally harmful pre-treatment.[3] Ionic liquids have provided a far more benign method of separating cellulose and this process is critical in the development of the functionalization of the resultant biopolymer.[4-9]

In 2004, the U.S. Department of Energy identified 5-hydroxymethylfurfural (HMF) as a key platform chemical, which can be the precursor to both chemical feedstocks and potential fuels, such as 2,5-dimethylfuran (40% higher energy density than ethanol).[10] The versatility of this synthetic building block is now widely recognised, leading to an increase in transformations using HMF being reported.[11,12]

In 2007, pioneering work by Zhao illustrated that an ionic liquid (IL), $[C_4C_1im]Cl$, could be used in combination with various metal salts to break down fructose to HMF in 70% yield at 120 °C over the course of 3 hours.[13] Chromium salts were found to provide the highest conversions and this has been confirmed by subsequent work in closely related studies.[14-17] While the 'green' credentials of ILs can be overstated,[19] they have environmental benefits such as their reusability and negligible vapour pressure. More importantly, they offer a vast improvement over the currently used process, which employs highly acidic aqueous solutions with all the attendant safety, environmental and containment issues.[3]

Over the last five years, a plethora of reports have appeared in which ILs have been employed to dissolve and breakdown sugars (fructose, sucrose, cellulose etc.) derived from biomass.[14-18] The majority of these have followed the original research in using imidazolium chloride ionic liquids, such as $[C_4C_1im]Cl$ and $[C_2C_1im]Cl$ (Figure 1). However, an overview of the catalytic literature using ILs illustrates that the presence of chloride (an excellent ligand) as part of the solvent system (and hence in huge concentration) in many cases inhibits the ability of transition metals to generate a vacant site in order to perform catalytically.[20]
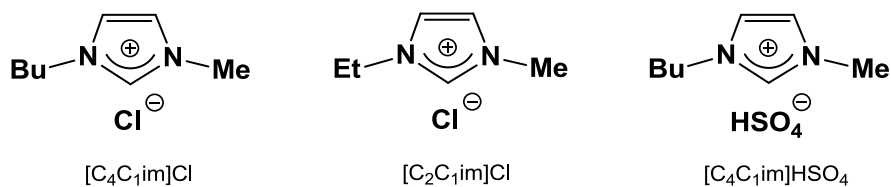
$[C_4C_1im]Cl$ $[C_2C_1im]Cl$ $[C_4C_1im]HSO_4$

Figure 1. Ionic liquids used in the dissolution and breakdown of biomass.

One of the many strengths of ionic liquids is the ability to tune their physical and chemical properties to provide the best medium for a specific transformation. The breakdown of fructose is known to be favoured by acidic conditions so the IL, $[C_4C_1im][HSO_4]$ was chosen as a suitable candidate for this transformation due to the mildly acidic proton located on the anion. Dilute acids have been reported to accelerate fructose conversion to HMF in both water[21] and ILs.[16] In addition, the absence of a chloride counterion and the presence of only a weakly coordinating hydrogensulfate anion were also important factors in the choice of this solvent.

The coordinating ability of the IL anion was demonstrated to be a significant factor by Hu et al when they reported the conversion of glucose to HMF using a Lewis acid ($SnCl_4$) in ILs with a range of anionic species while the cation used in all cases was $[C_4C_1im]^+$.[14] The best results was obtained when the anion was $[BF_4]^-$ while lower yields were obtained with the anions of ILs Cl⁻, Tf$_2$N⁻, TFA⁻, Trif⁻ and Sacc⁻, all of which have the ability to coordinate (Figure 2).[14] The coordinating anions would have stronger interactions with the metal centre which would compete with the interaction between sugar and catalyst and thus inhibit the formation of HMF.[14]
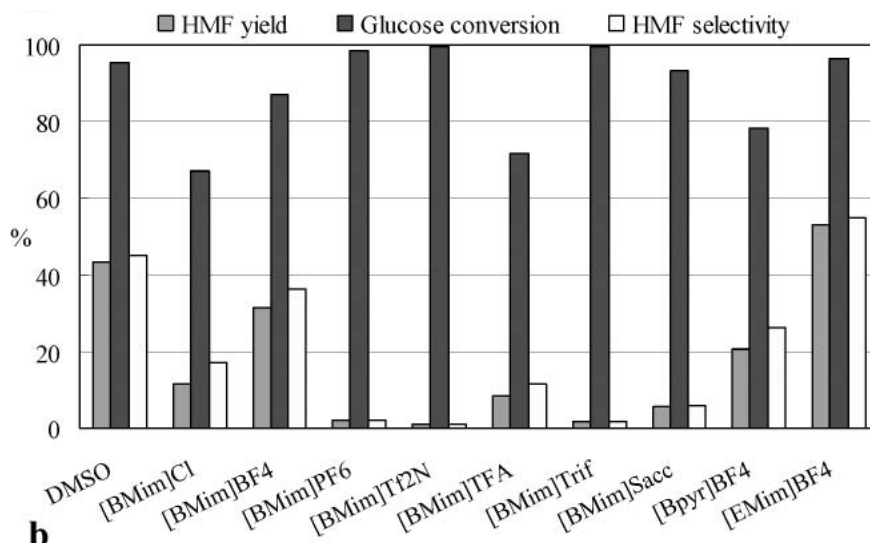

Figure 2. HMF yields in various ILs and DMSO. Reprinted with permission from reference 14.

It was proposed that a suitable medium should have strong solvent power for sugar dissolution but low coordination ability to metal centre.

Catalytic Studies

In order to ascertain the conversion of fructose to HMF without any additives, the sugar was heated at 80 °C in $[C_4C_1im][HSO_4]$ in air (Scheme 1) and the reaction monitored by removing aliquots after 0.5 hours, 1 hour, 3 hours and 24 hours. The conversion was determined by ^{1}H NMR analysis (methodology confirmed by HPLC comparison). This conversion is performed industrially in acidic aqueous media so it was not a surprise to see some HMF being formed after 0.5 hours (11%), rising to 38% conversion after 24 hours.
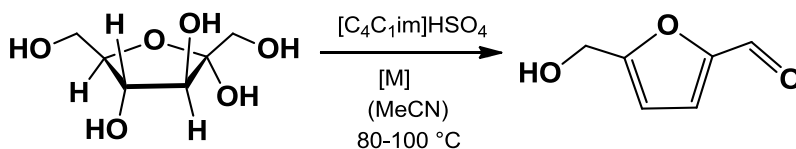
Scheme 1. Fructose conversion to 5-hydroxymethylfurfural (HMF).

Chromium salts have been shown to be particularly active in catalysing this transformation and so 7 mol% chromium(III) chloride hexahydrate was introduced, maintaining the same conditions as before. This resulted in substantial conversion after only 0.5 hours (54%), rising to 80% after 3 h, which was also the final conversion after 24 h (Table 1, Entry 2). This represented an improvement on the results obtained using $[C_4C_1im]Cl$ under the same conditions.[13] Using the hydrated salt, $CrCl_3 \cdot 6H_2O$, introduced a small amount of water into the system so anhydrous $CrCl_3$ was investigated and found to result in a much slower reaction (Table 1, Entry 4). However, when 15% water (v/v with the IL) was used, a higher overall conversion (at 80 °C) of 85% was observed (Table 1, Entry 1). The addition of 50% water slowed the conversion substantially, although the addition of other co-solvents, such as acetonitrile, did not lead to the same observed sluggishness. Anhydrous chromium(II) chloride was also found to be a reasonable catalyst for the formation of HMF, resulting in 74% conversion after 24 h. This is higher than the anhydrous chromium (III chloride, which performed very poorly in our system (only 6% conversion in the first 0.5 h, though increasing to 65% after 24 h). The anhydrous chromium (III) chloride salt did not dissolve in the anhydrous IL; only after approximately 1 h did the catalyst fully dissolve. We believe that the water yielded by the dehydration reaction was necessary to hydrate the chromium (III) chloride enough for it

to become soluble, and the catalyst performance therefore suffered until this condition was met.

Table 1. Fructose conversion to HMF

Entry	Metal salt	Conversion to HMF (%)			
		0.5 h	1 h	3 h	24 h
1	$CrCl_3 \cdot 6H_2O$ + 15% H_2O	11	30	65	85
2	$CrCl_3 \cdot 6H_2O$	54	60	80	80
3	$CrCl_2$ (anhydrous)	48	54	70	74
4	$CrCl_3$ (anhydrous)	6	11	32	65
5	$CrCl_3 \cdot 6H_2O$ + 50% H_2O	5	5	15	65
6	$CrCl_3 \cdot 6H_2O$ + 15% MeCN	54	60	80	65
7	WCl_4	49	54	60	65
8	$MoCl_3$	33	49	54	60
9	$Y(OTf)_3$	27	38	49	60
10	$LaCl_3$	11	22	38	60
11	$RuCl_3$	27	37	48	59
12	K_2PtCl_4	22	32	42	58
13	$NiCl_2$	22	37	41	54
14	$RhCl_3$	16	26	42	53
15	$La(OTf)_3$	22	33	49	49
16	$Sc(OTf)_3$	27	38	43	49
17	no catalyst + 15% water	5	5	11	44
18	$ZnCl_2$	16	21	32	38
19	no catalyst	11	21	27	38

7 mol% catalyst loading, 80 °C; Table ordered in terms of conversion after 24h. Entries numbered sequentially across both tables.

While other group 6 transition metal (Mo, W) salts led to acceptable conversions after 24 h, none tested here matched the chromium salts. This has been remarked upon in many reports and has been the subject of a combined experimental and computational study.[15] Metal salts from later in the transition series fared even worse. This led us to ponder whether the activity observed was an effect of Lewis acidity[14] and the general 'hard' nature of the metal compounds, as salts of higher oxidation state metals generally performed better against comparable related species. However, the strongly Lewis acidic lanthanide triflate ions showed unremarkable activity under the conditions tested (see Table 1).

Once variation of the duration of the reaction and the nature of the catalyst had been investigated, the effect of raising the temperature to 100 °C was analysed. Maintaining the other variables constant, this change led not only to the highest conversions observed in this study (96% after 3 h) but also to over 69% after only 0.5 hours (Table 2, Entry 20). At higher temperatures, high conversions were observed after only 0.5 h (87%, Table 2, entry 21). However, under these conditions, the formation of humins becomes an issue, leading to darkening of the ionic liquid and a lower conversion after 3h than at 100 °C. The addition of acetonitrile has previously been shown to limit this process.[22] Conducting the reaction 80 °C with 15% acetonitrile (v/v with the IL) leads to equally high yields (Table 2, Entry 6). There are several possible explanations for this result. As these ILs are highly viscous, acetonitrile may simply be acting as a diluent, reducing the viscosity of the solution, thereby enabling faster mass transport and accelerating the reaction. Acetonitrile also has a fairly high dielectric constant (ca. 36), which could affect the dissociation ability of the acidic IL solvent. In order to test this effect, we measured Hammett acidity values using the technique described by Fărcaşiu[23] for the IL with and without added acetonitrile. As Hammett acidity is intended as an extended pH scale, lower values indicate a more strongly acidic medium. Our measured value for pure $[C_4C_1im][HSO_4]$ ($H_0 = 1.96$) was noticeably lowered by the addition of 15% acetonitrile ($H_0 = 1.12$). This suggests that adding acetonitrile to the IL enhances the ability of the $[HSO_4]$ anion to protonate the substrate, increasing the acidity of the solvent medium. It should be noted that the Cr(II) chloride system also benefitted from higher temperature (conversion to 5-HMF increased from 70% at 80 °C to 87% at 100 °C after 3 hours), though the effect of acetonitrile on this system was negligible.

Adding 50% water (v/v) to the chromium(III) chloride system was found to decrease the final conversion after 24 h substantially (Table 1, entries 1 and 5). Adding such a large amount of water is likely to dissociate any metal-substrate complexes, and will also solvate the sugar substrates, likely retarding catalytic effects. Water will also stabilise the Cr(III) complex ions in solution, possibly reducing impetus for substrate binding. This same principle would lead to the formation of dehydrated intermediates being less favourable. As water is eliminated during this reaction, the water byproduct (or water from a 'wet' IL) is not likely to result in ligation to the Cr due to the solvation of the IL anion taking precedence (it is present in much higher concentration, though it is a poorer reaction partner).[19]

Table 2. Fructose conversion to HMF

Entry	Metal salt	Conversion to HMF (%)				
		Temp.	0.5 h	1 h	3 h	24 h
20	$CrCl_3 \cdot 6H_2O$	100 °C	69	87	96	-
21	$CrCl_3 \cdot 6H_2O$	120 °C	87	87	89	-
22	no catalyst	100 °C	51	69	69	-
23	no catalyst	120 °C	71	71	78	-
24	$CrCl_2$ (anhydrous)	100 °C	69	80	87	-
25	$CrCl_2$ (anhydrous) + 15% MeCN	100 °C	64	73	80	-
3	$CrCl_2$ (anhydrous)	80 °C	48	54	70	74
2	$CrCl_3 \cdot 6H_2O$	80 °C	54	60	80	80
6	$CrCl_3 \cdot 6H_2O$ + 15% MeCN	80 °C	54	60	80	65
1	$CrCl_3 \cdot 6H_2O$ + 15% H_2O	80 °C	11	30	65	85
5	$CrCl_3 \cdot 6H_2O$ + 50% H_2O	80 °C	5	5	15	65

7 mol% catalyst loading; Table ordered in terms of conversion after 3h. Entries numbered sequentially across both tables.

There are several possible reasons for the high performance of the IL $[C_4C_1im][HSO_4]$ as a solvent for HMF formation. The mildly acidic $[HSO_4]$ proton (pKa = 1.7) is likely to be acting as a co-catalyst for this reaction as well as acting as the solvent (and thus present in large excess). However, most strong acids promote over-dehydration of sugars to levulinic acid and formic acid, in both water[21] and ILs,[16] even in catalytic amounts. A large excess of a weaker acid appears to be a compromise between acid strength and concentration that optimises the formation of the dehydration intermediate HMF without promoting either levulinic acid or humin formation (as observed on adding concentrated H_2SO_4 to this system). The $[HSO_4]$ anion itself is also a mild hydrogen bond acceptor, compared to the much more basic chloride anion.[24] It is also less likely to compete with the substrate for the coordination sites at the metal catalyst, being a weakly coordinating anion. This result is in stark contrast to that found by Qi *et al.*[25] where a sulfonated zirconia catalyst was much more selective in $[C_4C_1im]Cl$ (89% HMF) than $[C_4C_1im][HSO_4]$ (43%), likely due to the over-acidity of the combined catalyst and solvent in the latter system.

Conclusions
In conclusion, a room temperature ionic liquid (IL) has been selected on the basis of the combination of the properties it provides as a medium for almost quantitative conversion

of fructose to 5-hydroxymethylfurfural (HMF) in the presence of a low loading of chromium(III) chloride. Previous to this report, the transformation of sugars to HMF in ILs had been carried out predominantly in dialkylimidazolium chloride salts. However, careful tailoring of the IL properties beyond the standard chloride salts improves the performance of the system substantially. The best condition that we report is 96% yield of 5-HMF in 3 hours at 100 °C. The selectivity of this process is indicated by the fact that no trace of levulinic acid or formic acid was encountered after conversion of fructose. This combination of the well-established advantages of ILs (negligible vapour pressure, recyclability) with a weakly acidic, weakly-coordinating medium provides an excellent environment for selective catalysis by a low toxicity metal species in only a few hours. Since HMF has recently become the starting point for scaled up production of 'green' beverage packaging,[26] the optimisation of high yielding routes to this platform chemical has never been more important or timely.

ASSOCIATED CONTENT

Supporting Information. Synthesis and preparation of ionic liquids and catalytic procedure for HMF formation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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For Table of Contents Use Only

Selective conversion of fructose to 5-hydroxymethylfurfural using mildly acidic ionic liquids

Sanan Eminov, James D. E. T. Wilton-Ely and Jason P. Hallett

The ionic liquid, $[C_4C_1im][HSO_4]$ provides an acidic solvent in which to convert fructose to 5-hydroxymethylfurfural rapidly and in high yield.
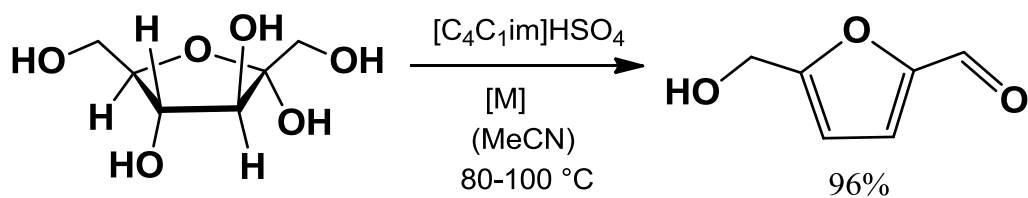
Metal-catalysed selective breakdown of fructose using ionic liquids

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Supplementary Information

Experimental Section

General Comments. All experiments were carried out under aerobic conditions apart from where stated. The ionic liquids used, [C$_4$C$_1$im]Cl, [C$_4$C$_1$im][MeSO$_4$] and [C$_4$C$_1$im][HSO$_4$] were prepared with only slight modifications to the literature routes.[S1] However, for convenience, the synthetic details are reproduced here along with selected data. The metal salts were obtained from commercial suppliers. Petroleum ether refers to the fraction boiling in the range 40-60 °C. Electrospray mass spectra were obtained using a Micromass LCT Premier instrument. Infrared data were obtained using a Perkin-Elmer Spectrum 100 FT-IR spectrometer. Unless otherwise indicated, NMR spectroscopy was performed at 25 °C using a Varian Mercury 300 spectrometer. All couplings are reported in Hertz.

Preparation of [C$_4$C$_1$im]Cl

A flask containing freshly distilled 1-methylimidazole (162 mL, 0.88 mol) and ethyl acetate (150 mL) was cooled in a dry ice bath. Freshly distilled 1-chlorobutane (100 mL, 0.96 mol) was added dropwise by dropping funnel under a nitrogen atmosphere. The reaction mixture was allowed to reach room temperature and then heated slowly under reflux for 1 hour until the solution became turbid. Then, the solution was heated under a nitrogen atmosphere to 70 °C for 48 hours. The solvent was removed by cannula filtration and the resultant viscous liquid was dissolved in an acetonitrile (25 mL) and ethyl acetate (75 mL) mixture. The solution was allowed to cool and kept at – 25 °C until crystals formed after 14 hours. The ethyl acetate and acetonitrile solvent mixture was removed by cannula filtration. The white crystals were washed with ethyl acetate (4 x 25 mL) and dried under vacuum overnight to give a 75 % yield of [C$_4$C$_1$im]Cl. ^{1}H NMR (400 MHz, DMSO) δ 9.45 (s, 1H, N$_2$CH), 7.86, 7.79 (m x 2, 2 x 1H, 2 x NCH), 4.20 (t, 2H, NCH$_2$, J_{HH} = 7.2 Hz), 3.88 (s, 3H, NCH$_3$), 1.77, 1.24 (m x 2, 2 x 2H, CCH$_2$), 0.90 (t, 3H, CCH$_3$, J_{HH} = 7.3 Hz) ppm. ^{13}C NMR (100 MHz, DMSO) δ 137.2 (N$_2$CH), 124.1, 122.7 (2 x NCH), 48.8 (NCH_2CH$_2$CH$_2$CH$_3$), 36.2 (NCH$_3$), 31.8 (NCH$_2$$CH_2CH_2CH_3$), 19.3 (NCH$_2CH_2$$CH_2CH_3$), 13.6 (N(CH$_2$)$_2CH_2$$CH_3$) ppm. MS (FAB, +ve mode): *m/z* (abundance) = 139 (100) [C$_4$C$_1$im]$^+$.

Preparation of [C$_4$C$_1$im][MeSO$_4$]

1-Butylimidazole (100 mL, 0.76 mol) was diluted in toluene (60 mL) and cooled in an ice bath. Dimethyl sulfate (72 mL, 0.76 mol) was added dropwise to the reaction mixture (flow rate 0.5

drops/sec) while stirring. The reaction mixture was stirred for a further hour at room temperature before the upper toluene layer was removed. The lower ionic liquid layer was washed with toluene (3 x 50 mL) before it was dried overnight at 65°C under vacuum with stirring. The yield was 92% and was used without further purification in the preparation of $[C_4C_1im][HSO_4]$.

Preparation of $[C_4C_1im][HSO_4]$

$[C_4C_1im][MeSO_4]$ (40 g, 0.16 mol) was diluted with deionized water (5 mL). The reaction vessel was kept open to the air and placed in a heating block at 215 °C. The internal temperature of the reaction mixture was continuously monitored and kept between 170 to 180°C for four hours by dropwise addition of deionized water. The reaction mixture was cooled to 65°C and kept under vacuum while stirring overnight to remove all residual water. The yield was 98%. ^{1}H NMR (400 MHz, DMSO) δ 9.19 (s, 1H, N$_2$CH), 7.79, 7.72 (m x 2, 2 x 1H, 2 x NCH), 4.17 (t, 2H, NCH$_2$, J_{HH} = 7.2 Hz), 3.86 (s, 3H, NCH$_3$), 1.74, 1.23 (m x 2, 2 x 2H, CCH$_2$), 0.88 (t, 3H, CCH$_3$, J_{HH} = 7.3 Hz) ppm. ^{13}C NMR (100 MHz, DMSO) δ 137.1 (N$_2$CH), 124.1 and 122.7 (2 x NCH), 48.9 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.1 (NCH$_3$), 31.8 (NCH$_2$$CH_2CH_2CH_3$), 19.2 (NCH$_2CH_2$$CH_2CH_3$), 13.7 (N(CH$_2$)$_2CH_2$$CH_3$) ppm. MS (FAB, +ve mode): m/z (abundance) = 139 (100) $[C_4C_1im]^+$, (FAB, −ve mode): m/z (abundance) = 97 (100) $[HSO_4]^-$.

Catalytic formation of 5-hydroxymethylfurfural (HMF)

In each run, fructose (1.00 g, 5.55 mmol) was added to a round bottomed flask containing $[C_4C_1im][HSO_4]$ (0.70 g, 2.96 mmol). The catalyst (0.39 mmol, 7 mol%) under study (CrCl$_2$, CrCl$_3$·6H$_2$O, CrCl$_3$, WCl$_4$, MoCl$_3$, LaCl$_3$, Sc(OTf)$_3$, La(OTf)$_3$, Y(OTf)$_3$, RuCl$_3$, K$_2$PtCl$_4$, NiCl$_2$, RhCl$_3$, ZnCl$_2$) was added to the flask. The flask was equipped with a reflux condenser and the reaction mixture was stirred at the desired temperature (60, 80, 100 or 120 ^{o}C) for 24 hours. Samples were collected after various reaction times (0.5, 1, 3, 24 hours) and analysed by NMR spectroscopy. HMF yields were calculated from the integration of HMF peaks against the ionic liquid $[C_4C_1im][HSO_4]$ itself. The ionic liquid was considered to be an internal standard, as it has negligible vapour pressure. For a selected group of conversions, HPLC-RI analysis was used to confirm the HMF selectivity. The HMF peak at the lowest field chemical shift value of 9.55 ppm was chosen for calculation of the yields as it does not interfere with any of the solvent resonances in ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, DMSO) δ 9.55 (s, 1H, CHO), 7.50 (d, 1H, furan-CH, J_{HH} = 3.5 Hz), 6.61 (d, 1H, furan-CH, J_{HH} = 3.5 Hz), 5.57 (t, 1H, OH, J_{HH} = 6.0 Hz), 4.51 (d, 2H, CH$_2$O, J_{HH} = 6.0 Hz) ppm.

S1.   M. A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N. H. Hassan, J. P. Hallett, P. A. Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16831-16840.