Supporting Information for

Conversion of fructose to 5-hydroxymethylfurfural using ionic liquids prepared from renewable materials

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Materials

D-Fructose (99%) was purchased from Alfa Aesar, 5-hydroxymethylfurfural (99%) was purchased from Aldrich, and the other starting materials (A. R. grade) were purchased from Beijing Chemical Reagents Company and used without further purification.

Analysis methods

The methods of analysis of fructose and HMF by HPLC

5-hydroxymethylfurfural (HMF): Supelcosil LC-18 5μm column at 25 °C, Shimadzu LC-20AT pump, Sama UV-Vis LC-830 detector at 282.0 nm, methanol/water (50/50 V/V) as flowing phase at 0.8 mL/min. And the amount of HMF was calculated by using an external standard.

Fructose: Hypersil NH2 5μm column at 40 °C, Shimadzu LC-20AT pump, Shimadzu RID-10A detectors at 40 °C, acetonitrile/water (75/25 V/V) as flowing phase at 0.8 mL/min. And the amount of fructose was calculated by using an external standard.

HMF Characterization

HMF was characterized by ^{1}H NMR spectra which was recorded as solutions in $CDCl_3$ at room temperature on a Brucker spectrometer at 400 MHz and by GC/MS (GC: Agilent technologies 6890N; MS: Agilent technologies 5973 inert MS Detector)

5-hydroxymethylfurfural (2): M.S.: m/z (% of max intensity) 50 (8), 69 (32), 81 (7), 97 (100), 109 (11), 126 (75); ^{1}H NMR (400M, $CDCl_3$) δ (ppm): 4.75 (s, 2 H), 6.54 (d, *J*=3.4 Hz, 1 H), 7.24 (d, *J*=3.4 Hz, 1 H), 9.62 (s, 1 H).

Experimetal procedures

Preparation of the choline chloride-based Ils

The ILs were synthesized following the procedures reported in the literature.[S1,S2] The molar ratios of the choline chloride (ChoCl) and molecular donors of the ILs are given in Supporting Table S1.

General procedures of conversion of fructose to HMF in ILs

Fructose (99%) (91.0 mg, 0.5 mmol) and known amount of IL were added into the reactor in a constant temperature oil bath, and the reaction system was stirred for desired time. After reaction, the reactor was cooled to room temperature immediately. The yields and conversions were analyzed by HPLC. Each reaction had been repeated at least three times.

Biphasic procedure

Fructose (99%) (91.0 mg, 0.5 mmol) and choline chloride/citric acid (1.47 g, 3 mmol) were added into the reactor in a constant temperature oil bath of 80 ^oC. After stirring for 1 min, the desired amount of ethyl acetate was added into the reactor. After reaction, the reaction system was cooled to room temperature. Then the ethyl acetate phase was poured out from the reactor and collected. The amounts of HMF in the two phases were analyzed by HPLC respectively and the yield was calculated. Each procedure had been repeated at least three times.

The procedure of intermittent extraction in the biphasic reaction system

Fructose (99%) (91.0 mg, 0.5 mmol) and choline chloride/citric acid (1.47 g, 3 mmol) were added into the reactor in a constant temperature oil bath of 80 ^oC. After stirring for 1 min, ethyl acetate

(1.47 g) was added into the above mixture. The reaction system was stirred for 20 min at 80 ^{o}C. Then the reactor was taken out from the constant temperature oil bath and the ethyl acetate phase was poured out and collected. The above procedures were repeated other two times, and the ethyl acetate solutions collected in the three runs were combined. The amounts of HMF in the two phases were analyzed by HPLC respectively and the yield was calculated. This procedure had been repeated at least three times.

The procedure of continuous extraction in the biphasic reaction system

Fructose (99%) (91.0 mg, 0.5 mmol) and choline chloride/citric acid (1.47 g, 3 mmol) were added into the reactor in an constant temperature oil bath of 80 ^{o}C, and the reaction mixture was stirred. After certain time, ethyl acetate was pumped into the IL phase (0.20 mL/min). During the reaction, the ethyl acetate phase flowed out from the reactor after pumping AcOEt for 15 min. After desired time, the reactor was taken out from the constant temperature oil bath, and the residual ethyl acetate phase was poured out from the reactor and was combined with the flowed-out ethyl acetate solution. The amounts of HMF in the two phases were analyzed by HPLC respectively and the yield was calculated. Each procedure had been repeated at least three times.

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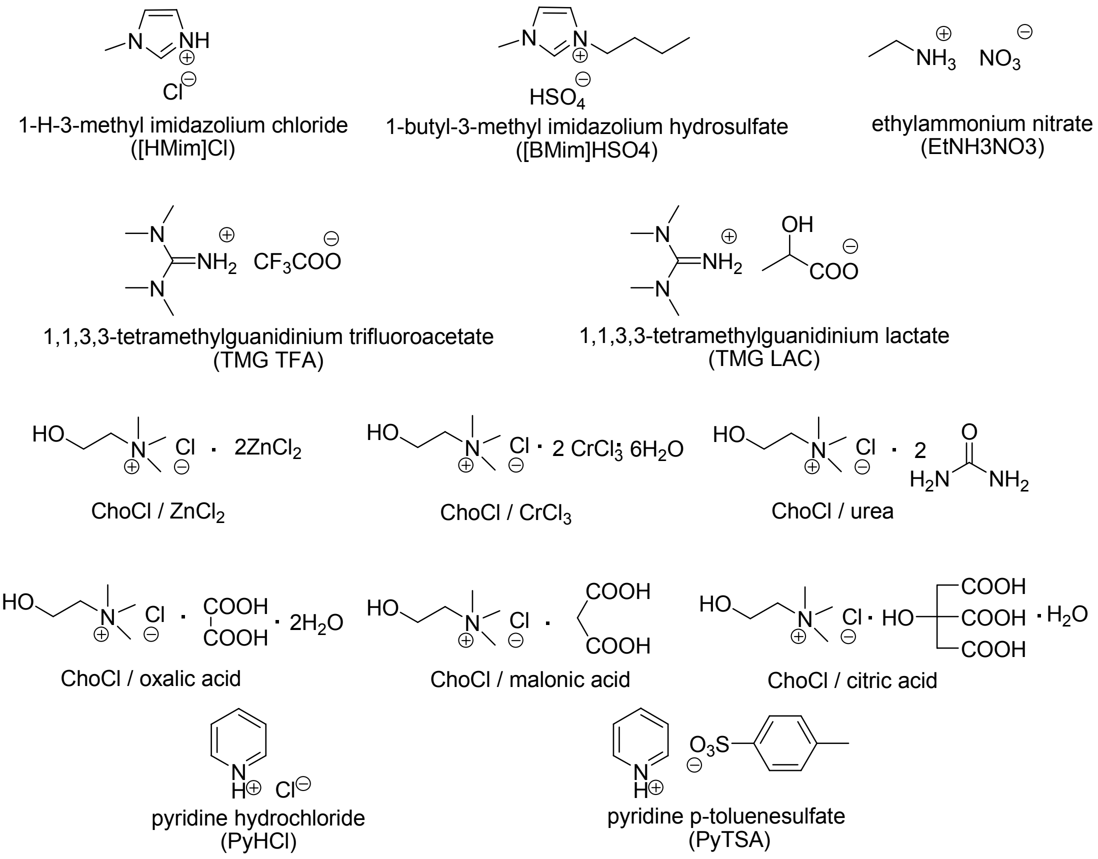
Supporting Scheme S1.



Supporting Tables

Supporting Table S1. Molar ratios of choline chloride (ChoCl) to molecular donor.

IL	Molecular donor	Molar ratio
ChoCl/urea	urea	1:2
ChoCl/$ZnCl_2$	anhydr. $ZnCl_2$	1:2
ChoCl/$CrCl_3$	$CrCl_3$ •6 H_2O	1:2
ChoCl/malonic acid	malonic acid	1:1
ChoCl/oxalic acid	oxalic acid•$2H_2O$	1:1
ChoCl/citric acid	citric acid •H_2O	2:1
ChoCl/anhydr. citric acid	anhydr. citric acid	2:1

Supporting Table S2. Results of the conversion of HMF from fructose in ChoCl/citric acid and pyridine hydrochloride (PyHCl).

Entry	Ionic liquid	Molar ratio	Tempera -ture (°C)	Time (h)	Yield (%)	Conversion (%)	Selectivity (%)
1	ChoCl/citric acid	2	80	1	41.3	83.0	49.4
2	ChoCl/citric acid	3	80	1	54.3	86.0	63.1
3	ChoCl/citric acid	4	80	1	67.0	89.0	75.1
4	ChoCl/citric acid	5	80	1	76.3	91.1	83.8
5	ChoCl/citric acid	6	80	1	77.8	93.2	83.5
6	ChoCl/citric acid	7	80	1	78.1	93.2	84.4
7	ChoCl/citric acid	6	80	0.5	60.7	85.2	71.2
8	ChoCl/citric acid	6	80	2	77.2	95.4	80.9
9	ChoCl/citric acid	6	80	3	77.7	96.5	80.5
10	ChoCl/citric acid	6	70	1	41.3	45.3	91.2
11	ChoCl/citric acid	6	90	1	76.4	94.2	81.1
12	ChoCl/citric acid	6	100	1	75.6	94.6	80.0
13	PyHCl	1	80	1	36.0	81.2	44.3
14	PyHCl	2	80	1	51.0	87.8	58.1
15	PyHCl	3	80	1	61.8	93.5	66.1
16	PyHCl	4	80	1	66.9	94.4	70.9
17	PyHCl	5	80	1	69.4	92.1	75.4
18	PyHCl	6	80	1	72.3	96.9	74.6
19	PyHCl	7	80	1	69.1	95.6	72.3

Fructose (99%) 91.0mg 0.5 mmol, the molar ratio of ILs to fructose is from 1 to 7.

Supporting Table S3. HMF converted from Fructose in the biphasic system of Choline chloride/citric acid and AcOEt at 80 ^{o}C for 1 h: fructose (99%) 91.0mg 0.5 mmol, choline chloride/citric acid 1.47 g 3 mmol.

Entry	W_{AcOEt}/ W_{IL}[a]	Total yield (%)	Conve -rsion (%)	Selec -tivity (%)	Yield in AcOEt (%)	W_{HMF}/ W_{AcOEt}	W_{HMF}/ W_{IL}	R[b]	Extraction rate (%)[c]
1	0	77.8	93.2	83.5	-	-	-	-	-
2[d]	1	85.4	92.5	92.3	31.9	0.0137	0.0230	0.60	37.4
3[d]	2	86.8	94.2	92.1	47.7	0.0102	0.0167	0.61	55.0
4[d]	3	85.6	93.2	91.8	55.6	0.0079	0.0129	0.61	64.9
5[e]	1+1+1	82.1	91.7	89.5	63.0	0.0090[g]	0.0082	1.10	77.0
6[f]	6.1	80.7	89.8	89.9	64.3	0.0045[g]	0.0069	0.65	80.0
7[f	4.9	91.4	97.6	93.6	66.0	0.0058[g]	0.0109	0.53	72.2

[a] W_{AcOEt}/W_{IL} is the ratio of weight of AcOEt to weight of IL. [b] R is equal to the ratio of W_{HMF}/W_{AcOEt} to W_{HMF}/W_{IL}. [c] Extraction rate is the ratio of yield in AcOEt to the total yield. [d]AcOEt were added into IL phase in the beginning of reaction. [e] The intermittent extraction: added fresh AcOEt (W_{AcOEt}/W_{IL}=1) into IL phase and poured AcOEt phase out after biphasic system reacted for 20 min, repeated 2 times and the total reaction time was 1 h. [f] The continuous extraction: pumped AcOEt (0.2 mL/min) into the IL mixture after the reaction run for 10 and 20 min, respectively. [g] The average value.

Supporting references

[S1] A. P. Abbott, G. Capper, D. L. Davies, R. K. Rasheed and V. Tambyrajah, *Chem. Comm.* 2003, 70-71.

[S2] A. P. Abbott, D. Boothby, G. Capper, D. L. Davies, R. K. Rasheed, *J. Am. Chem. Soc.* 2004, **126**, 9142-9147.