Supporting Information

Conversion of glucose into 5-hydroxymethylfurfural catalyzed by acid-base bifunctional heteropolyacid-based ionic hybrids

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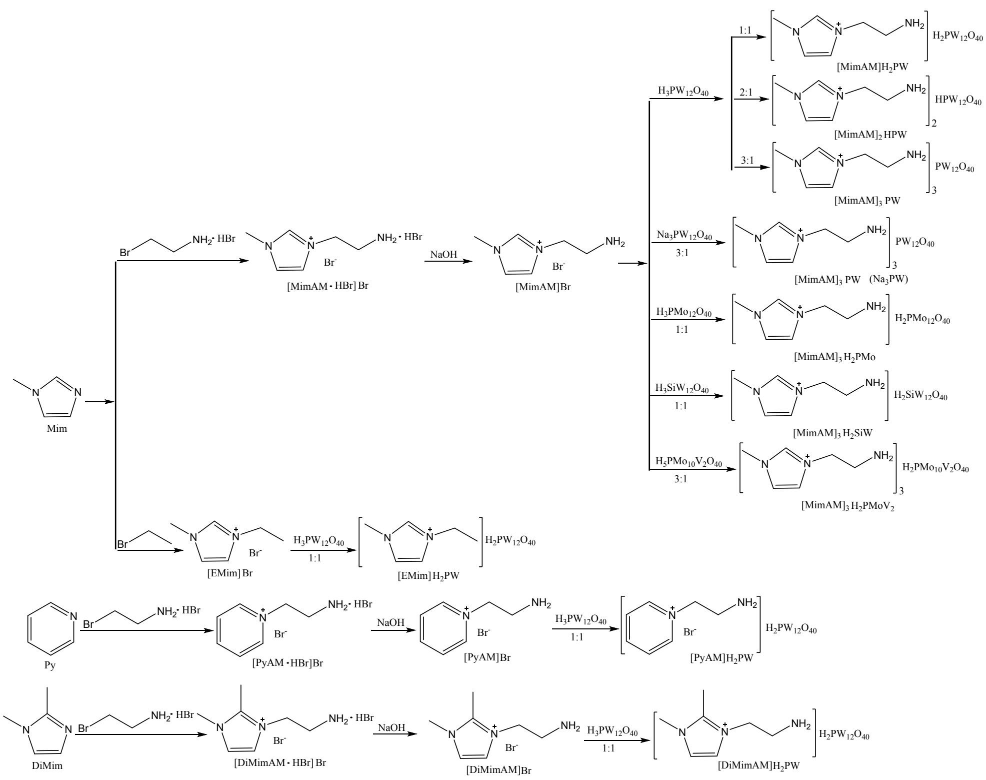

Scheme S1 Synthesis of amino-functionalized HPA-based ionic hybrid catalysts and various counterparts

Table S1 The elemental analysis of $[MimAM]_nH_{3-n}PW$

	$[MimAM]H_2PW$		Recovered $[MimAM]H_2PW$	$[MimAM]_2HPW$		$[MimAM]_3PW$	
	Calcd	Found	Found	Calcd	Found	Calcd	Found
C (wt%)	2.09	1.99	2.11	4.75	4.74	5.99	6.09
N (wt%)	1.00	1.15	1.05	2.74	2.74	3.50	3.54
H (wt%)	0.40	0.39	0.32	1.00	1.01	1.26	1.26

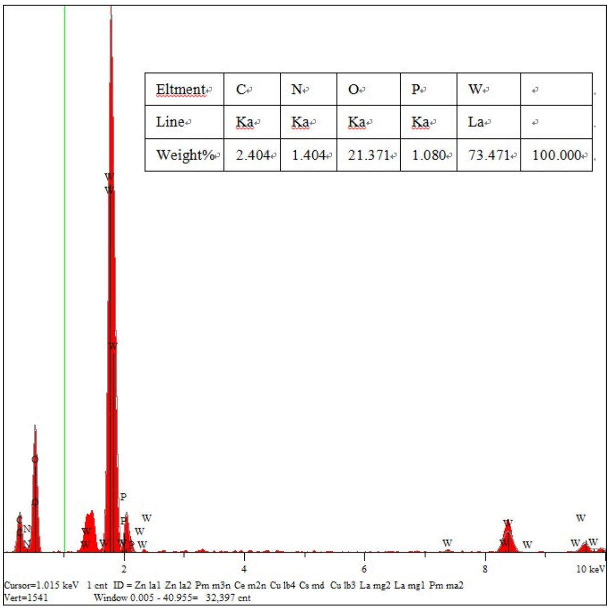

Fig. S1 SEM-EDX analysis of $[MimAM]H_2PW$.

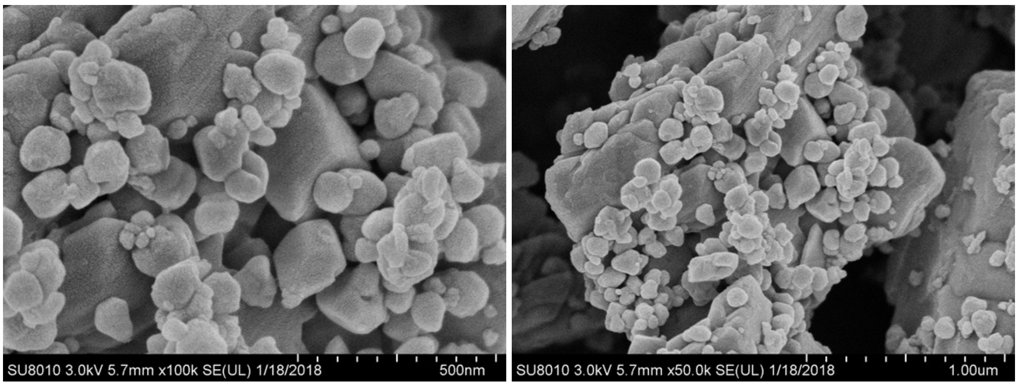

Fig. S2 SEM images of $[MimAM]H_2PW$.

Table S2 The acidity of $[MimAM]_nH_{3-n}PW_{12}O_{40}$ (n = 0-3).

Catalyst	$H_3PW_{12}O_{40}$	$[MimAM]H_2PW$	$[MimAM]_2HPW$	$[MimAM]_3PW$
Total acidity [a] (mol mol^{-1})	12.12	8.90	6.68	5.17

[a] 0.05 g of solid was suspended in 45 mL of acetonitrile and stirred for 3 h. Measured by titration with a solution of *n*-butylamine in acetonitrile (0.05 M) using the indicator anthraquinone (pK_a = −8.2).

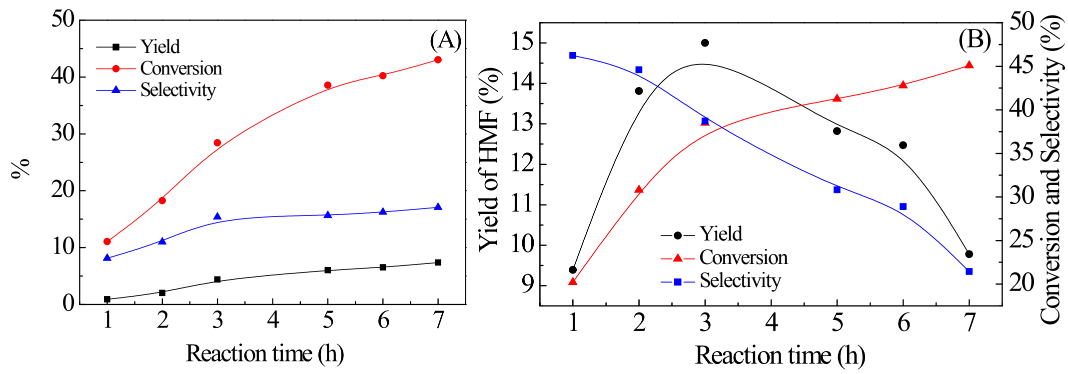

Fig. S3 $[EMim]H_2PW$ (A) and $[MimAM]_3PW(Na_3PW)$ (B) catalyzed glucose dehydration to HMF. Reaction conditions: 0.1 g gluose, 0.37 g NaCl and 30 μmol catalyst in 12 mL solvent (H_2O : THF=1 : 2) at 160 °C.

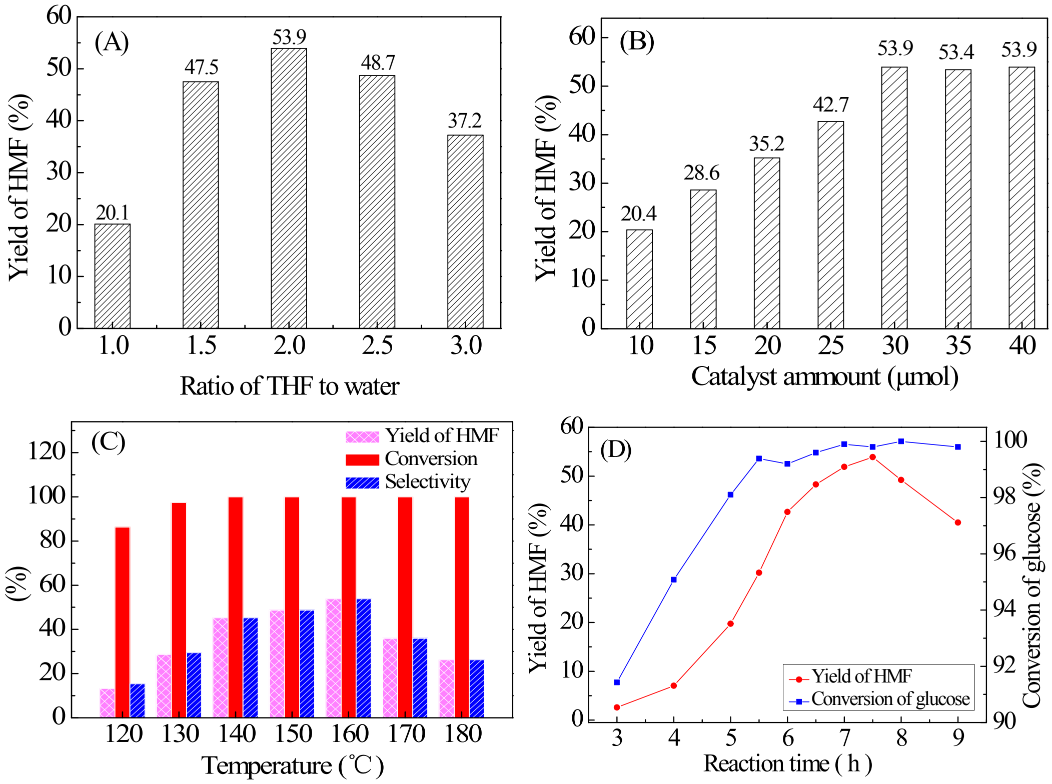

Fig. S4 Influences of reaction conditions on the hydrolysis of glucose to HMF over [MimAM]H_2PW. (A) Molar ratio of THF to water. (B) Catalyst amount. (C) Reaction temperature. (D) Reaction time. Reaction conditions: 0.1 g gluose, 0.37 g NaCl and 30 μmol catalyst in 12 mL solvent (H_2O : THF=1 : 2) at 160 ^{o}C for 7.5 h; for each figure there is a specific parameter changed.

Table S3 The effect of [MimAM]H_2PW on the different substrates hydrolysis.

Entry	Substrate	Conversion (%)	Yield of HMF (%)[a]
1	Glucose	99.8	53.9
2	Cellulose	23.6	8.2
3	Sucrose	94.3	23.5
4	Starch	54.1	12.4
5	Fructose	100	40.1

[a] Reaction conditions: 0.1 g gluose, 0.37 g NaCl and 30 μmol catalyst in 12 mL solvent (H_2O : THF=1 : 2) at 160 ^{o}C for 7.5 h.

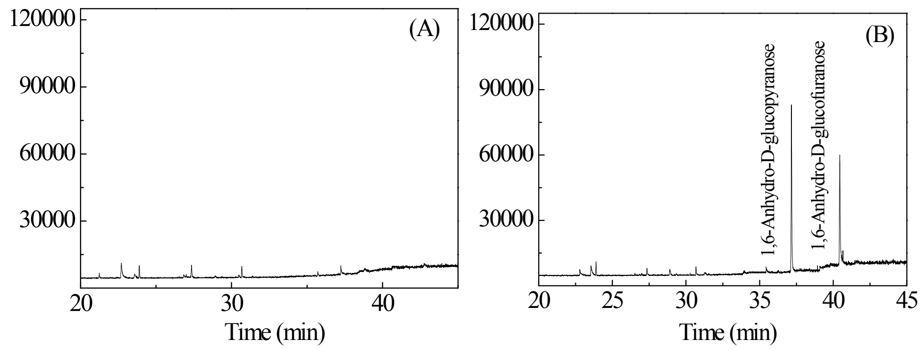

Fig. S5 GC-MS spectrogram of fructose (A) and glucose (B) dehydration to HMF. Reaction conditions: 0.1 g gluose, 0.37 g NaCl and 30 μmol catalyst in 12 mL solvent (H_2O : THF=1 : 2) at 160 ^oC.

The thermal filtration recovery experiments

We conduct a reaction of just the catalyst in the solvent (without reactant glucose) at the optimal condition, and then filter the catalyst out. The filtrate is used as solvent, and then plus reactant glucose for the next reaction, which gives 5.6% yield of HMF.