Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

-Supporting Information-

A universal solvent effect on the formation of soluble humins in glucose dehydration to 5-hydroxymethylfurfural

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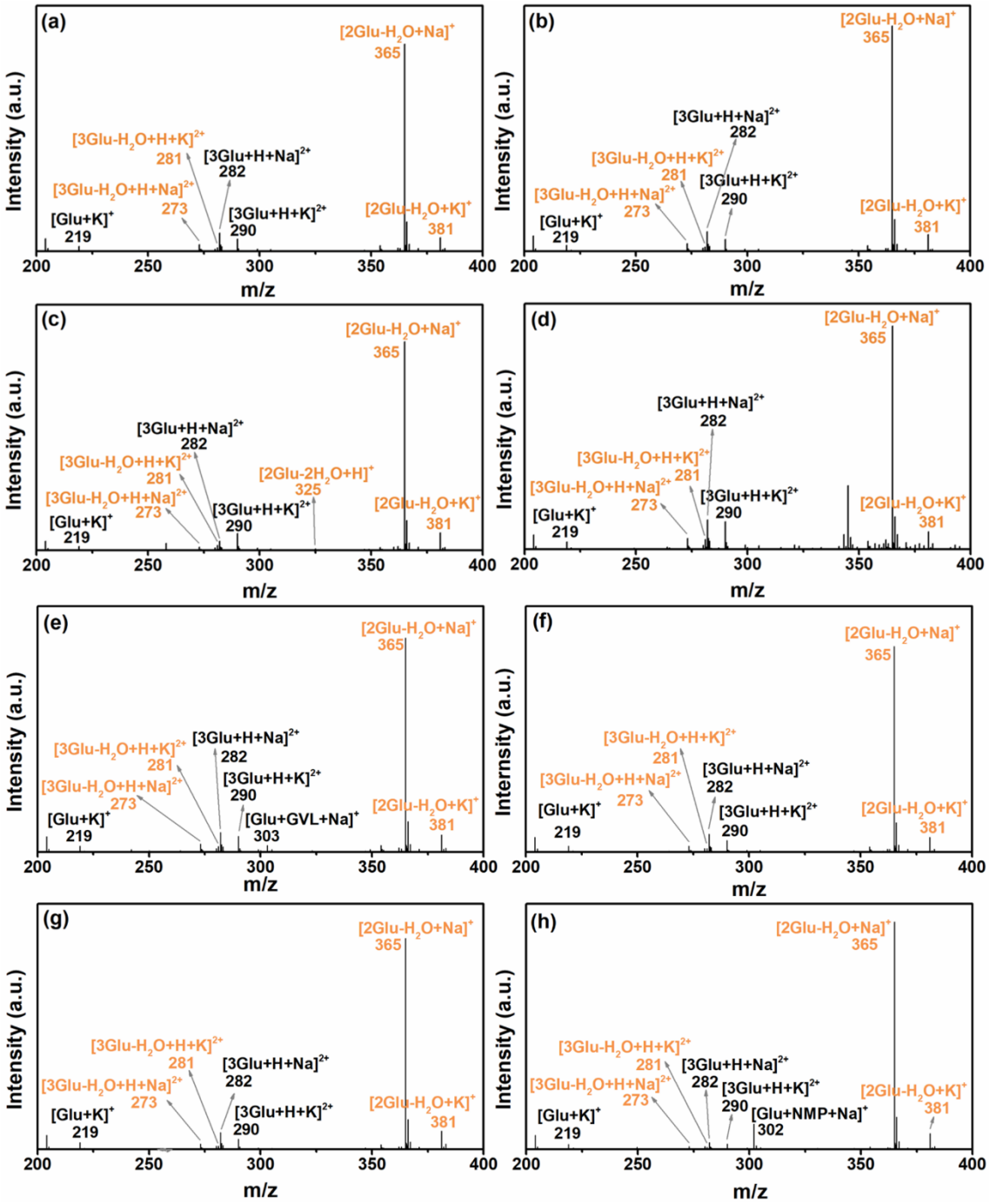

Figure S1. ESI-MS spectra of glucose (4.5 *wt*.%) in various solvents at room temperature. (a) H_2O, (b) MIBK-H_2O, (c) MTHF-H_2O, (d) DMF-H_2O, (e) GVL-H_2O, (f) THF-H_2O, (g) DIO-H_2O, and (h) NMP-H_2O.

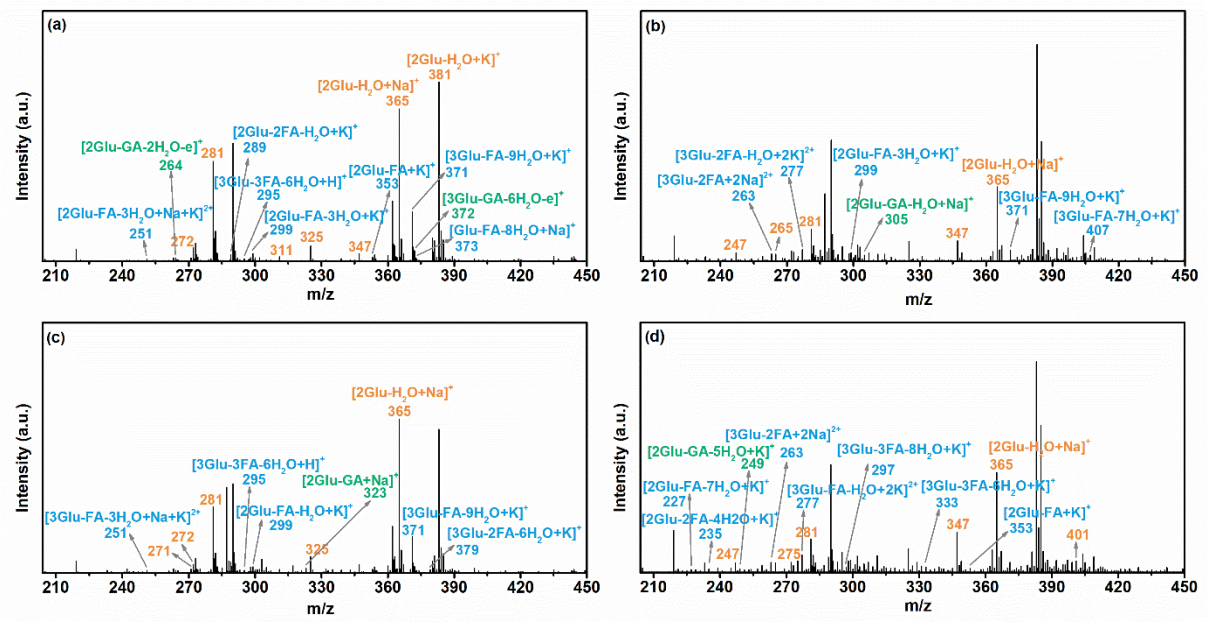

Figure S2. ESI-MS spectra of reaction mixture after reacting glucose at 120 °C for 4 h in presence of various acid catalysts. (a) H_2O with 0.075 mM HCl, (b) H_2O with 0.075 mM $AlCl_3 \cdot 6H_2O$, (c) MTHF-H_2O with 0.075 mM HCl and (d) MTHF-H_2O with 0.075 mM $AlCl_3 \cdot 6H_2O$. Species marked in different colors represents different paths for humin formation: etherification-dehydration-condensation (orange, humins **I**); degradative (− FA) condensation (blue, humins **II**); degradative (− GA) condensation (green, humins **III**).

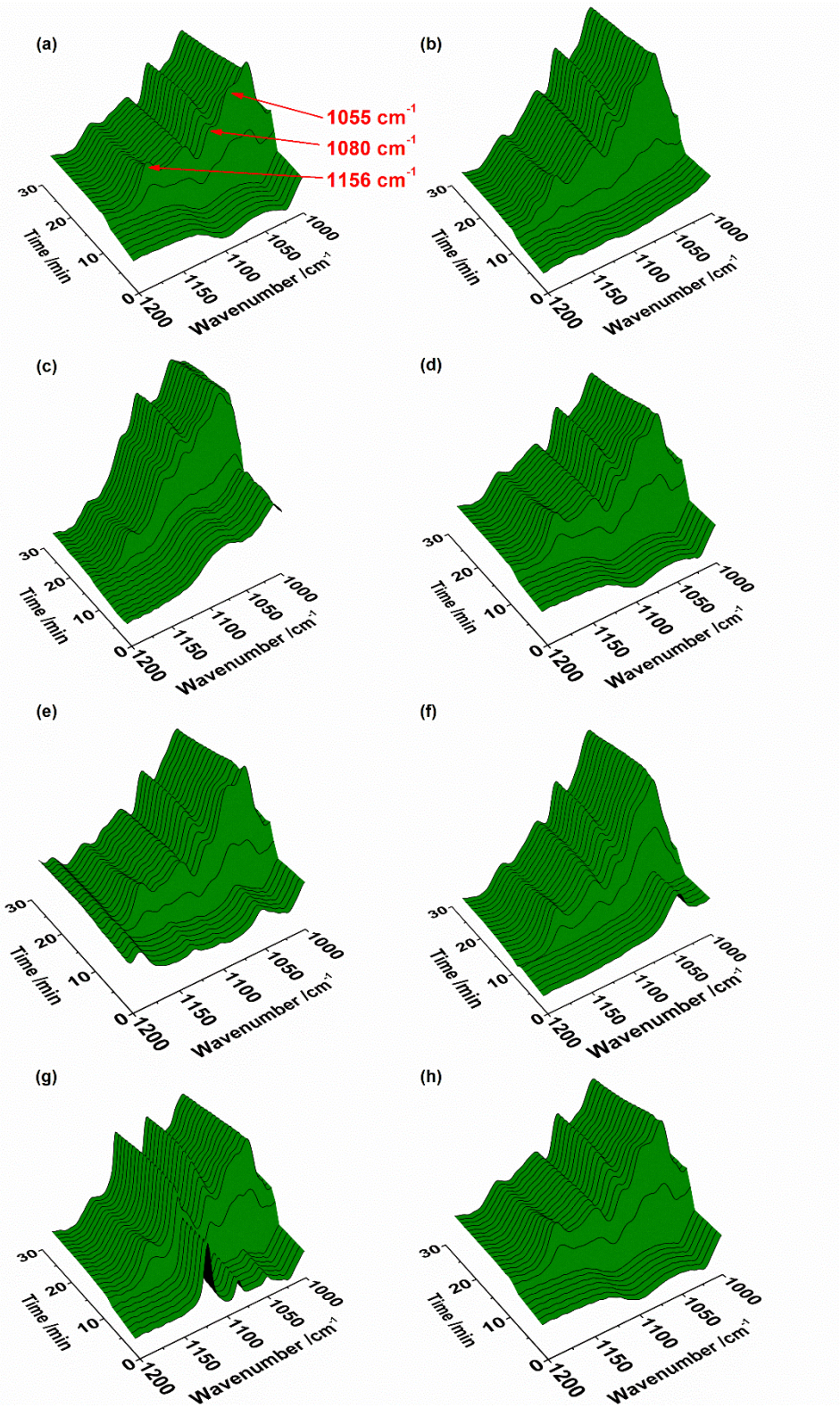

Figure S3. *In situ* ATR-IR spectra of the reaction mixture containing glucose in various solvents. (a) H_2O, (b) MIBK-H_2O, (c) MTHF-H_2O, (d) DMF-H_2O, (e) GVL-H_2O, (f) THF-H_2O, (g) DIO-H_2O, and (h) NMP-H_2O. The FT-IR peaks at 1055 cm^{-1} and 1080 cm^{-1} are selected as the characteristic peaks of α-D-glucopyranose and β-D-glucopyranose, respectively; and IR peak at 1156 cm^{-1} represents the vibration of pyranose ring. Reaction conditions: 10 g of glucose, 50 mL of solvents, 70 °C.

Table S1. Physical properties and Kamlet-Taft parameters of the polar aprotic organic solvents.

Entry	Solvents	Boiling point (°C)	Solubility in water	Density g/mL	V_{H2O}/V_{org}	Kamlet-Taft parameters		
						α	β	π
1	MIBK	115.8	1.7 g/100 mL	0.801	49/1	0	0.48	0.65
2	MTHF	78-80	15.0 g/100 mL	0.860	85/15	0	0.45	0.53
3	DMF	92-94	0.26 g/100 mL	0.905	399/1	0	-	-
4	GVL	207-208	miscible	1.050	-	0	0.60	0.83
5	DIO	101.3	miscible	1.034	-	0	0.37	0.55
6	THF	66	miscible	0.887	-	0	0.55	0.58
7	NMP	203	miscible	1.028	-	0	0.75	0.90

Table S2. Conversion of glucose in mixed solvents with V_{H2O}/V_{org} of 90/10.

Entry	$V_{H2O}/V_{org.}$	Solvent	Conv. of gluc. /%	Yield / %			Selectivity of FA /%
				Fruc.	HMF	FA	
1	90/10	GVL+H_2O	3.0	0.2	-	1.0	33.3
2		THF+H_2O	6.0	3.1	-	1.7	28.3
3		DIO+H_2O	3.5	1.2	-	1.5	42.8
4		NMP+H_2O	6.7	1.4	-	2.5	37.3

Reaction conditions: 4.5 *wt*.% Glucose, 1 mL solvent, 120 °C, 4 h.

Table S3. The structural formula of the ionic species deconvoluted from the ESI-MS spectra of the reaction mixture after reacting glucose in various solvents at 120 °C for 4 h.

m/z	Possible structural formula	m/z	Possible structural formula
209	$[3Glu\text{-}2FA\text{-}3H_2O+H+Na]^{2+}$	300	$[2Glu\text{-}GA\text{-}e]^{+}$
235	$[2Glu\text{-}2FA\text{-}4H_2O+K]^{+}$	301	$[2Glu\text{-}FA\text{-}2H_2O+Na]^{+}$
239	$[3Glu\text{-}6H_2O+2Na]^{2+}$	305	$[2Glu\text{-}GA\text{-}H_2O+Na]^{+}$
243	$[2Glu\text{-}FA\text{-}4H_2O+H]^{+}$	309	$[2Glu\text{-}5H_2O+K]^{+}$
249	$[2Glu\text{-}GA\text{-}5H_2O+K]^{+}$	311	$[2Glu\text{-}4H_2O+Na]^{+}$
250	$[3Glu\text{-}2FA\text{-}11H_2O\text{-}e]^{+}$	321	$[2Glu\text{-}GA\text{-}H_2O+K]^{+}$
251	$[3Glu\text{-}FA\text{-}3H_2O+Na+K]^{2+}$	325	$[2Glu\text{-}2H_2O+H]^{+}$
261	$[3Glu\text{-}FA\text{-}H_2O+2Na]^{2+}$	329	$[2Glu\text{-}3H_2O+Na]^{+}$
263	$[3Glu\text{-}2FA+2K]^{2+}$	339	$[2Glu\text{-}GA+K]^{+}$
272	$[3Glu\text{-}2H_2O+H+K]^{2+}$	340	$[3Glu\text{-}2FA\text{-}6H_2O\text{-}e]^{+}$
281	$[3Glu\text{-}H_2O+H+K]^{2+}$	347	$[2Glu\text{-}2H_2O+Na]^{+}$
289	$[2Glu\text{-}2FA\text{-}H_2O+K]^{+}$	353	$[2Glu\text{-}FA+K]^{+}$
293	$[2Glu\text{-}5H_2O+Na]^{+}$	365	$[2Glu\text{-}H_2O+Na]^{+}$
294	$[3Glu\text{-}2GA\text{-}7H_2O\text{-}e]^{+}$	377	$[3Glu\text{-}2FA\text{-}4H_2O+H]^{+}$
298	$[4Glu\text{-}4FA\text{-}H_2O+2K]^{2+}$	381	$[2Glu\text{-}H_2O+K]^{+}$
299	$[4Glu\text{-}2FA\text{-}3H_2O+H+Na]^{2+}$	415	$[3Glu\text{-}7H_2O+H]^{+}$

Table S4. Conversion of glycolaldehyde dimer in various solvents.

Entry	Solvent	Yield of FA /%
1	H_2O	38.0
2	MIBK+H_2O	36.7
3	MTHF+H_2O	42.6
4	DMF+H_2O	24.0
5	GVL+H_2O	32.0
6	THF+H_2O	32.9
7	DIO+H_2O	41.8
8	NMP+H_2O	28.4

Reaction conditions: 0.25 mmol glycolaldehyde dimer, 1 mL solvent, 120 ^oC, 4 h.

Table S5. The protophilic energy (ΔG) of different solvents.

Entry	Solvent	ΔG /KJ·mol^{-1}
1	H_2O	217.1
2	MIBK	-13.0
3	MTHF	-24.1
4	DMF	62.3
5	GVL	-9.8
6	THF	-22.4
7	DIO	-4.6
8	NMP	-34.3