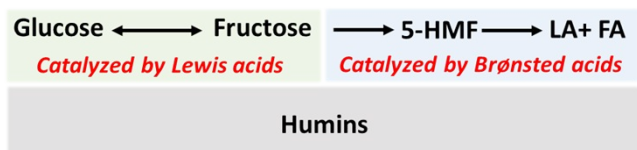**Effect of Metal Chlorides on Glucose Mutarotation and Possible Implications on Humin Formation**

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Supporting Information

Scheme S1: Simplified tandem reaction scheme of glucose conversion to HMF

Experimental

Materials

Tin (IV) chloride pentahydrate ($SnCl_4.5H_2O$), chromium (III) chloride hexahydrate ($CrCl_3.6H_2O$), aluminum chloride hexahydrate ($AlCl_3.6H_2O$), Glucose (Dextrose, D(+)Glucose) were purchased from Sigma-Aldrich and used without further purification. Sulfuric acid (H_2SO_4 5 M Fluka Analytical) and hydrochloric acid (36% w/w aqueous solution Alfa Aesar) were also used for the Brønsted acid mutarotation reaction.

Catalytic reactions

In a typical experiment, the metal chloride hydrates were dissolved in deionized water to prepare 10mM, 50mM and 100mM solutions. Then, appropriate amount of glucose was used so that the final solution contains 0.8M of the monosaccharide. Appropriate amount of Brønsted acids (HCl and H_2SO_4) were also mixed in water to prepare solution in the 0.01-0.1M concentration range.

In another experiment, solutions of 1.6M of glucose in water were also prepared and left under stirring for 5 hours to reach anomeric equilibrium. Then, metal chloride hydrates were dissolved in deionized water and mixed with the glucose solutions to study any deviation from the equilibrium.

Spectroscopic characterization

Raman spectra were recorded using a Horiba LabRAM HR Evolution high spatial and spectral resolution spectrometer. The incident beam (532nm, 80mW) was directed via a 90° macro lens of 40 mm focal length in the middle of a quartz cuvette containing each reaction mixture. The scattered light was collected through backscattering geometry and analysed with a 1800gr/mm grating. Collection of the scattered light was achieved with an air-cooled open electrode 1024x256 pixels CCD -75°C. The acquisition time of each spectrum was 50-60secs, the number of accumulations varied in the range of 6-12 and the spectral slit was fixed at 100μm. A 25% neutral density filter was
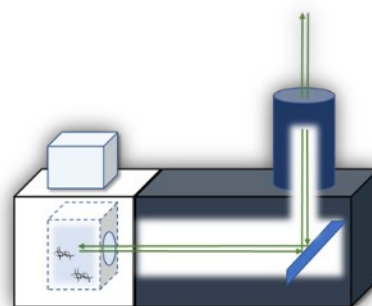

Figure s1: Schematic of the in-situ Raman setup

also used to avoid local overheating of the liquid sample which can cause change in the measured reaction kinetics.

Kinetics Analysis

The simplified glucose mutarotation scheme shown next (since the open chain aldehyde form was not detected herein) can be used to estimate the observed rate constant $k = (k_a + k_\beta)$ assuming a first order reaction. Utilizing the differential form of the rate law:

$$\alpha\text{-Glucose} \underset{k_\beta}{\overset{k_\alpha}{\rightleftharpoons}} \beta\text{-Glucose}$$
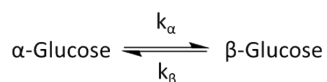
$$\frac{d[a]}{dt} = -k_\alpha[\alpha] + k_b[\beta]$$

After integration, we can calculate the observed rate constant via:

$$ln\frac{([a] - [a]_{eq})}{([a]_0 - [a]_{eq})} = -(k_a + k_\beta)t$$

Table S1: Rate constants for the forward and reverse reaction

	k_{obs} (min^{-1})	k_a (min^{-1})	k_β (min^{-1})
H$_2$O	0.02325	0.01604	0.00721
10mM AlCl$_3$	0.02167	0.01344	0.00823
50mM AlCl$_3$	0.02267	0.01496	0.00771
100mM AlCl$_3$	0.03586	0.02456	0.0113
10mM CrCl$_3$	0.01935	0.01258	0.00677
50mM CrCl$_3$	0.02315	0.01331	0.00984
100mM CrCl$_3$	0.02396	0.01234	0.01162
10mM SnCl$_4$	0.03088	0.02115	0.00973
50mM SnCl$_4$	0.02325	0.01604	0.00721

Table S2: pH of the solutions at different stages

	Salt dissolution ($t = 0min$)	Salt dissolution ($t = 24h$)	Glucose addition ($t = 0min$)	Glucose addition ($t = 24hr$)
10mM AlCl$_3$	3.81	3.78	3.83	3.86
50mM AlCl$_3$	3.09	3.27	3.37	3.35
100mM AlCl$_3$	2.88	3.09	3.23	3.25
10mM CrCl$_3$	3.42	2.86	2.92	2.93
50mM CrCl$_3$	2.85	2.7	2.79	2.79
100mM CrCl$_3$	2.66	2.52	2.66	2.61
10mM SnCl$_4$	1.8	1.74	1.80	2.03
50mM SnCl$_4$	1.23	1.21	1.31	1.42
100mM SnCl$_4$	0.95	0.86	1.02	1.12

Figure s2: In Situ Raman data of 10mMAlCl3, 100mMAlCl3, 10mMCrCl3, 100mMCrCl3, 10mMSnCl4 and 100mMSnCl4
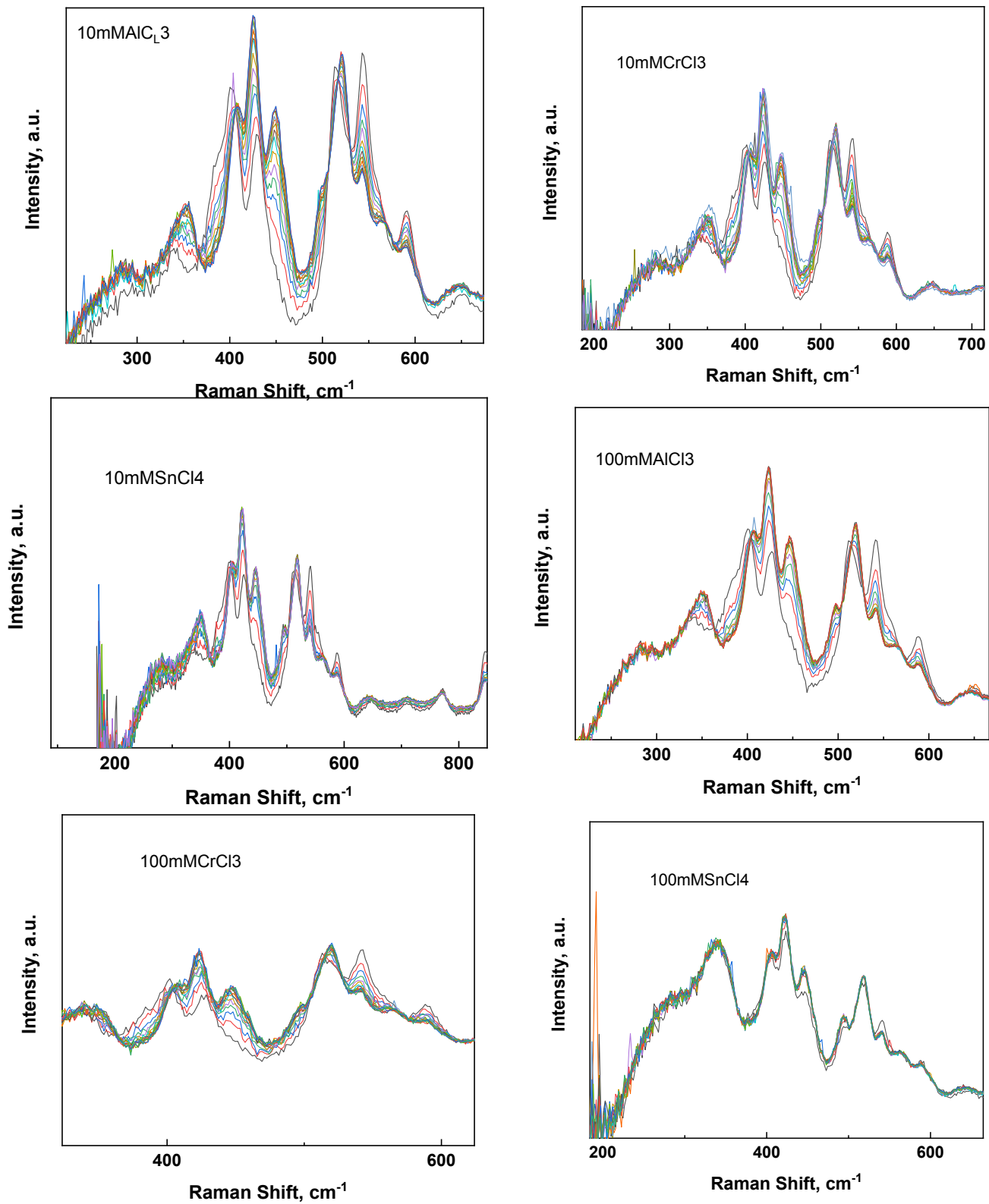
Figure s3: Kinetic data analysis for glucose mutarotation in the presence of HCl or H_2SO_4
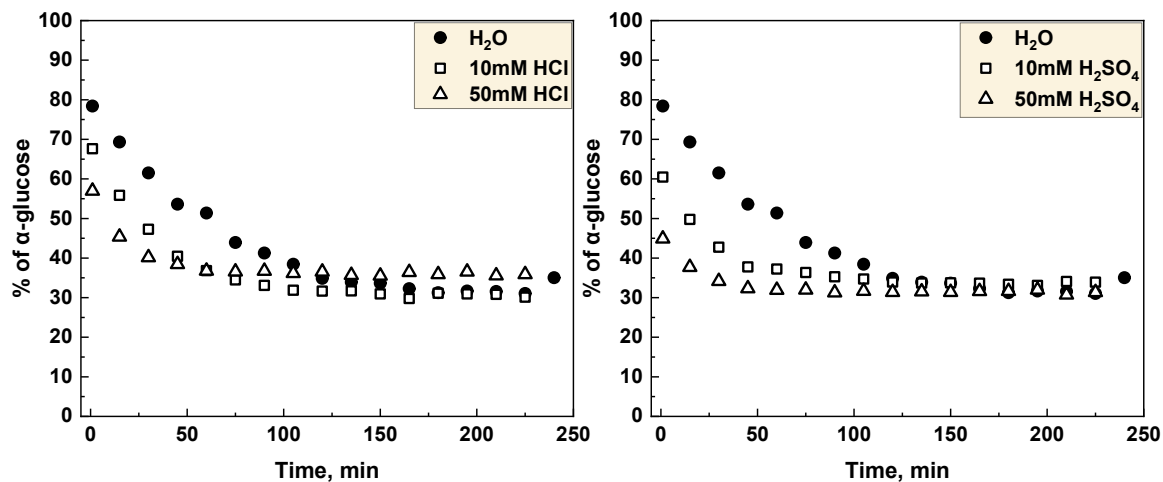

Figure s4: Raman and ATR-FTIR data of humins at earlier stages of their formation and relevant photos during reaction