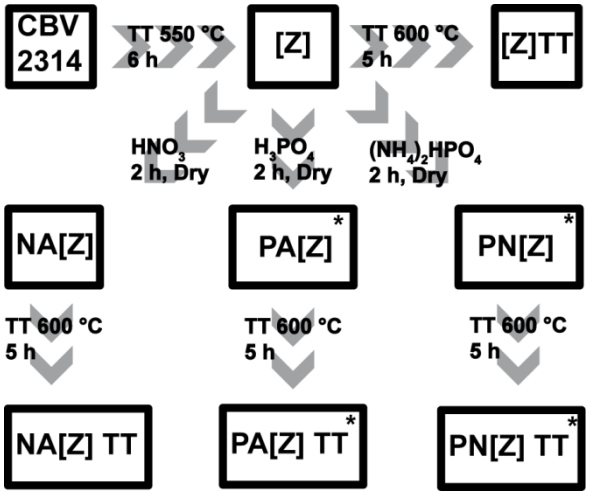
Electronic Supplementary Information



Scheme S1. Preparation scheme of the samples under study: TT = Thermal treatment, HT = Hydrothermal treatment, and * = Sample contains an eluted variety.

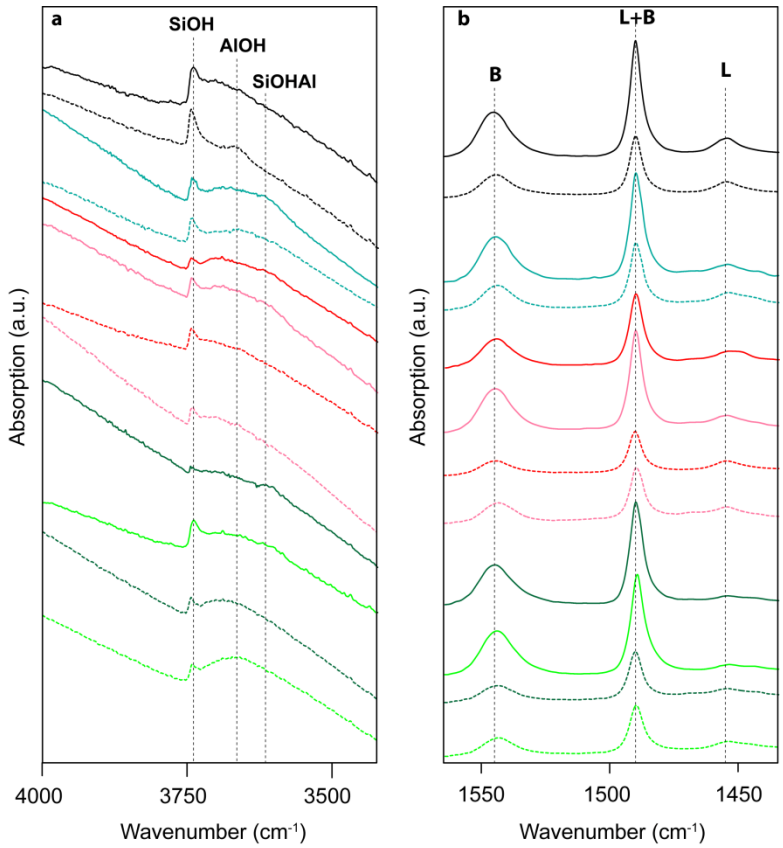


Fig. S1 FT-IR spectra of pyridine TPD at 200°C for a) the O-H stretch region and b) the N-H stretch region of the following samples: ■ = [Z], ■ dashed = [Z]TT, ■ = NA[Z], and ■ dashed = NA[Z]TT ■ = PA[Z], ■ = PA[Z]e, ■ = PB[Z], and ■ = PB[Z]e ■ dashed = PA[Z]TT, ■ dashed = PA[Z]TTe, ■ dashed = PB[Z]TT, and ■ dashed = PB[Z]TTe

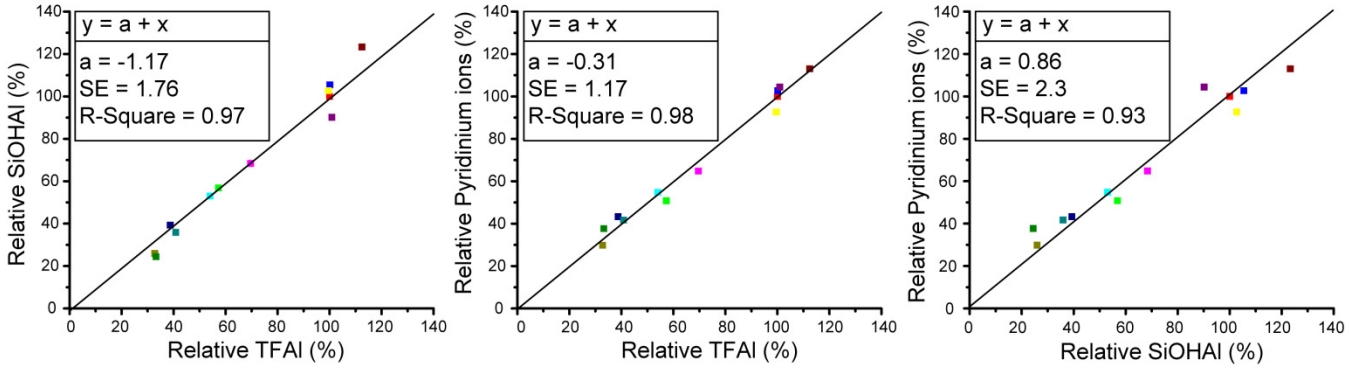


Fig. S2 Relation between SiOHAl groups, TFAl species and Brønsted acid sites. Values of SiOHAl correspond to the area of the deconvoluted 3600 cm^{-1} band of each sample, relative to the area of the deconvoluted 3600 cm^{-1} band of **[Z]**. Details of the deconvolution procedure can be found in Table S2. Values for TFAl correspond to the relative contribution of the deconvoluted 55 ppm peaks of each sample relative to the relative contribution of the deconvoluted 55 ppm peaks of **[Z]**. Details of the deconvolution procedure can be found in Table S-3. Values for the pyridinium ions correspond to the baseline corrected area of the 1540 cm^{-1} pyridinium ion N-H stretch band of each sample, relative to area of the 1540 cm^{-1} band for sample **[Z]** at 200 °C.

Table S1. Relative amounts of SiOHAl, TFAl and Pyridinium ion

Sample	SiOHAl (%)[a]	TFAl (%) [a]	Pyridimium ions (%) [a]
[Z]	100	100	100
[Z] TT	57	57	51
NA[Z]	105	100	103
NA[Z] TT	53	53	55
PA[Z]	68	70	65
PA[Z] e	103	100	93
PA[Z] TT	26	33	30
PA[Z] TT e	39	39	43
PB[Z]	90	101	104
PB[Z] e	123	112	113
PB[Z] TT	24	33	38
PB[Z] TT e	36	41	42

[a] Relative to sample **[Z].**

Table S2. Parameters used for the deconvolution of the FT-IR spectra.

Type	Center	Height	FWHM	Type
0 Quadratic	-	-	-	
1 Lorentzian	3603[a], 3603[b], 3605[c], 3603[d], 3605[e], 3603[f], 3602[g], 3602[h], 3603[i], 3603[j], 3604[k], 3604[l]	0.25[a], 0.17[b], 0.32[c], 0.19[d], 0.20[e], 0.37[f], 0.06[g], 0.13[h], 0.19[i], 0.55[j], 0.05[k], 0.09[l]	38.14[a], 43.70[b], 37.62[c], 44.43[d], 44.36[e], 37.79[f], 41.31[g], 46.70[h], 34.76[i], 34.45[j], 43.21[k], 47.40[l]	Si-OH-Al
2 Lorentzian	3718[a], 3724[b], 3718[c], 3723[d], 3719[e], 3718[f], 3720[g], 3720[h], 0[i], 3726[j], 3718[k], 3719[l]	0.03[a], 0.03[b], 0.05[c], 0.05[d], 0.04[e], 0.05[f], 0.03[g], 0.06[h], 0.00[i], 0.03[j], 0.03[k], 0.04[l]	35.03[a], 24.13[b], 38.42[c], 25.20[d], 20.39[e], 36.61[f], 31.24[g], 33.45[h], 0.00[i], 16.75[j], 27.44[k], 27.38[l]	Si-OH (internal)
3 Lorentzian	3740[a], 3741[b], 3740[c], 3741[d], 3737[e], 3739[f], 3741[g], 3740[h], 0[i], 3740[j], 3741[k], 3740[l]	0.04[a], 0.06[b], 0.06[c], 0.09[d], 0.02[e], 0.05[f], 0.03[g], 0.05[h], 0.00[i], 0.07[j], 0.03[k], 0.03[l]	9.65[a], 8.57[b], 9.45[c], 9.41[d], 8.25[e], 10.34[f], 7.51[g], 8.66[h], 0.00[i], 8.64[j], 7.04[k], 8.25[l]	Si-OH (external)
4 Lorentzian	0[a], 3658[b], 0[c], 3658[d], 3685[e], 0[fe], 3653[g], 3659[h], 0[i], 0[j], 3656[k], 3659[l]	0.00[a], 0.07[b], 0.00[c], 0.10[d], 0.02[e], 0.00[f], 0.03[g], 0.06[h], 0.00[i], 0.00[j], 0.04[k], 0.04[l]	0.00[a], 32.40[b], 0.00[c], 35.53[d], 38.63[e], 0.00[f], 78.30[g], 64.23[h], 0.00[i], 0.00[j], 62.71[k], 54.72[l]	Al-OH
5 Lorentzian	3355[a], 3355[b], 3355[c], 3355[d], 3355[e], 3355[f], 3355[g], 3355[h], 3355[i], 3355[j], 3355[k], 3355[l]	0.05[a], 0.05[b], 0.07[c], 0.06[d], 0.07[e], 0.07[f], 0.03[g], 0.07[h], 0.04[i], 0.09[j], 0.02[k], 0.03[l]	436.85[a], 436.85[b], 436.85[c], 436.85[d], 436.85[e], 436.85[f], 436.85[g], 436.85[h], 436.85[i], 436.85[j], 436.85[k], 436.85[l]	unknown
6 Lorentzian	3544[a], 3544[b], 3544[c], 3544[d], 3544[e], 3544[f], 3544[g], 3544[h], 3544[i], 3544[j], 3544[k], 3544[l]	0.03[a], 0.03[b], 0.04[c], 0.04[d], 0.05[e], 0.05[f], 0.04[g], 0.06[h], 0.02[i], 0.04[j], 0.03[k], 0.04[l]	153.26[a], 153.26[b], 153.26[c], 153.26[d], 153.26[e], 153.26[f], 153.26[g], 153.26[h], 153.26[i], 153.26[j], 153.26[k], 153.26[l]	unknown

[a] [Z] [b] [Z]TT [c] NA[Z] [d] NA[Z]TT [e] PA[Z] [f] PA[Z]e [g] PA[Z]TT [h] PA[Z]TT e [i] PN[Z] [j] PN[Z]e [k] PN[Z]TT [l] PN[Z]TT e.

Table S3. Isotropic chemical shifts and second-order quadrupolar effect parameters (SOQE) estimated from the analysis of ^{27}Al MQ MAS spectra.

Sample	**[Z]TT**		**PA[Z]**		**PA[Z] e**		**PA[Z]TT**		**PA[Z]TT e**		**PB[Z]**		**PB[Z]TT e**	
	δ_{iso} (ppm)	SOQE (MHz)	δ_{iso} (ppm)	SOQE (MHz)	δ_{iso} (ppm)	SOQE (MHz)	δ_{iso} (ppm)	SOQE (MHz)	δ_{iso} (ppm)	SOQE (MHz)	δ_{iso} (ppm)	SOQE (MHz)	δ_{iso} (ppm)	SOQE (MHz)
1	56.6	2.6	56.6	2.6	58.7	4.6	56.6	3.1	55.8	2.1	56.8	2.6	56.5	2.8
2	1.27	2.8	0.9	2.5	3.1	4.7	1.1	3.0	0.3	2.4	-	-	0.9	3.6
3	-	-	51.7	6.6	58.9	7.7	51.7	6.5	51.6	6.6	55.8	6.7	52.0	6.7
4	-	-	-2.6	2.6	-0.3	5.1	-2.45	3.2	-3.0	2.7	-4.2	3.6	-2.1	3.8
5	-	-	-5.1	3.4	-2.9	4.8	-5.12	3.4	-5.1	2.9	-7.1	3.6	-5.0	3.8
6	-	-	-9.1	3.6	-	-	-9.0	3.6	-9.7	2.9	-10	3.7	-8.9	3.6
7	58.5	6.5	-	-	-	-	-	-	-	-	-	-	-	-

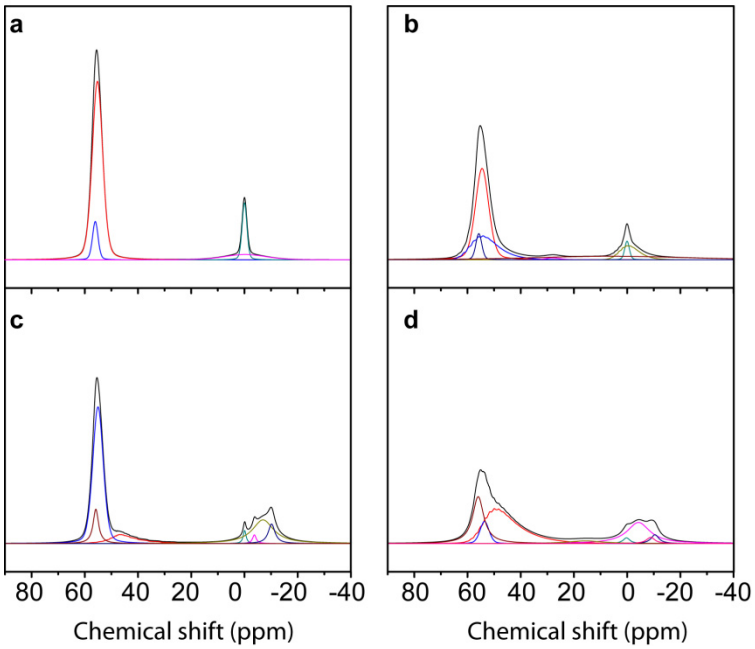


Fig. S3 Examples of ^{27}Al 1D MAS NMR spectra and corresponding deconvolution for the following samples: a) **[Z]**, b) **[Z]TT**, c) **PA[Z]**, and d) **PA[Z]TT.**

Table S4. ^{27}Al 1D MAS NMR contributions of deconvoluted resonances.

Sample	TFAl (%)	$TFAl_{dis}$ (%)	Al(V) (%)	OFAl (%)	Al(VI) (%)	Al(IV)[a]/Al(IV)[b]
[Z]	85	-	-	15	-	5.5
[Z] TT	49	22	1	3	9	5.8
NA[Z]	85	-	-	15	-	5.6
NA[Z] TT	46	22	2	4	10	4.8
PA[Z]	59	8	-	2	33	2.0
PA[Z] e	84	-	-	7	9	16
PA[Z] TT	28	38	4	2	29	2.2
PA[Z] TT e	33	29	-	7	13	3.1
PB[Z]	85	1	-	-	14	6.2
PB[Z] e	95	-	-	-	5	19.0
PB[Z] TT	28	39	4	2	28	2.2
PB[Z] TT e	35	29	-	4	17	3.0

[a] Al (IV) = TFAl + $TFAl_{dis}$ [b] Al (IV) = OFAl + Al(VI).

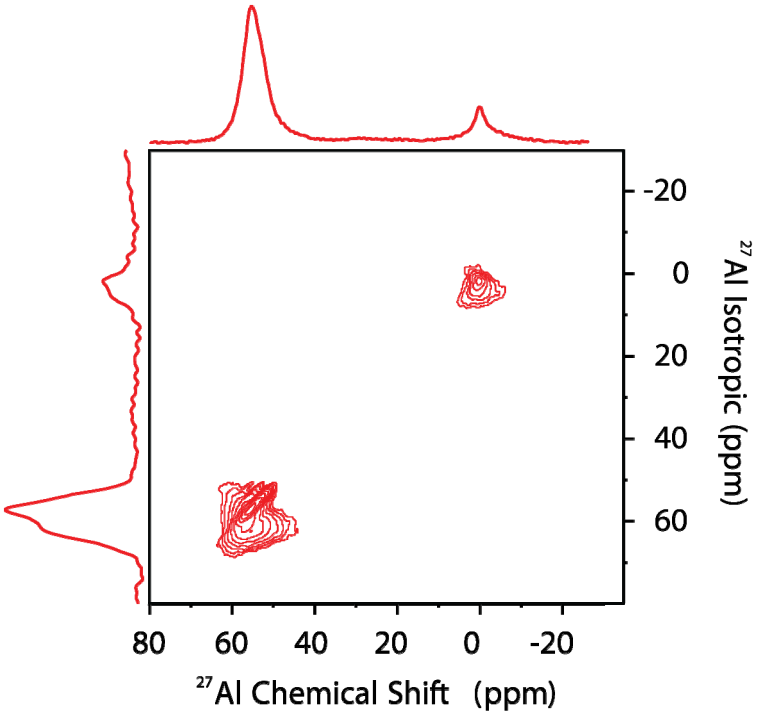


Fig. S4 ^{27}Al MQ MAS NMR spectra of sample **[Z]TT**.

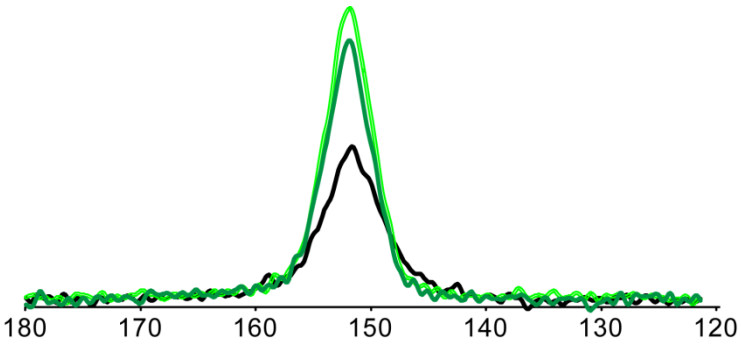


Fig. S5 ^{27}Al MQ MAS NMR spinning sideband of the 55 ppm resonance of the following samples: ■ = **[Z]**, ■ = **PB[Z]**, and ■ = **PB[Z]e.**

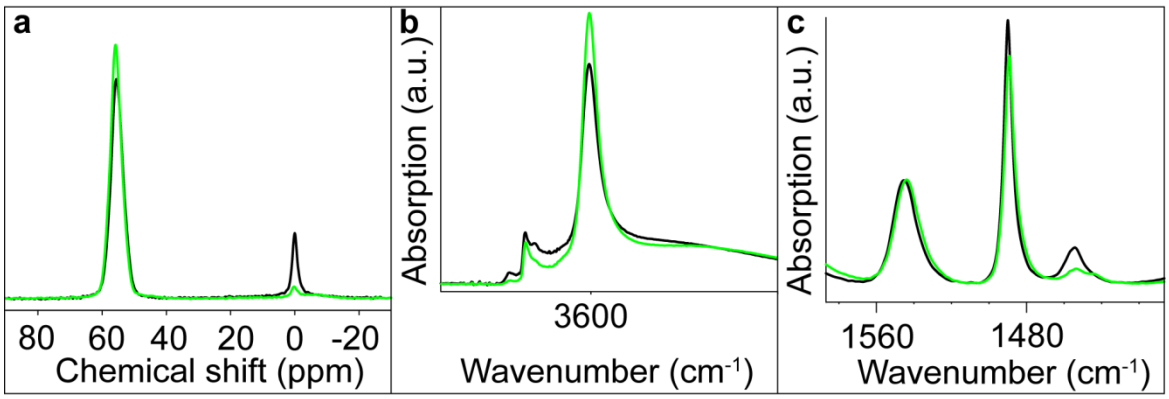


Fig. S6 a) ^{27}Al MAS NMR spectra, b) FT-IR spectra, highlighting the OH-stretch region and c) FT-IR spectra, highlighting the N-H stretch region at 200°C after temperature programmed desorption of the following samples: ■ = **[Z]**, and ■ = **PB[Z]e**.

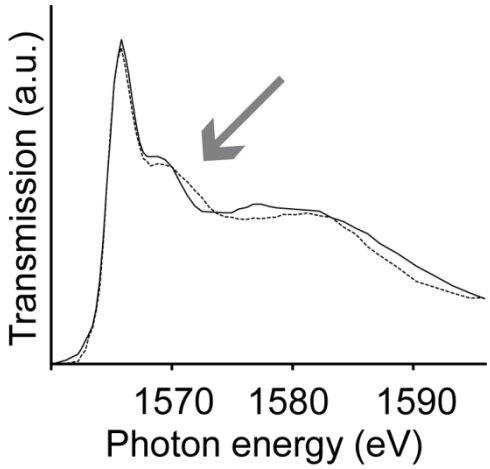


Fig. S7 Aluminium K-edge XANES spectra of the following samples: ■ = **[Z]**, ■ dashed = **[Z]TT**. The broadening of the post-edge feature marked by the arrow indicates the formation of partially dislodged aluminium species.

Table S5. ICP results for phosphorus-containing samples.

Sample	P-content (wt%)	Remaining[a] (%)	Sample	P-content (wt%)	Remaining[a] (%)
PA[Z]	2.26	-	PB[Ze]	1.01	43
PA[Ze]	0.56	25	PB[ZTT]	2.30	98
PA[ZTT]	2.18	96	PB[ZTTe]	1.73	75
PA[ZTTe]	1.59	73	TT[ZPA]	2.19	-
PN[Z]	2.35	-	TT[ZPAe]	0.82	37

[a] Relative to the parent material of the sample.

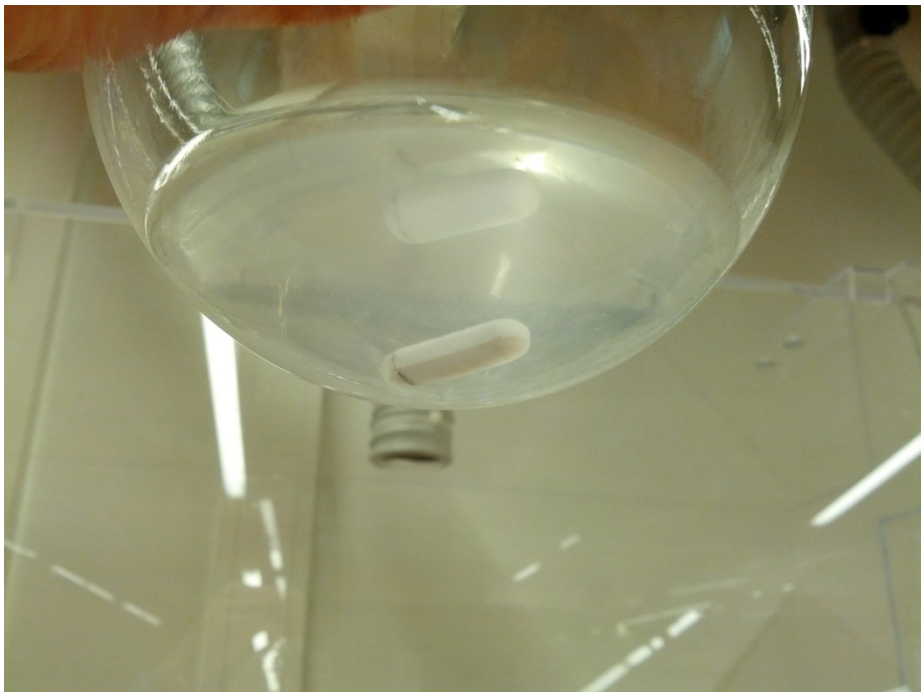


Fig. S8 H_3PO_4 (85%) was calcined in static air at 600°C for 5 h. Afterwards 100 mg of the newly formed white powder was suspended in 200 ml hot water (80°C) and stirred for 2 h. The solution was clearly turbid and a high amount of sediment was observed. Prolonged stirring (4 h) and sonication did not proof effective in further solving the condensed phosphates.

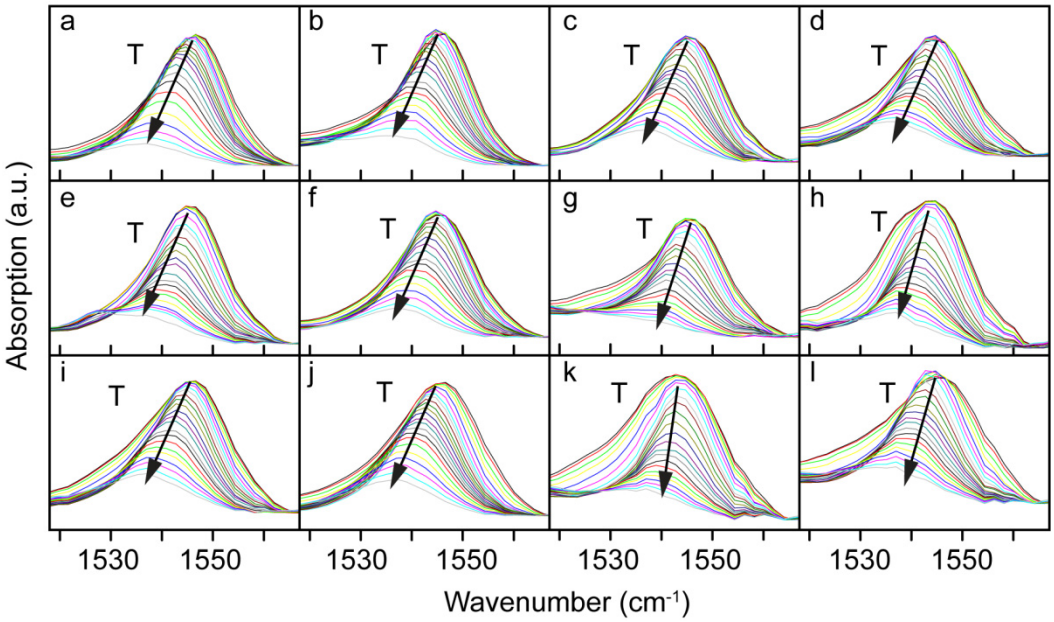


Fig. S9 FT-IR spectra of the pyridinium ion N-H stretch band evolution from 50 to 600°C. The band shifts to lower wavenumbers with increasing temperature, due to the effect of heat on the molecular vibration energies. Bands are not normalized with respect to sample weight. a) [Z], b) [Z]TT, c) NA[Z], d) NA[Z]TT, e) PA[Z], f) PA[Z] e, g) PA[Z]TT, h) PA[Z]TT e, i) PB[Z], j) PB[Z] e, k) PB[Z]TT, and l) PB[Z]TT e.

