Electronic Supplementary Material (ESI) for RSC Sustainability.

Supplementary material

Stability Study of a Superbase-derived Ionic Liquid [mTBNH][OAc] with Enhanced Cellulose Dissolution Ability: Thermal and Natural Degradation

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Thermal degradation by-products

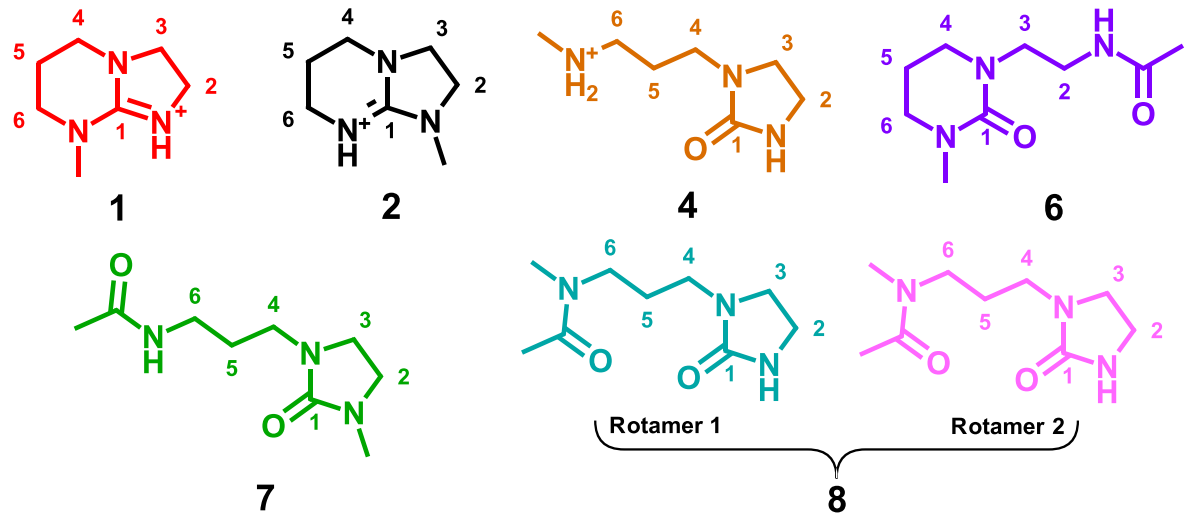


Figure S1. By-products of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample. Structural confirmation was achieved by means of ^{1}H and ^{13}C NMR spectroscopy.

Table S1: ^{1}H chemical shifts of thermal by-products of [mTBNH][OAc].

Pos.	1	2	4	6	7	8 rotamer-1	8 rotamer-2
2	3.49	3.45	3.19	3.09	3.20	n.d.	n.d.
3	3.52	3.51	3.28	3.19	3.20	n.d.	n.d.
4	3.17	3.24	3.03	3.22	3.03	3.02	2.97
5	1.95	1.84	1.58	1.83	1.53	1.67	1.57
6	3.24	3.22	2.48	3.16	2.98	3.23	3.21
N-CH_3	2.98	2.89	2.27	2.75	2.61	2.76	2.92
Ac-CH_3	-	-	-	1.76	1.77	1.95	1.94

n.d. = not detected due to signal overlap

Table S2: ^{13}C chemical shifts of thermal by-products of [mTBNH][OAc].

Pos.	1	2	4	6	7	8 rotamer-1	8 rotamer-2
1	156.61	155.07	162.43	155.62	161.18	162.47	162.37
2	41.03	47.68	37.56	37.28	n.d.	n.d.	n.d.
3	49.05	46.88	44.49	47.24	42.21	n.d.	n.d.
4	41.74	37.92	40.94	46.29	41.77	40.67	40.94
5	20.43	19.82	26.31	22.01	27.42	26.09	25.32
6	46.54	42.27	47.95	47.40	36.41	47.58	44.58
N-CH_3	37.20	31.73	34.93	35.24	31.22	32.55	35.83
Ac-CO	-	-	-	169.34	169.15	169.38	169.61
Ac-CH_3	-	-	-	22.71	22.71	21.14	21.82

n.d. = not detected due to signal overlap

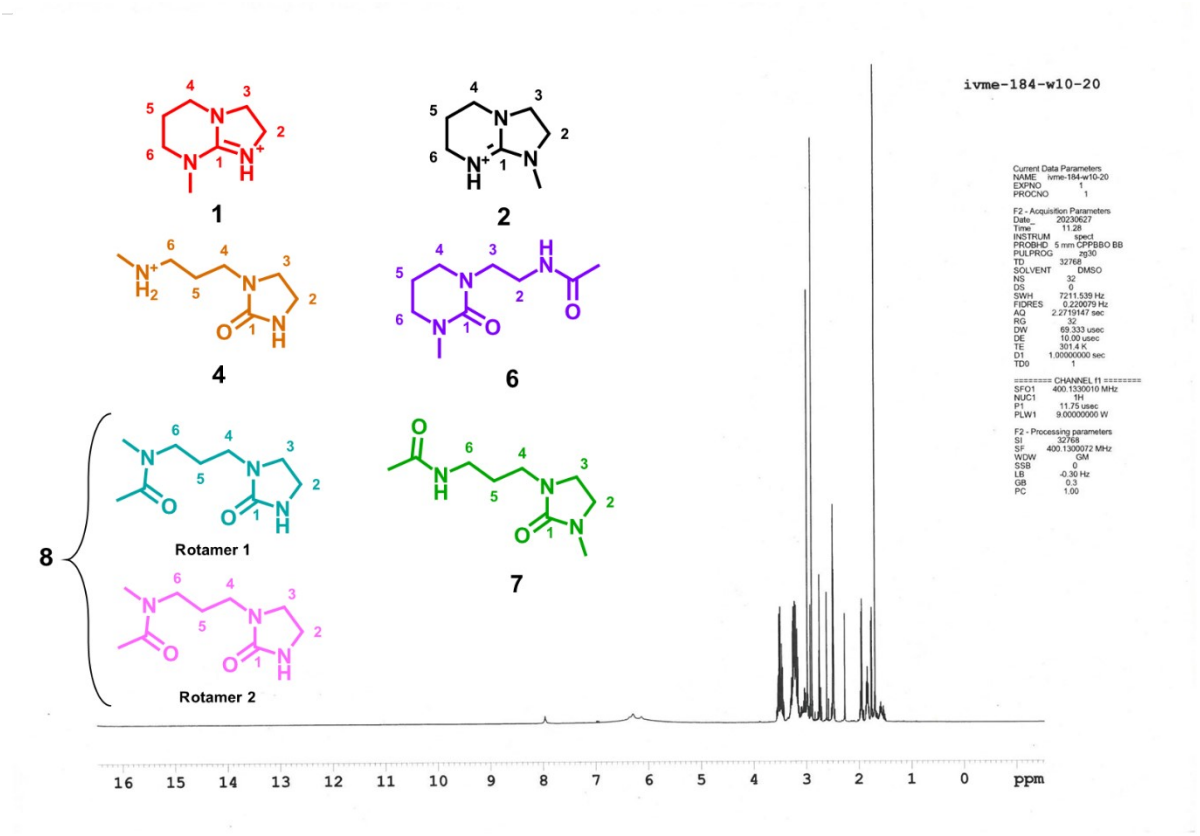


Figure S2. ^{1}H NMR spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample.

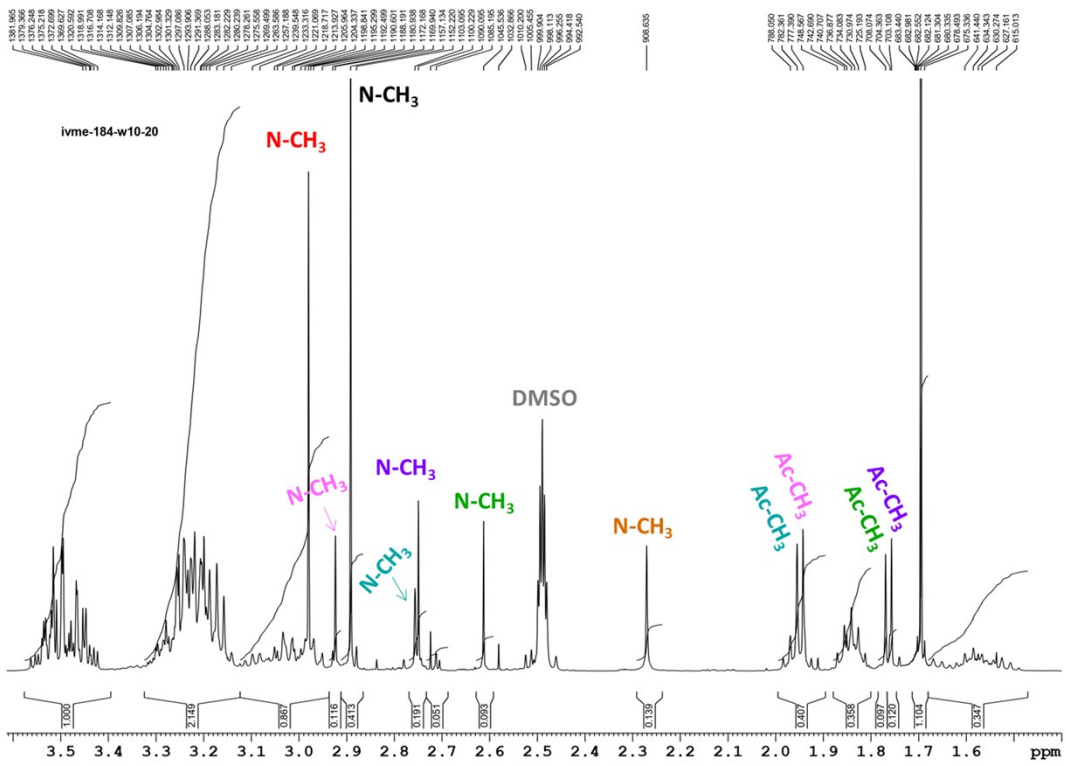


Figure S3. ^{1}H NMR spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample with assigned peaks.

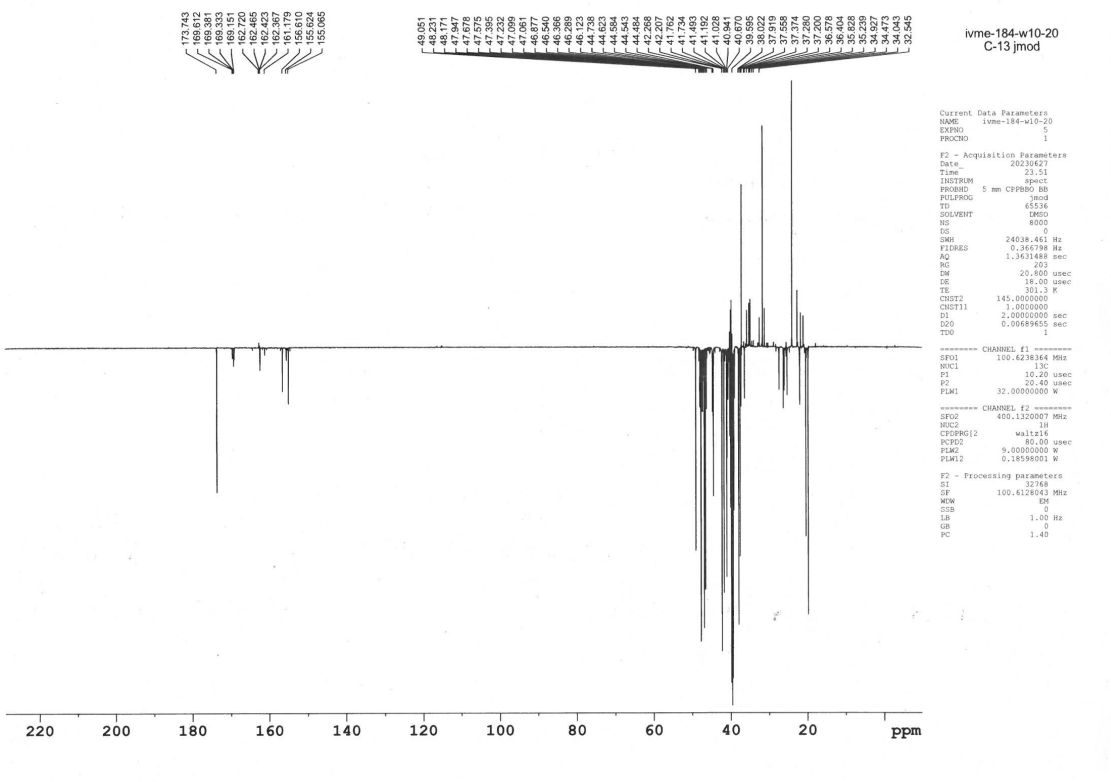


Figure S4. ^{13}C NMR spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample.

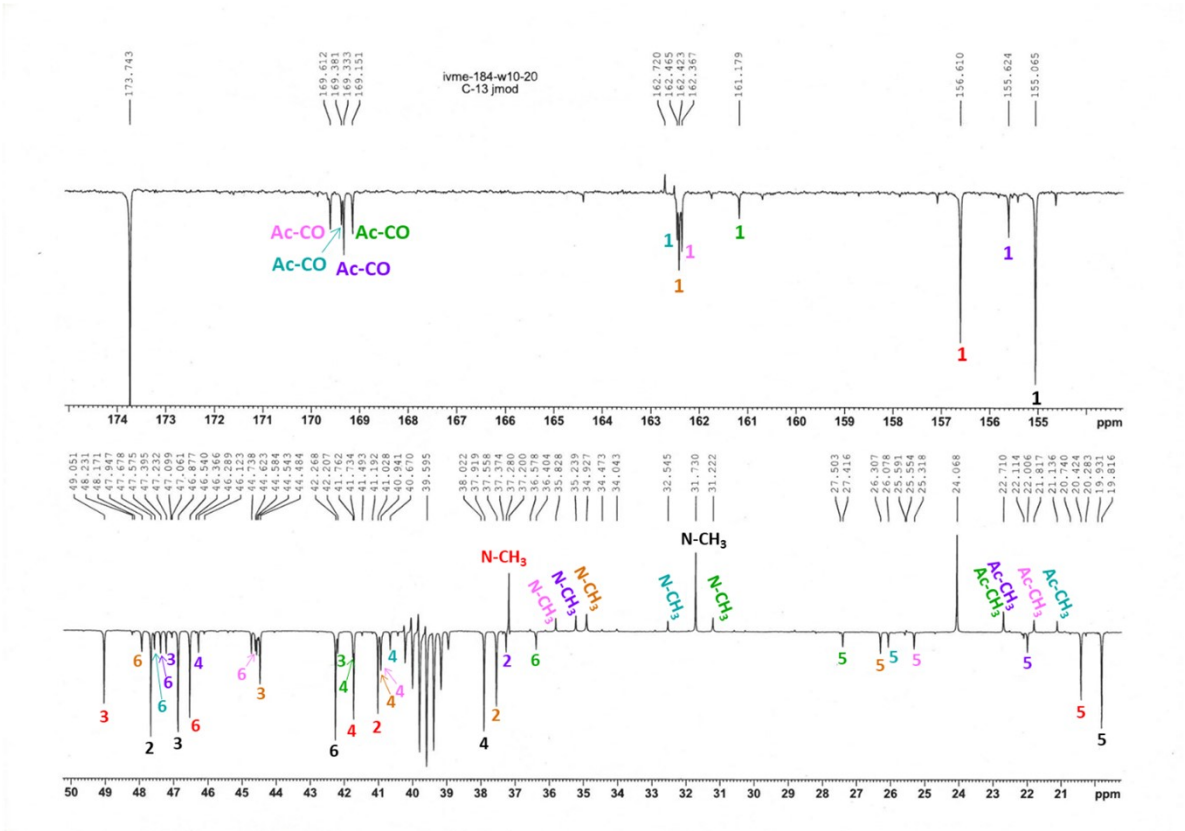


Figure S5. ^{13}C NMR spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample with assigned peaks.

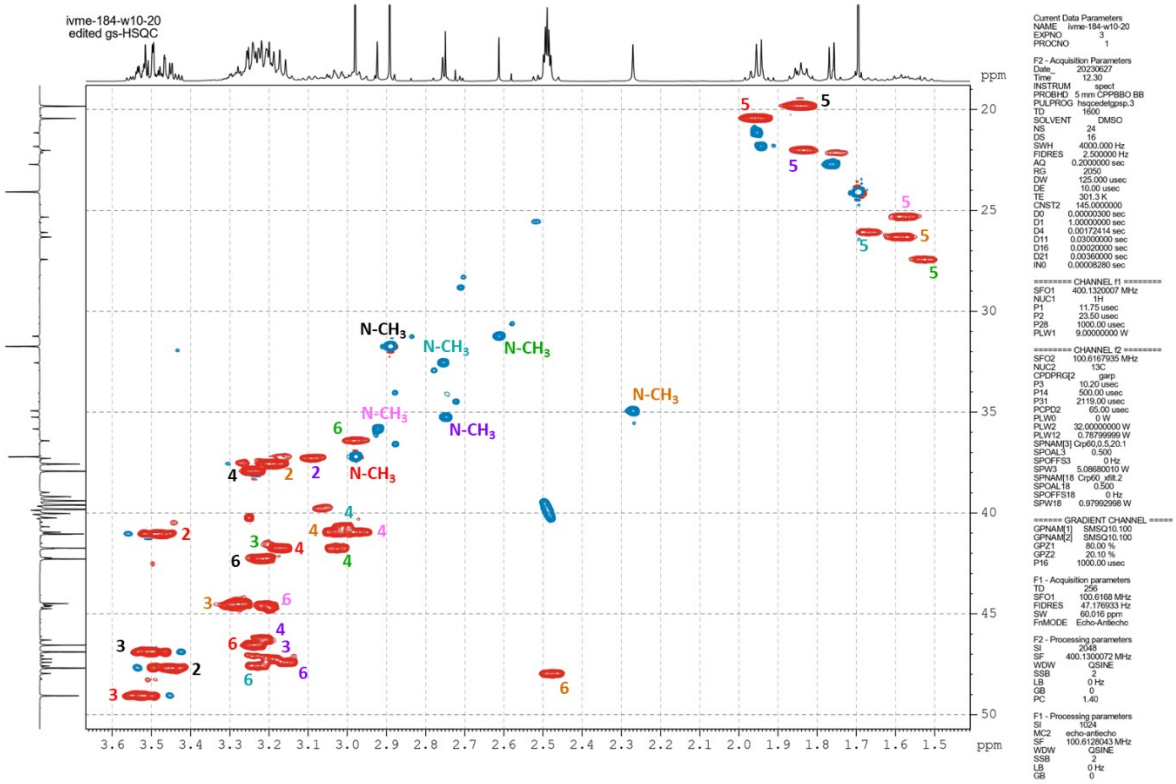


Figure S6. HSQC spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample with assigned peaks.

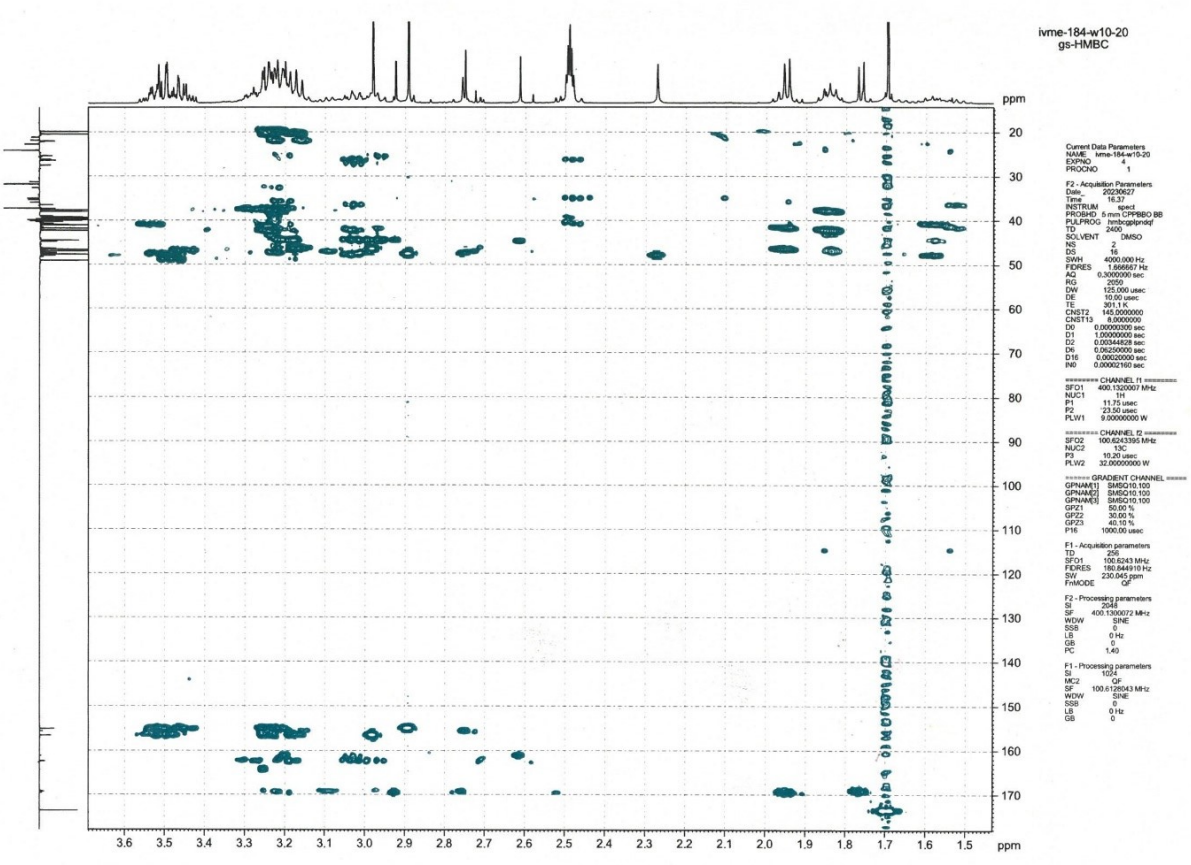


Figure S7. HMBC spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample.

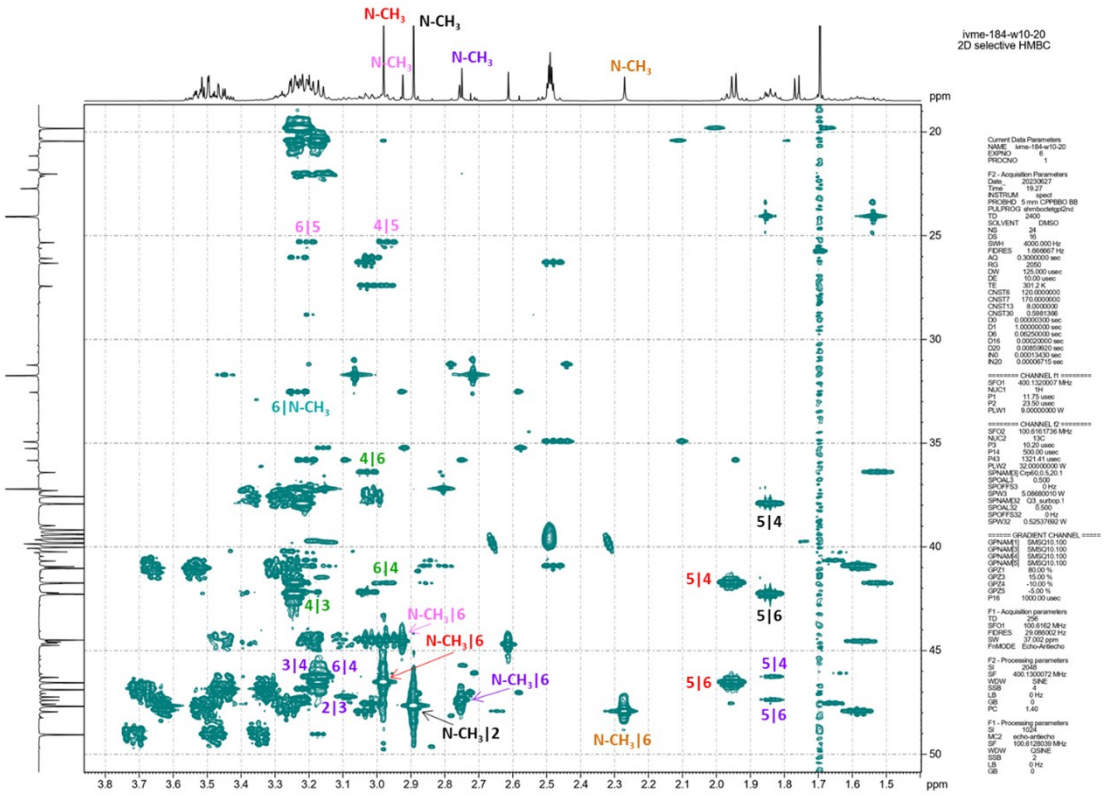


Figure S8. 2D selective HMBC spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample with assigned peaks.

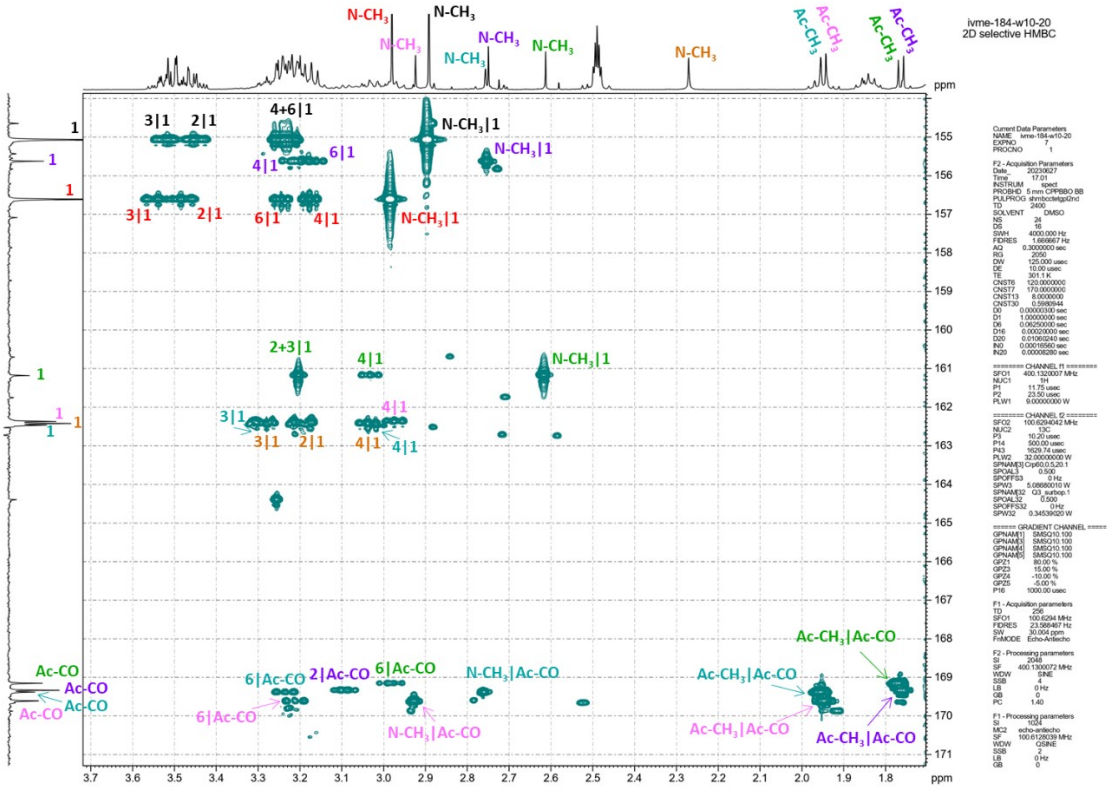


Figure S9. 2D selective HMBC spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample with assigned peaks.

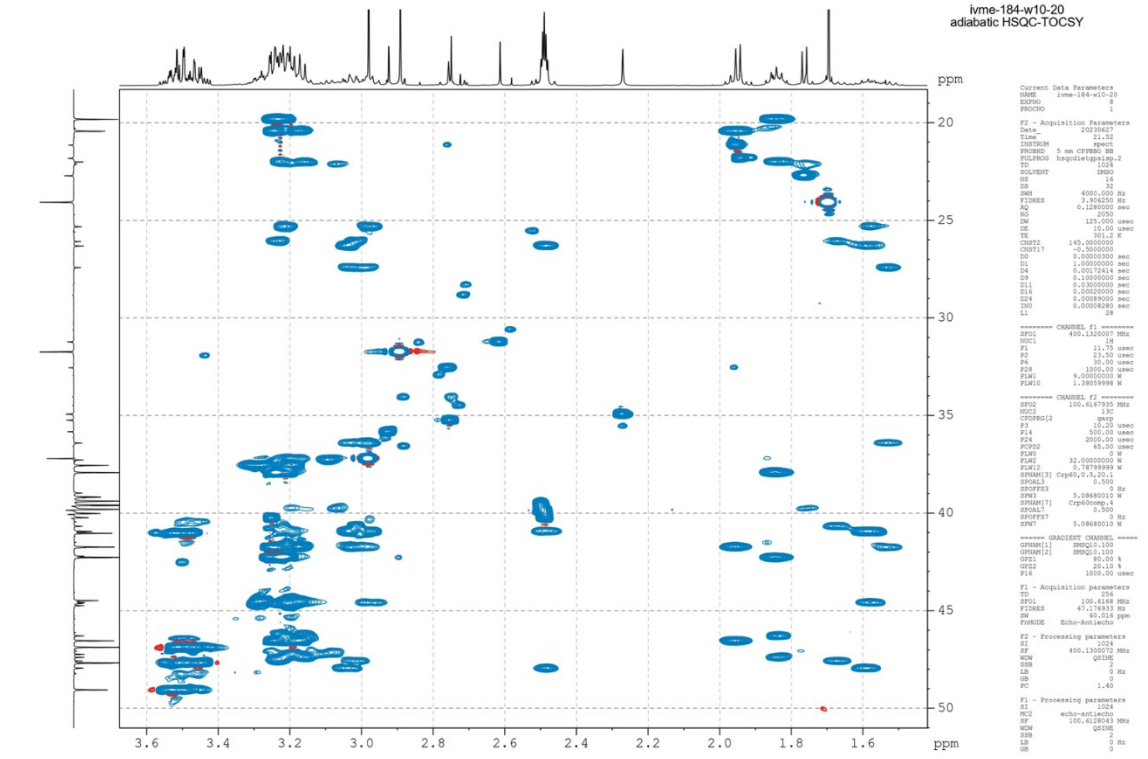


Figure S10. HSQC-TOCSY spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample.

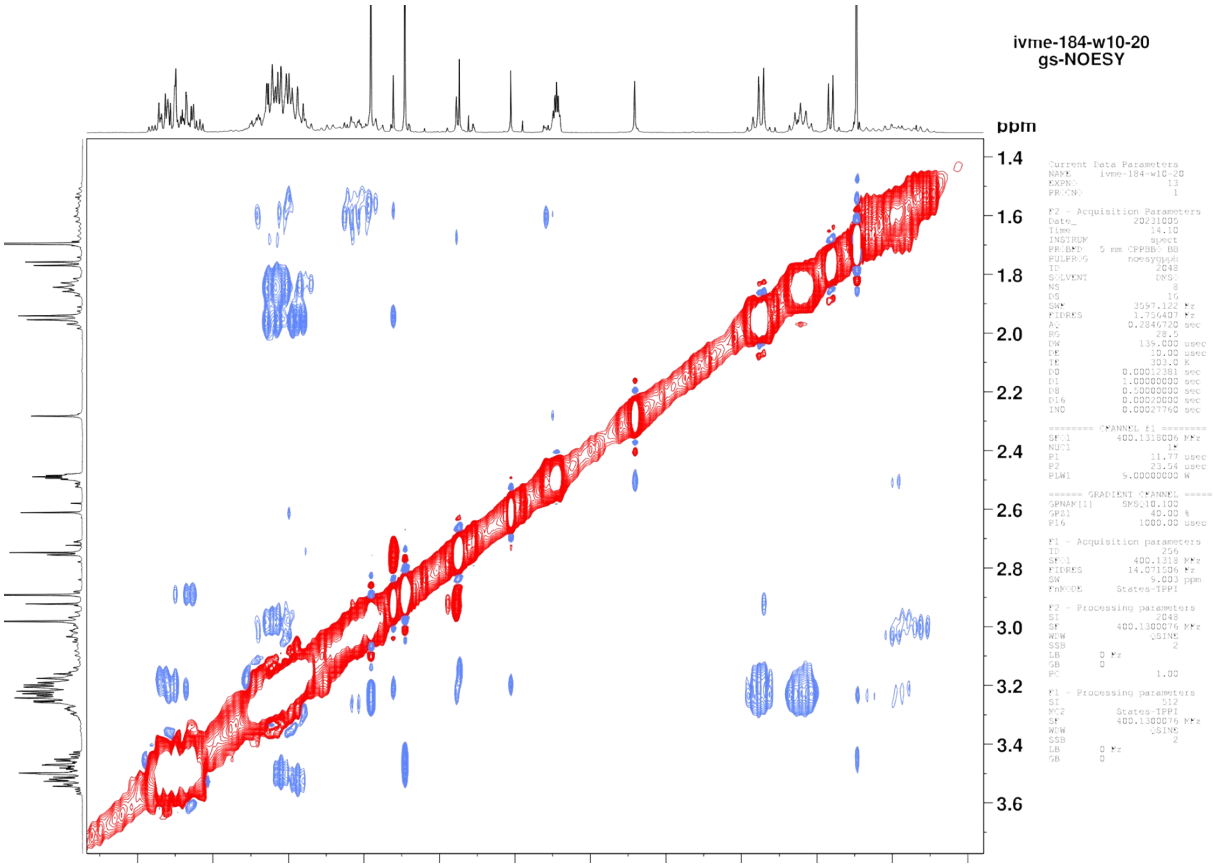
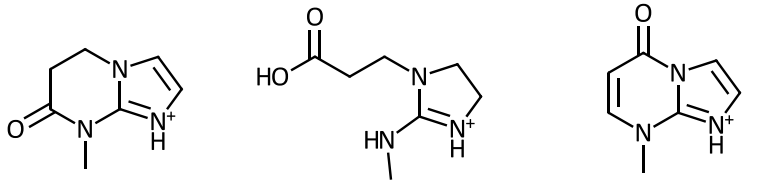


Figure S11. NOESY spectrum of thermally aged (95°C, 20 days, 10 % wt water) [mTBNH][OAc] sample.

Natural degradation by-products



9

peak i
m/z 152.0827
$C_7H_{10}N_3O^+$

10

peak t
m/z 172.1086
$C_7H_{14}N_3O_2^+$

11

peak x
m/z 150.0669
$C_7H_8N_3O^+$

Figure S12. By-products isolated by means of flash column chromatography from a naturally aged [mTBNH][OAc] sample (rt, no light, 2 years). Structural confirmation was achieved by means of ^1H and ^{13}C NMR spectroscopy. Peaks names relate to Figure 6, Table 1 and Scheme 2.

7-Methyl-4,5-dihydro-1,3a,7-triaza-1-indenium-6(7H)-one (9)

^1H NMR (400 MHz, CD_3OD) δ 6.88 (d, *J* = 1.6 Hz,1H), 6.79 (d, *J* = 1.6 Hz,1H), 4.12 (t, *J* = 7.1 Hz, 2H), 3.34 (s, 3H), 2.90 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ 168.71, 145.23, 126.14, 117.92, 40.26, 32.00, 29.04. ESI-QToF-MS: *m/z* calcd for $C_7H_{10}N_3O^+$ (M^+) 152.0823, found 152.0827.

3-[2-(Methylamino)-2-imidazolidinylium-1-yl]propionate (10)

^1H NMR (400 MHz, CD_3OD) δ 3.77−3.71 (m, 2H), 3.67−3.61 (m, 2H), 3.49 (t. *J* = 12.2 Hz, 2H), 2.88 (s, 3H), 2.42 (t. *J* = 12.2 Hz, 2H). ^{13}C NMR (101 MHz, CD_3OD) δ 178.93, 160.70, 49.72, 43.96, 42.07, 36.43, 29.18. ESI-QToF-MS: *m/z* calcd for $C_7H_{14}N_3O_2^+$ (M^+) 172.1086, found 172.1086.

7-Methyl-1,3a,7-triaza-1-indenium-4(7H)-one (11)

^1H NMR (400 MHz, CD_3OD) δ 7.88 (d, *J* = 7.6 Hz,1H), 7.67 (d, *J* = 1.7 Hz, 1H), 7.27 (d, *J* = 1.7 Hz, 1H), 5.84 (d, *J* = 7.6 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 160.14, 145.20, 144.96, 129.85, 110.71, 96.95, 38.58. ESI-QToF-MS: *m/z* calcd for $C_7H_8N_3O^+$ (M^+) 150.0667, found 150.0669.

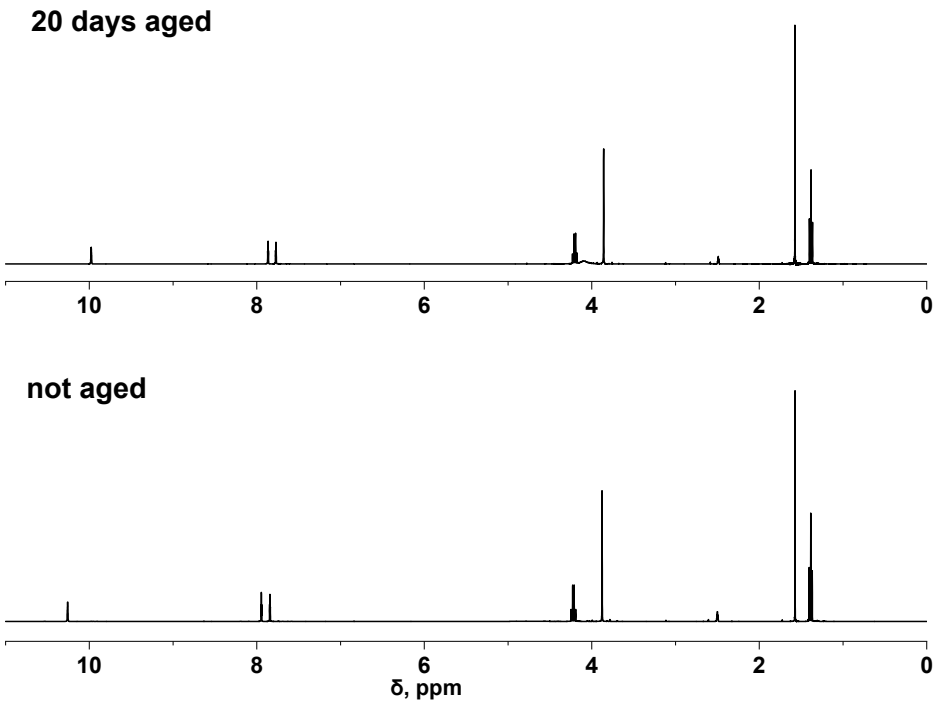


Figure S13. ^{1}H NMR of fresh and aged (20 days, 95°C, 10 % wt water) [Emim][OAc] samples.

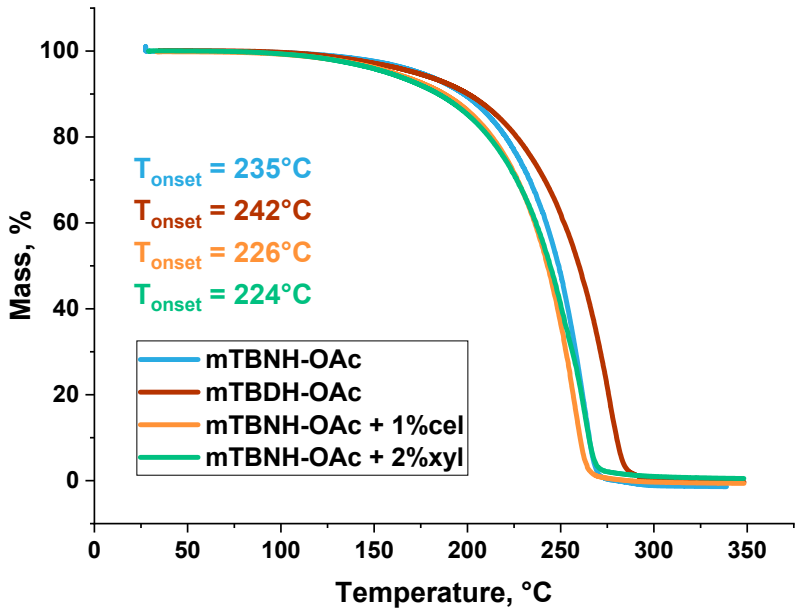


Figure S14. Dynamic decomposition curves of [mTBDH][OAc] and [mTBNH][OAc] (pure and with additives) obtained from thermogravimetric analysis in nitrogen atmosphere at ramp mode (ramp 10°C/min to 350°C).

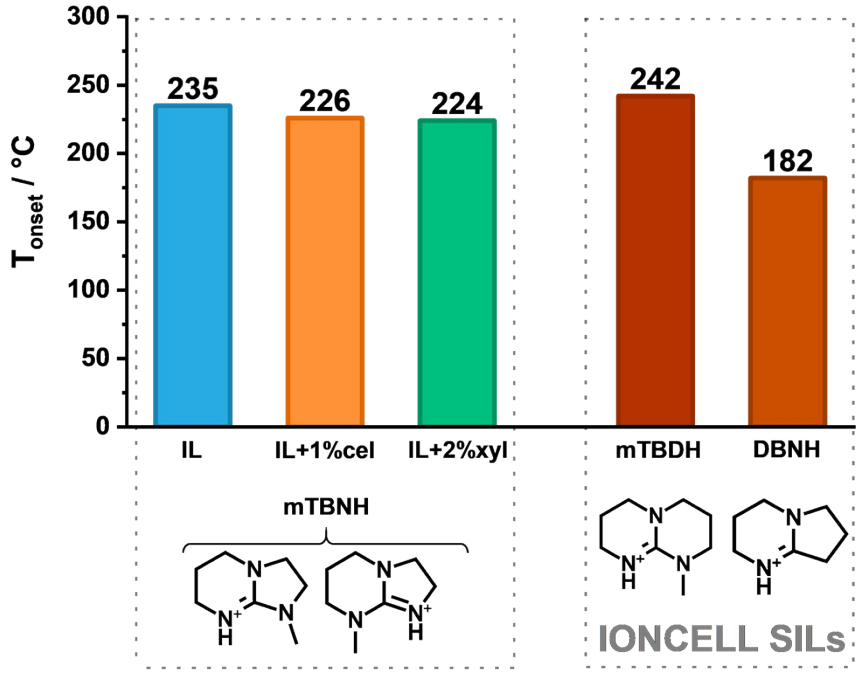


Figure S15. Thermal temperature of decomposition (T_{onset}) of SILs. T_{onset} of [DBNH][OAc] was measured by Kuzmina et al.[1]

Reference

1 O. Kuzmina, J. Bhardwaj, S. R. Vincent, N. D. Wanasekara, L. M. Kalossaka, J. Griffith, A. Potthast, S. Rahatekar, S. J. Eichhorn and T. Welton, *Green Chem.*, 2017, **19**, 5949–5957.