Supporting information

Pyrrolidinium-based Gel Composites for Reprocessable, Flame-Retardant Electrolytes

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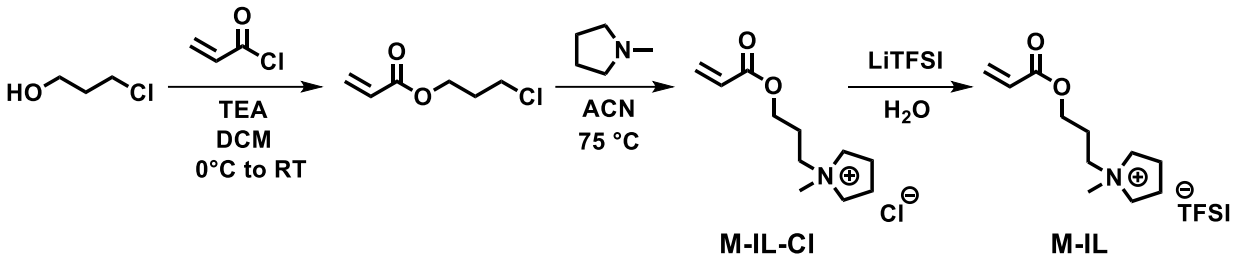
Synthesis of ionic liquid monomer - M-IL



Step 1: A two-neck flask was charged with dry dichloromethane (DCM) (50 mL), triethylamine (TEA) (5.20 mL), and 3-chloro-1-propanol (2.75 mL, 33 mmol). The reaction mixture was cooled to 0 °C in an ice-water bath, after which acryloyl chloride (2.83 mL, 35 mmol) was added dropwise under stirring. Upon completion of the addition, the reaction mixture was allowed to warm to room temperature and stirred for 16 h. The resulting mixture was filtered, and the filtrate was poured into saturated aqueous $NaHCO_3$ (30 mL). The organic phase was separated using a separatory funnel and washed with water (3 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure using a rotary evaporator at 35 °C. The crude product was purified by distillation under high vacuum (0.05 mbar) at 35 °C, affording a colorless, transparent liquid in 80% yield.

^{1}H-NMR (400 MHz, Chloroform-d): δ 6.41 (dd, J = 17.3, 1.4 Hz, 1H), 6.12 (dd, J = 17.3, 10.4 Hz, 1H), 5.84 (dd, J = 10.4, 1.4 Hz, 1H), 4.31 (t, J = 6.1 Hz, 2H), 3.63 (t, J = 6.4 Hz, 2H), 2.14 (p, J = 6.3 Hz, 2H).
^{13}C-NMR (101 MHz, Chloroform-d): δ 166.13, 131.12, 128.34, 77.48, 77.16, 76.84, 61.37, 41.30, 31.75.

Step 2: The obtained 3-chloropropyl acrylate (5.2 g, 28 mmol) and N-methylpyrrolidine (2.42 g, 28 mmol) were dissolved in anhydrous acetonitrile (80 mL) in a single-neck round-bottom flask equipped with a reflux condenser and a magnetic stir bar under an inert atmosphere. The reaction mixture was refluxed at 80 °C overnight. After completion, the solvent was removed under reduced pressure at 35 °C. The resulting crude product was dissolved in water and washed with dichloromethane (15 mL) three times. The aqueous phase was then concentrated under reduced pressure to afford the product (**M-IL-Cl**) as a viscous oil (yield: 85%).

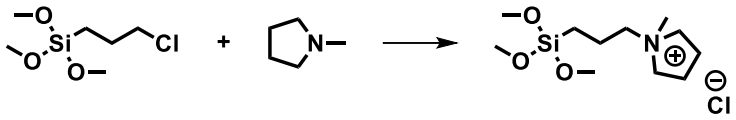
^{1}H-NMR (400 MHz, DMSO-d_6): δ 6.38 (dd, J = 17.3, 1.5 Hz, 1H), 6.18 (dd, J = 17.3, 10.4 Hz, 1H), 5.98 (dd, J = 10.4, 1.5 Hz, 1H), 4.18 (t, J = 6.2 Hz, 2H), 3.60 – 3.42 (m, 6H), 3.03 (s, 3H), 2.17 – 2.02 (m, 6H).
^{13}C-NMR (101 MHz, DMSO-d_6): δ 165.33, 131.96, 128.04, 63.49, 61.35, 60.16, 47.45, 22.86, 21.03.

Step 3: The obtained product (**M-IL-Cl**) (2.6 g, 11 mmol) was dissolved in water (30 mL). Lithium bis(trifluoromethylsulfonyl)imide (3.7 g, 13 mmol) was dissolved in water (20 mL) and added to the **M-IL-Cl** solution. The resulting mixture was stirred at room temperature overnight. After completion, the product was extracted with dichloromethane (3 × 15 mL). The combined organic layers were washed with water (3 × 15 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was removed under reduced pressure using a rotary evaporator at 35 °C. The obtained ionic liquid monomer was further dried under high vacuum overnight over P_2O_5 to afford the product **M-IL** (yield: 50%).

^{1}H-NMR (400 MHz, DMSO-d_6): δ 6.38 (dd, J = 17.3, 1.5 Hz, 1H), 6.17 (dd, J = 17.3, 10.4 Hz, 1H), 5.96 (dd, J = 10.4, 1.5 Hz, 1H), 4.19 (t, J = 6.2 Hz, 2H), 3.58 – 3.39 (m, 6H), 3.02 (s, 3H), 2.19 – 2.04 (m, 6H). (Figure S 1)

^{13}C-NMR (101 MHz, DMSO-d_6): δ 165.34, 131.65, 128.04, 124.35, 121.15, 117.95, 114.75, 63.69, 61.22, 60.50, 47.56, 22.88, 21.06. (Figure S 2)
^{19}F-NMR (376 MHz, DMSO-d_6): δ -78.74. (Figure S 3)

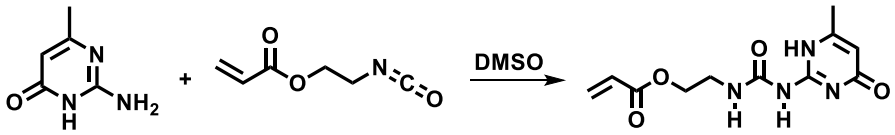
Synthesis of N-[3-(trimethoxysilyl)propyl]-N-methylpyrrolidinium chloride



Initially N-[3-(trimethoxy silyl)propyl]-N-methylpyrrolidinium chloride was prepared with the following procedure: N-methylpyrrolidinium (5 mL, 47 mmol) and (3-chloropropyl) trimethoxysilane (8.57 mL, 47 mmol) mixture was kept at 80 °C while stirring for 48 hours under inert atmosphere. Red/orangish mixture was washed using diethyl ether (4 times) and obtained product was dried in vacuum (yield 45%).

^{1}H NMR (400 MHz, Chloroform-d): δ 3.78 – 3.61 (m, 4H), 3.54 – 3.47 (m, 2H), 3.45 (s, 9H), 3.19 (s, 3H), 2.27 – 2.08 (m, 4H), 1.80 – 1.68 (m, 2H), 0.61 – 0.53 (m, 2H). (Figure S 4)
^{13}C NMR (101 MHz, Chloroform-d): δ 65.36, 64.15, 50.62, 48.40, 21.5, 17.59, 5.77. (Figure S 5)

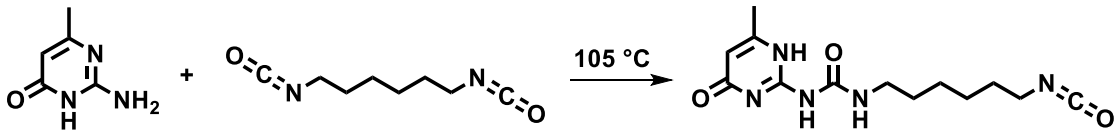
Synthesis of ureidopyrimidinone monomer – M-UPy



2-Amino-6-methylpyrimidin-4(3H)-one (3.12 g, 25 mmol) was charged into a dry round-bottom flask equipped with a magnetic stir bar. Anhydrous DMSO (120 mL) was added, and the mixture was heated to 120 °C with stirring until complete dissolution was achieved. The solution was then cooled to 80 °C, and 2-isocyanatoethyl acrylate (3.1 mL, 25 mmol) was added via syringe. The reaction mixture was allowed to cool to room temperature and stirred for an additional 3 h. The resulting solid was collected by suction filtration and washed with n-hexane (3 times). The product was dried under reduced pressure using a rotary evaporator and further dried under high vacuum to afford the final compound (yield: 60%).

^{1}H NMR (400 MHz, Chloroform-d): δ 12.96 (s, 1H), 11.94 (s, 1H), 10.47 (s, 1H), 6.44 (dd, J = 17.4, 1.5 Hz, 1H), 6.13 (dd, J = 17.4, 10.5 Hz, 1H), 5.85 – 5.74 (m, 2H), 4.29 (t, J = 5.7 Hz, 2H), 3.57 (q, J = 5.7 Hz, 2H), 2.23 (s, 3H).

Synthesis of 1-(6-isocyanatohexyl)-3-(4-methyl-6-oxo-1,6-dihydropyrimidin-2-yl)urea – UPy-NCO



2-amino-4-hydroxy-6-methylpyrimidine (3.0 g, 24 mmol) and hexamethylene diisocyanate (30 mL, 187 mmol) were combined in a flask under an inert atmosphere. The reaction mixture was stirred at 105 °C for 16 h. After cooling to room temperature, the product was precipitated in n-hexane and washed with n-hexane (4 times). The resulting solid was collected and dried under vacuum to afford the final product (yield: 94%).

^{1}H NMR (400 MHz, Chloroform-d): δ 13.10 (s, 1H), 11.85 (s, 1H), 10.17 (t, J = 5.4 Hz, 1H), 5.81 (t, J = 1.3 Hz, 1H), 3.35 – 3.18 (m, 4H), 2.22 (3H), 1.67 – 1.56 (m, 5H), 1.46 – 1.33 (m, 4H).(Figure S 6)
^{13}C NMR (101 MHz, Chloroform-d): δ 173.20, 156.75, 154.86, 148.40, 106.83, 43.03, 39.93, 31.34, 29.44, 26.37, 26.31, 19.07. (Figure S 7)

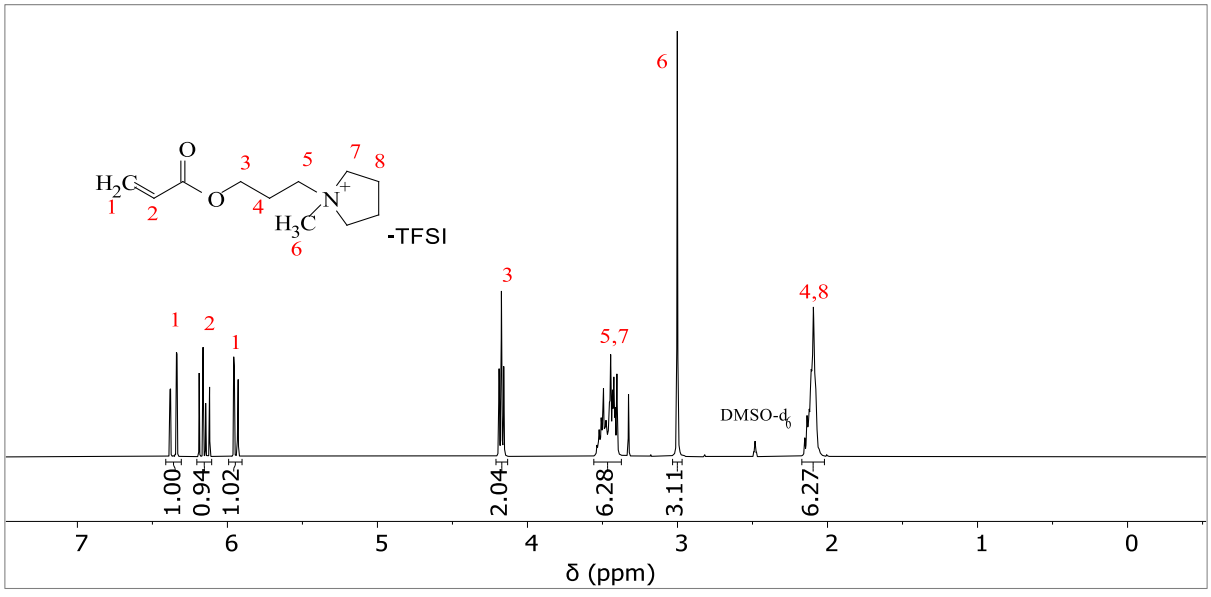


Figure S 1. ^{1}H NMR spectrum of **M-IL** in DMSO-d_6.

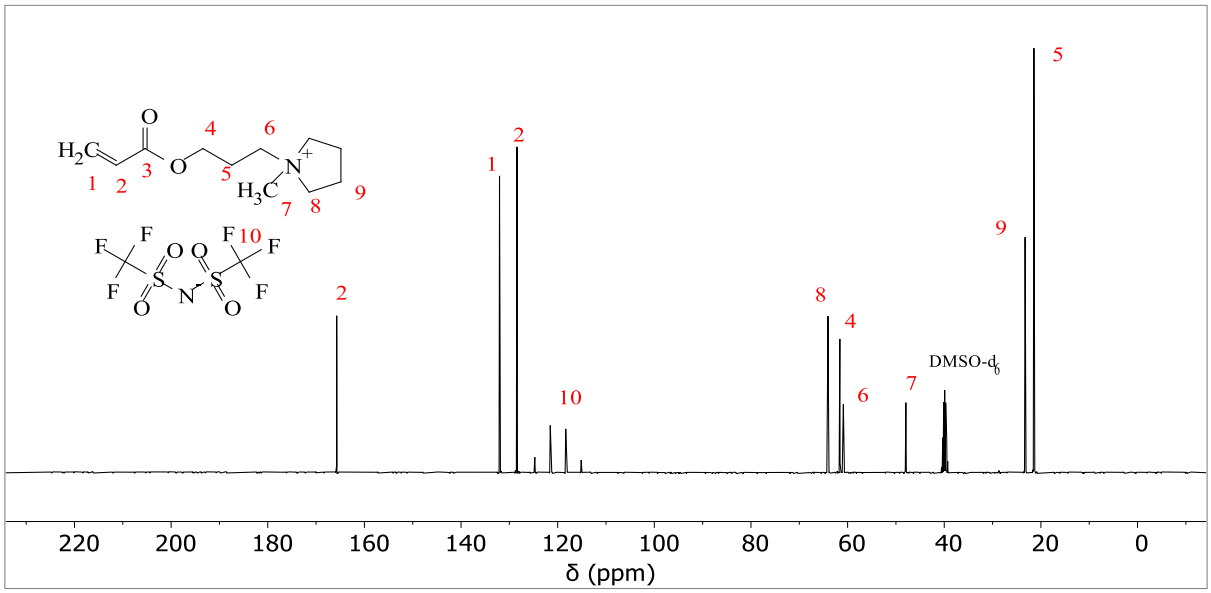


Figure S 2. ^{13}C NMR spectrum of **M-IL** in DMSO-d_6.

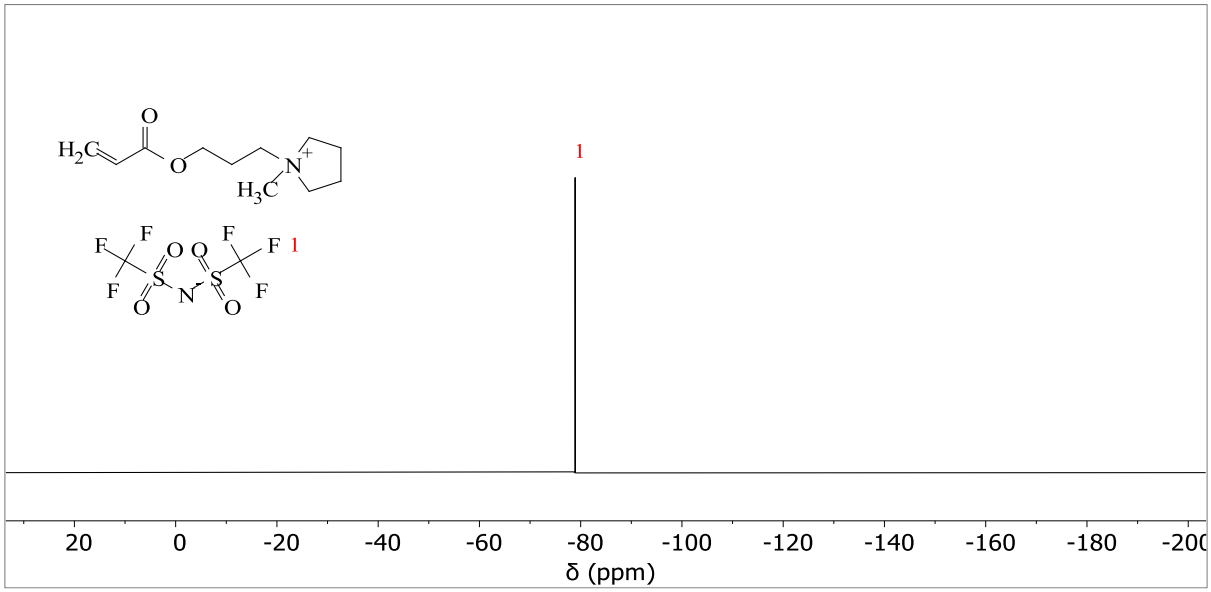


Figure S 3. ^{19}F NMR spectrum of **M-IL** in DMSO-d_6.

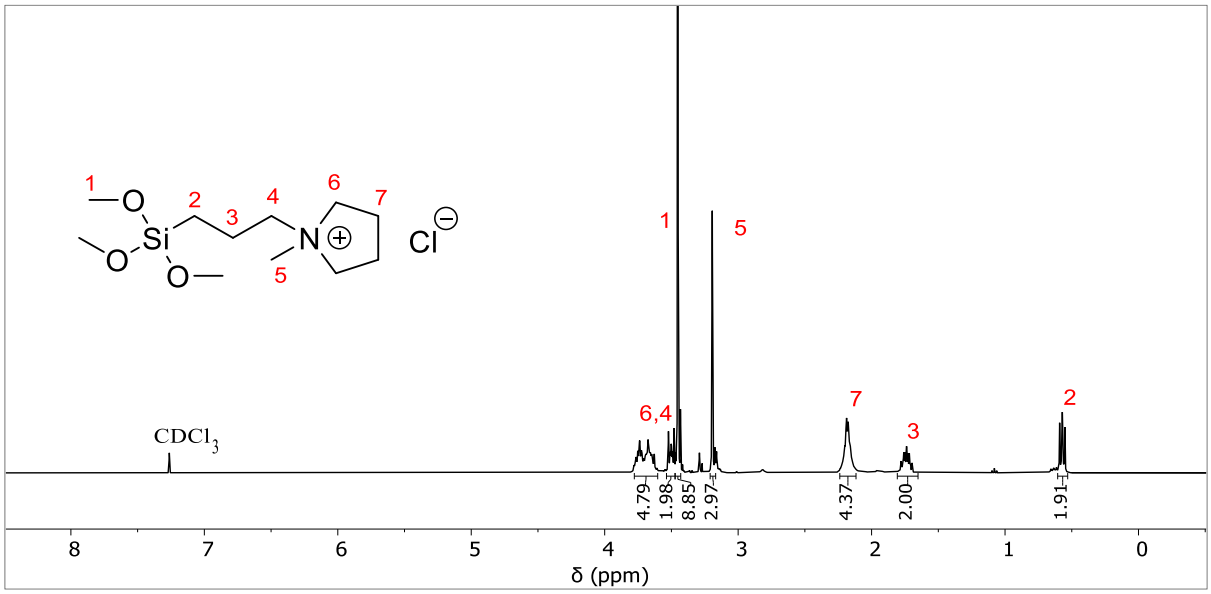


Figure S 4. ^{1}H NMR spectrum of N-[3-(trimethoxysilyl)propyl]-N-methylpyrrolidinium chloride in Chloroform-d.

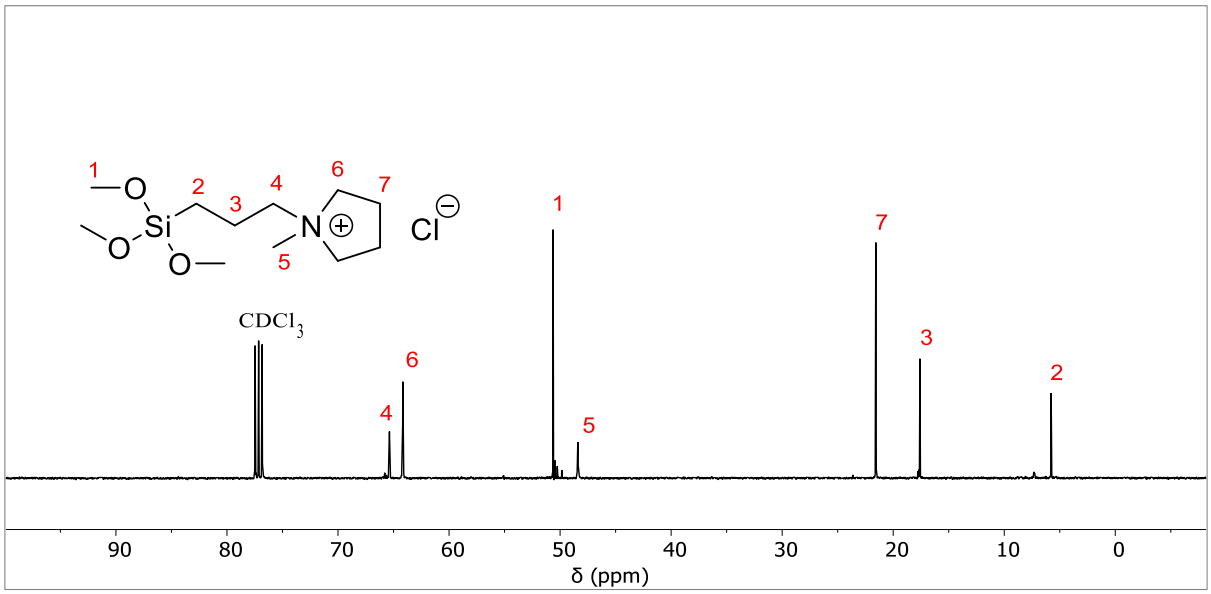


Figure S 5. ^{13}C NMR spectrum of N-[3-(trimethoxysilyl)propyl]-N-methylpyrrolidinium chloride in Chloroform-d.

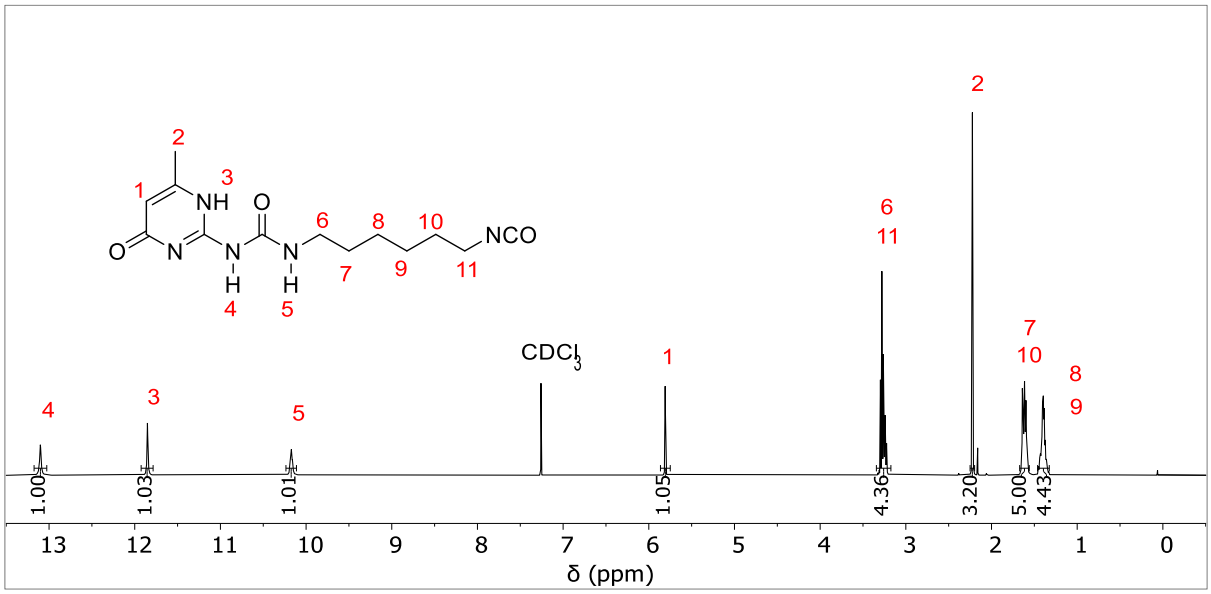


Figure S 6. ^{1}H NMR spectrum of **UPy-NCO** in Chloroform-d.

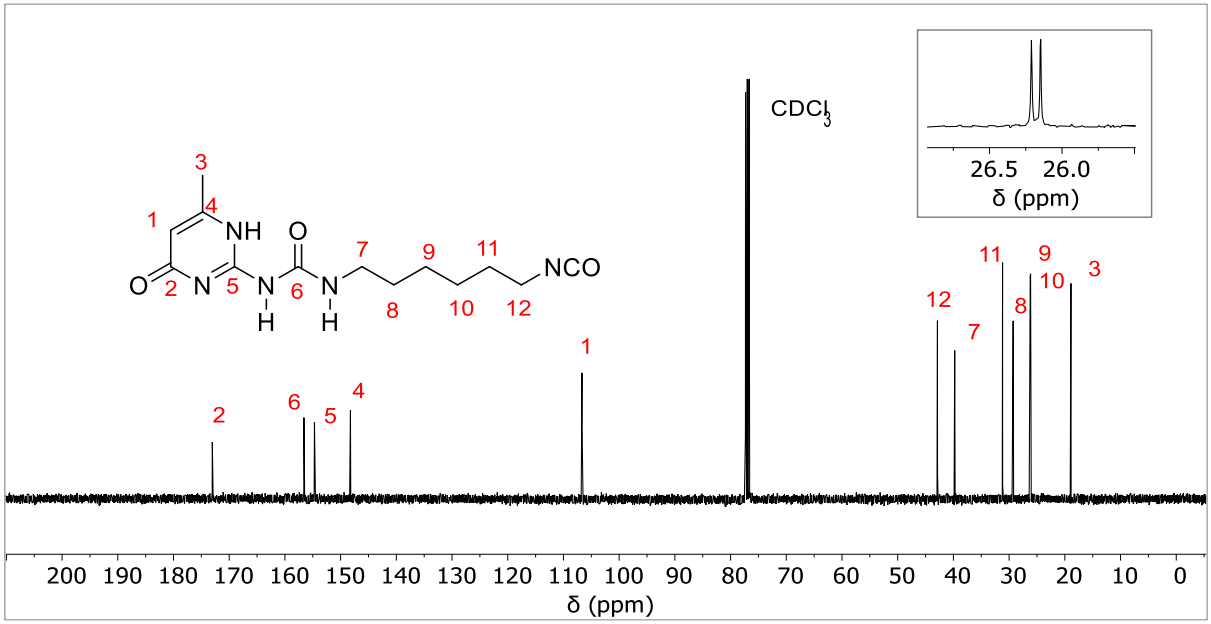


Figure S 7. ^{13}C NMR spectrum **UPy-NCO** in Chloroform-d.

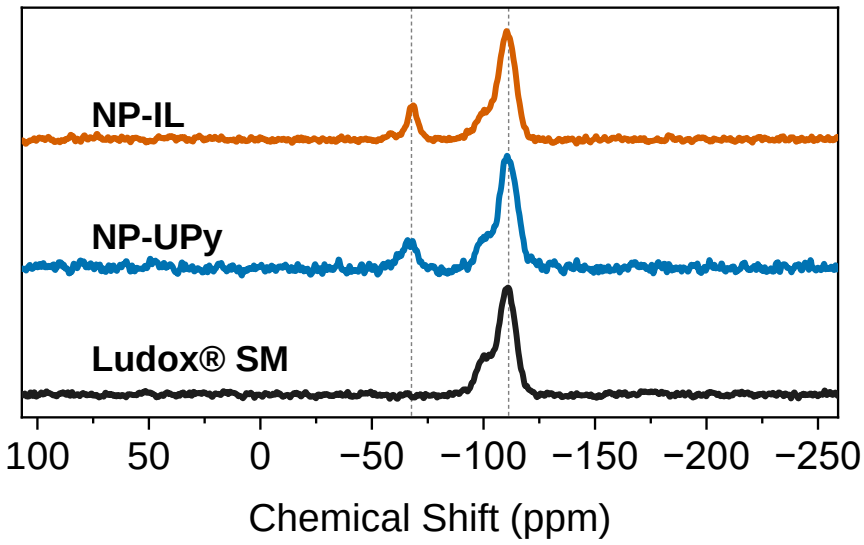


Figure S 8. MAS Si^{29} of surface modified nanoparticles (**NP-IL**, **NP-UPy**) and Ludox® SM.

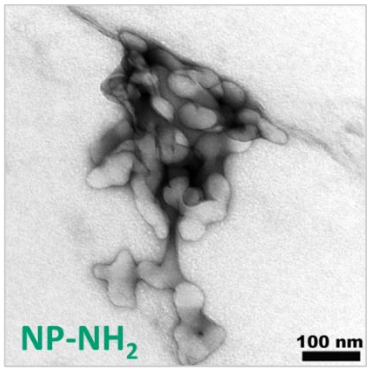


Figure S 9. TEM image of **NP-NH_2**.

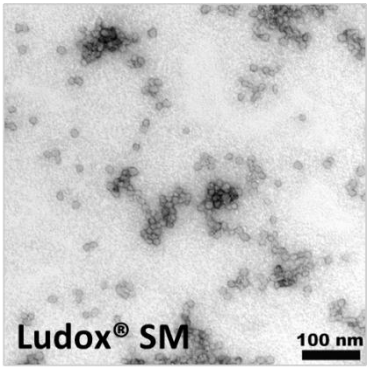


Figure S 10. TEM image of **Ludox® SM**.

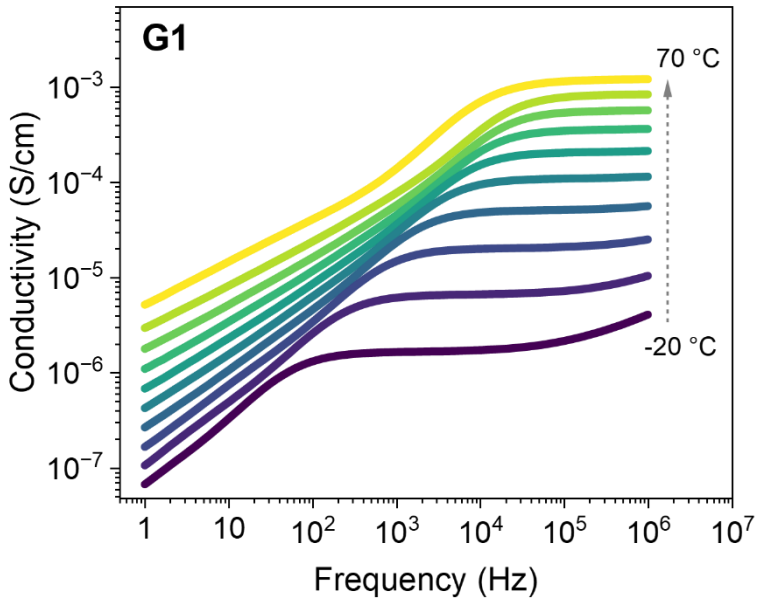


Figure S 11. BDS measurement of **G1** in the temperature range of -20 to 70 °C.

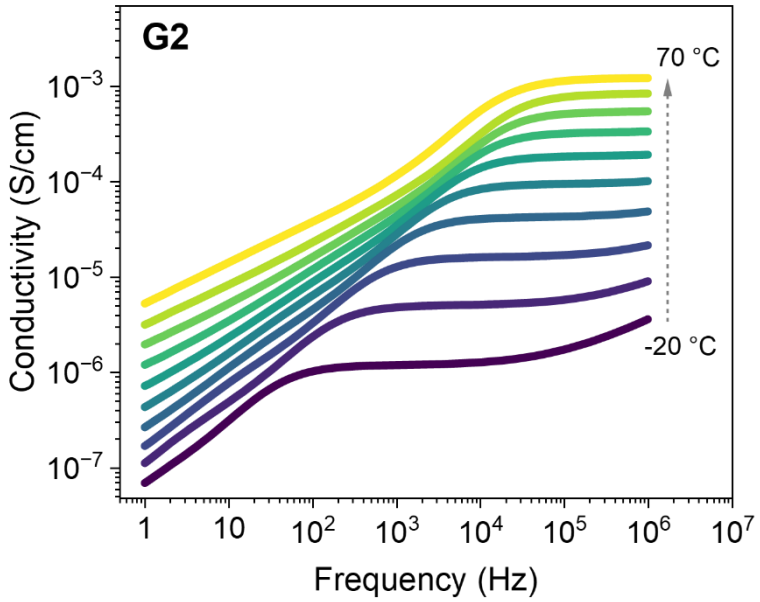


Figure S 12. BDS measurement of **G2** in the temperature range of -20 to 70 °C.

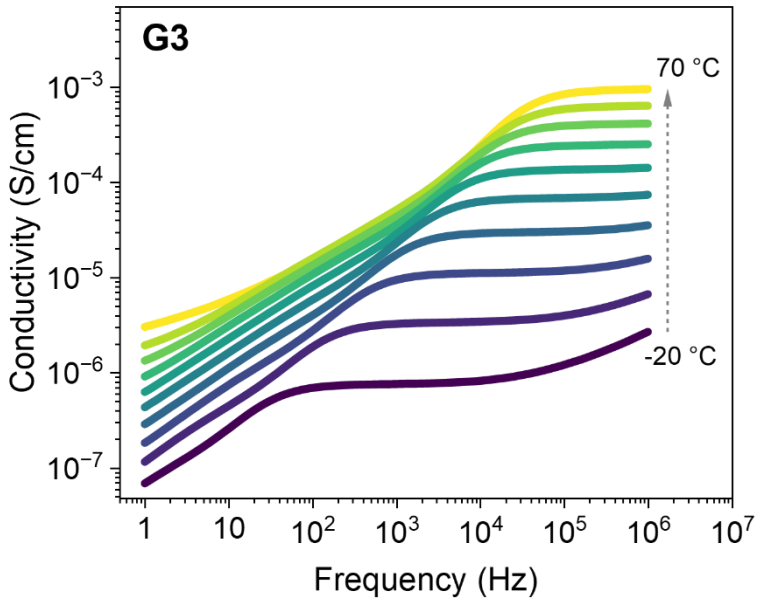


Figure S 13. BDS measurement of **G3** in the temperature range of -20 to 70 °C.

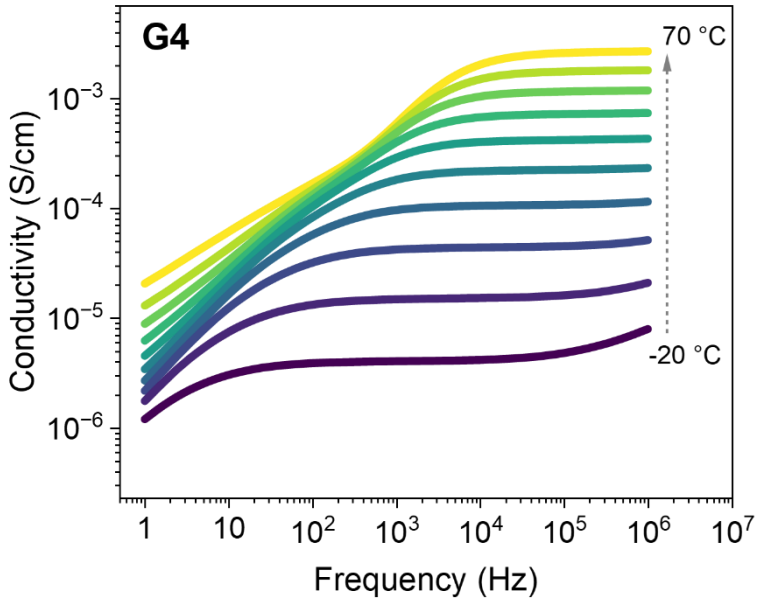


Figure S 14. BDS measurement of **G4** in the temperature range of -20 to 70 °C.

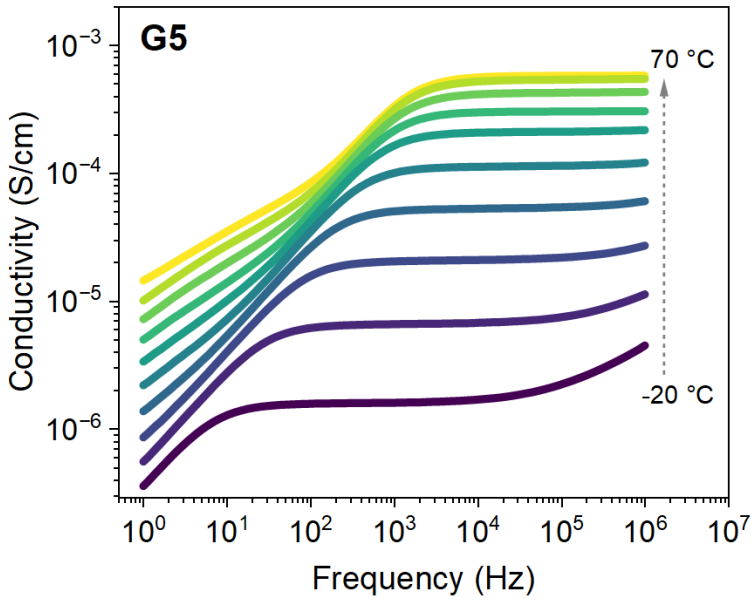


Figure S 15. BDS measurement of **G5** in the temperature range of -20 to 70 °C.

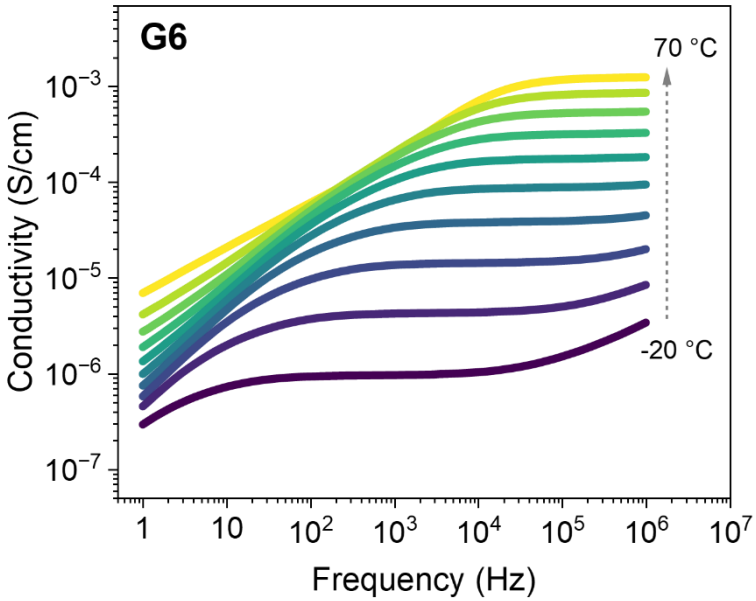


Figure S 16. BDS measurement of **G6** in the temperature range of -20 to 70 °C.

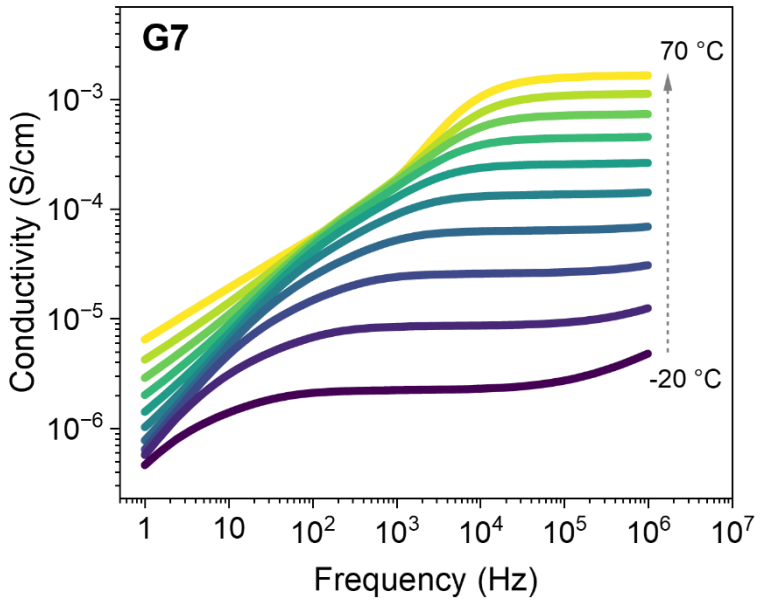


Figure S 17. BDS measurement of **G7** in the temperature range of -20 to 70 °C.

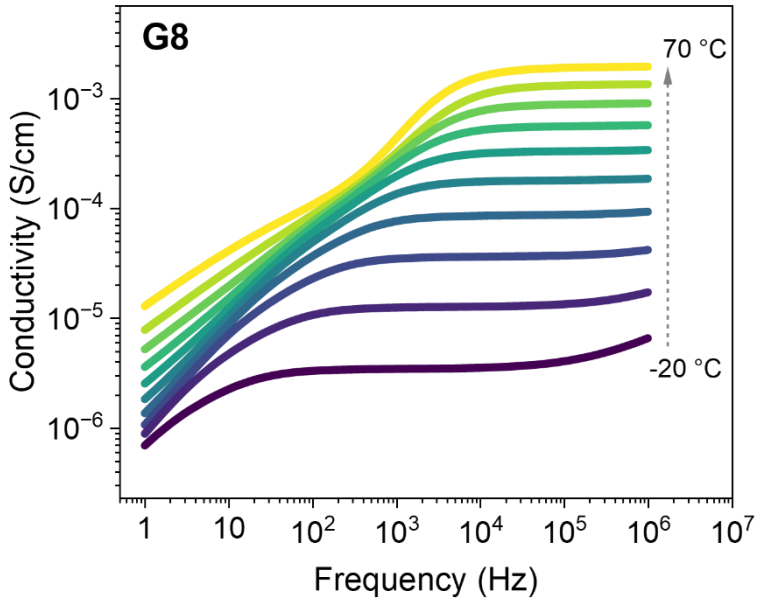


Figure S 18. BDS measurement of **G8** in the temperature range of -20 to 70 °C.

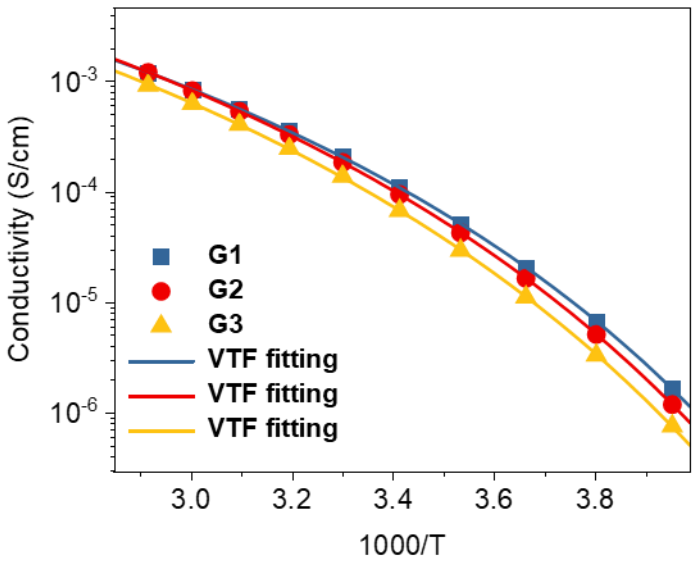
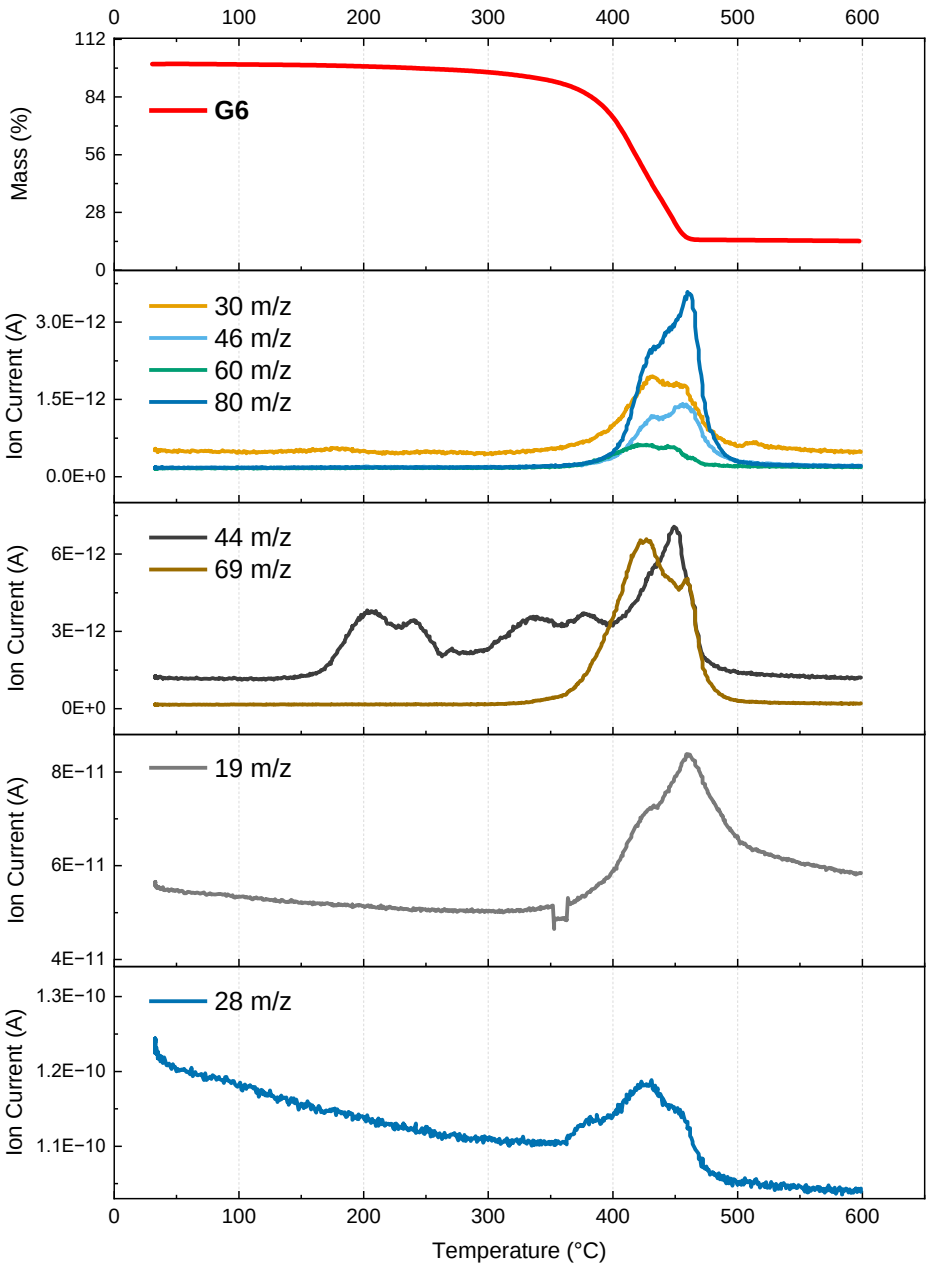
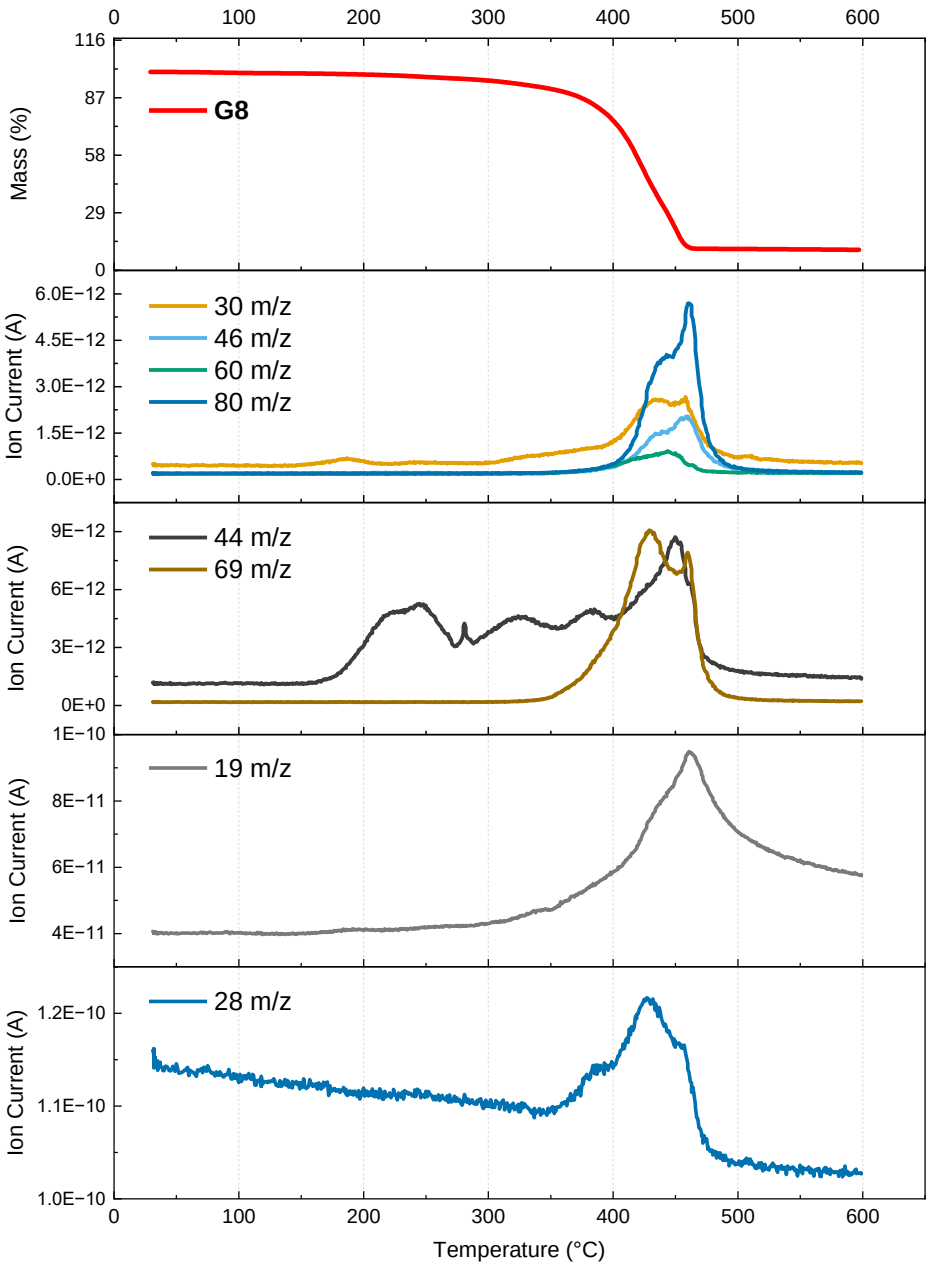


Figure S 19. Ionic conductivity as a function of inverse temperature and corresponding VTF fitting of **G1**, **G2** and **G3**.



m/z	Structure
19	F
28	CO
30	NO
44	CO_2
46	NO_2
60	H_2N O NH_2
69	CF_3
80	SO_3

Figure S 20. TGA-MS of **G6** with heating up to 600 °C in Ar at 5 K min^{-1}.



m/z	Structure
19	F
28	CO
30	NO
44	CO_2
46	NO_2
60	H_2N, O, NH_2
69	CF_3
80	SO_3

Figure S 21. TGA-MS of **G8** with heating up to 600 °C in Ar at 5 K min^{-1}.

Flammability test according to UL 94 V

Each sample was analyzed with a 20 mm large flame for 2x10 seconds. The second flaming time starts when the burning sample self-extinguishes or if the sample doesn't burn. The samples show dripping material, but no burning of the cotton material. The samples passed the test with UL 94 V-0 for specimens of dimension 125 mm x 13 mm x 1 mm (Table S 1, Figure S 22).

Table S 1. Flammability test according to UL 94 V

Specimen	Thickness (mm)	Burn time duration (s)		
		1. After flaming	2. After flaming	Total time
1	1.1	0	0	0
2	1.0	0	0	0
3	0.9	0	0	0
4	1.0	0	0	0
5	0.8	0	0	0
Time (s)		**0**	**0**	**0**
Remarks:				
Cotton burning: No		**Dripping: Yes**	**Coal: No**	**Smoke: No**

Figure S 22. Gel composite specimen before and after flammability test.

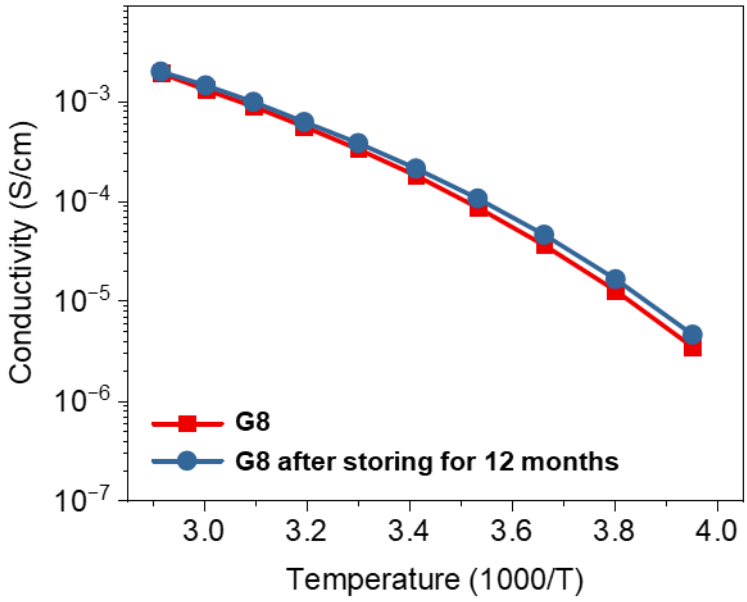


Figure S 23. Ionic conductivity as a function of inverse temperature of **G8** after storing for 12 months.