NJC

Supporting Information

Alkoxycyanoborates: metal salts and low viscosity ionic liquids

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1. NMR spectroscopic Details

Table S1: Selected NMR spectroscopic data[a] of alkoxytricyanoborate anions.

Anion	^{11}B	$^3J_{BH}$	^{19}F	$^3J_{FH}$	^{1}H		$^3J_{HH}$	^{13}C				$^1J_{CB}$	$^1J_{FC}$
	δ		δ (CF_3)		δ (–CH_2–)	δ (–CH_3)		δ (–CH_2–)	δ (–CH_3)	δ (–CF_3)	δ (–CN)		
	[ppm]	[Hz]	[ppm]	[Hz]	[ppm]		[Hz]	[ppm]				[Hz]	
$[CH_3OB(CN)_3]^-$[a]	−18.42	3.8	-	-	-	3.21	-	-	52.22	-	127.79	70.2	-
$[C_2H_5OB(CN)_3]^-$	−18.99	1.7	-	-	3.42	1.09	7.0	16.91	60.39	-	128.15	69.9	-
$[CF_3CH_2OB(CN)_3]^-$	−19.03	1.5	−75.96	9.09	3.80	-	-	63.27	-	124.60	126.61	71.7	277
$[(CF_3CH_2O)_2B(CN)_2]^-$[a]	−6.67	2.0	−76.08	9.41	3.78	-	-	62.15	-	126.40	130.23	73.8	280

Table S2: Selected calculated[a] NMR spectroscopic data of alkoxytricyanoborate anions.

Anion	^{11}B	$^3J_{BH}$	^{19}F	$^3J_{FH}$	^{1}H		$^3J_{HH}$	^{13}C				$^1J_{CB}$	$^1J_{FC}$
	δ		δ (CF_3)		δ (–CH_2–)	δ (–CH_3)		δ (–CH_2–)	δ (–CH_3)	δ (–CF_3)	δ (–CN)		
	[ppm]	[Hz]	[ppm]	[Hz]	[ppm]		[Hz]	[ppm]				[Hz]	
$[CH_3OB(CN)_3]^-$[a]	−24.22	3.7	-	-	-	3.41	-	-	53.66	-	132.36	74.0	-
$[C_2H_5OB(CN)_3]^-$	−24.72	1.1	-	-	3.59	1.15	6.3	62.71	19.42	-	132.49	74.0	-
$[CF_3CH_2OB(CN)_3]^-$	−24.92	1.2	−98.43	7.3	3.94	-	-	67.04	-	138.85	130.96	75.7	−349

[a] B3LYP/6-311++G(2d,p)//B3LYP/6-311++G(d,p)

2. Thermal and Electrochemical Properties

Table S3 Selected thermal and electrochemical parameters of $[EMIm]^+$ salts in the temperature range of 293–353 K.

anion	M	density ρ					dynamic viscosity η					concentration $c = \rho \cdot M^{-1}$				
		20 °C	40°C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C
	[g·mol^{-1}]	[g·mL^{-1}]					[mPa·s]					[mol·L^{-1}]				
$[CH_3OB(CN)_3]^-$	232.07	1.04	1.03	1.01	1.00	1.00	18.8	11.0	6.9	5.6	4.7	4.48	4.43	4.35	4.31	4.31
$[C_2H_5OB(CN)_3]^-$	246.10	1.03	1.01	1.00	0.99	0.99	25.2	12.6	7.7	6.2	5.1	4.19	4.10	4.06	4.02	4.02
$[CF_3CH_2OB(CN)_3]^-$	300.07	1.18	1.16	1.14	1.13	1.13	24.4	12.6	7.6	6.1	5.0	3.93	3.87	3.80	3.77	3.77
$[B(CN)_4]^-$ [e]	226.05	1.04	1.02	1.01	1.00	0.99	22.6	11.4	7.0	5.7	4.7	4.60	4.53	4.46	4.43	4.40

anion	specific conductivity σ					$\log(\Lambda_{imp})$ [a]					$\log(\eta^{-1})$				
	20 °C	40 °C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C	20 °C	40 °C	60 °C	70 °C	80 °C
	[mS·cm^{-1}]					[log(S·cm^2·mol^{-1})]					[log(cm·s·g^{-1})]				
$[CH_3OB(CN)_3]^-$	10.1	16.7	24.0	28.1	32.3	0.3530	0.5763	0.7417	0.8142	0.8747	0.7258	0.9586	1.1612	1.2521	1.3279
$[C_2H_5OB(CN)_3]^-$	5.6	9.7	14.7	17.4	20.9	0.1260	0.3740	0.5588	0.6363	0.7159	0.5986	0.8996	1.1135	1.2076	1.2924
$[CF_3CH_2OB(CN)_3]^-$	5.5	9.3	14.3	16.3	18.6	0.1460	0.3808	0.5756	0.6358	0.6932	0.6126	0.6126	0.8996	1.2147	1.300
$[B(CN)_4]^-$ [e]	12.1	20.7	31.0	36.6	42.4	0.4211	0.6588	0.8410	0.9171	0.9845	0.6612	0.9582	1.1791	1.2705	1.3520

[a] $\Lambda_{imp} = \sigma \cdot c^{-1}$.

Table S3. continued.

anion	D^+ [b]			D^- [c]			Λ_{NMR}			Λ_{imp} [d]			$I = \Lambda_{imp} \cdot \Lambda_{NMR}^{-1}$		
	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C
	$[10^{-11} \cdot m^2 \cdot s^{-1}]$			$[10^{-11} \cdot m^2 \cdot s^{-1}]$			$[cm^2 \cdot S \cdot mol^{-1}]$			$[cm^2 \cdot S \cdot mol^{-1}]$			[–]		
$[CH_3OB(CN)_3]^-$	7.2	14.5	23.5	5.5	11.2	18.5	4.84	9.19	14.12	2.25	3.77	5.52	0.46	0.41	0.39
$[C_2H_5OB(CN)_3]^-$	5.8	12.3	20.8	3.9	8.4	14.7	3.71	7.40	11.93	1.34	2.37	3.62	0.36	0.32	0.30
$[CF_3CH_2OB(CN)_3]^-$	6.9	14.1	23.1	5.0	10.5	17.6	4.55	8.80	13.68	1.40	2.40	3.76	0.31	0.27	0.27
$[B(CN)_4]^-$ [e]	6.3	13.3	22.5	5.4	11.8	20.1	4.47	8.98	14.32	2.64	4.56	6.93	0.59	0.51	0.48

[b] D^+ was determined by ^{1}H NMR DOSY, mean value of all signals. [c] D^- was determined by ^{1}H and ^{11}B NMR DOSY, mean value of all signals. [d] calcd. by: $\Lambda_{NMR} = (D^+ + D^-) \cdot N_A \cdot e^2 \cdot k_B^{-1} \cdot T^{-1}$. [e] Lit.[2]

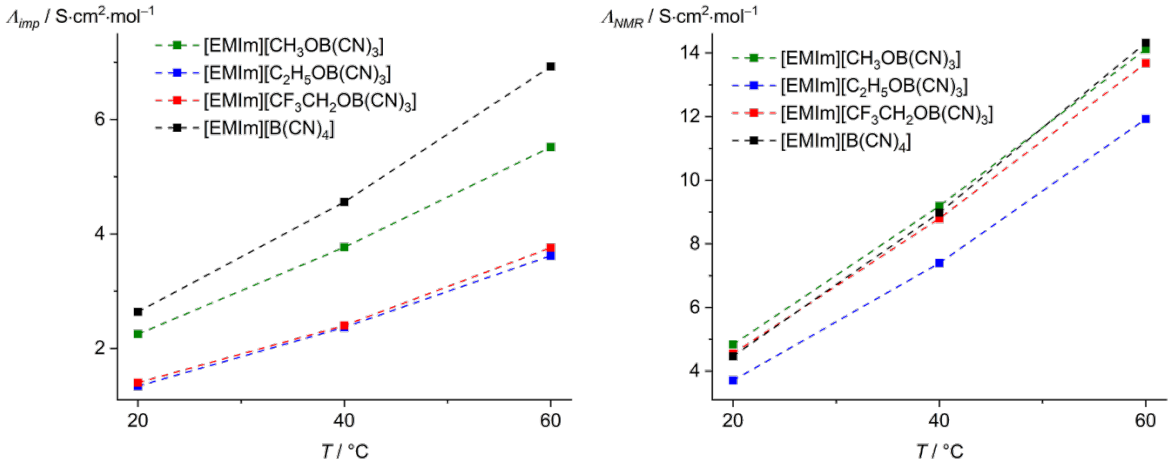

Figure S1. Plots of molar conductivities of EMIm-ILs versus temperature ($\Lambda_{NMR:}$ calculated from diffusion constants derived from DOSY NMR experiments; Λ_{imp}: measuered via impedance spectroscopy).

3. Thermal Properties

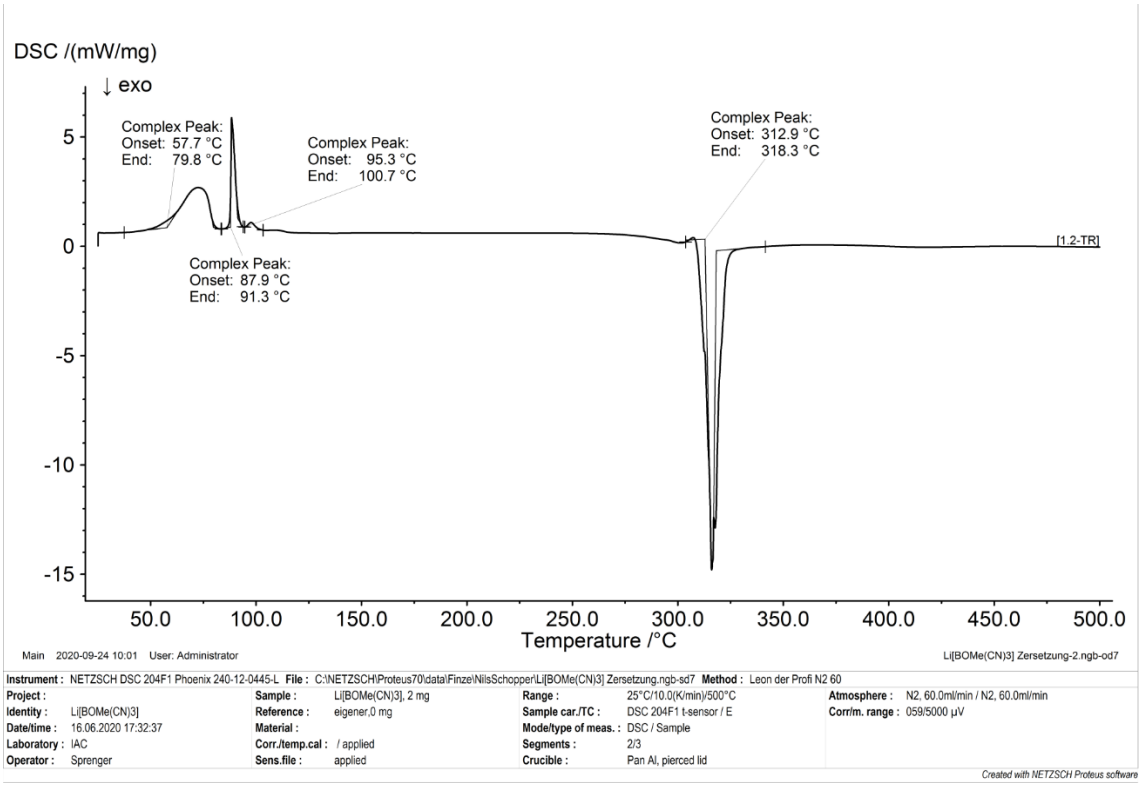

Figure S2. DSC curve of $Li[B(OCH_3)(CN)_3]\cdot H_2O$.

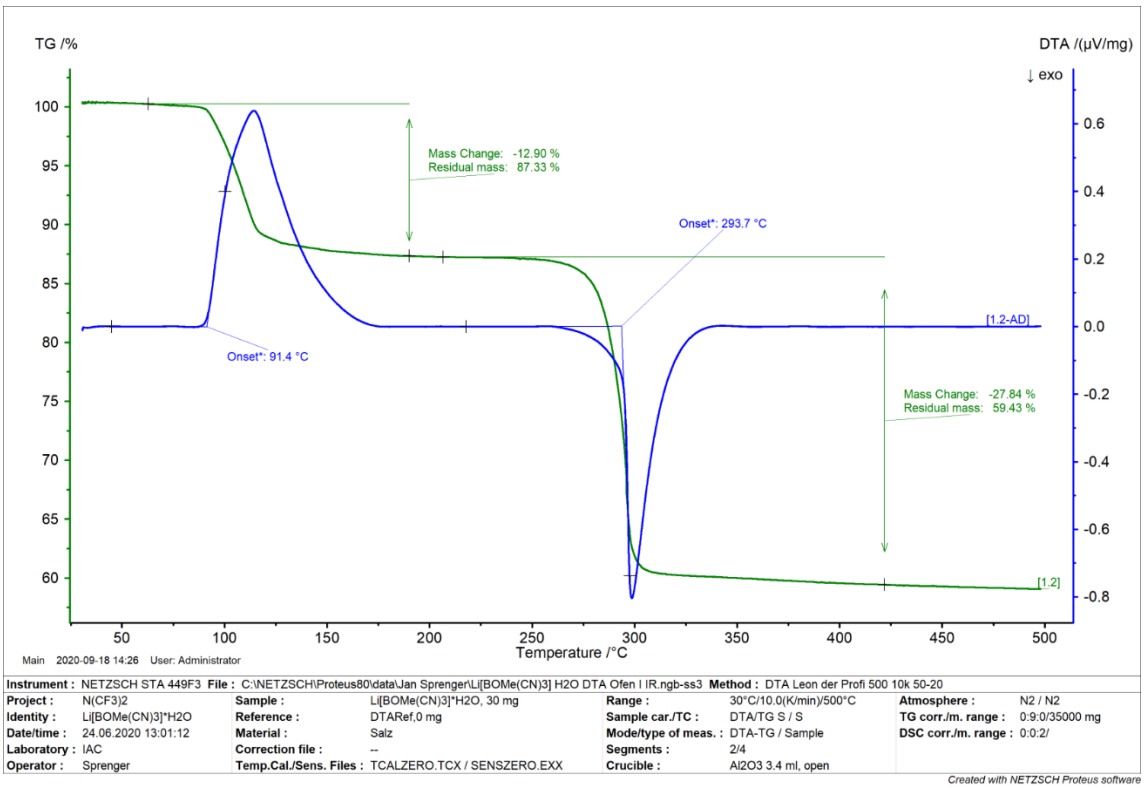

Figure S3. DTA/TG curves of $Li[B(OCH_3)(CN)_3]\cdot H_2O$.

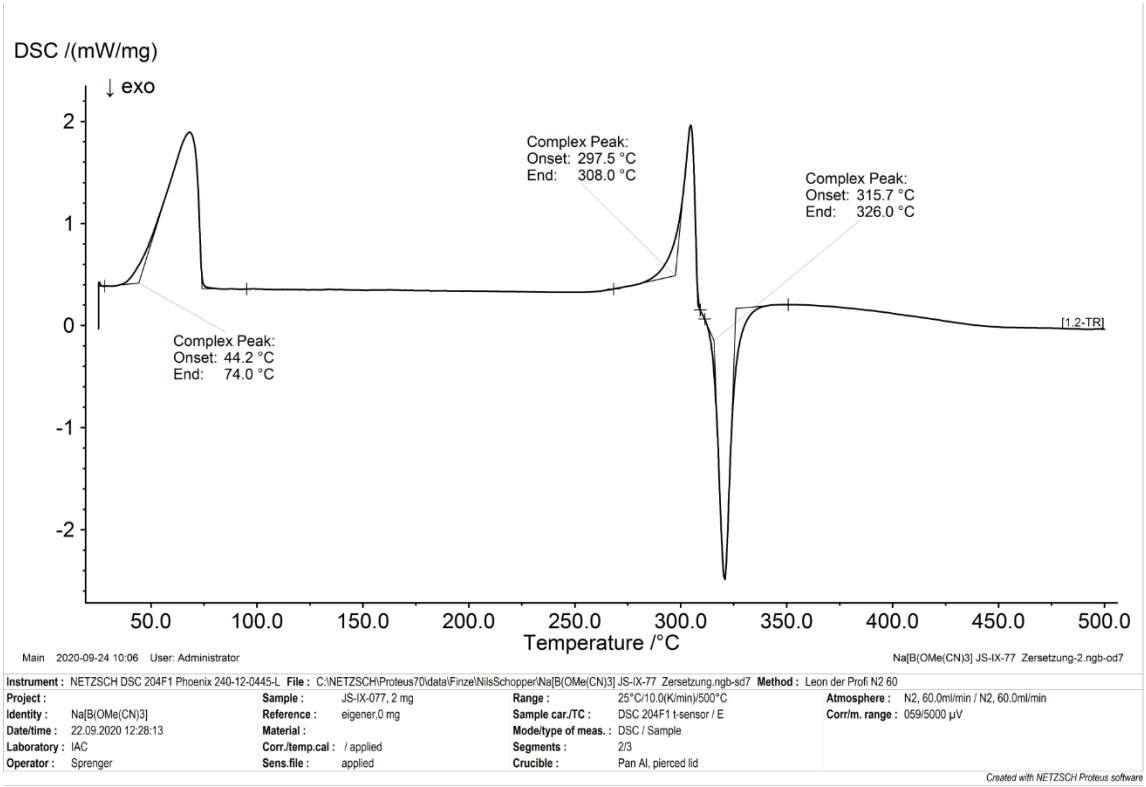

Figure S4. DSC curve of $Na[B(OCH_3)(CN)_3]\cdot H_2O$.

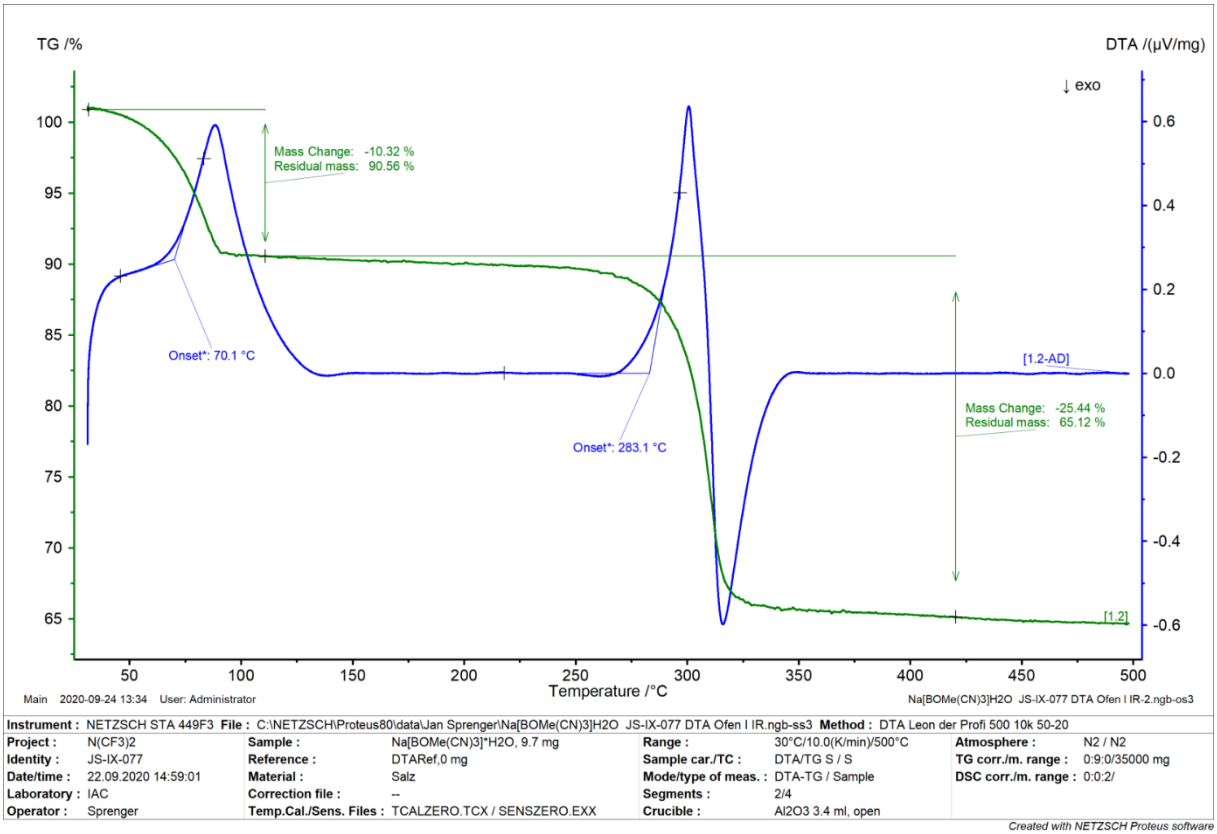

Figure S5. DTA/TG curves of $Na[B(OCH_3)(CN)_3]\cdot H_2O$.

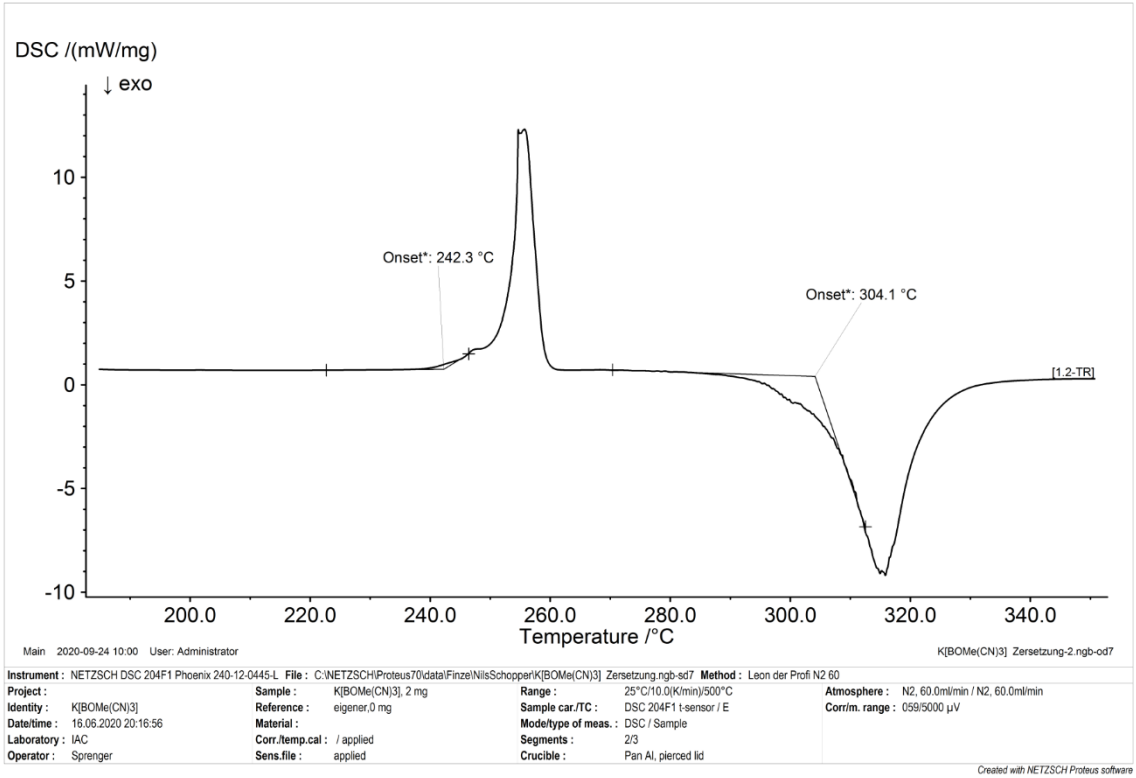

Figure S6. DSC curve of $K[B(OCH_3)(CN)_3]$.

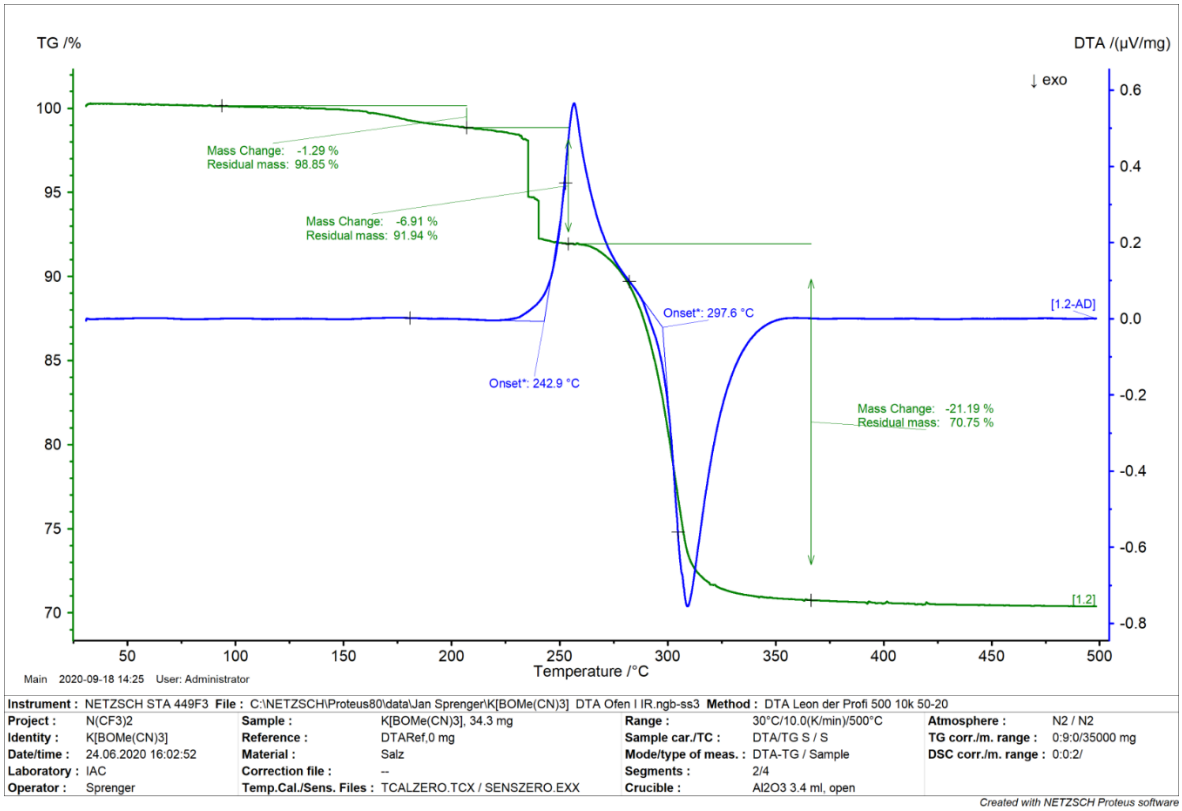

Figure S7. DTA/TG curves of $K[B(OCH_3)(CN)_3]$.

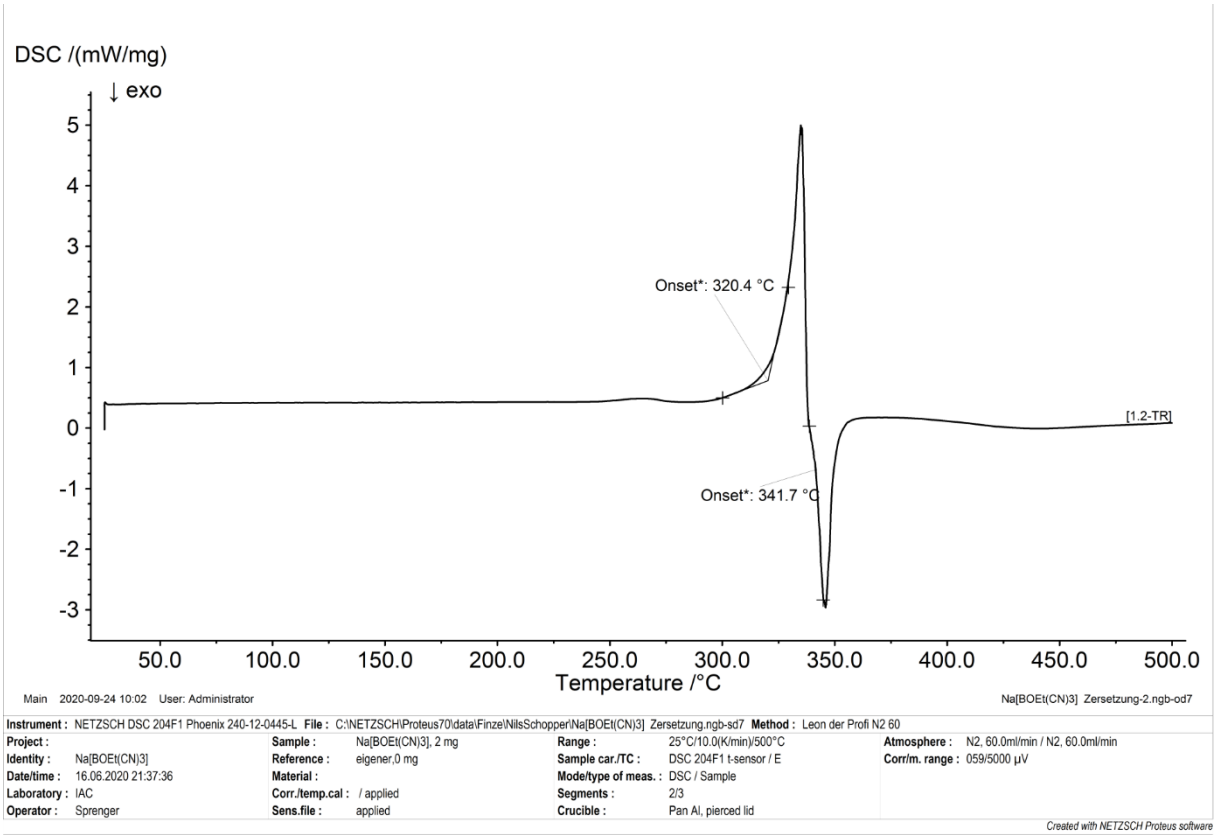

Figure S8. DSC curve of $Na[B(OC_2H_5)(CN)_3]$.

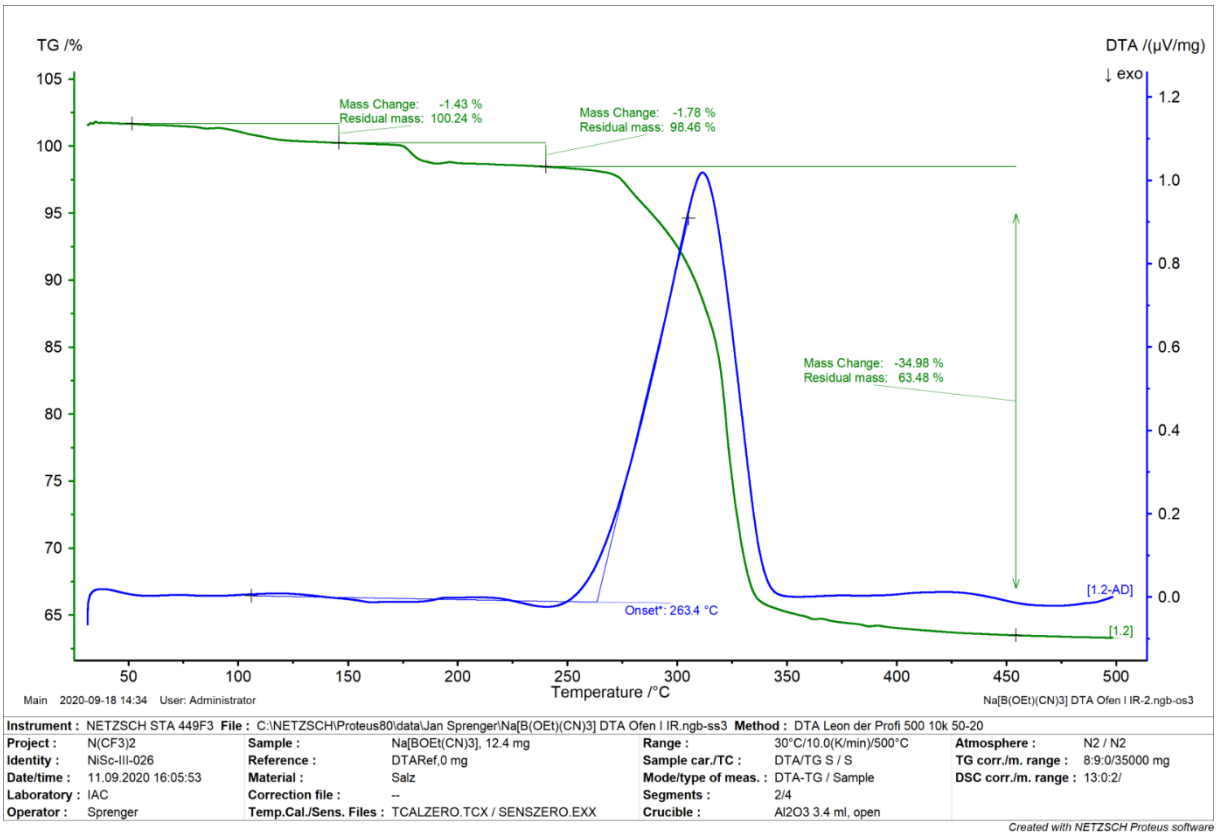

Figure S9. DTA/TG curves of $Na[B(OC_2H_5)(CN)_3]$.

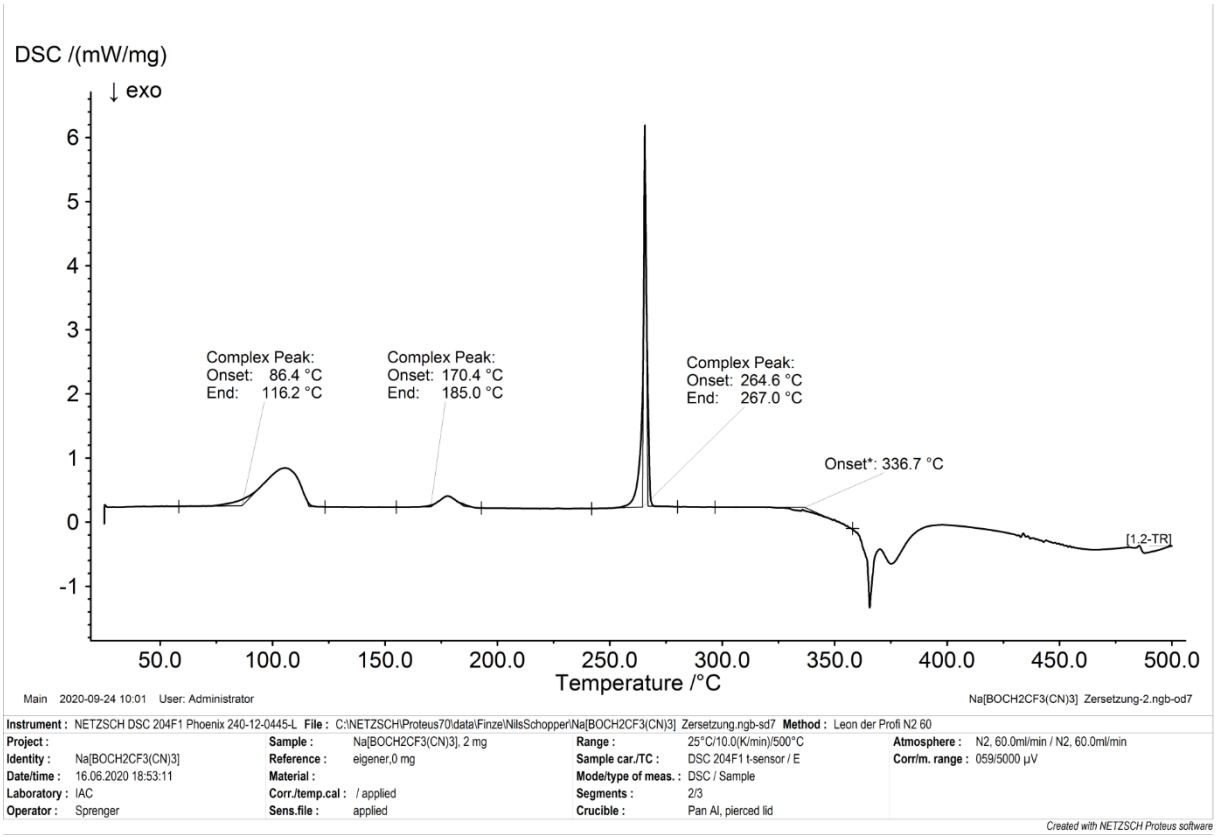

Figure S10. DSC curve of $Na[B(OCH_2CF_3)(CN)_3]\cdot 0.5H_2O$.

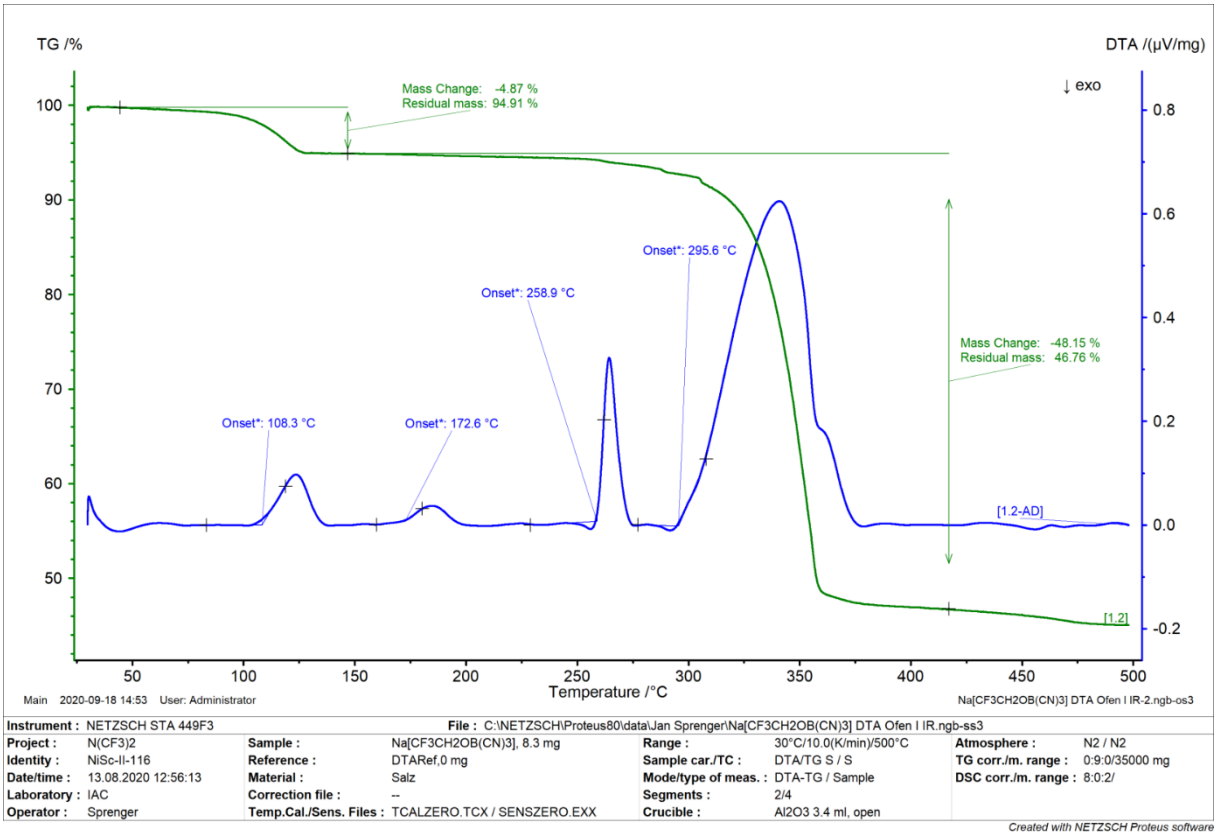

Figure S11. DTA/TG curves of $Na[B(OCH_2CF_3)(CN)_3]\cdot 0.5H_2O$.

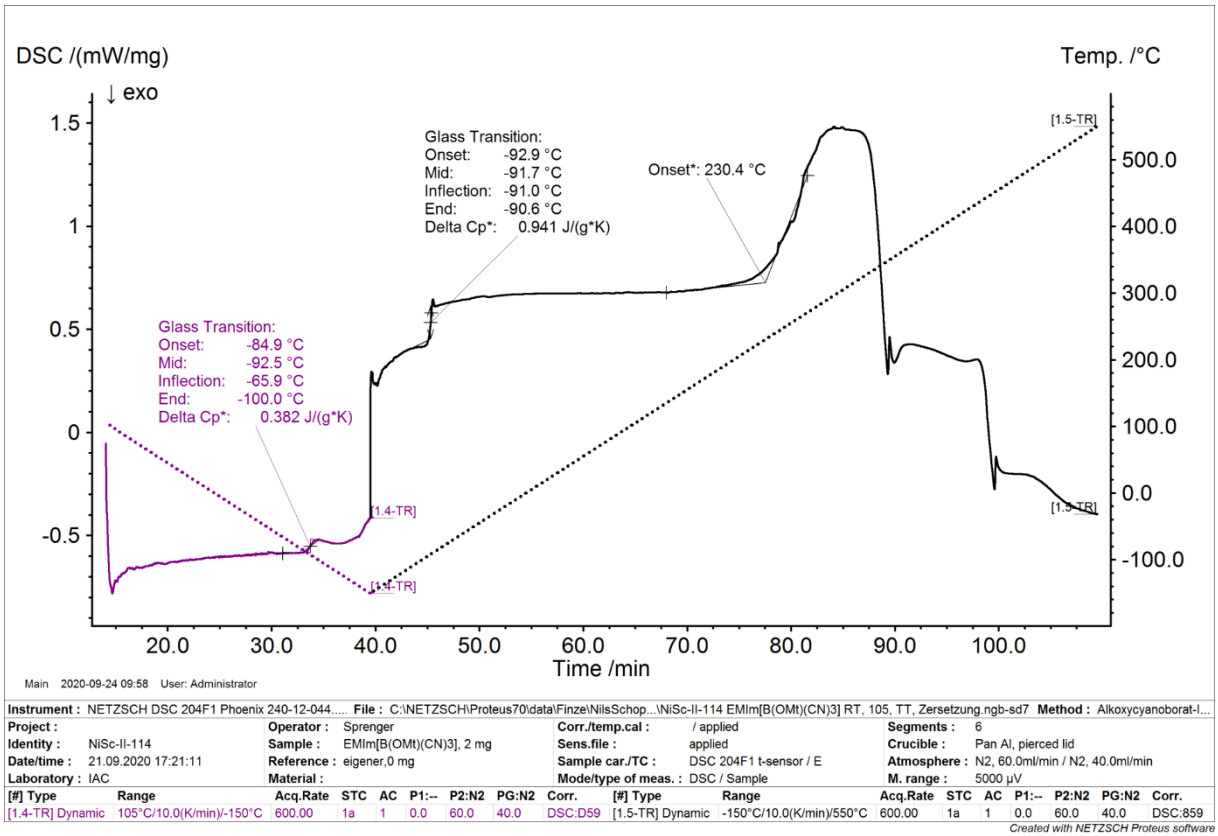

Figure S12. DSC curve of [EMIm][B(OCH$_3$)(CN)$_3$].

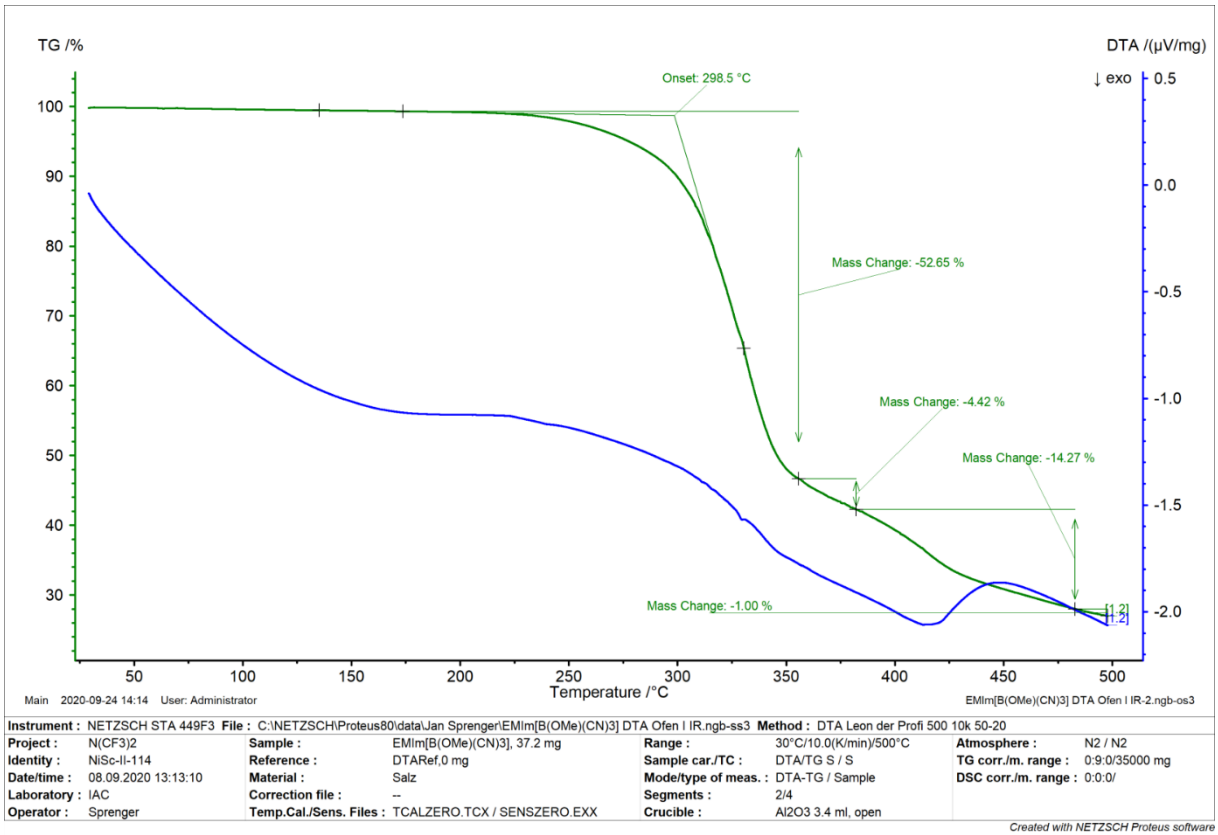

Figure S13. DTA/TG curves of [EMIm][B(OCH$_3$)(CN)$_3$].

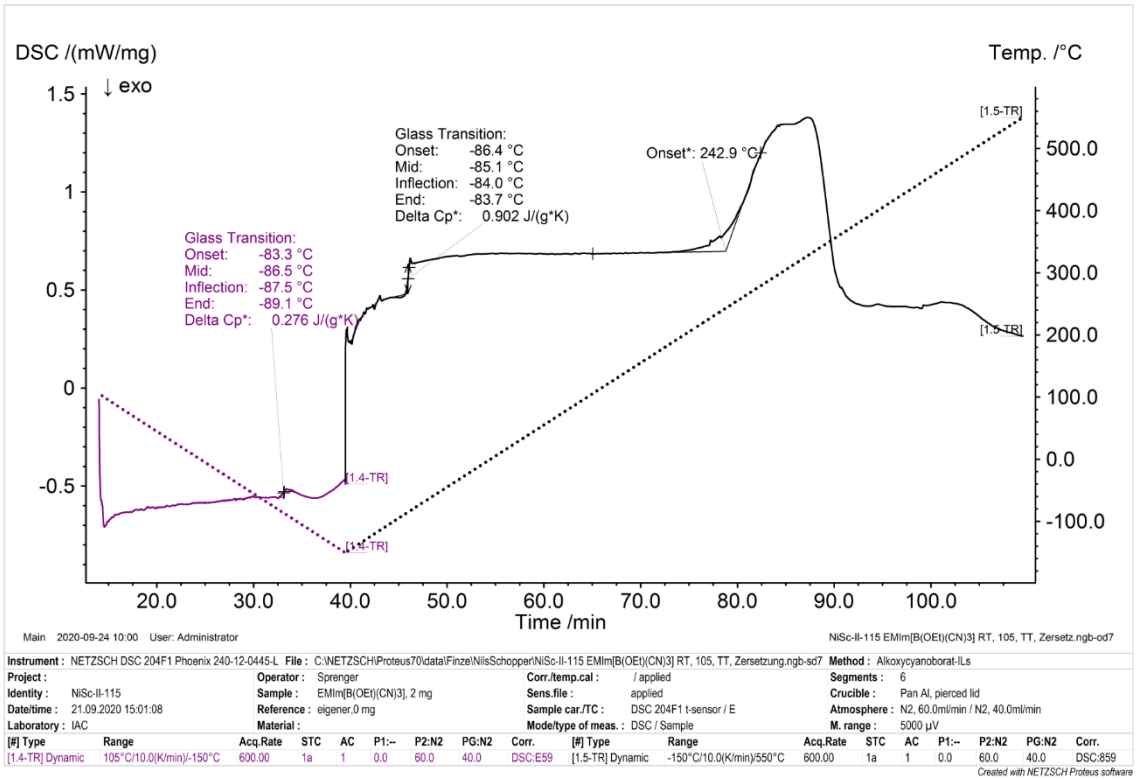

Figure S14. DSC curve of [EMIm][B(OC$_2$H$_5$)(CN)$_3$].

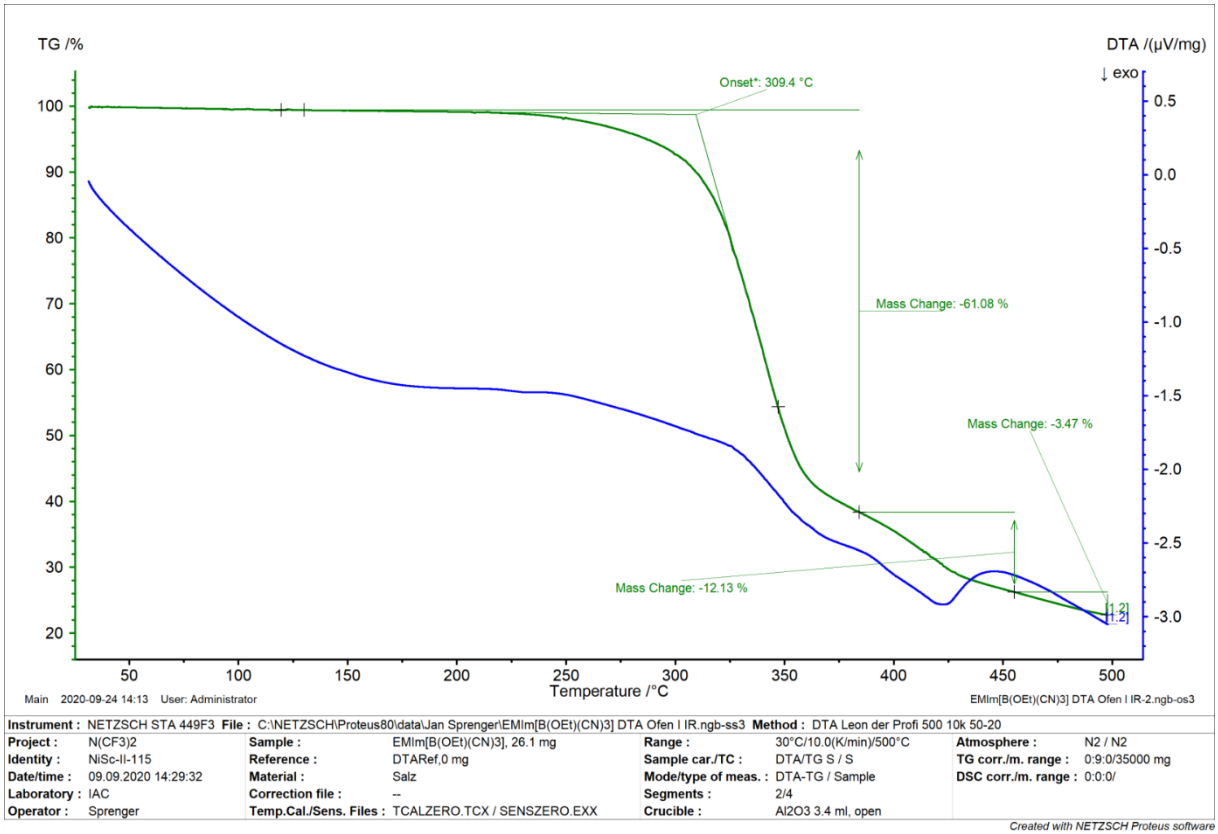

Figure S15. DTA/TG curves of [EMIm][B(OC$_2$H$_5$)(CN)$_3$].

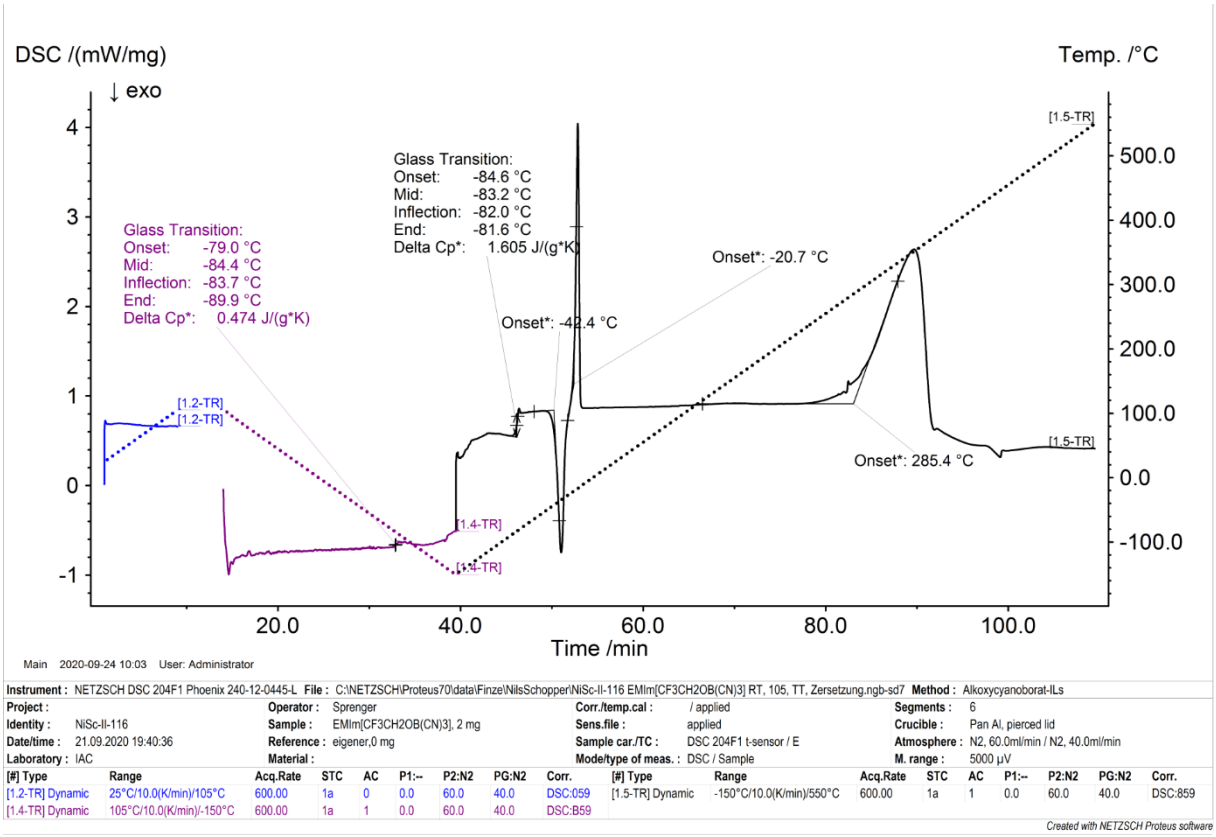

Figure S16. DSC curve of [EMIm][B(OCH$_2$CF$_3$)(CN)$_3$].

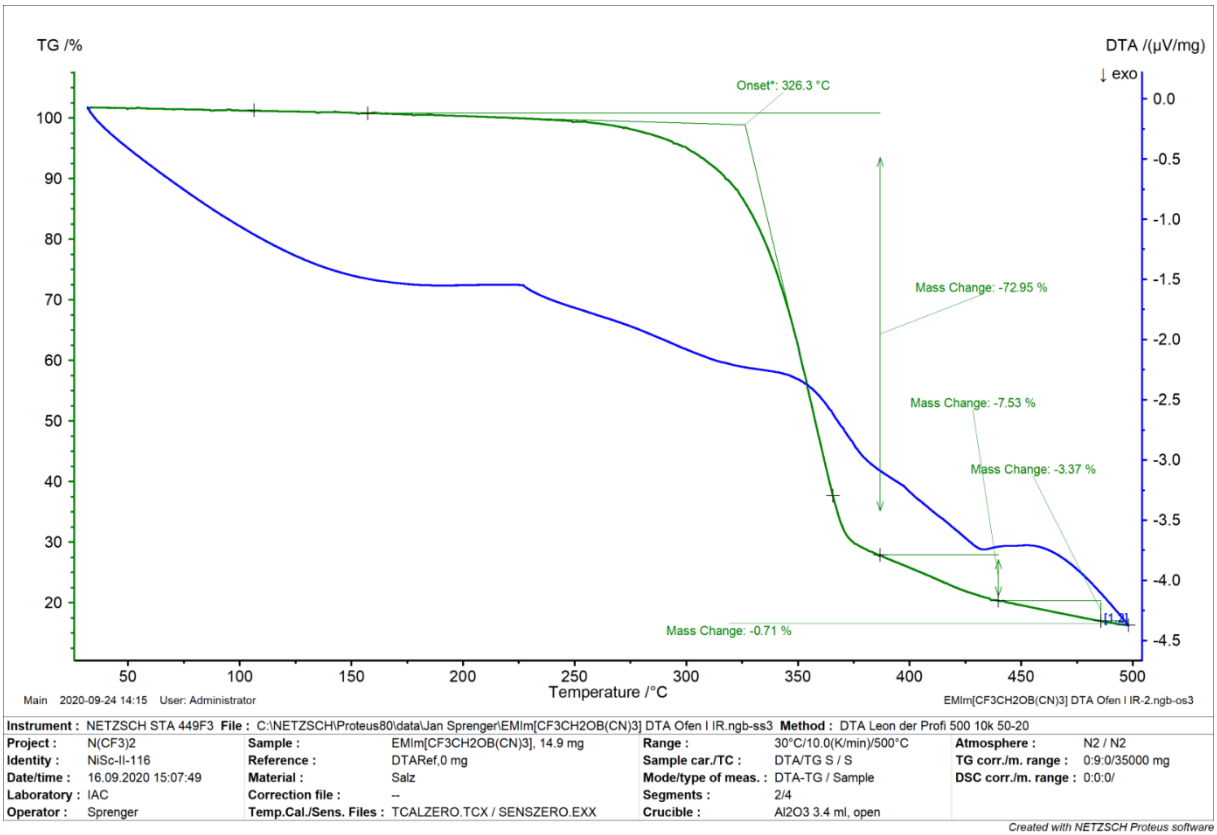

Figure S17. DTA/TG curves of [EMIm][B(OCH$_2$CF$_3$)(CN)$_3$].

4. Single Crystal X-ray Diffraction

Table S4: Crystallographic data of $Li[(CH_3O)B(CN)_3]\cdot H_2O$ and $Na[(CH_3O)B(CN)_3]\cdot H_2O$.

compound	**$Li[(CH_3O)B(CN)_3]\cdot H_2O$**	**$Na[(CH_3O)B(CN)_3]\cdot H_2O$**
Formula	$C_4H_5BLiN_3O_2$	$C_4H_5BN_3NaO_2$
M_w [g mol^{-1}]	144.86	160.91
T [K]	100(2)	290(2)
Colour	colourless	colourless
Crystal size [mm^3]	0.350 x 0.210 x 0.190	0.40 x 0.30 x 0.20
Crystal system	monoclinic	triclinic
Space group	*Cc*	$P\bar{1}$
a [Å]	5.9444(0)	6.2298(3)
b [Å]	17.4508(2)	8.0256(4)
c [Å]	7.4613(0)	8.9101(4)
α [°]	90	105.478(4)
β [°]	96.637(01)	101.298(4)
γ [°]	90	97.248(4)
V [Å^3]	768.80(7)	413.44(4)
Z	4	2
ρ_{calc} [Mg m^{-3}]	1.252	1.293
μ [mm^{-1}]	0.800	0.143
Absorption correction	Gaussian	semi-empirical
F(000) [e]	296	164
Device, radiation, wavelength	XtaLAB Synergy, Dualflex, HyPix, (CuK_α = 1.54184 Å)	Oxford Xcalibur, Eos (MoK_α = 0.71073 Å)
Theta range [°]	5.069 to 77.310	4.136 to 29.994
refelctions collected / independent	6190 / 1302	7746 / 2413
refelctions observed [$I > 2\sigma(I)$]	1299	
R(int)	0.0248	0.0158
Data / restraints / parameters	1302 / 2 / 110	2413 / 0 / 110
R_1 [$I > 2\sigma(I)$][a]	0.0220	0.0300
wR_2 (all data)[b]	0.0610	0.0651
Goodness-of-fit F^2[c]	1.062	1.025
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ [e Å^{-3}]	0.205 / −0.117	0.222 / −0.160
CCDC no.	2035891	2033370

[a] $R1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, weight map: $w = [\sigma^2 F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0,F_o^2) + 2F_c^2]/3$; [b1] a = 0.0406, b = 0.1464; [b2] a = 0.0160, b = 0.1. [c] GooF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(m-n)]^{0.5}$; ($m$ = reflections, n = variables)

Table S5: Crystallographic data of K[$(CH_3O)B(CN)_3$] and Na[$(C2H_5O)B(CN)_3$] .

compound	**K[$(CH_3O)B(CN)_3$]**	**Na[$(C_2H_5O)B(CN)_3$]**
Formula	$C_4H_3BKN_3O$	$C_5H_5BN_3NaO$
M_w [g mol^{-1}]	159.00	156.92
T [K]	100(2)	100(2)
Colour	colourless	colourless
Crystal size [mm^3]	0.450 x 0.280 x 0.140	0.345 x 0.171 x 0.139
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a [Å]	13.8805(2)	7.3884(2)
b [Å]	7.5052(0)	7.7824(2)
c [Å]	15.3649(2)	8.09230(10)
α [°]	90	82.094(2)
β [°]	95.168(0)	71.472(2)
γ [°]	90	63.968(2)
V [Å^3]	1594.15(4)	396.426(17)
Z	8	2
ρ_{calc} [Mg m^{-3}]	1.325	1.315
μ [mm^{-1}]	5.333	1.240
Absorption correction	Gaussian	Gaussian
F(000) [e]	640	160
Device, radiation, wavelength	XtaLAB Synergy, Dualflex, HyPix, (CuK_α = 1.54184 Å)	XtaLAB Synergy, Dualflex, HyPix, (CuK_α = 1.54184 Å)
Theta range [°]	5.783 to 77.246	5.766 to 77.333
refelctions collected / independent	8580 / 1670	8262 / 1658
refelctions observed [$I > 2\sigma(I)$]	1640	1584
R(int)	0.0296	0.0309
Data / restraints / parameters	1670 / 0 / 95	1658 / 0 / 101
R_1 [$I > 2\sigma(I)$][a]	0.0251	0.0289
wR_2 (all data)[b]	0.0687	0.0764
Goodness-of-fit F^2[c]	1.018	1.072
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ [e Å^{-3}]	0.243 / −0.248	0.321 / −0.235
CCDC no.	2035889	2035890

[a] $R1 = (\Sigma|\,|F_o| - |F_c|\,|)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, weight map: $w = [\sigma^2 F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0,F_o^2) + 2F_c^2]/3$; [b1] a = 0.0419, b = 1.0863; [b2] a = 0.038, b = 0.1253. [c] GooF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(m - n)]^{0.5}$;
(m = reflections, n = variables)

Table S6: Crystallographic data of $Na[(CF_3CH_2O)B(CN)_3]\cdot 0.5H_2O$.

compound	**$Na[(CF_3CH_2O)B(CN)_3]\cdot 0.5H_2O$**
Formula	$C_{10}H_6B_2F_6N_6Na_2O_3$
$\underline{M}_w$ [g mol^{-1}]	439.81
T [K]	100(2)
Colour	colourless
Crystal size [mm^3]	0.190 x 0.146 x 0.047
Crystal system	monoclinic
Space group	$C2/c$
a [Å]	15.4584(2)
b [Å]	7.76240(10)
c [Å]	15.2266(2)
α [°]	90
β [°]	99.7870(10)
γ [°]	90
V [Å^3]	1800.51(4)
Z	4
ρ_{calc} [Mg m^{-3}]	1.622
μ [mm^{-1}]	1.823
Absorption correction	Gaussian
F(000) [e]	872
Device, radiation, wavelength	XtaLAB Synergy, Dualflex, HyPix, (CuK_α = 1.54184 Å)
Theta range [°]	5.809 to 74.504
refelctions collected / independent	10105 / 1844
refelctions observed [$I > 2\sigma(I)$]	1741
R(int)	0.0287
Data / restraints / parameters	1844 / 1 / 136
R_1 [$I > 2\sigma(I)$][a]	0.0289
wR_2 (all data)[b]	0.0798
Goodness-of-fit F^2[c]	1.004
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ [e Å^{-3}]	0.346 / −0.267
CCDC no.	2035892

[a] $R1 = (\Sigma||F_o|-|F_c||)/\Sigma|F_o|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$, weight map: $w = [\sigma^2 F_o + (aP)^2 + bP]^{-1}$; $P = [\max(0,F_o^2) + 2F_c^2]/3$; [b1] a = 0.0492, b = 1.3813; [b2] a = 0.1337, b = 1.1987. [c] GooF: $S = [\Sigma w(F_o^2 - F_c^2)^2/(m - n)]^{0.5}$; ($m$ = reflections, n = variables)

5. References

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