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Understanding the ionic liquid [NC_{4111}][NTf_2] from individual building blocks: an IR spectroscopic study

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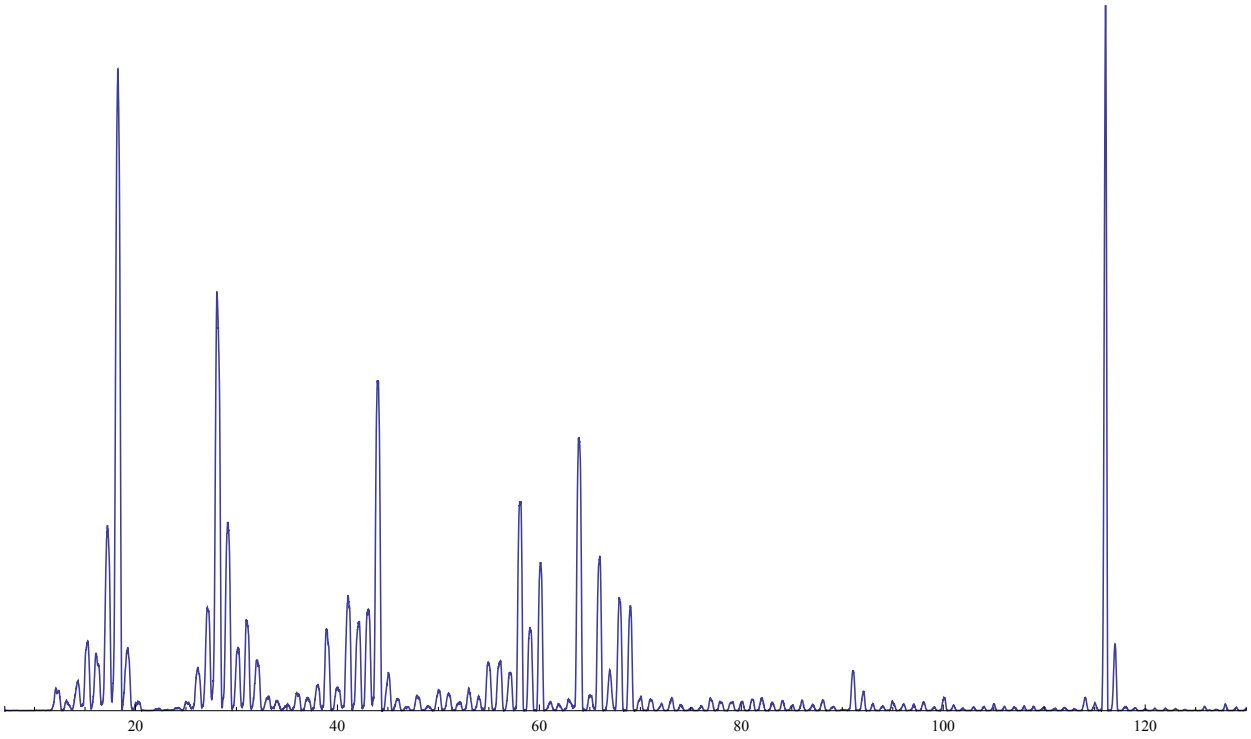

Fig. S 1. Gas phase mass spectrum of $[NC_{4111}][NTf_2]$. $m/z = 116$ is the cation mass. Peaks at $m/z = 58$, 60, 64, 69 result from the fragments Bu+H^+, $N(CH_3)_3$+H^+, SO_2^+ and CF_3^+ of anion and cation, respectively. The water, nitrogen and CO_2 signals at $m/z = 18$, 28, 44 are due to the background in the QMS chamber.

Mass spectrosocopic measurements This work present a line-of-sight mass spectroscopic measurement of the evaporated $[NC_{4111}][NTf_2]$ at an evaporation temperature of 450(1) K. In Figure S1 we show the gas phase mass spectrum of $[NC_{4111}][NTf_2]$. m/z = 116 corresponds to the cation mass. Peaks at m=z = 58, 60, 64, 69 result from the fragments $Bu + H^+$, $N(CH_3)_3 + H^+$, SO_2^+ and CF_3^+ of anion and cation, respectively. The water, nitrogen and CO_2 signals at m/z = 18, 28, 44 are due to the background in the QMS chamber. We observed a signal at m/z = 116 corresponding to the cation as well as fragments of the anion. After switching off the ionization filament no signal below m/z = 1000 could be observed. This supports the results of earlier studies that aprotic ILs evaporate in ultrahigh vacuum as classical ion pairs (see reference 27,74).

IR spectra for the IL using the deuterated cation Figure S2 displays the recorded IR spectra of the IL building blocks of the deuterated cation d_9. From top to bottom: CIVP

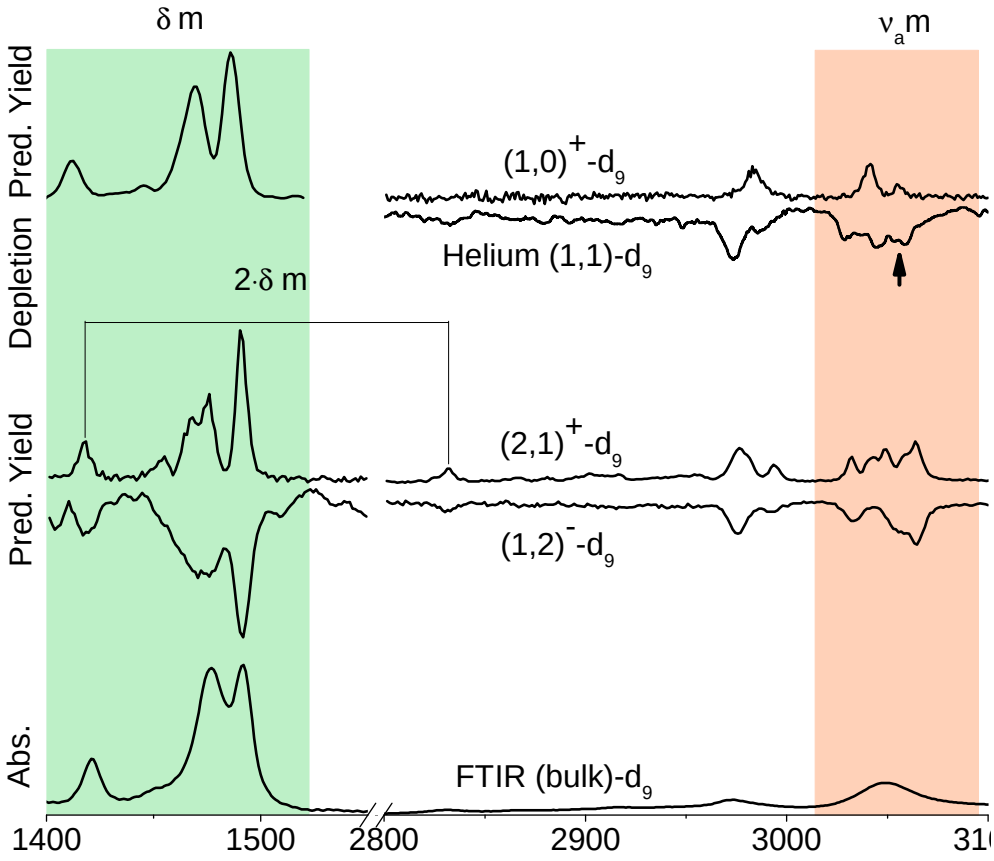

Fig. S 2. From top to bottom: CIVP spectra of the deuterated cation (1,0)-d_9; IR spectrum of $[d_9{-}NC_{4111}][NTf_2]$ measured in helium droplet Helium (1,1)-d_9; CIVP spectra of the deuterated (2,1) and (1,2) clusters and the FTIR bulk spectrum of $[d_9{-}NC_{4111}][NTf_2]$, labeled (2,1)-d_9, (1,2)-d_9 and FTIR (bulk)-d_9, respectively. Note that the vertical axes are arbitrarily scaled on either side of the break in the abscissa. The arrow marks the position of the VTMA measurement.

spectrum of the deuterated cation $d_9-(1,0)$. $[d_9-NC_{4111}][NTf_2]$ ion pair measured in helium droplet Helium d9-(1,1); CIVP spectra of the deuterated $(2,1)$ and $(1,2)$ clusters and the FTIR bulk spectrum of $[d_9-NC_{4111}][NTf_2]$, labeled $d_9-(2,1)$, $d_9-(1,2)$ and room temperature FTIR d_9-(bulk), respectively. Vertical lines, corresponding to the most intense (d_9-(1,0) features, aid to identify spectral changes. IR transitions are arbitrarily scaled on either side of. The arrow marks the position of the VTMA measurement.

Results of the theoretical predictions in comparison to the experimental results

TABLE I. Harmonic frequencies and assignments obtained by MP2/cc-pwCVTZ (scaled by 0.968) of the anion in trans ((0,1) *trans*) and cis ((0,1) *cis*) conformation; center frequencies of the anion ((0,1)) measured by CIVP; anion bands from two harmonic frequency calculations of an ion pair with the anion in trans ((1,1) *trans*) and cis ((1,1) *cis*) and the cation both in ap/ap conformation obtained by MP2/aug-cc-pwCVDZ (unscaled); center frequencies of anion bands in cm^{-1}. Band frequencies from resonances shifted due to different local environments are separated by a semicolon. Predicted frequencies in italics.

assignment[a]	(0,1) *trans*	(0,1) *cis*	(0,1)	(1,1) *trans*	(1,1) *cis*	(1,2)	(2,3)	(2,1)	(3,2)	bulk FTIR	Neon	Argon
δCSN	*616*	*595*[b]	626	*601*	*581*[b]	626	625	621	616	617	606;609;621;626	603;608;620;624
δSNS	*615*	*642*	–	*615*	*637*	–	669	–	643	656	656;672	655;670
$\delta_s CF_3$	*734*	*735*	–	*726**	*728**	737	740	–	–	741	742	741
νCS	*748*	*749*	–	*739**	*743**	756	760	–	–	763	769	767
ν_sSN	*788*	*784*	–	*777**	*772**	788	793	–	–	791	794	792
ν_aSN	*1077*	*1080*	1069	*1022*	*1029*	1063;1074	1059;1073	1055	1057	1060	1053;1058;1065	1056;1063
–	–	–	–	*1100**	*1102**	–	–	–	–	–	–	–
$\nu_s^{o.p.} SO_2$	*1144*	*1142*	–	*1105*[b]*	*1106*[b]*	1144	1148	1140	1130	1139	1134;1141	1132;1139
$\nu_s^{i.p.} SO_2$	*1148*	*1148*	–	*1118*[b]*	*1115*[b]*	1153	1152	1149	1142	–	1146;1151	1143;1149
νCF_3	*1173*	*1176*[b]	1178	*1142*[b]	*1152*[b]	1171	1184	1182	–	1177	–	–
νCF_3	*1179*	*1178*[b]	–	*1148*[b]	*1166*[b]	–	–	1190	–	–	–	–
νCF_3	*1181*	*1187*	1186	*1190*	*1191*	1183	–	1202	1195	–	1197;1200	1193
νCF_3	*1207*	*1203*	1205	*1202*	*1198*	1204;1215	1202;1216	1216	1212;1220	1199	1208;1213	1203
$\nu_a CF_3$	*1234*	*1238*	1229	*1214*	*1213*	1234	1235	–	1226	1226	1222	–
$\nu_s CF_3$	*1246*	*1245*	1236	*1225*	*1222*	1249	–	1255	1241	–	1237	1234
$\nu_a^{o.p.} SO_2$	*1359*	*1358*	1348	*1322**	*1314**	1347;1368	1330	1342	1327	1335	1321;1332	1321;1331
$\nu_a^{i.p.} SO_2$	*1379*	*1375*	1370	*1352**	*1338**	1362;1379	1361;1368	1368	1349	1355	1350;1361	1345 sh;1348 sh;1355

[a] The symbols have their usual meaning: ν, stretching; δ, bending; $_s$, symmetric; $_a$, antisymmetric; $^{i.p.}$, in-phase; $^{o.p.}$, out-of-phase; sh, shoulder. [b] Vibration is localized on either moiety. *Strongly coupled band.

TABLE II. Harmonic frequencies and group assignments obtained by MP2/cc-pVTZ (scaled by 0.94) of the cation in ap/ap conformation (ap/ap); center frequencies of cation bands as shown in the main document and in argon matrix in cm^{-1}. Band frequencies from resonances shifted due to different local environments are separated by a semicolon. Calculated frequencies are written in italics.

assignment[a]	ap/ap	(1,0)	(2,1)	(3,2)	(1,2)	(2,3)	bulk FTIR	Helium (1,1)	Helium (2,2)+	Neon	Argon
	2889	2884	2880	2880 sh	2885	2869	2874 sh	2880 sh	2880 sh	2882 sh	2875 sh
	2897	2895	2892	2889	–	2886	2883	2889	2889	2891	2887
ν_sb	*2902*	–	2901	–	–	–	–	–	–	–	–
	2911	–	–	–	–	–	–	–	–	–	–
	2915	–	2915	2914	2916	2912	–	2913	2913	2918 sh	–
ν_sm	*2918*	–	–	–	–	–	–	–	–	–	–
	2921	–	–	–	–	–	–	–	–	–	–
	2933	2950 sh	2939	–	–	2935	–	2931	2930 sh	2929	2924
	2956	2959	2950	2949	2946	2947	2942	2949	2948	2951	2946
ν_ab	*2975*	–	–	–	–	–	–	–	–	–	–
	2979	2979	2976; 2978 sh	2973	2970	2971; 2977 sh	2972	2975	2975	2979	2975
	2991	2996	2988; 2990 sh	2979 sh	2980 sh	2985 sh		2984	2982 sh	2990 sh	2984 sh
	3018	–	3014	–	3014	3006	–	3009	3009	3017	–
	3019	–	–	–	–	–	–	–	–	–	–
	3023	3039	3031	3030	3032	3024	–	3030	3034	3037 sh	3029 sh
ν_am	*3023*	–	–	–	–	–	–	–	–	–	–
	3035	–	–	–	–	–	–	–	–	–	–
	3038	3055	3042;3048	3040;3048	3053	3050	3048	3046	3051	3048	3043 sh
	–	–	3057;3064	3060	3063	3063 sh	–	3058	3057 sh	3057	3053

[a] The symbols have their usual meaning: ν, stretching; $_s$, symmetric; $_a$, antisymmetric; sh, shoulder.

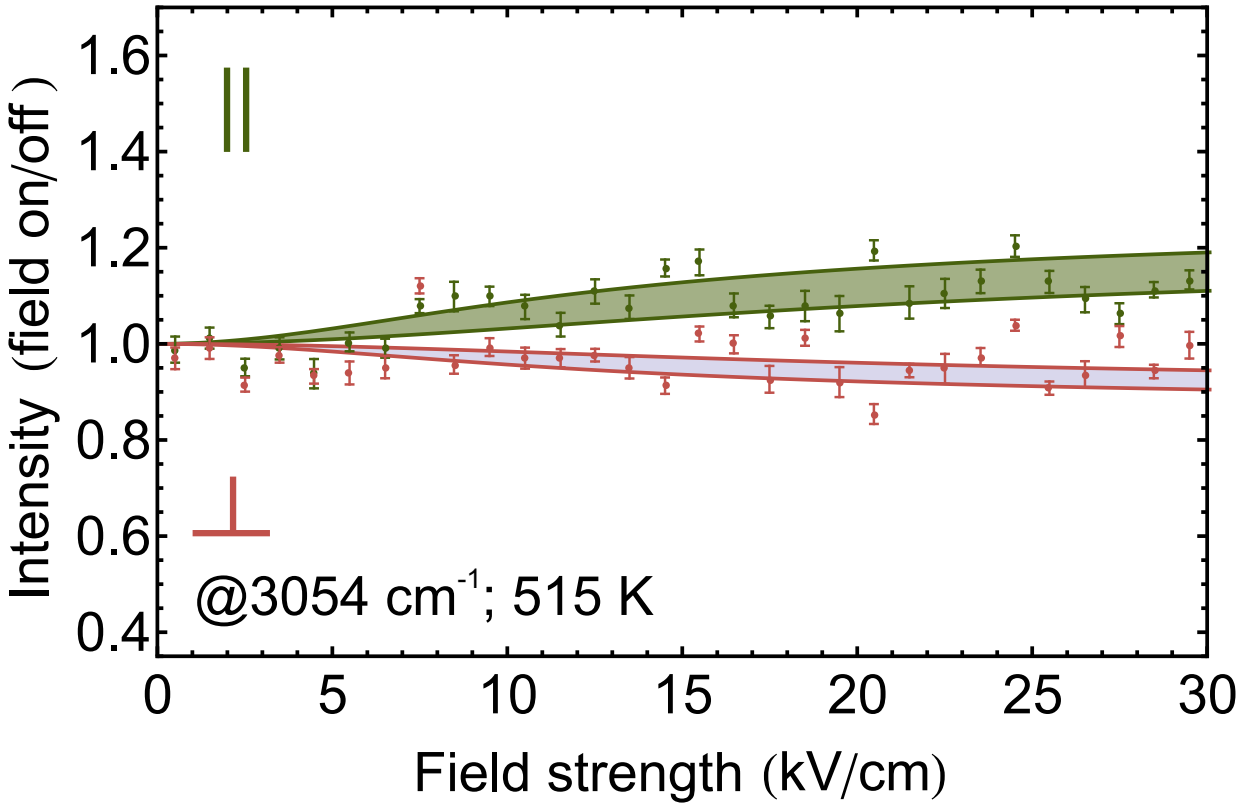

Fig. S 3. Recorded intensity ratio with field on/off as a function of the electric field strength for the 3054 cm-1 band at an evaporation temperature of 515 K. Results for the laser polarization parallel/perpendicular to the electric field are displayed in green and red, respectively.

TABLE III. Harmonic frequencies and group assignments obtained by MP2/cc-pVTZ (scaled by 0.94) of the cation in different conformations; cation bands from two harmonic frequency calculations of an ion pair with the anion in trans ((1,1) *trans*) and cis ((1,1) *cis*) and the cation both in ap/ap conformation obtained by MP2/aug-cc-pwCVDZ (scaled by 0.945).

assignment[a]	ap/ap	ap/sc	sc/ap	ac/ap	sc/sc	ac/sc	(1,1) *trans*	(1,1) *cis*
	2889	*2891*	*2880*	*2892*	*2892*	*2892*	*2880*	*2885*
	2897	*2900*	*2894*	*2896*	*2894*	*2905*	*2888*	*2887*
ν_sb	*2902*	*2903*	*2897*	*2904*	*2900*	*2906*	*2889*	*2890*
	2911	*2913**	*2911**	*2912**	*2914**	*2914**	*2907*	*2906*
	2915	*2915**	*2914**	*2915**	*2917**	*2918**	*2911*	*2911*
ν_sm	*2918*	*2918*	*2917*	*2918*	*2918**	*2918**	*2917*	*2916*
	2921	*2921*	*2924***	*2921*	*2924**	*2922**	*2924*	*2920*
	2933	*2951*	*2924***	*2933*	*2941*	*2947*	*2955*	*2958*
	2956	*2957*	*2945*	*2952*	*2947*	*2952*	*2968*	*2969*
ν_ab	*2975*	*2973*	*2974*	*2974*	*2971*	*2972*	*2976*	*2979*
	2979	*2981*	*2979*	*2976*	*2978*	*2978*	*2995*	*2986*
	2991	*2987*	*2992*	*2991*	*2987*	*2989*	–	–
	3018	*3018*	*3017*	*3019*	*3017*	*3018*	*3015*	*3015*
	3019	*3019*	*3018*	*3020*	*3018*	*3019*	*3019*	*3018*
	3023	*3023*	*3022*	*3023*	*3022*	*3023*	*3025*	*3024*
ν_am	*3023*	*3023*	*3024*	*3024*	*3024*	*3024*	*3029*	*3026*
	3035	*3035*	*3032*	*3033*	*3032*	*3034*	*3032*	*3029*
	3038	*3038*	*3056*	*3037*	*3054*	*3037*	*3035*	*3034*
	–	–	–	–	–	–	*3059*	*3054*

[a] The symbols have their usual meaning: ν, stretching; $_s$, symmetric; $_a$, antisymmetric. $^{*}\nu_s$b and ν_sm coupled band. $^{**}\nu_s$m and ν_ab coupled band.

TABLE IV. Harmonic frequencies and group assignments obtained by MP2/cc-pVTZ (scaling factors see computational methods) of the deuterated cation in ap/ap conformation (ap/ap - d_9); center frequencies of deuterated cation bands in cm^{-1}. Band frequencies from resonances shifted due to different local environments are separated by a semicolon. Calculated frequencies are written in italics.

assignment[a]	ap/ap - d_9	(1,0) - d_9	(2,1) - d_9	(1,2) - d_9	Helium (1,1) - d_9	bulk FTIR - d_9
	1419		1418	1418		1421
	1420		–	–		–
	1461		1455	1455 sh		1455 sh
	1461		–	–		–
δm	*1470*	no data	–	–	no data	–
	1471		–	–		–
	1491		1467	1470		
	1493		1476	1476		1476
	1508		1491	1491		1492
	2082		2078	2078		2078
ν_sb	*2104*	no data	–	–	no data	–
	2112		2115	2116		2117
	2116		–	–		–
	2177		–	2145		2147
	2195		2221	2215		2226
ν_ab	*2207*	no data	–	–	no data	–
	2210		–	–		–
	2216		2231	2235 sh		–
	2915	–	–	–	–	–
ν_sm	*2918*	–	–	–	–	–
	2920	–	–	–	–	–
	–	2983	2976;2980 sh	2976	2974	2972
	–	–	2994	2994	2987	2983 sh
	3018	–	–	–	–	–
	3019	–	–	–	–	–
	3023	–	–	–	–	–
ν_am	*3023*	3041	3032	3033	3029	–
	3035	–	–	–	–	–
	3037	3055	3043;3049	3055 sh	3044	3049
	–	–	3059 sh;3064	3064	3059	–

[a] The symbols have their usual meaning: δ bending; ν, stretching; $_s$, symmetric; $_a$, antisymmetric; sh, shoulder.