Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Electronic Supplementary Information:

Ion-ion and ion-solvent interactions in lithium imidazolide electrolytes studied by Raman spectroscopy and DFT models

Johan Scheers,*[a] Leszek Niedzicki,[b,c] Grażyna Z. Żukowska,[b,c] Patrik Johansson,[a,c] Władysław Wieczorek[b,c] and Per Jacobsson[a]

[a]*Department of Applied Physics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden.*

[b]*Polymer Ionics Research Group, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, PL-00664 Warsaw, Poland.*

[c]*ALISTORE-European Research Institute*

*Corresponding author. Tel.: +46 31 772 3177; fax: +46 31 772 2090.

E-mail address: johan.scheers@chalmers.se

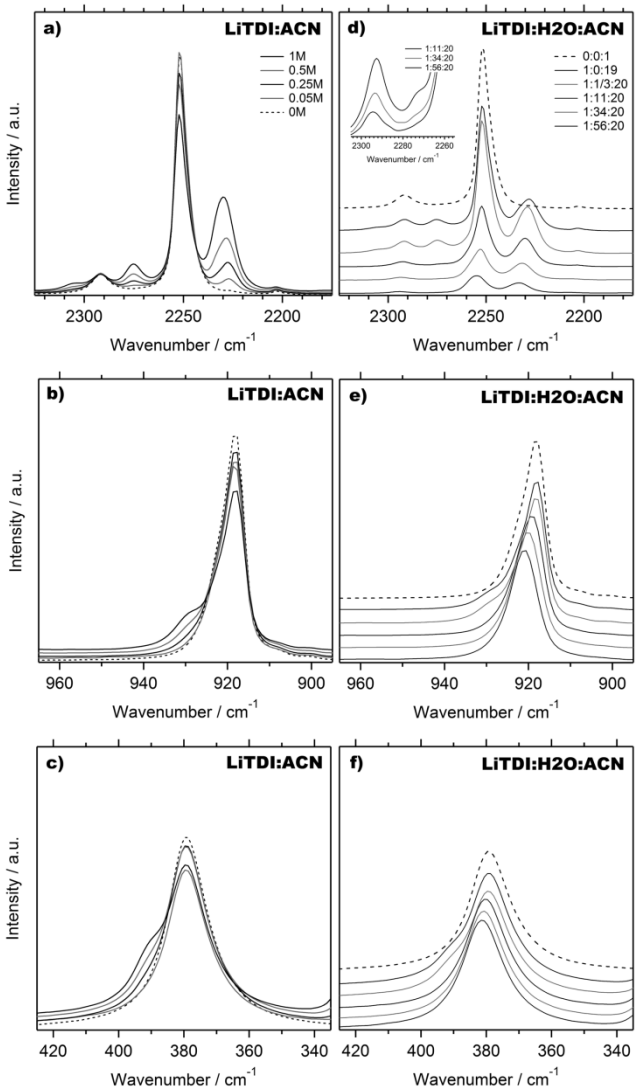

Figure S1. Raman spectra showing Li^+ coordination effects on the vibration modes of ACN; in LiTDI:ACN only (a, b, and c) and in the presence of water (d, e, f).

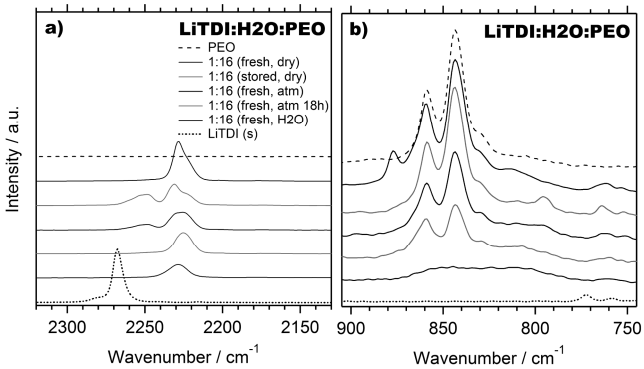

Figure S2. Raman spectra showing the effect of water on a) the ν(C3-N2) modes and b) the polymer backbone in PEO-based electrolytes.

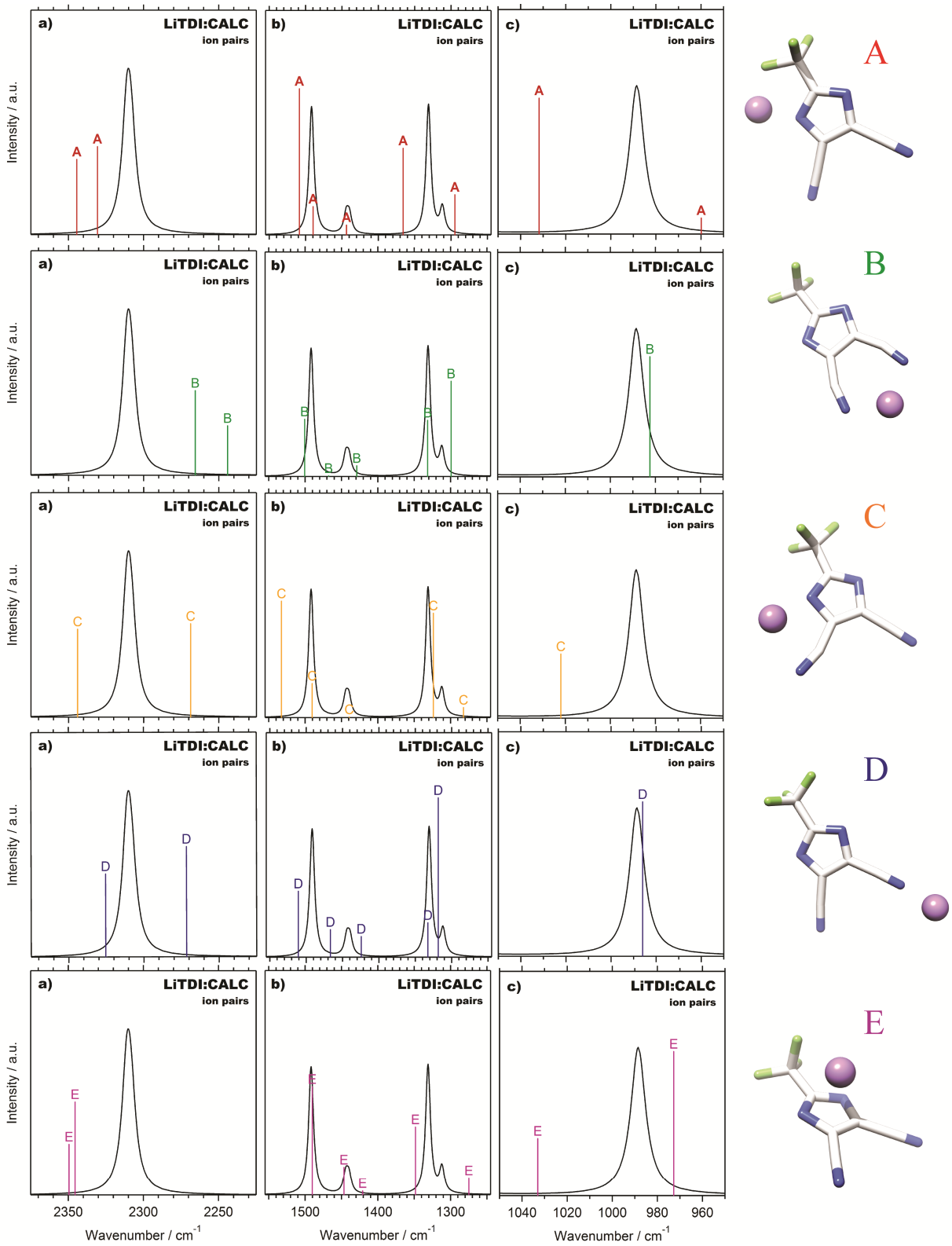

Figure S3. Calculated Raman spectra of the vibrational shifts resulting from different LiTDI ion pair configurations (vertical lines) in comparison with TDI (envelopes) in three different regions; a-c) (vacuum, B3LYP/6-311+G(d)).

Table S1. Assigned vibrational spectrum of TDI, based on the calculated energy minimum structure in vacuum. Experimental data are given for a 1M LiTDI:H_2O electrolyte (wavenumbers and qualitative band features).

Mode	υ_{exp} /cm^{-1}	I_{exp} /a.u.	υ_{calc} / cm^{-1}	IR_{Int} /$km \cdot mol^{-1}$	R_{Act} /$Å^4 \cdot amu^{-1}$	Tentative assignment
33	2238	s	2311	136	565	ν_s(C3-N2)
32			2308	159	378	ν_{as}(C3-N2)
31	1499	s	1492	63	149	ν(C4-C1; C2-C2*)$_{o.o.ph.}$
30	1460	m	1444	61	21	ν(C1-N1; C2*-C3*)$_{i.ph.}$
29			1440	82	19	ν(C1-N1*; C2-C3)$_{i.ph.}$
28	1317	s	1331	44	124	ν_{as}(N1-C2)
27			1312	35	24	ν_s(N1-C2)
26	1187	w,br	1189	297	6	[ν(C4-C1)$_{o.o.ph}$; ν_s(C1-N1)]$_{i.ph.}$
25	1136	w,br	1171	45	4	ν_{as}(N1-C2); ν(C4-C1)
24			1118	322	14	δ(C4)
23			1073	314	3	π(C4)
22	996	m	988	92	16	δ(N1-C1-N1*)
21	765	w,br	757	7	< 1	π(C1)
20	757	w,sh	755	2	1	$\delta(CF_3)$
19	708	w,br	715	< 1	2	π(C2; C2*)$_{o.o.ph.}$
18			684	5	1	δ_{as}(C2-C3-N2)
17	679	m	677	7	10	$\delta(CF_3)$; ν_s(C2-C3)
16			586	4	< 1	ν_{as}(C2-C3)
15	566	vw	580	2	2	π_s(C2; C3)$_{o.o.ph.}$
14			540	5	2	π_s(C3)
13	525	w	522	< 1	2	δ(F2-C4-F2*); ν_{as}(C2-C3)
12	482	w	506	4	5	δ_s(C2-C3-N2)
11	466	w	497	< 1	2	π_{as}(C3)
10			391	3	< 1	π(NCN*)
9	392	w	391	2	2	δ(F1-C4-C1; F2-C4-F2*)$_{i.ph.}$
8	334	m	330	2	5	ν(C4-C1)
7			250	4	< 1	δ(F1-C4-C1)
6			209	5	< 1	π(C2C2*)$_{i.ph.}$
5			151	< 1	< 1	π(C2C2*)$_{o.o..ph.}$
4			124	1	< 1	δ(C4-C1-N1*)
3			111	2	9	δ_s(C2*-C2-C3)
2			88	2	4	$\pi(CF_3)$
1			-8	< 1	1	$(CF_3)_{rotation}$

br = broad; s = strong; sh = shoulder; w = weak; vw = very weak; ν = stretching (ν_s -symmetric; ν_{as} -asymmetric) ; δ = in plane bending or motion of atoms; π = out of plane bending or motion of a single atom/group of atoms; i.ph. = in phase; o.o.ph. = out of phase.

Table S2. Selected geometry parameters and normal modes for model structures.

Model	d(Li-N) /Å	d(Li-F) /Å	∠(Li-N1-C2)	$\Delta\nu_1$[a] /cm^{-1}	$\Delta\nu_2$[b] /cm^{-1}	$\Delta\nu_3$[c] /cm^{-1}
Ion pairs:						
LiTDI (***A***)	1.878	1.924	145.5	+17	+35	+43
$LiTDI(ACN)_1$ (***F***)	1.923	2.049	141.3	+16	+27	+53
$LiTDI(ACN)_2$ (***G***)	2.004	2.648	130.2	+14	+16	+20
$LiTDI(ACN)_3$ (***H***)	2.074	2.908	129.1	+9	+14	+12
$LiTDI(H2O)_1$ (***I***)	1.908	2.132	137.5	+24	+23	+57
$LiTDI(H2O)_2$ (***J***)	1.988	3.281	122.1	+24	+13	+16
$LiTDI(H2O)_3$ (***K***)	2.054	3.286	124.5	+19	+16	+12
$LiTDI_{ACN}$ (***L***)[d]	2.059/2.075	2.980/2.946	127.1/122.9	+5/+7	+7/+9	+15/+16
$LiTDI_{H2O}$ (***M***)[d]	2.064/2.082	2.988/2.953	127.2/122.8	+5/+8	+7/+9	+15/+15
$[LiTDI(H2O)_3]_{ACN}$ (***N***)[d]	2.135/2.120	3.230/3.342	126.2/126.1	+3/+6	+5/+7	+13/+13
Multiplets:						
Li_2TDI (***O1***)	1.947/2.009	1.987/4.207	142.6/99.0	+9/+67	+21	+15/+82
Li_2TDI (***O2***)	1.946	1.902	147.6	+17	+6/+26	-17/+38
$Li(TDI)_2$ (***P***)	1.977/1.978	2.140/2.150	140.9/141.4	+13	+24	+15/+18
Li_2TDI_2 (***Q***)	1.941/1.956	2.047/2.047	142.1/142.1	+17	+18	+5/+58
$Li_2TDI(ACN)_6$ (***R1***)	2.097	2.868	130.2	+13	+5	+14
$Li_2TDI(ACN)_5$ (***R2***)	2.086/2.167	2.924	128.8	+10	-1	+12
$LiTDI_2(ACN)_2$ (***S***)	2.138/2.144	2.509/2.678	132.0/135.4	+7	+22	+11
$Li_2TDI_2(ACN)_4$ (***T***)	2.078/	2.132	137.5	+11	+5	+15
$Li_2TDI(H2O)_6$ (***U1***)	2.091/2.095	2.884/3.362	125.2/122.4	+35	+19	+31
$Li_2TDI(H2O)_6$ (***U2***)	2.077/2.001	3.220	125.6	+20	+5	+14
$LiTDI_2(H2O)_2$ (***V***)	2.096/2.114	3.196/3.309	125.5/126.0	+7/+12	+10/+21	-2/+6
$Li_2TDI_2(H2O)_4$ (***W***)	2.032/2.055	2.691/2.692	130.1/130.2	+12	+10	+16
$[Li_2TDI]_{ACN}$ (***X1***)	2.081/2.112	2.629/3.265	131.2/131.4	+13	+21	+31
$[Li_2TDI]_{ACN}$ (***X2***)	2.092	2.932	123.6	+6	+8	+16
$[Li(TDI)_2]_{ACN}$ (***Y***)	2.089/2.089	3.116/3.116	126.8/126.8	+6	+8	+16
$[Li_2TDI_2]_{ACN}$ (***Z***)	2.112/2.113	2.901/2.902	123.3/123.3	+8	+4	+17
Experimental:						
1M LiTDI/ACN				**+4**	**+8**	**+13/+24**

[a] ν(C4-C1;C2-C2*); [b] ν_{as}(N1-C2); [c] δ(N1-C1-N1*); [d]shifts are reported for UAKS/UFF radii.