Structural and dynamic characterization of Li–ionic liquid electrolyte solutions for application in Li-ion batteries: a Molecular Dynamics Approach

Michele A. Salvador[**,1], Rita Maji[2], Francesco Rossella[1,4], Elena Degoli[3,4,5], Alice Ruini[1,4,5], and Rita Magri[*,1,4,5]

[1]Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia,Via Campi 213/A, 41125 Modena, Italy

[2]Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia,Via Amendola 2 Padiglione Tamburini , I-42122 Reggio Emilia, Italy

[3]Dipartimento di Scienze e Metodi dell'Ingegneria, Università di Modena e Reggio Emilia and Centro Interdipartimentale En&Tech, Via Amendola 2 Padiglione Morselli, I-42122 Reggio Emilia, Italy

[4]Centro S3, Istituto Nanoscienze-Consiglio Nazionale delle Ricerche (CNR-NANO),Via Campi 213/A, 41125 Modena, Italy
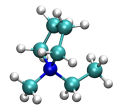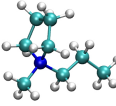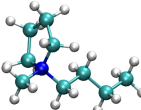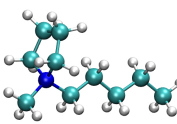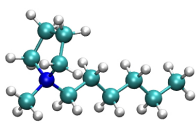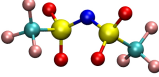
[5]Centro Interdipartimentale di Ricerca e per i Servizi nel settore della produzione, stoccaggio ed utilizzo dell'Idrogeno H2-MO.RE., Via Università 4, 41121 Modena, Italy

[*]corresponding author 1: Rita Magri (rita.magri@unimore.it)

[**]corresponding author 2: Michele A. Salvador (michelesalvador@gmail.com)

Supplementary Material

Table S1: Identification of all species considered in this paper. *code: identification of the species throughout the paper.

| code*	name	composition	image
Pyr12	*1-methyl-1-ethyl pyrrolidinium*	$C_7H_{16}N^+$	
Pyr13	*1-methyl-1-propyl pyrrolidinium*	$C_8H_{18}N^+$	
Pyr14	*1-methyl-1-butyl pyrrolidinium*	$C_{10}H_{20}N^+$	
Pyr15	*1-methyl-1-pentyl pyrrolidinium*	$C_{11}H_{22}N^+$	
Pyr16	*1-methyl-1-hexyl pyrrolidinium*	$C_{12}H_{24}N^+$	
BF4	*tetrafluoroborate*	BF_4^-	
PF6	*hexafluorophosphate*	PF_6^-	
TFSI	*bis(trifluoro-methane)sulfonimide*	$(CF_3SO_2)2N^-$	
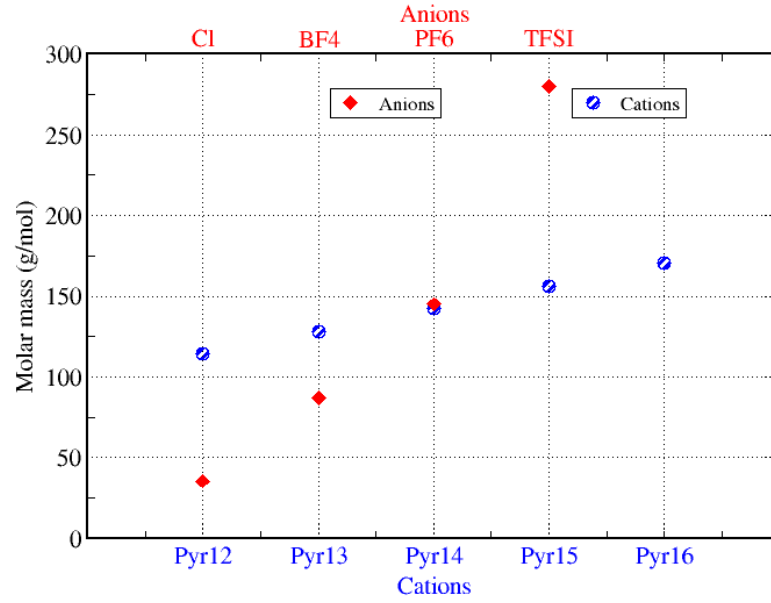
Figure S1: Calculated molar mass of cations and anions.

Table S2: Energy values obtained from DFT calculations of each species. ΔE: single point energy; E_{zp}: zero-point energy; ΔG: Gibbs free energy; ΔH: enthalpy. Unit: a.u.: Hartree.

Species	ΔE (a.u.)	E_{zp} (a.u.)	ΔG (a.u.)	ΔH (a.u.)
Pyr12	-330.818	0.231	-330.619	-330.577
Pyr13	-370.123	0.260	-369.897	-369.852
Pyr14	-409.427	0.289	-409.176	-409.126
Pyr15	-448.732	0.317	-448.453	-448.401
Pyr16	-488.036	0.346	-487.730	-487.675
BF4	-424.434	0.014	-424.447	-424.414
PF6	-940.413	0.017	-940.427	-940.388
TFSI	-1826.590	0.043	-1826.589	-1826.529

(a) Pyr12-anion
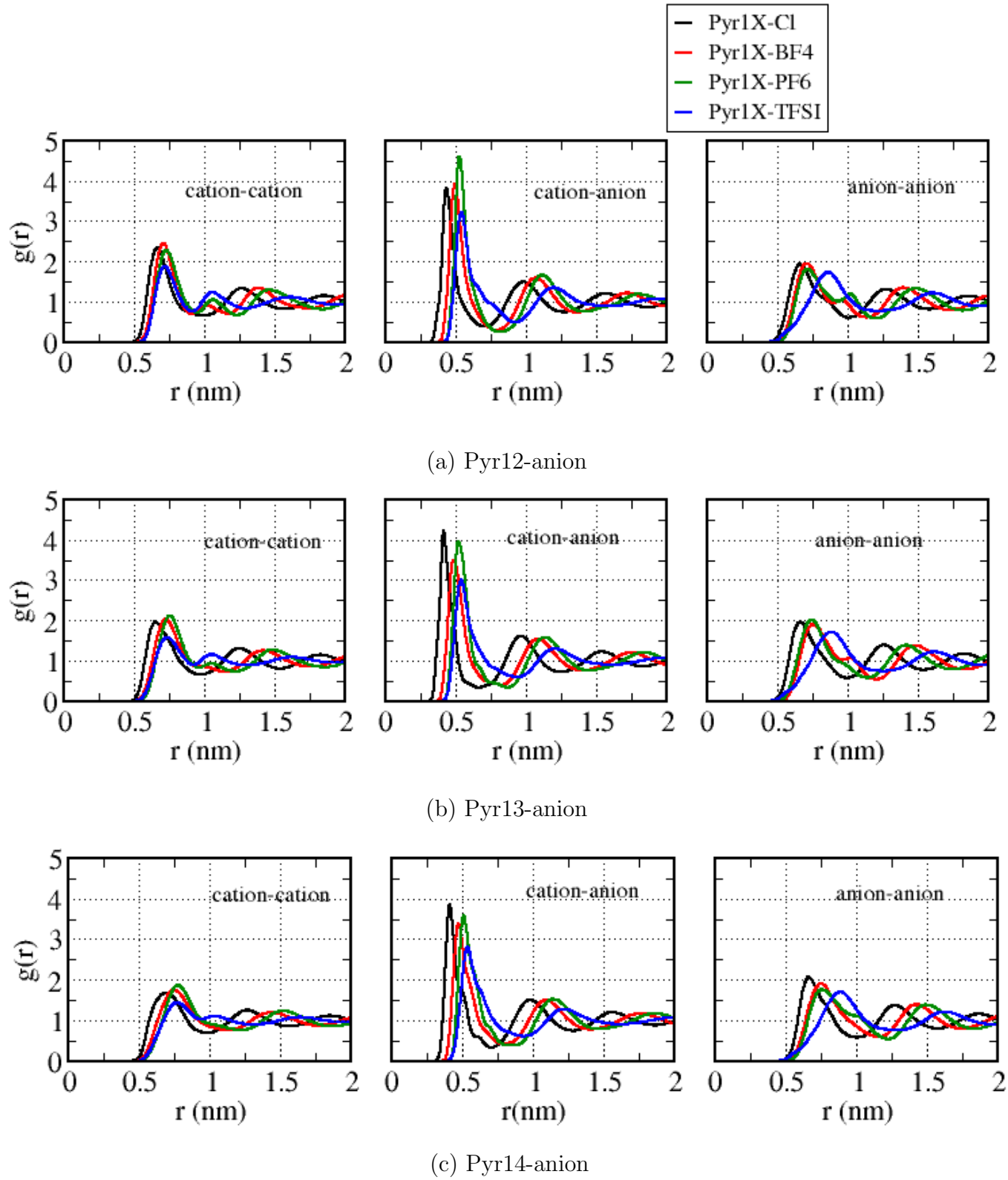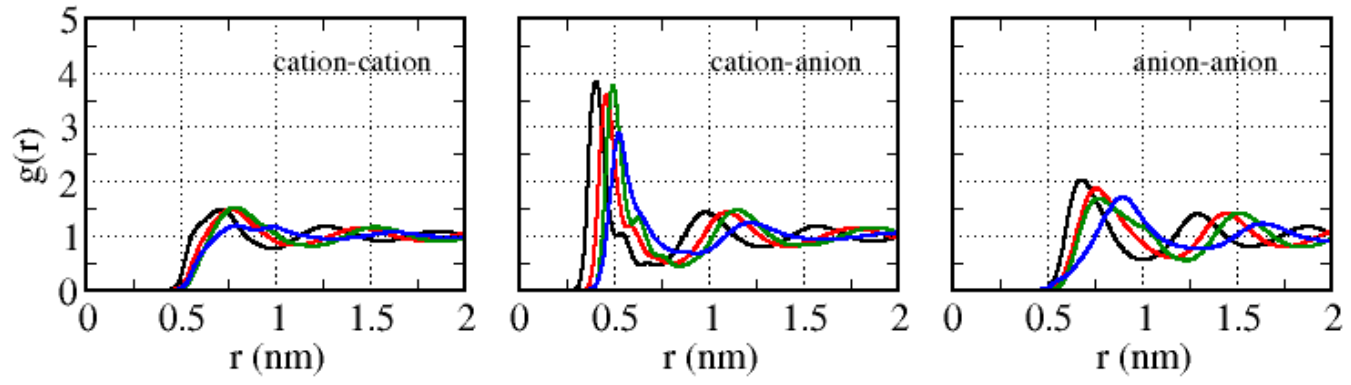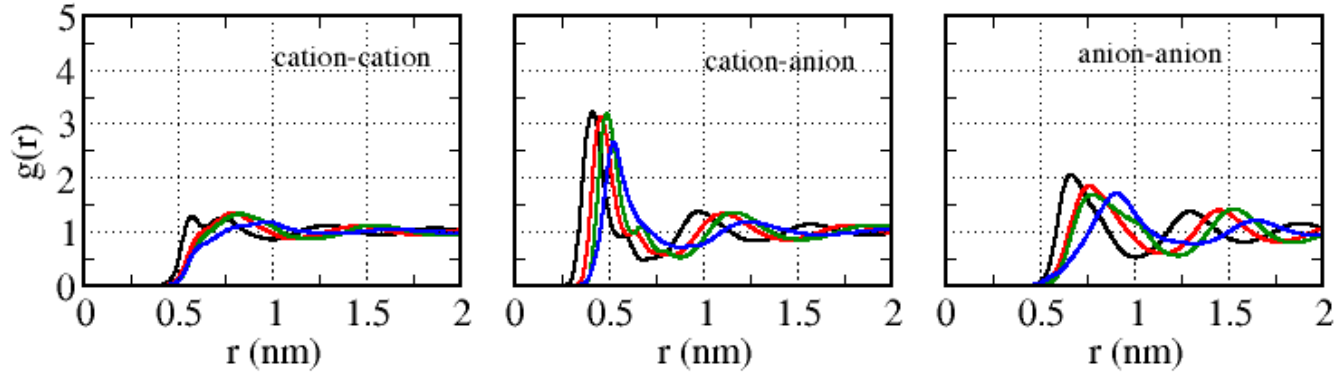
(b) Pyr13-anion

(c) Pyr14-anion

Figure S2: Center-of-mass cation-cation, cation-anion and anion-anion pair correlation functions ($g(r)$) for all the cation-anion combinations with: (a) Pyr12 as cation, (b) Pyr13, (c) Pyr14

(a) Pyr15-anion

(b) Pyr16-anion

Figure S3: Center-of-mass cation-cation, cation-anion and anion-anion pair correlation functions (g(r)) for all the cation-anion combinations with: (a) Pyr15 as cation, (b) Pyr16 as a cation.
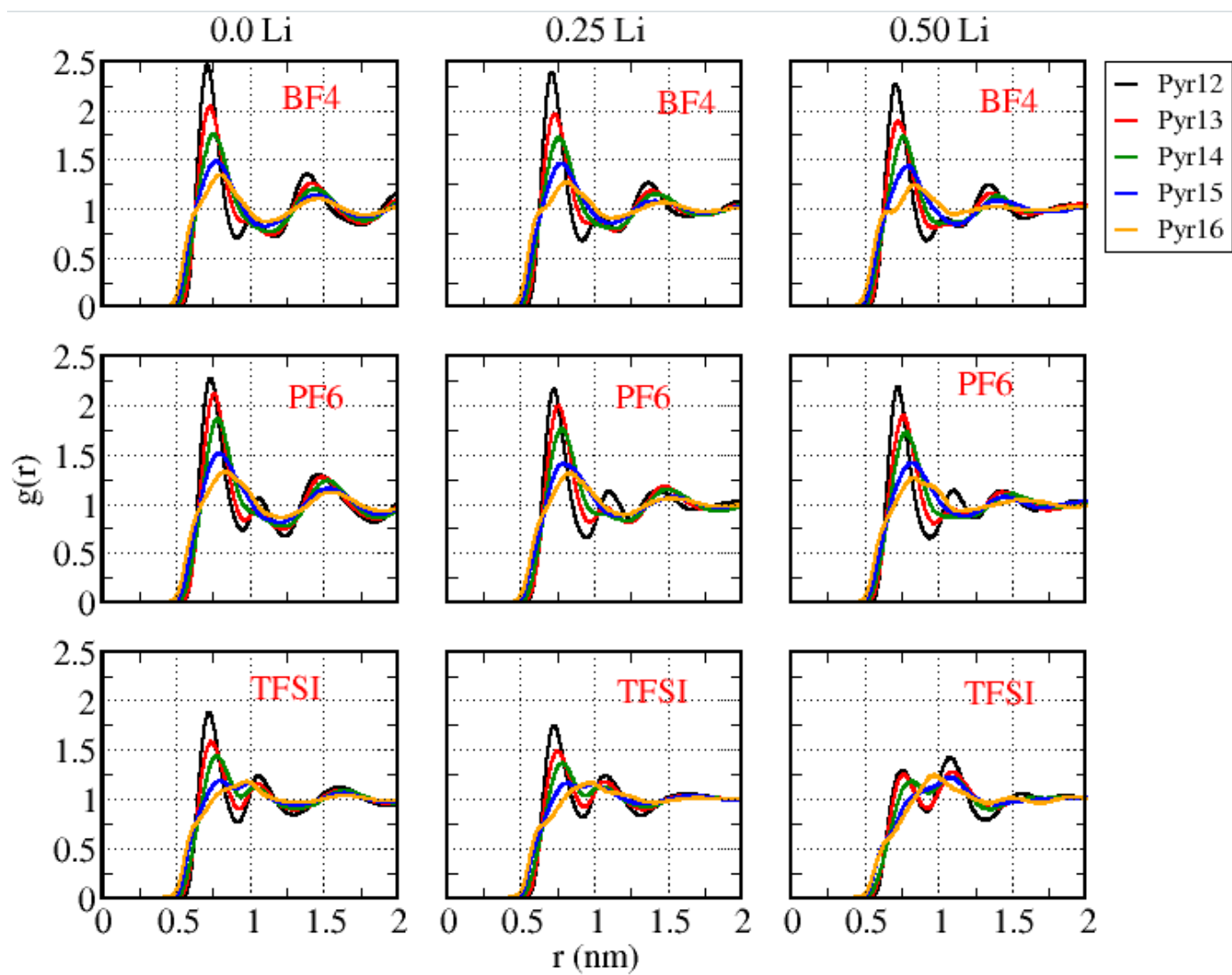
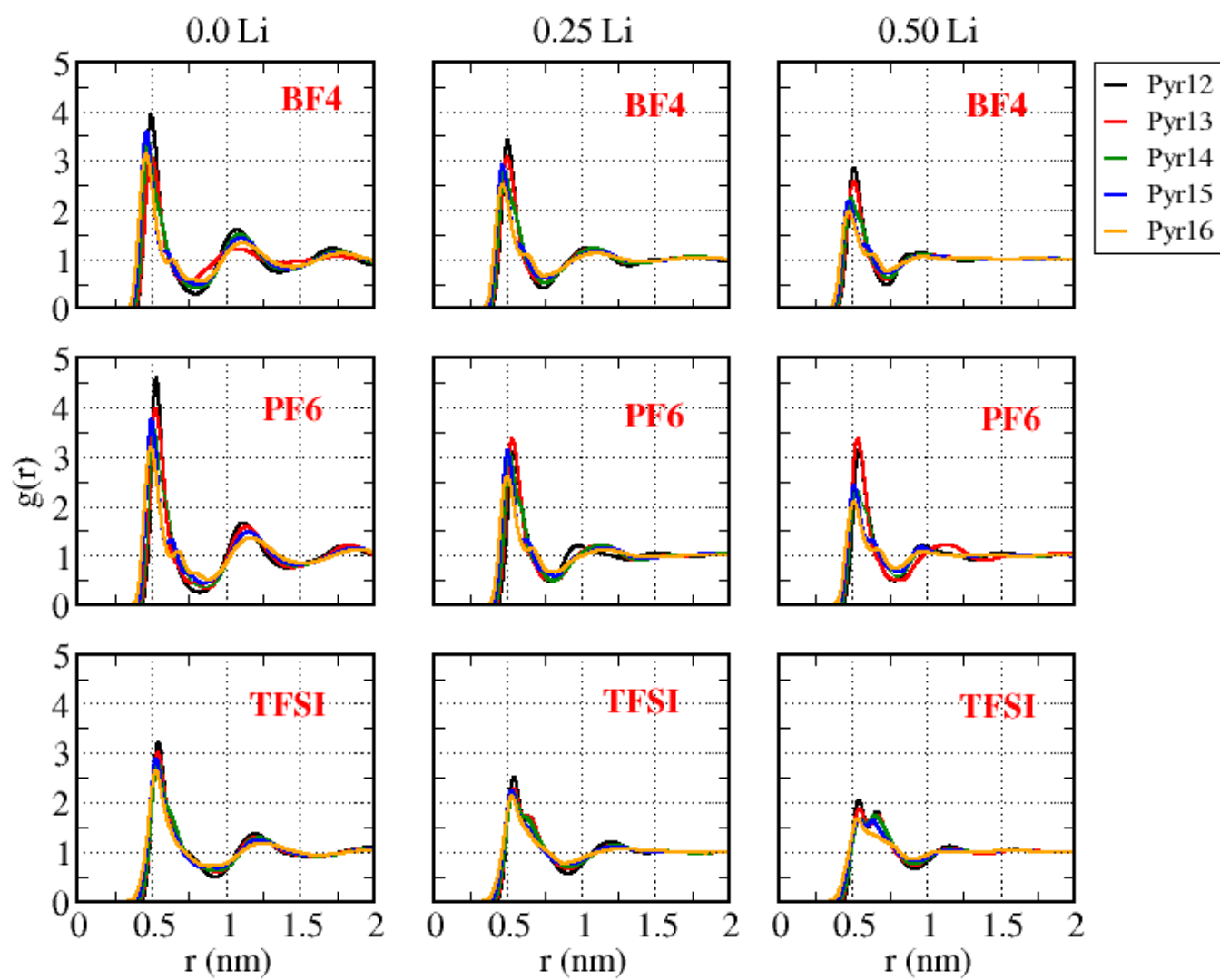Figure S4: Center-of-mass cation-cation g(r) with all fractions of Li.

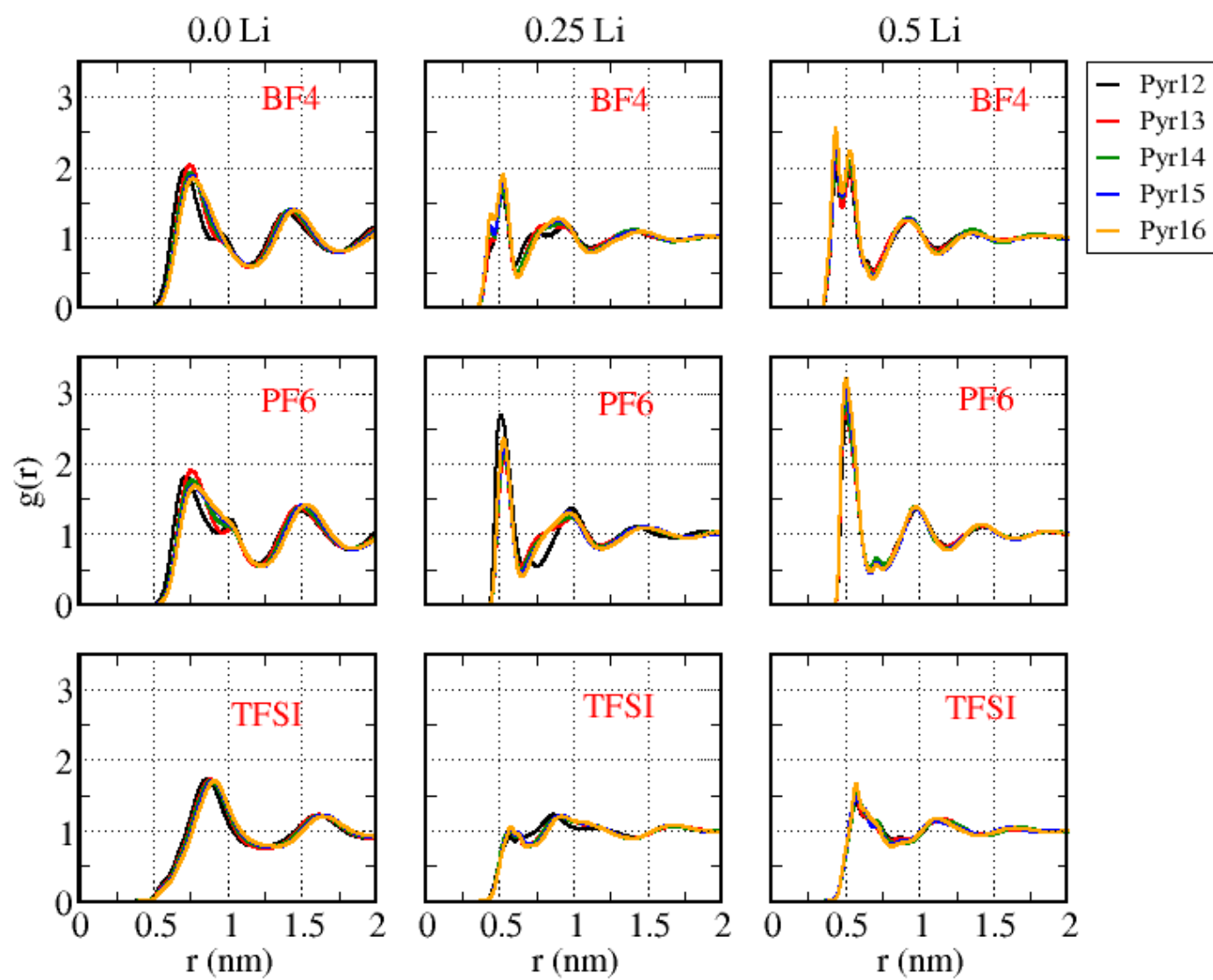Figure S5: Center-of-mass cation-anion g(r) with all fractions of Li.

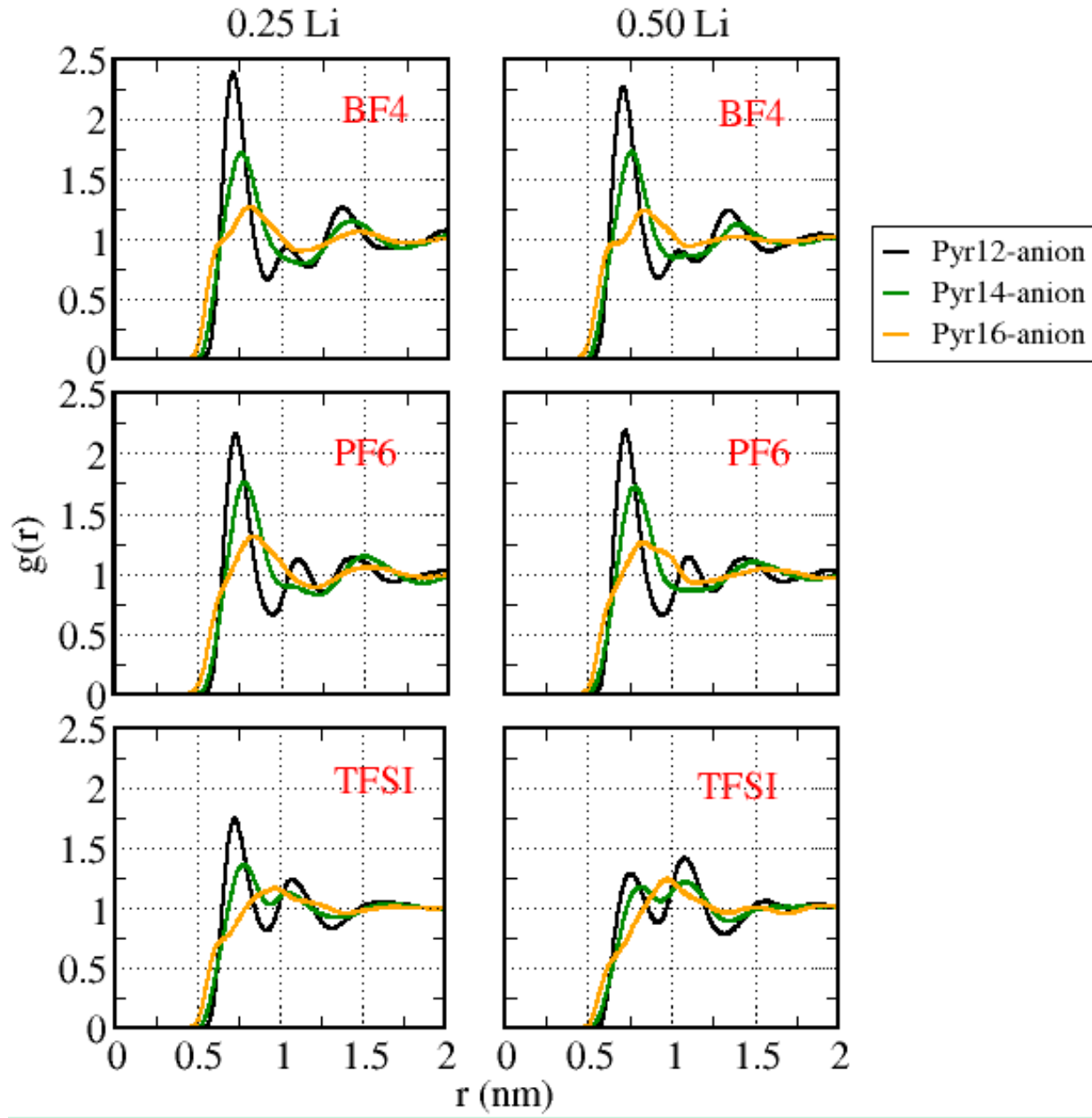Figure S6: Center-of-mass anion-anion g(r) with all fractions of Li.

Figure S7: Center-of-mass cation-cation $g(r)$ for systems Pyr12-anion, Pyr14-anion and Pyr16-anions.