Electronic Supplementary Information

Molecular insights of nanoconfinement effect on the structure and dynamics of ionic liquids in carbon nanotubes

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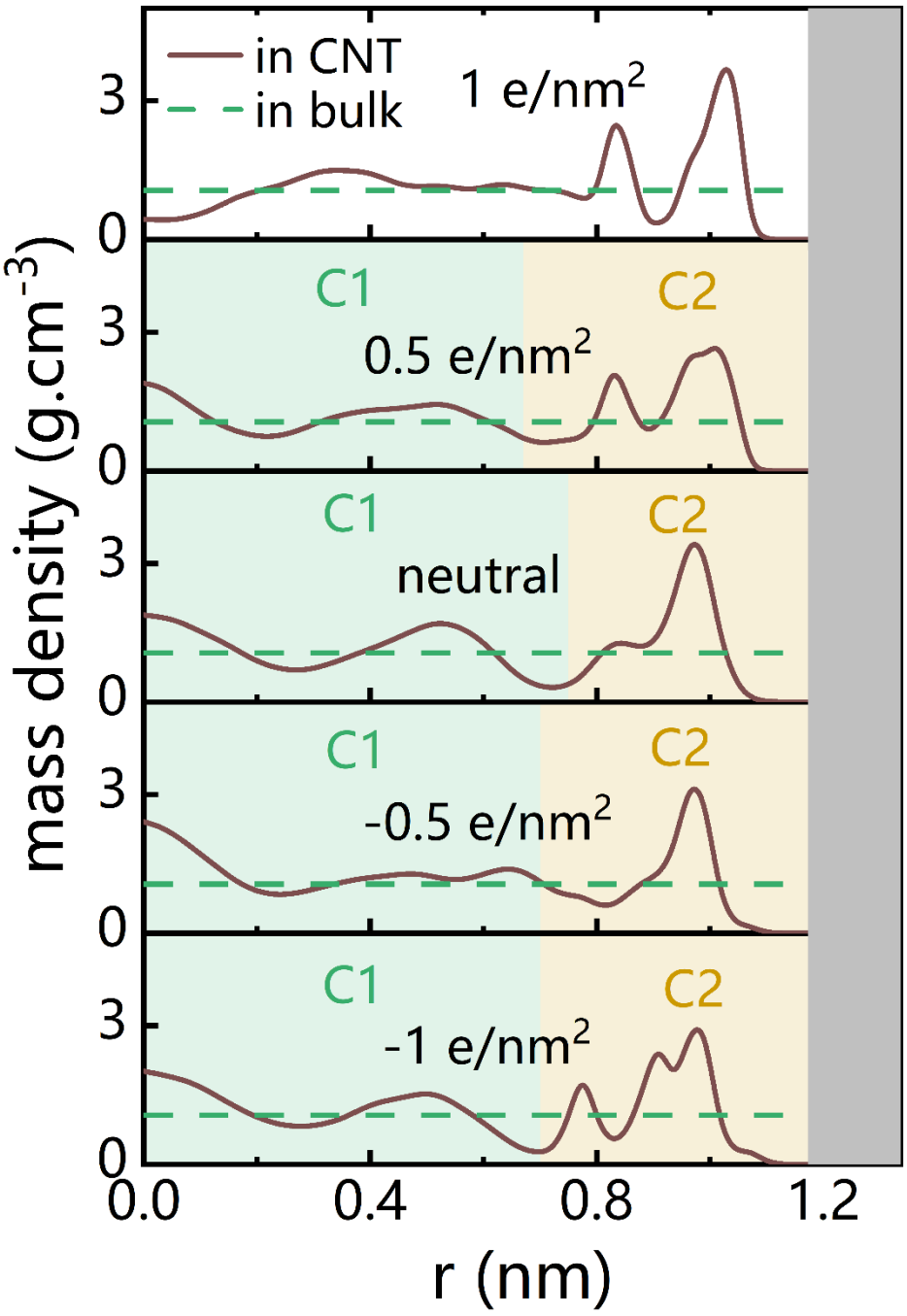

Fig. S1 Mass density profiles of the IL [BMIM][BF_4] in the five CNTs with the charge densities of 1, 0.5, 0 (neutral), -0.5, and -1 e/nm^2, different background colors represent different regions defined based on the distribution of cations, where the green color means central region (Region C1), and the yellow color corresponds to the boundary region (Region C2). The green dashed lines represent the bulk density of the IL at identical temperature.

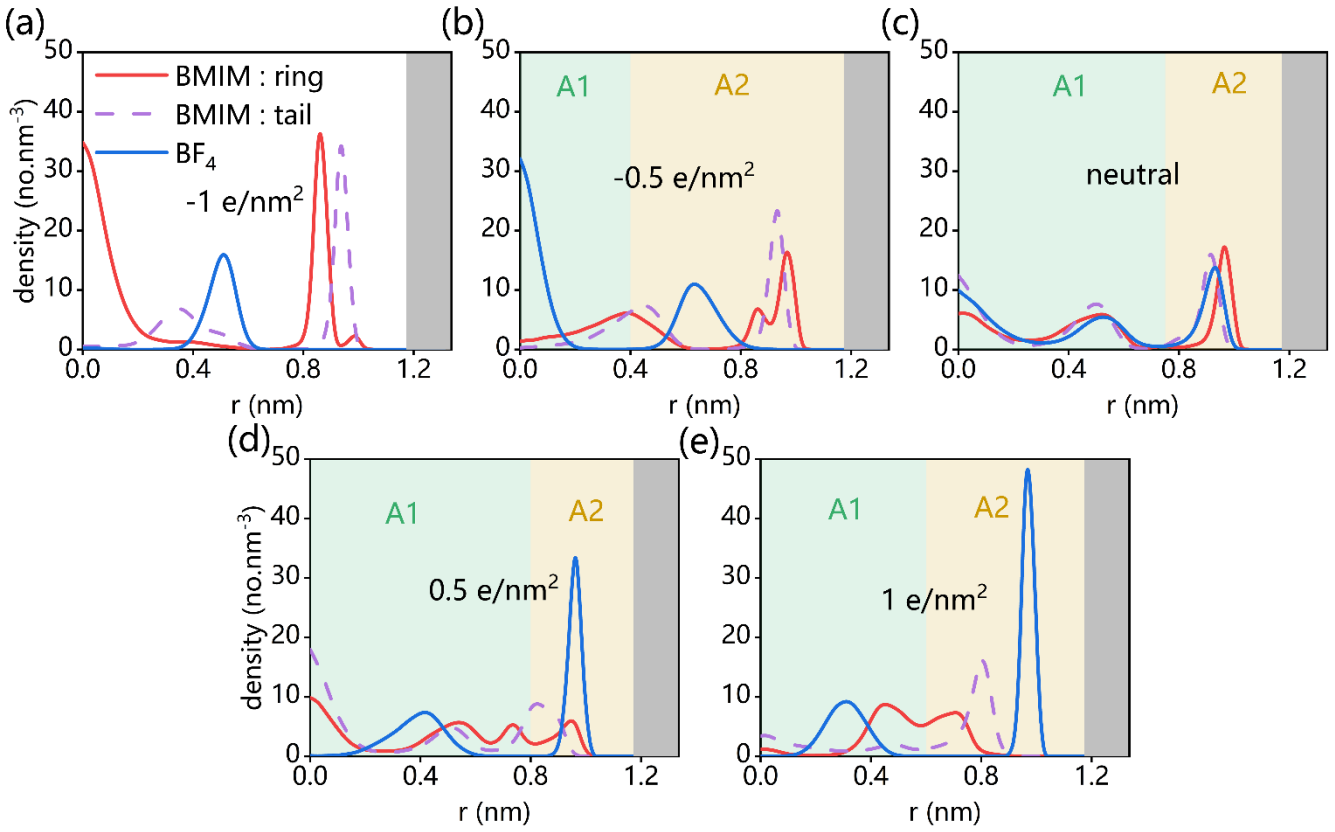

Fig. S2 Number density profiles of the IL [BMIM][BF_4] in the five CNTs with the charge densities of (a)1, (b) 0.5, (c) 0 (neutral), (d) -0.5, and (e) -1 e/nm^2. Different background colors represent different regions based on the distribution of cations, where the green color means the central region (Region A1), and the yellow color corresponds to the boundary region (Region A2).

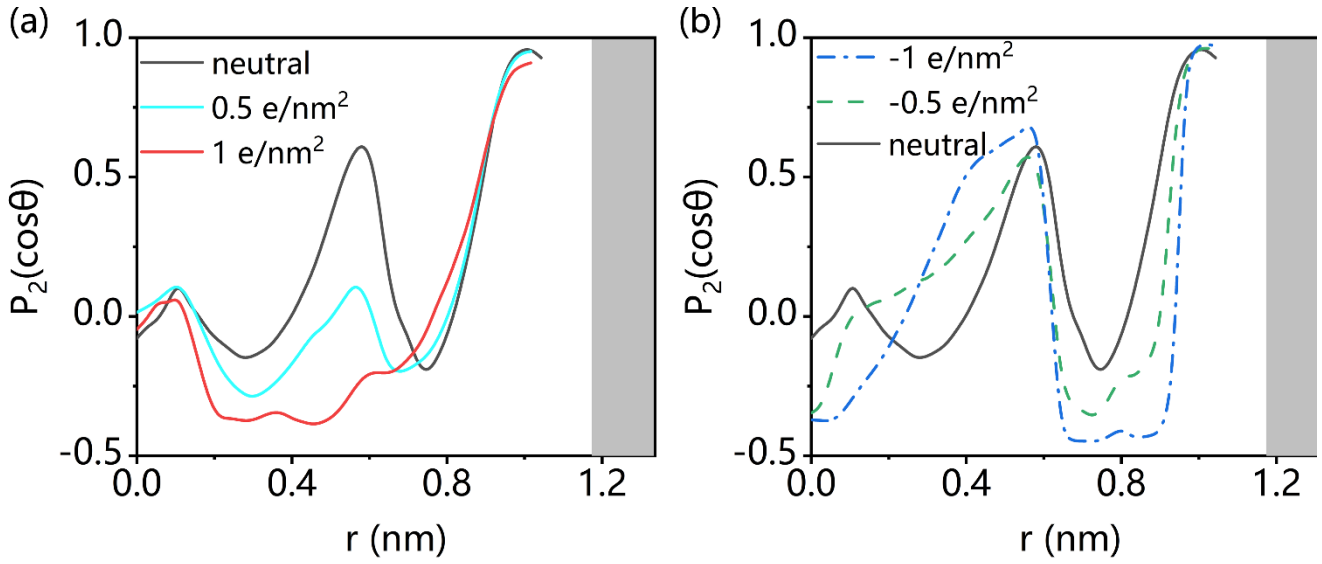

Fig. S3 Orientation profiles of imidazole rings along the radial direction as a function of distance from central axes in CNTs with (a) positive charge and (b) negative charge by comparing with the results in neutral CNT.

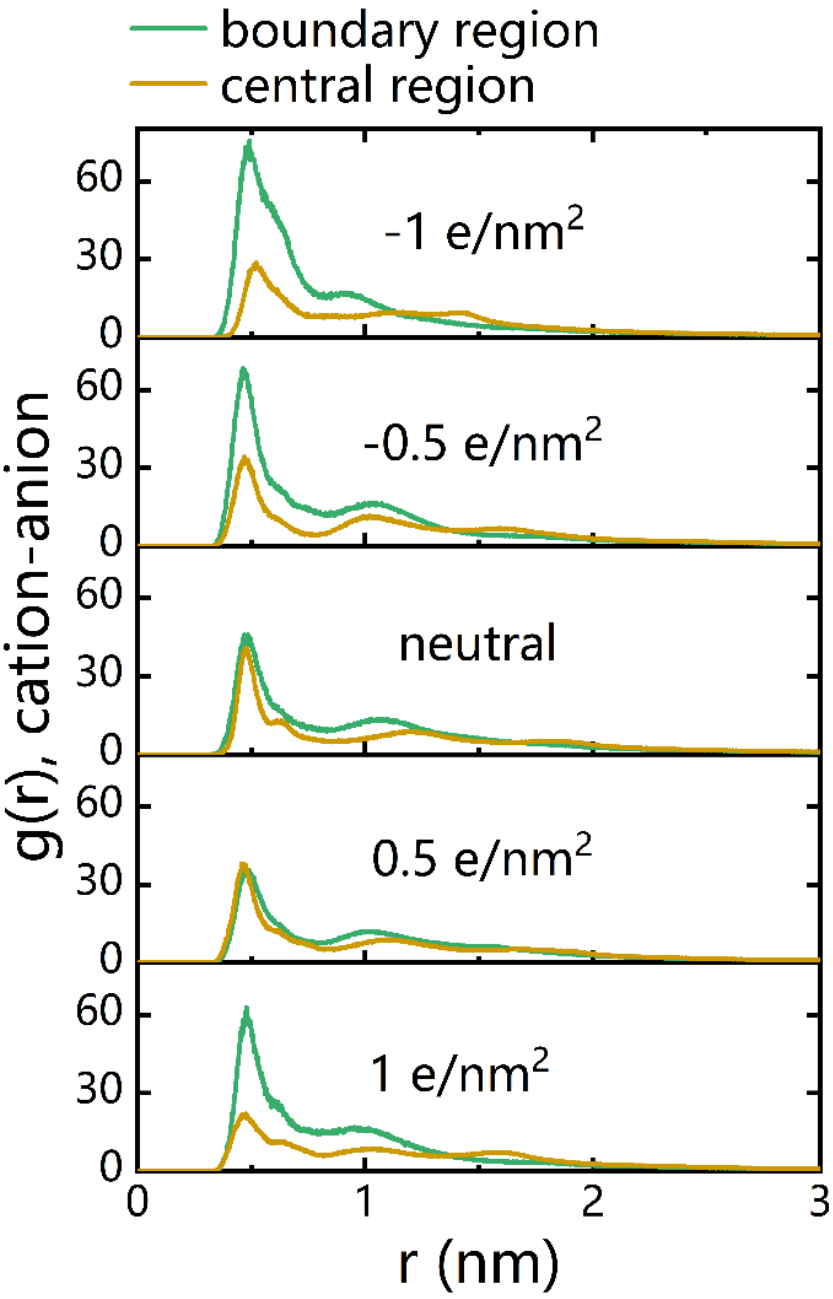

Fig. S4 RDFs between COMs of cation - anion pairs in different regions of CNTs with different charge densities of -1, -0.5, 0 (neutral), 0.5, and 1 e/nm^2, respectively.

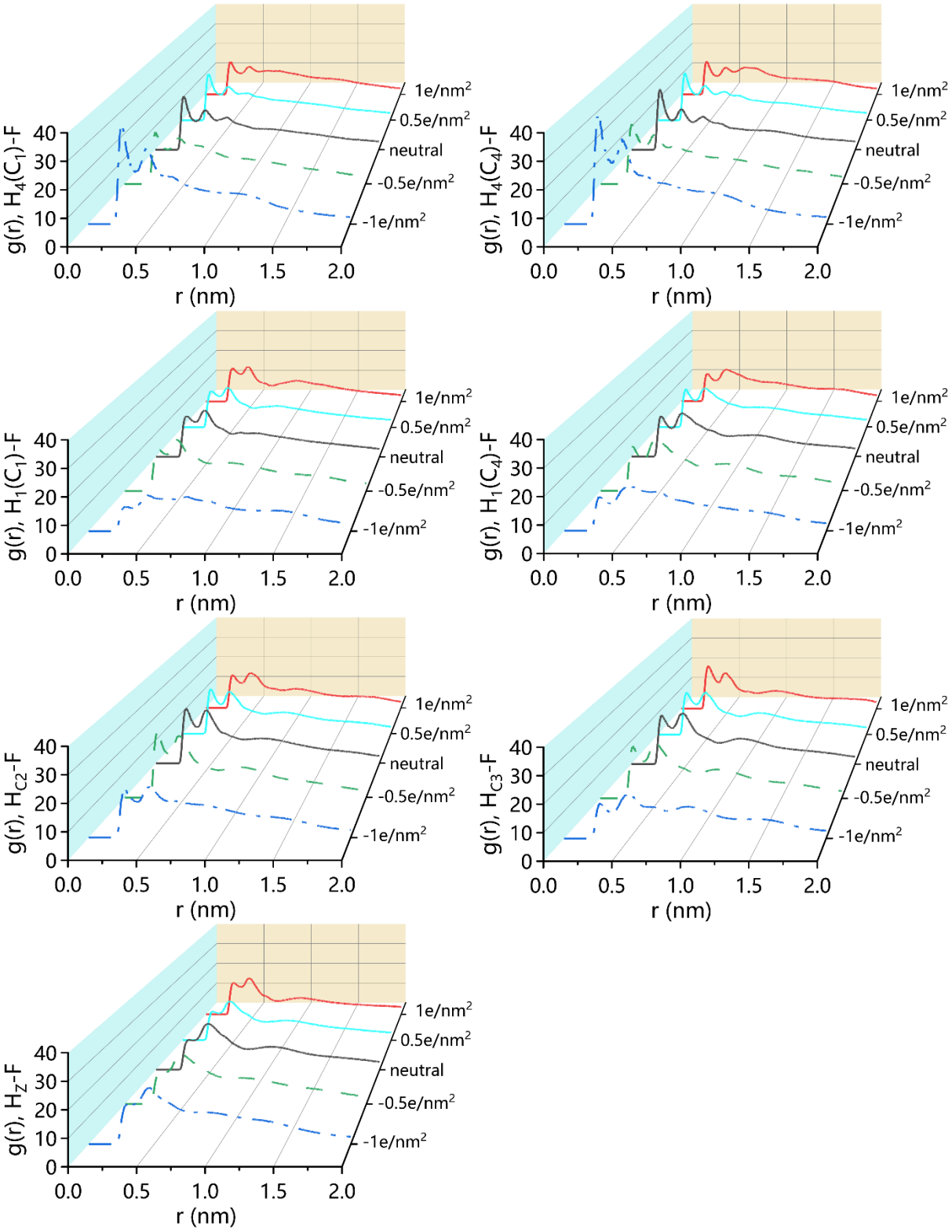

Fig. S5 RDFs based on the arrangements of different H atoms in cations and F atoms in anions, in the CNTs with different charge densities.

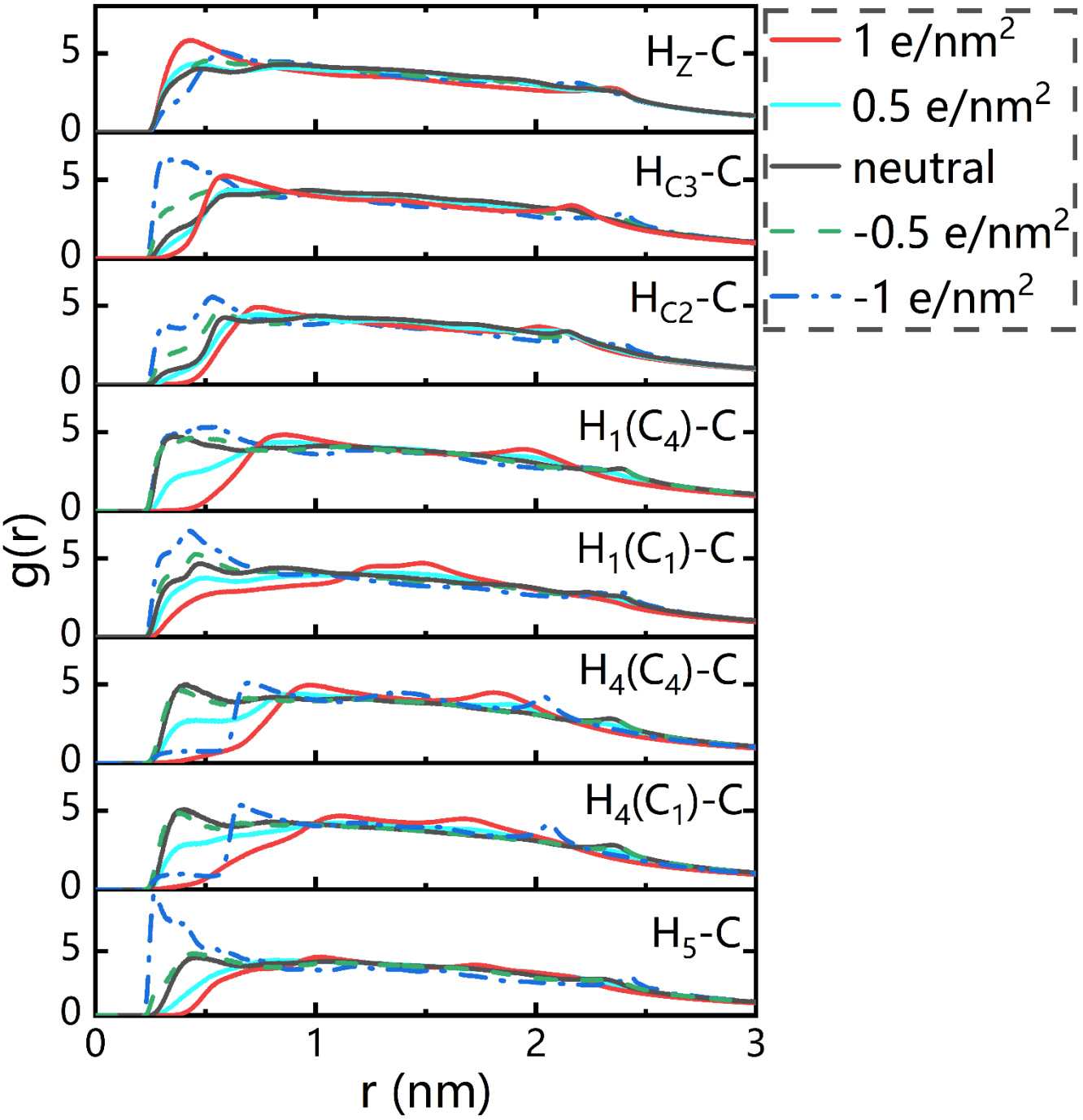

Fig. S6 RDFs based on the arrangements of different H atoms in cations and C atoms in CNTs with different charge densities.

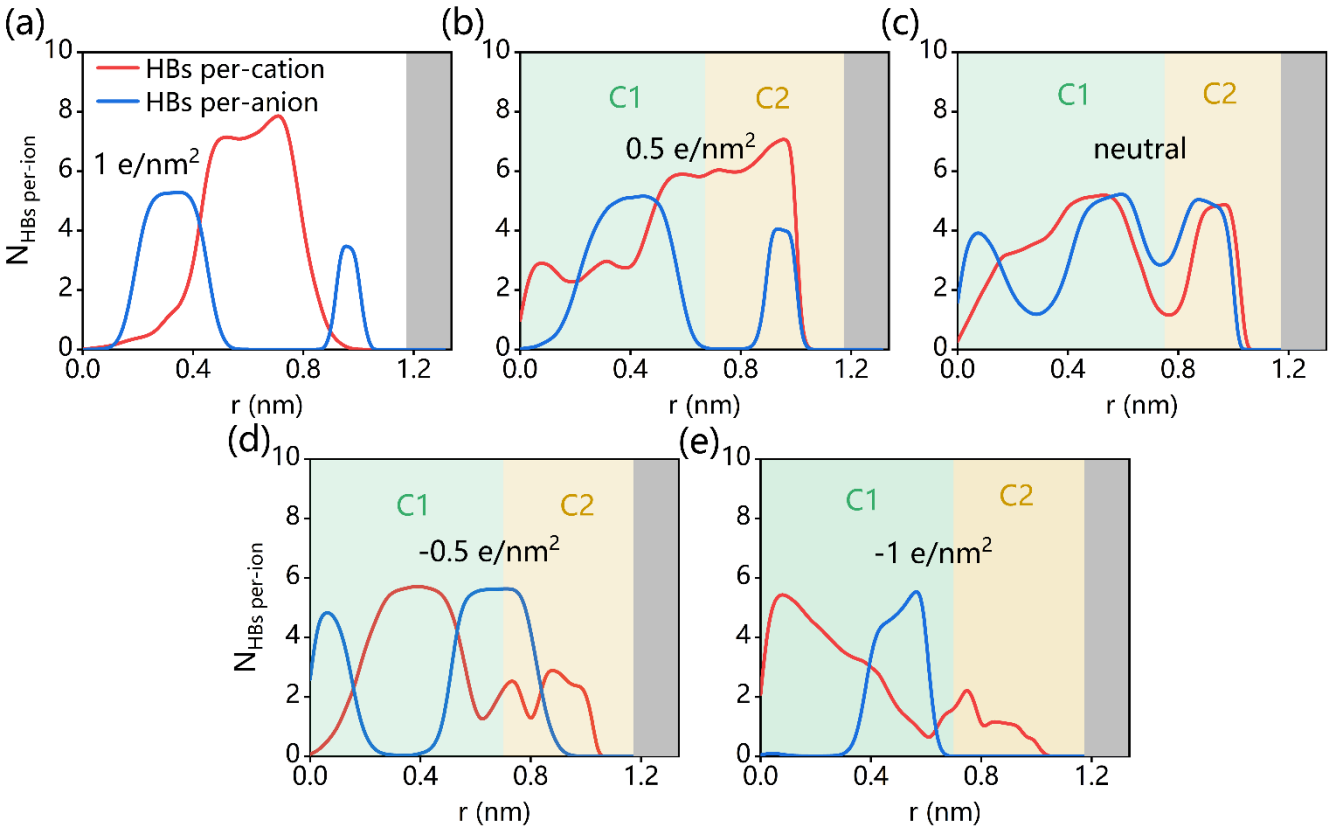

Fig. S7 Average HBs number per cation (red lines) and per anion (blue lines) distributions along the radial direction in CNTs with charge densities of (a)1, (b) 0.5, (c) 0 (neutral), (d) -0.5, and (e) -1 e/nm^2, where the regions were divided based on the distribution of cations.

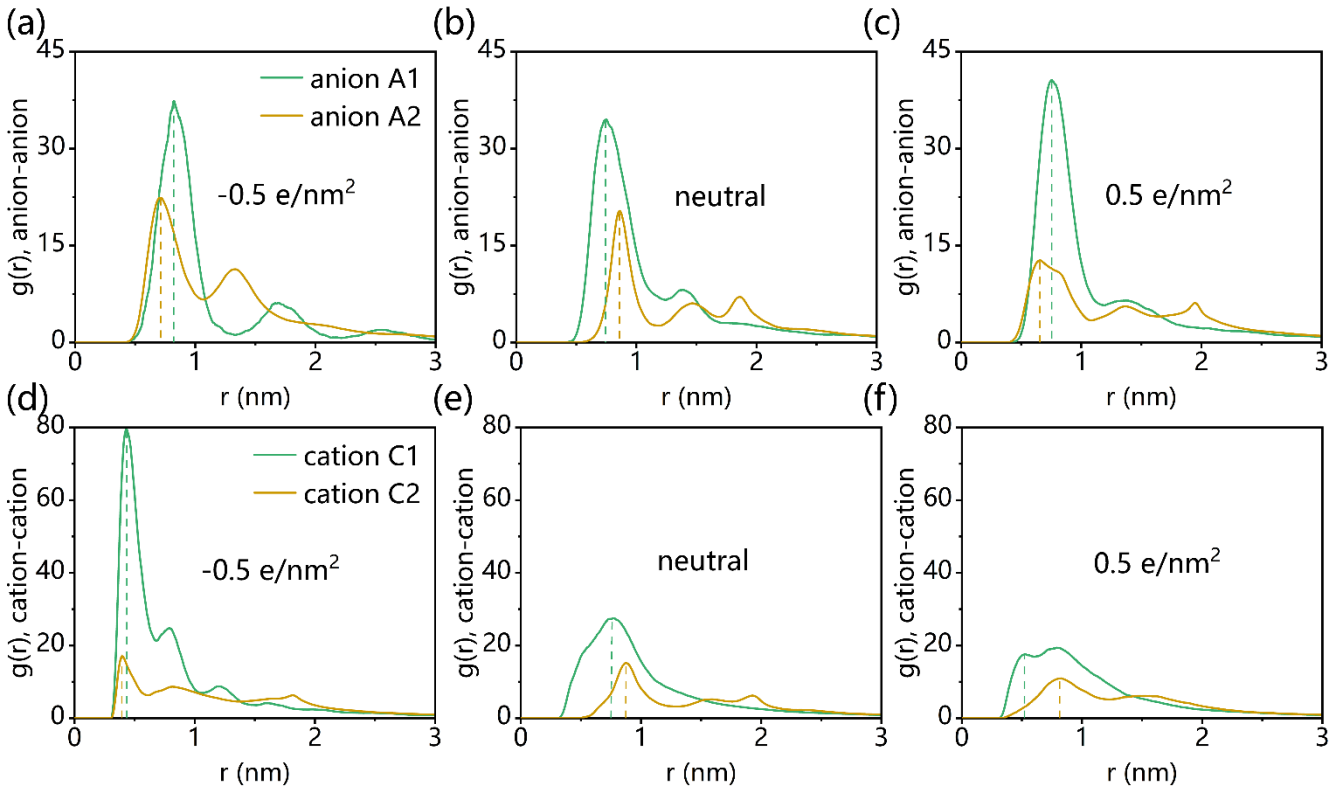

Fig. S8 RDFs of anion pair BF_4 –BF_4 in different regions of CNTs with charge densities of (a) -0.5, (b) 0 (neutral), and (c) 0.5 e/nm^2, and RDFs of cation pair BMIM – BMIM in different regions of CNTs with charge densities of (d) -0.5, (e) 0 (neutral), and (f) 0.5 e/nm^2.

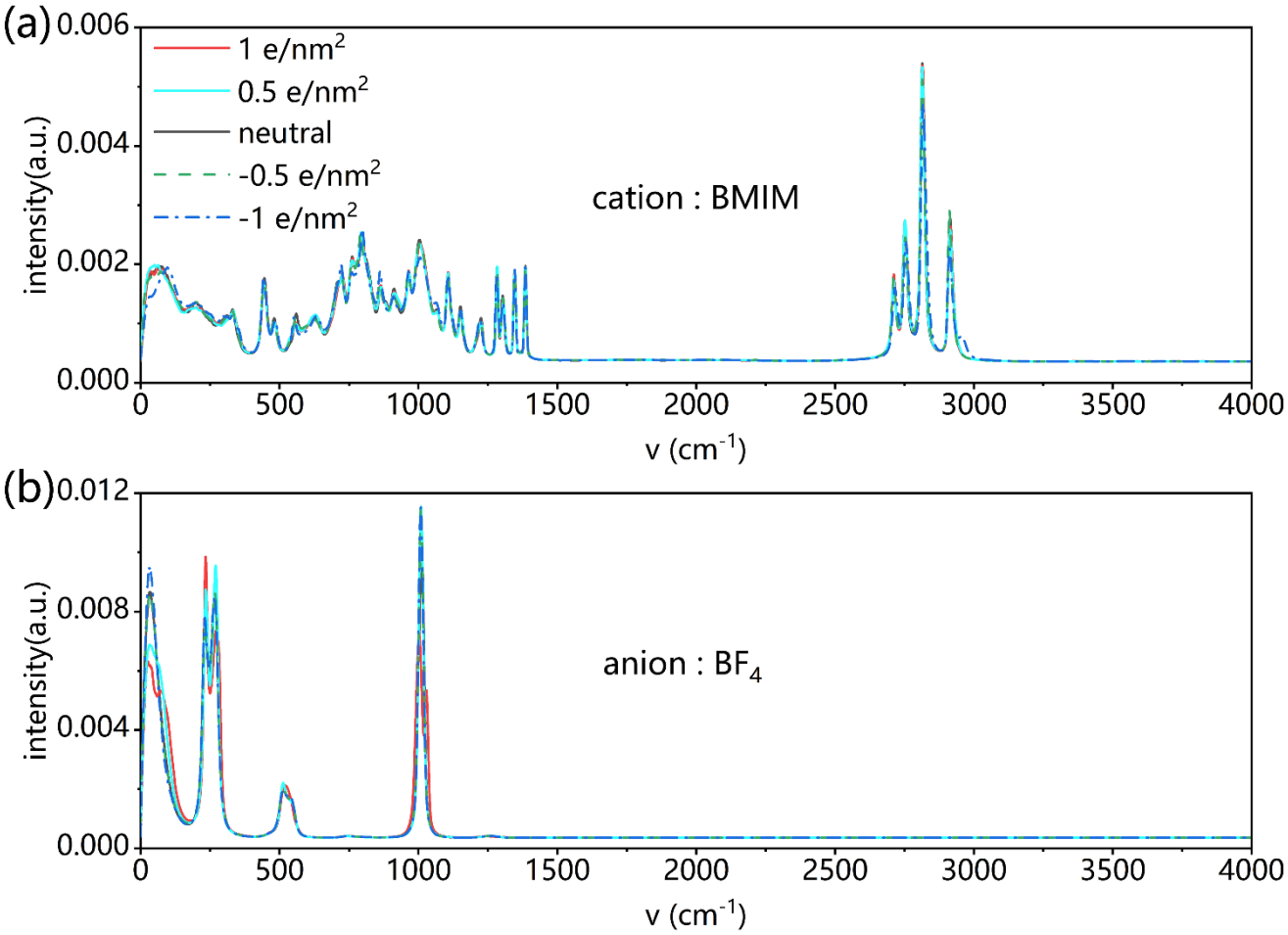

Fig. S9 Complete densities of vibrational states of (a) cations and (b) anions in CNTs with different charge densities, with the wavenumber range from 0 ~ 4000 cm^{-1}.

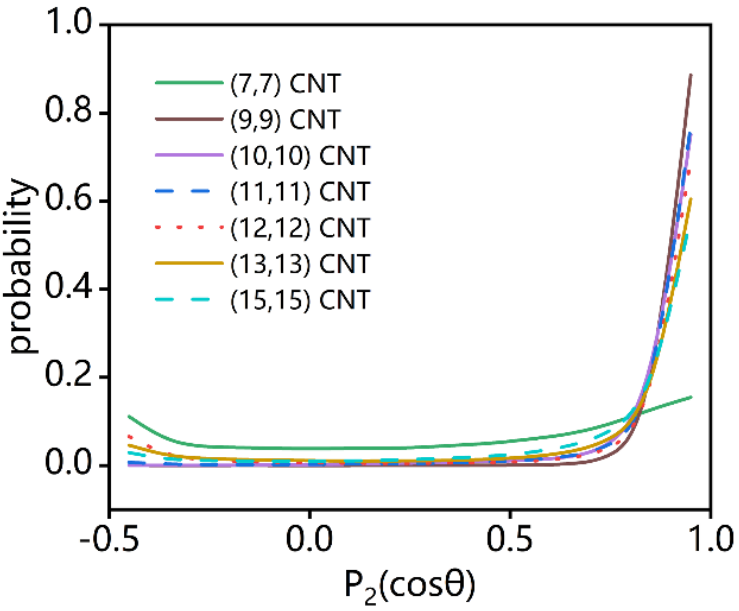

Fig. S10 Normalized orientation probability distribution functions (PDF) of the orientations of imidazole rings in CNTs with different pore sizes.

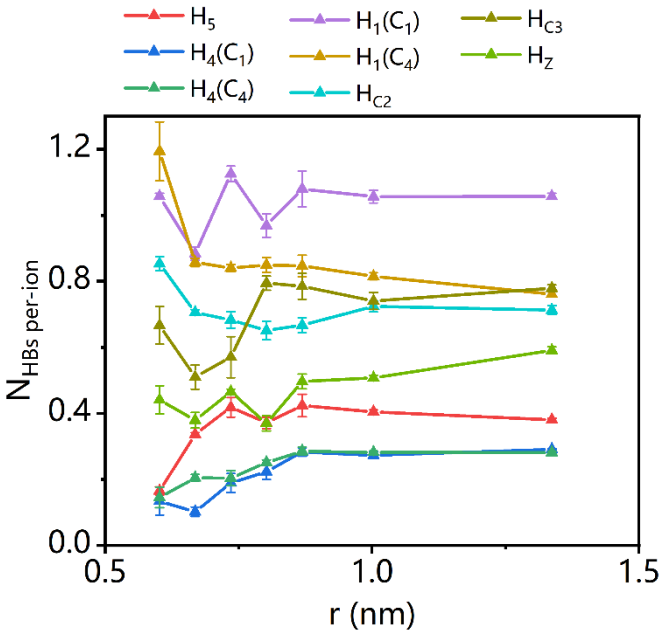

Fig. S11 Average HBs number per ion formed by different H atoms in cations and F atoms in anions as a function of the radii of CNTs, the error bars were based on at least five independent simulations.

Table S1. Intermolecular interactions per ion between different types of ions pairs and the interactions between ions and CNTs.

interaction (kJ/mol)		charge density of CNTs				
		-1 e/nm^2	-0.5 e/nm^2	neutral (0 e/nm^2)	0.5 e/nm^2	1 e/nm^2
cation-anion	Coulomb	-1008.72±13.97	-1453.19±17.00	-1918.98±20.80	-2418.83±21.85	-2972.31±28.45
	LJ	-9.59±0.35	-14.52±0.53	-17.95±0.63	-22.20±0.77	-26.19±0.85
cation-cation	Coulomb	2003.80±12.20	1835.11±14.14	1705.66±13.73	1620.11±13.38	1596.75±9.83
	LJ	-67.85±0.94	-53.07±0.89	-48.72±0.94	-49.41±1.02	-54.78±0.94
cation-nanotube	Coulomb	-1060.86±0.62	-527.33±0.48	0	523.22±0.51	1041.66±0.58
	LJ	-53.31±0.56	-57.13±0.61	-53.87±0.75	-40.39±0.78	-27.75±0.49
interaction (kJ/mol)		charge density of CNTs				
		-1 e/nm^2	-0.5 e/nm^2	neutral (0 e/nm^2)	0.5 e/nm^2	1 e/nm^2
anion-cation	Coulomb	-2555.99±29.88	-2231.32±25.18	-1916.97±19.87	-1684.01±15.50	-1529.56±13.20
	LJ	-24.30±0.86	-22.25±0.80	-17.93±0.62	-15.46±0.52	-13.47±0.43
anion-anion	Coulomb	1093.84±10.39	1411.58±15.56	1637.95±29.60	2028.45±11.80	2442.95±9.27
	LJ	-2.04±0.12	-2.18±0.10	-2.14±0.07	-2.84±0.11	-4.60±0.11
anion-nanotube	Coulomb	1032.10±0.77	518.53±0.58	0	-529.48±0.43	-1064.01±0.40
	LJ	-2.13±0.04	-4.24±0.15	-13.10±0.27	-15.92±0.31	-14.73±0.39

Table S2. Intermolecular interactions of ions in different regions of CNTs with different charge densities (neutral, 0.5, and 1 e/nm^2 were placed in this page, -0.5 and -1 e/nm^2 were in the next page), where the interactions of ions with CNT were also involved, and E_{ion} indicates the total intermolecular interactions obtained from the summations of interactions of the referred ions with counter-ions and co-ions. The first lines in gray areas indicate the referred ions, and the second lines indicate the objects interacted with the referred ions.

charge density of CNT: 1 e/nm²						
type of	anion in Region A2			anion in Region A1		
interaction	cation	anion	CNT	cation	anion	CNT
Coulomb (kJ/mol)	-1411.31±13.79	2334.78±9.10	-1067.06±0.89	-2078.74±25.70	2960.57±31.00	-1015.29±1.91
LJ (kJ/mol)	-11.50±0.44	-4.94±0.10	-17.75±0.44	-22.71±1.24	-3.65±0.13	-1.24±0.02
E_{ion} (kJ/mol)	907.03±14.13		---	856.92±26.03		---
charge density of CNT: 0.5 e/nm²						
type of	cation in Region C2			cation in Region C1		
interaction	anion	cation	CNT	anion	cation	CNT
Coulomb (kJ/mol)	-2276.60±33.15	1498.89±23.13	528.62±1.24	-2596.08±41.46	1779.60±25.40	515.45±1.61
LJ (kJ/mol)	-20.18±1.25	-40.20±1.45	-62.93±2.22	-23.74±1.24	-60.86±1.65	-17.10±1.71
E_{ion} (kJ/mol)	-826.14±30.71		---	-904.68±34.61		---
type of	anion in Region A2			anion in Region A1		
interactions	cation	anion	CNT	cation	anion	CNT
Coulomb (kJ/mol)	-1541.48±14.94	1886.08±12.23	-534.73±0.51	-2107.96±25.91	2438.90±24.59	-511.68±1.06
LJ (kJ/mol)	-12.77±0.58	-2.80±0.08	-20.80±0.38	-23.36±1.09	-3.45±0.11	-1.59±0.05
E_{ion} (kJ/mol)	329.03±11.74		---	304.13±17.03		---
charge density of CNT: neutral (0 e/nm²)						
type of	cation in Region C2			cation in Region C1		
interaction	anion	cation	CNT	anion	cation	CNT
Coulomb (kJ/mol)	-1740.12±21.22	1512.41±22.16	0	-2191.02±29.20	1949.39±31.44	0
LJ (kJ/mol)	-14.47±0.80	-36.12±0.95	-83.89±1.01	-23.13±1.04	-66.25±1.61	-9.15±0.81
E_{ion} (kJ/mol)	-278.30±22.46		---	-331.01±27.67		---
type of	anion in Region A2			anion in Region A1		
interaction	cation	anion	CNT	cation	anion	CNT
Coulomb (kJ/mol)	-1754.83±21.99	1473.98±29.19	0	-2202.09±32.76	1912.23±35.83	0
LJ (kJ/mol)	-14.76±0.78	-1.57±0.06	-19.85±0.40	-23.29±1.05	-3.11±0.12	-2.07±0.11
E_{ion} (kJ/mol)	-297.18±31.62		---	-316.26±40.83		---

charge density of CNT: -0.5 e/nm²

type of	cation in Region C2			cation in Region C1		
interaction	anion	cation	CNT	anion	cation	CNT
Coulomb (kJ/mol)	-1284.98±16.45	1656.38±23.35	-533.51±0.62	-1826.48±27.08	2151.11±33.82	-511.72±1.11
LJ (kJ/mol)	-10.67±0.54	-44.54±1.12	-80.90±1.10	-22.80±1.19	-68.91±1.71	-6.47±0.38
E_{ion} (kJ/mol)	316.18±21.45		---	232.92±30.00		---
type of	anion in Region A2			anion in Region A1		
interaction	cation	anion	CNT	cation	anion	CNT
Coulomb (kJ/mol)	-2198.84±24.44	1369.41±15.21	519.38±0.72	-2533.75±54.59	1720.53±37.32	506.93±2.18
LJ (kJ/mol)	-21.95±0.85	-2.18±0.09	-4.73±0.18	-24.98±2.29	-3.28±0.18	-0.80±0.01
E_{ion} (kJ/mol)	-853.55±20.99		---	-842.76±30.62		---

charge density of CNT: -1 e/nm²

type of	cation in Region C2			cation in Region C1		
interaction	anion	cation	CNT	anion	cation	CNT
Coulomb (kJ/mol)	-913.28±12.6	1871.60±23.07	-1062.68±1.02	-1440.50±23.26	2398.02±33.25	-1014.81±2.45
LJ (kJ/mol)	-7.09±0.31	-65.43±1.30	-65.42±0.73	-20.62±1.35	-71.35±2.07	-5.19±0.66
E_{ion} (kJ/mol)	885.8±20.51		---	865.54±29.37		---