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ESI

Macrocyclic Host Appended Carbon Nanotubes for Selective Adsorption of Metal Ions: Combined Experimental, DFT and MD Studies

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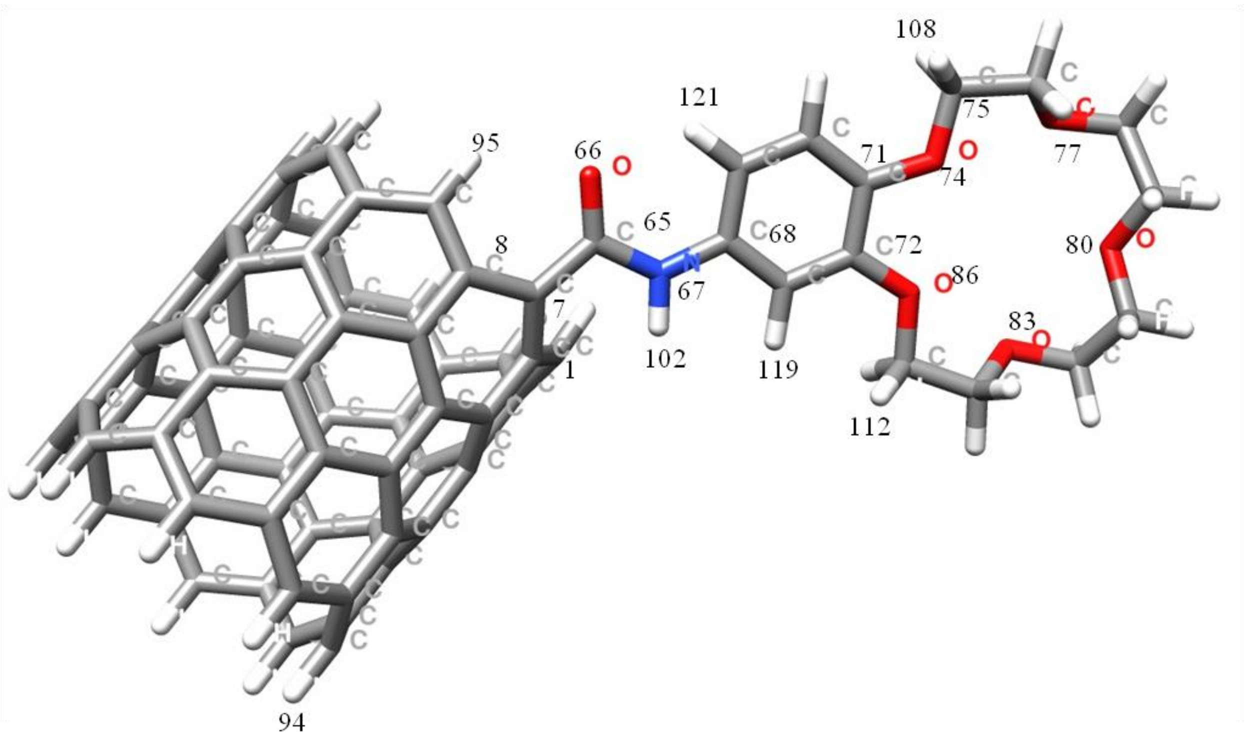

Fig. S1: Atoms position of CNT-B15C5 used in MD simulations.

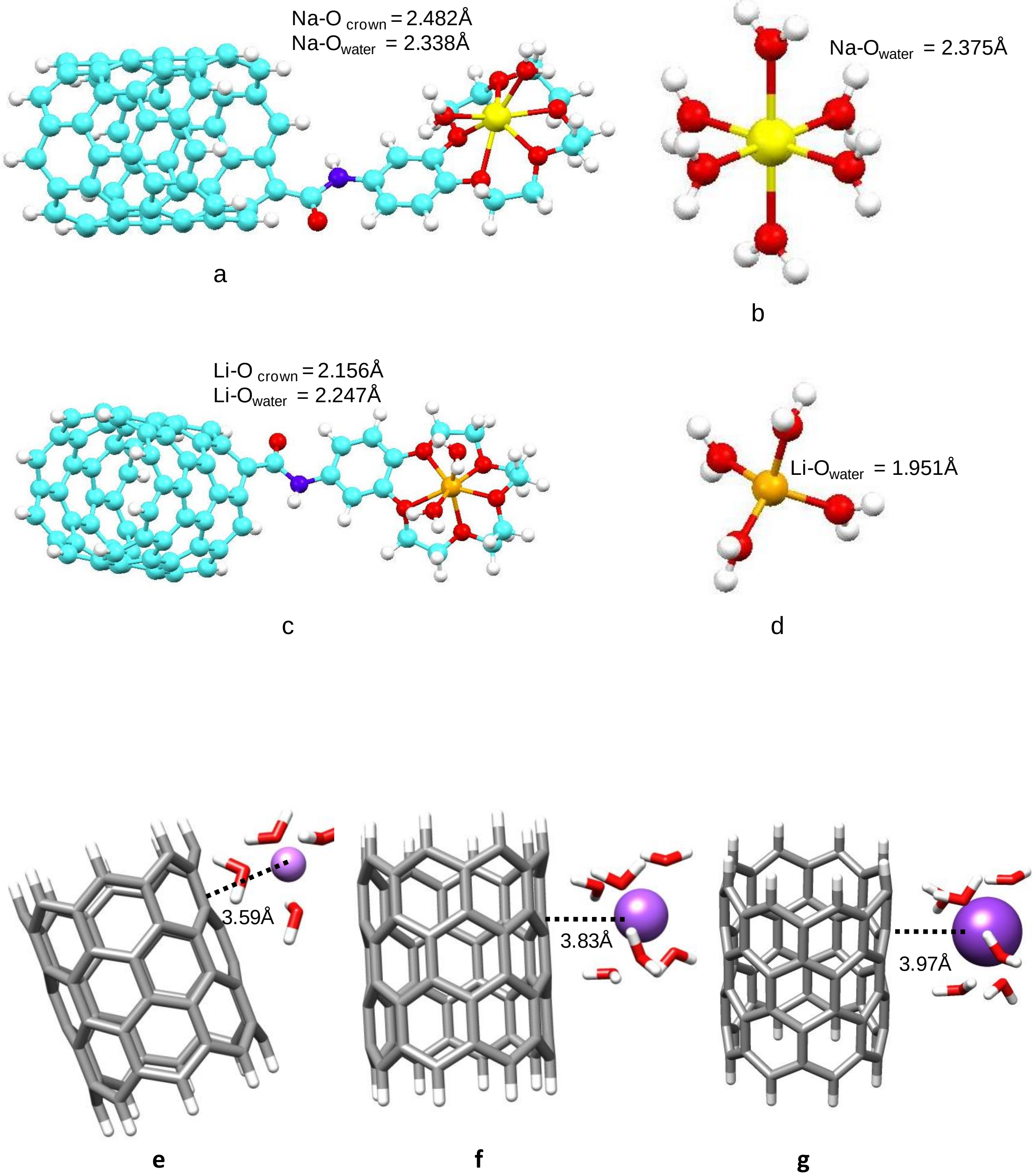

Fig. S2. Optimized structures of Na$^+$ ion with (a) CNT-B15C5 and (b) Water and Li$^+$ ion with (c) CNT-B15C5 and (d) Water (e)[CNT-Li-(H$_2$O)$_4$]$^+$, (f) [CNT-Na(H$_2$O)$_6$]$^+$, and (g) [CNT-K(H$_2$O)$_6$]$^+$

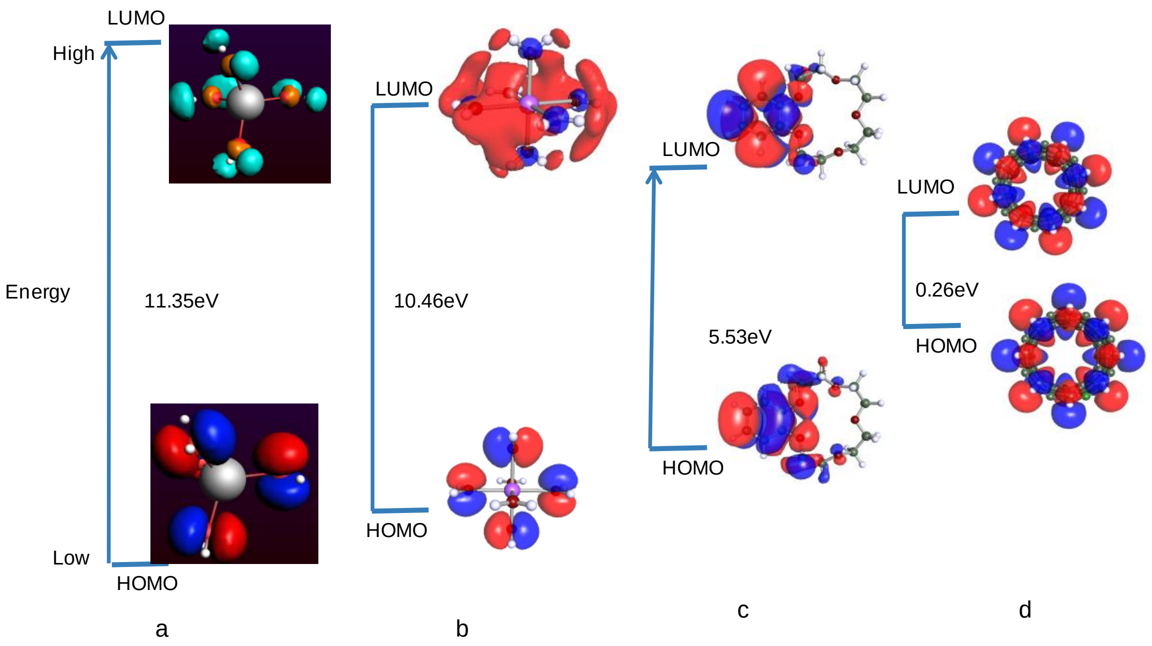

Fig. S3: HOMO-LUMO orbitals of (a) $[Li\text{-}(H_2O)_4]^+$ (b) $[Na\text{-}(H_2O)_6]^+$ (c) B15C5 and (d) CNT(8, 0)

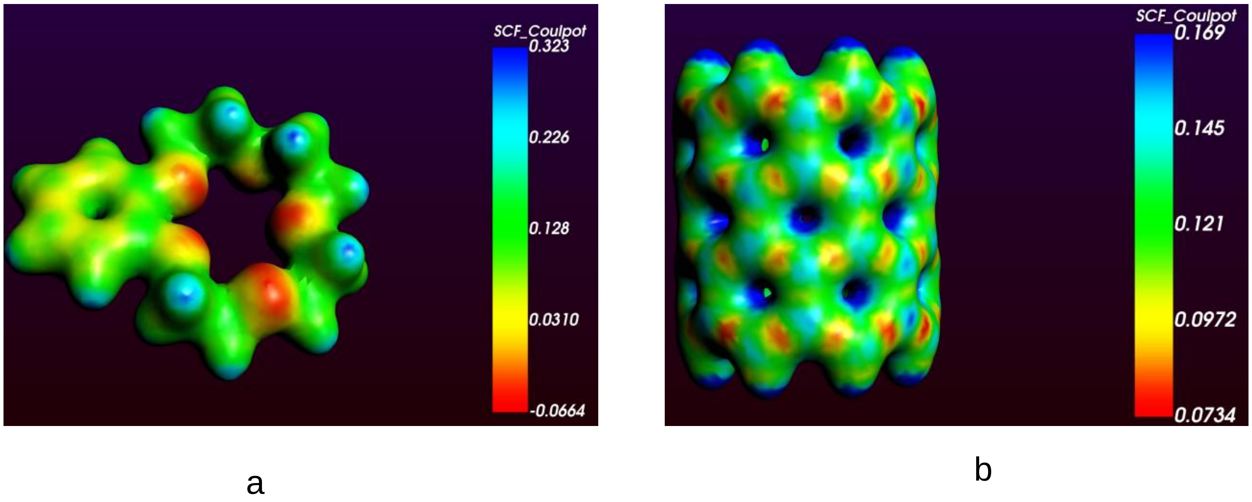

Fig. S4: MEP of of (a) B15C5 and (b) CNT(8,0)

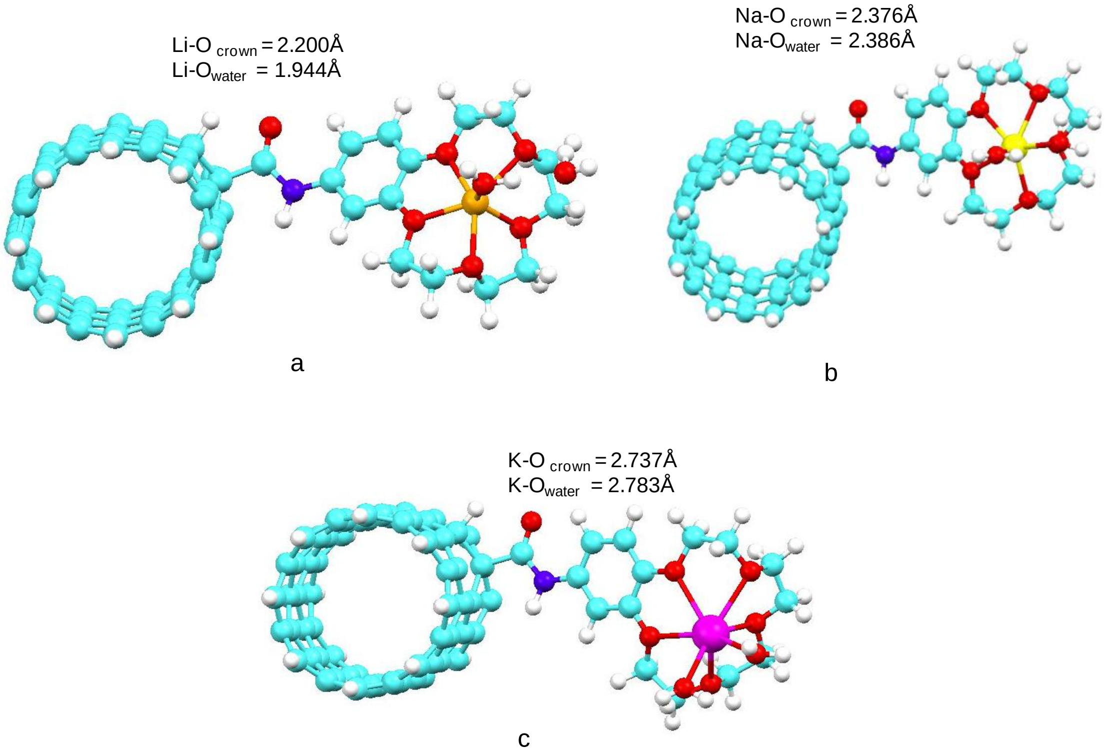

Fig. S5. Optimized structures of the (a) functionalized B15C5 at the sidewall of the CNT and its complexes with (b) Li^+ ion , (c) Na^+ ion and (d) K^+ ion

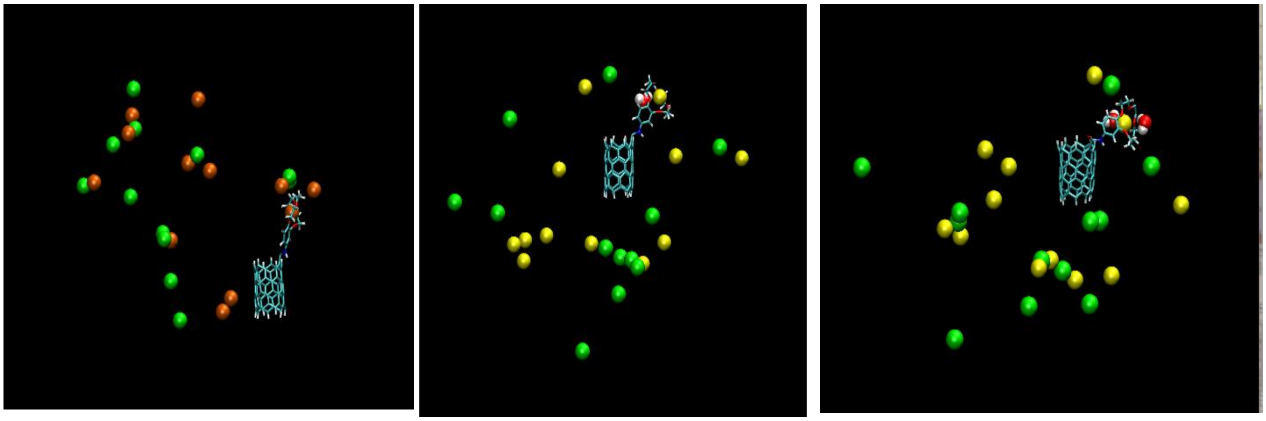

Fig. S6: Snapshots of the equilibrated structures of systems containing CNT-B15C5 for pure salt-water systems P1, P2 and P3, with the considered salt KCl, NaCl and LiCl respectively (color code Orange: K; green: Cl; red: O; cyan: C and white: H; yellow: Na and Li) CNT-B15C5 are shown by dynamic bonds. Ions are encapsulated by host B15C5 and hydrated water are shown by red-white.

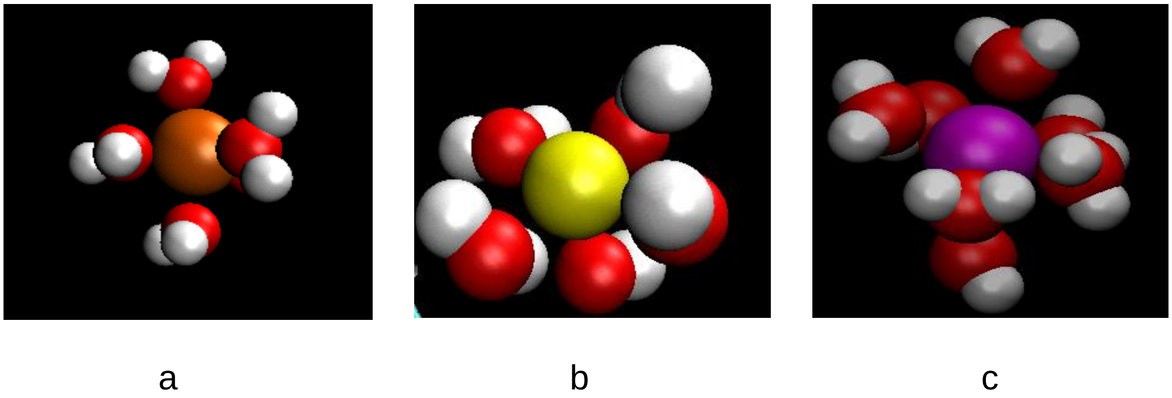

Fig. S7: Snap shot of coordinated ion-water for bulk system (a) Li (b) Na and (c) K ion.

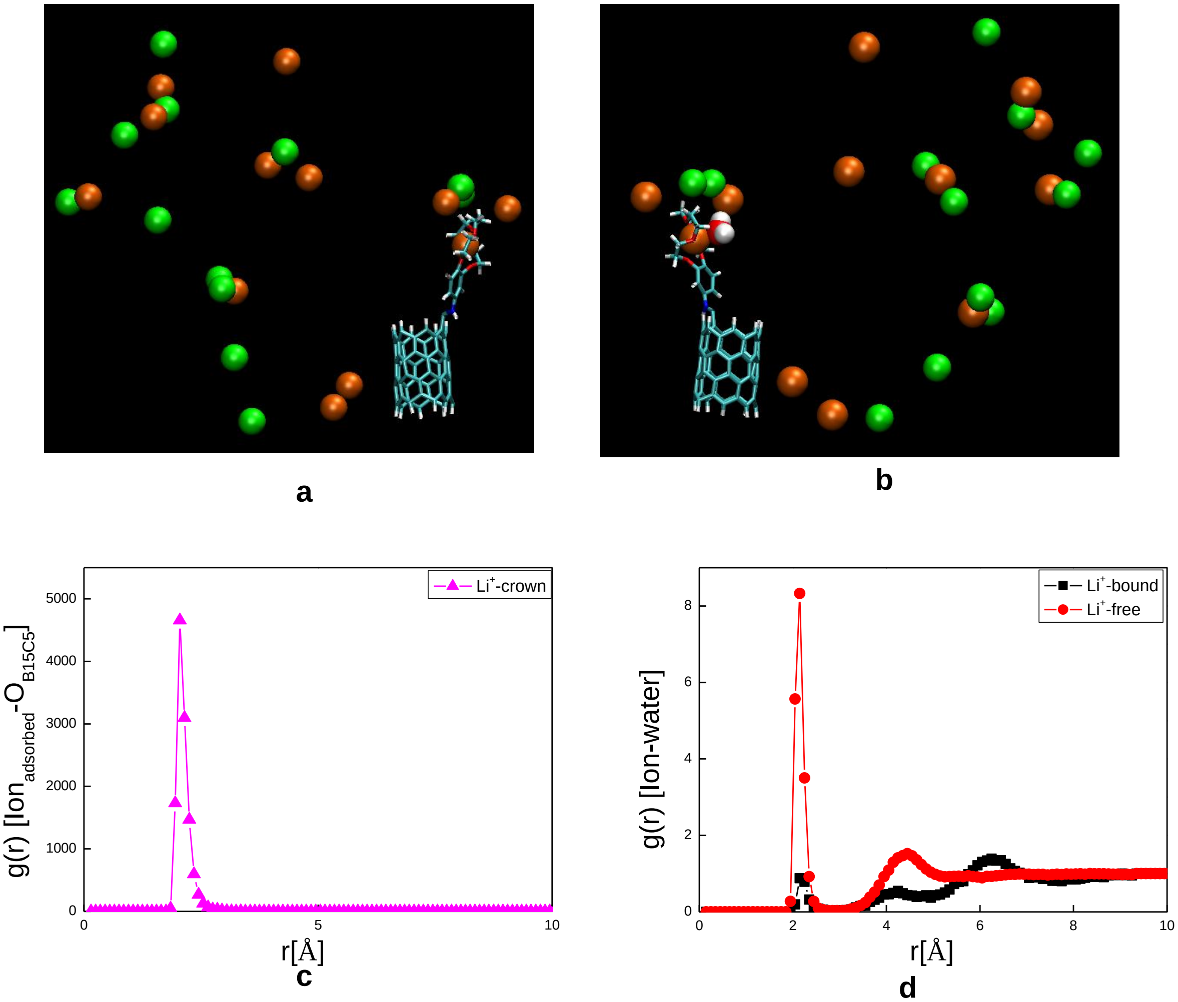

Fig.S8. (a) Snap shot of simulated system displaying the capture of Li$^+$ ion within the cavity of crown ether (b) Snap shot of simulated system displaying the number of water molecules coordinating to Li$^+$ ion bound to the crown ether cavity. (c) Radial distribution function of crown ether oxygen and Li$^+$ ion indicating strong interaction(d) water molecules around Li$^+$ in bulk solutions and in crown ether cavity. Owing to the confinement effect, the water density in the first hydration shell of Li$^+$ is significantly reduced, and the second hydration shell nearly disappears. Color code: Orange: Li; green: Cl; red: O; cyan: C and white: H.

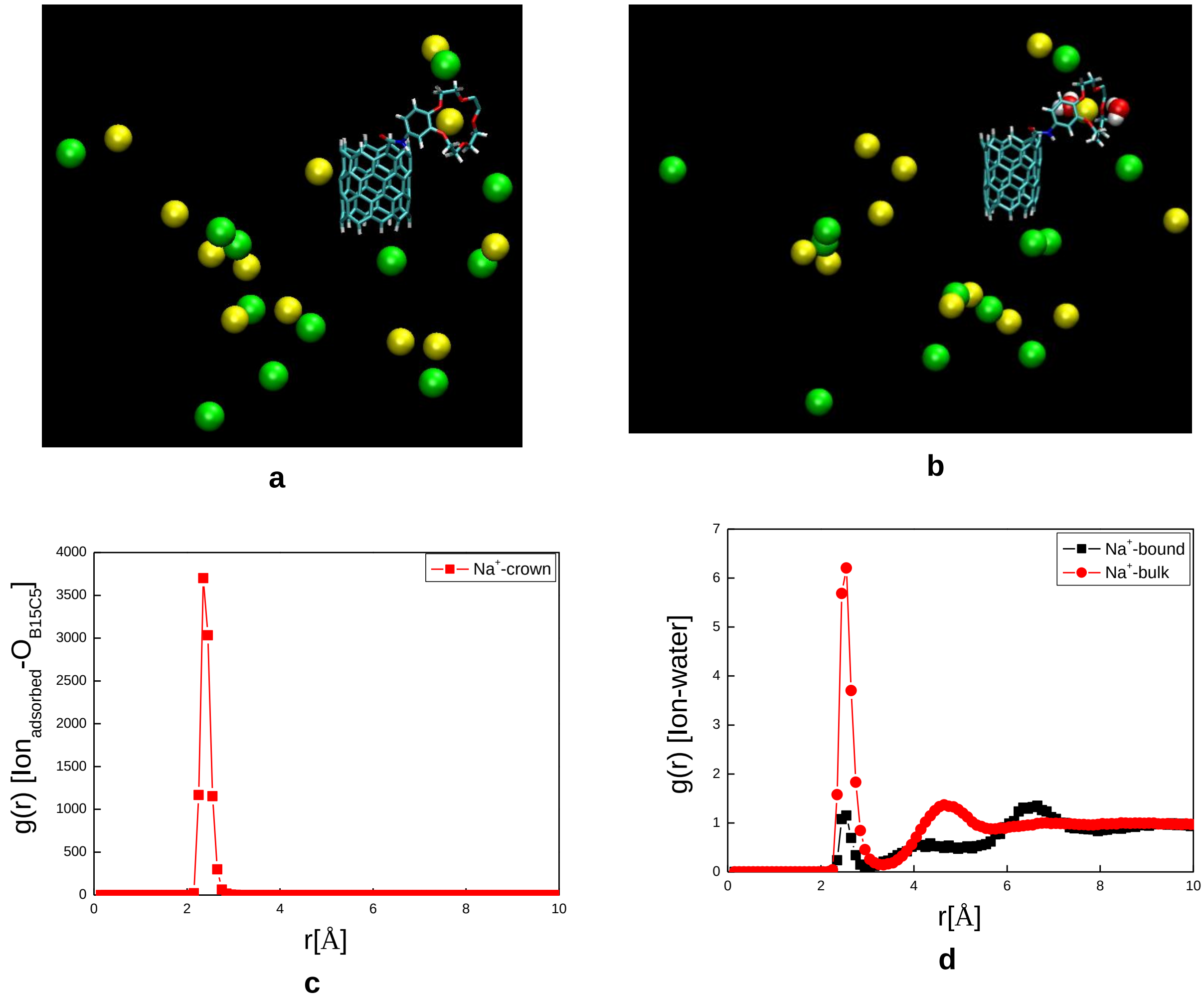

Fig.S9. (a) Snap shot of simulated system displaying the capture of Na$^+$ ion within the cavity of crown ether (b) Snap shot of simulated system displaying the number of water molecules coordinating to Na$^+$ ion bound to the crown ether cavity. (c) Radial distribution function of crown ether oxygen and Na$^+$ ion indicating strong interaction(d) water molecules around Li$^+$ in bulk solutions and in crown ether cavity. Owing to the confinement effect, the water density in the first hydration shell of Na$^+$ is significantly reduced, and the second hydration shell nearly disappears. Color code: Yellow: Li; green: Cl; red: O; cyan: C and white: H.

S1: Synthesis of designed CNT-B15C5

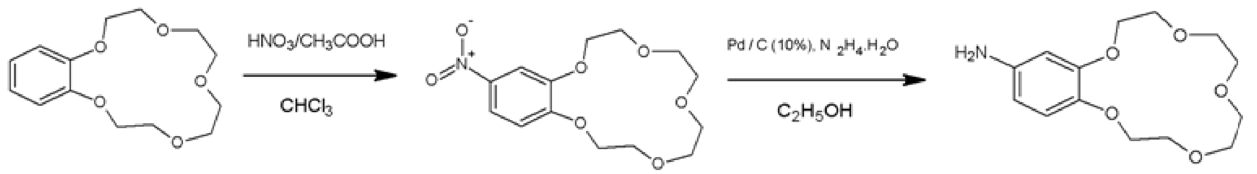

Fig. S10. Scheme of synthesis of amino B15C5

Synthesis of 4′-aminobenzo-15-crown-5

Synthesis 4′ -nitroB15C5 (NB15C5) from B15C5 and then 4`-aminoB15C5 (AB15C5) from 4 nitroB15C5 was carried out by following method (**Fig. S10**) described in literature[S1, S2]. A brief procedure is as follows.

5g of B15C5 was dissolved in mixture of 70ml chloroform and 60ml acetic acid, 17ml of nitric acid (70%) was added drop-wise over a 30 min time period under magnetic stirring. The stirring was continued for next 24 hours at room temperature. The mixture was then neutralized with aqueous Na_2CO_3 and chloroform layer was separated. The remaining aqueous layer was re-extracted 2-3 times with $CHCl_3$. The combined chloroform extracts were dried over $MgSO_4$ and distilled in vacuum distillation unit at about 50^{0}CA a yellow-colored solid crude NB15C5 product was obtained. m.p. 70^{o}C. Yield 75%. IR(KBr): 3090, 2945, 2870, 1587, 1520, 1450, 1338, 1280, 1137, 1090, 1048, 950, 925, 875, 806, 745, 650 cm^{-1}. 1H NMR (500 MHz, TMS): 3.756 (m, 16 –CH_2-), 6.866-7.911 (m, 3 ArH).

The crude NB15C5 was dissolved in 100ml of boiling ethanol under reflux condition. 0.5 g of Pd/C (10%) was added to the yellow reaction mixture by portions. 25 mL of hydrazine hydrate was added very slowly through the wall of the RBF keeping mind the effervescences getting generated. The mixture was then refluxed for 7 hours and immediately filtered in hot condition through Whatman 541 filter paper. The filtrate was mixed with water and extracted with chloroform. The chloroform layer was dried over $MgSO_4$ and distilled to get brown color oil of AB15C5 which solidified upon standing. Yield 65%. IR (KBr): 3336, 3220, 2876, 2361, 1617, 1510, 1457, 1350, 1300, 1225, 1123, 1190, 943, 980, 847, 650 cm^{-1}. 1H NMR (500 MHz, TMS): 3.451 (m, 16 –CH_2-), 5.340 (s, broad, 2H, NH_2), 6.193-6.264 (ds, 1H, H_b), 6.706-6.726 9dd, 1H, H_c), 7.266 (s, 1H, H_a). FTIR and 1H NMR spectra of B15C5, NB15C5, and AB15C5 are shown in **Fig. S13** and **Fig. S14**.

Carboxylation of CNTs

Carboxylation on the MWCNTs was carried out by already known process (**Fig.S11**) of oxidation[S3] with 3:1 ratio of H_2SO_4 and HNO_3. A brief process is described below.

500mg of MWCNTs was mixed in 200ml mixture of H_2SO_4 and HNO_3 in 3:1 (v/v) ratio, sonicated for 10 min and kept for stirring for about 4 hours at 85^{o}C. The black viscous suspension diluted with de-ionized water and filtered through 0.2µm PTFE membrane in a vacuum filtration assembly. The solid was then washed several times with de-ionized water till the pH of the filtrate reach the pH of the de-ionized water being used and then dried at 80^{0}C under reduced pressure.

Coupling of Aminobenzo-15-Crown-5 Ether and MWCNT-COOH

A simple process (**Fig.S12**) of preparing B15C5 functionalized MWCNTs described by Camerenaet. al[S4] was followed. 100mg of MWCNT-COOH was sonicated with 100ml of DMF for 10 minutes. The black suspension was then stirred with a magnetic stirrer at room temperature. 260mg of DCC amidation coupling agent was added into the mixture followed 15mg of DMAP. After 10 minutes of stirring, AB15C5 was added to the reaction mixture and the mixture was stirred for next 24 hours at room temperature. The product was filtered using 0.2µm PTFE membrane and the residue was washed with DMF and methanol, and then dried at 50^0C under reduced pressure.

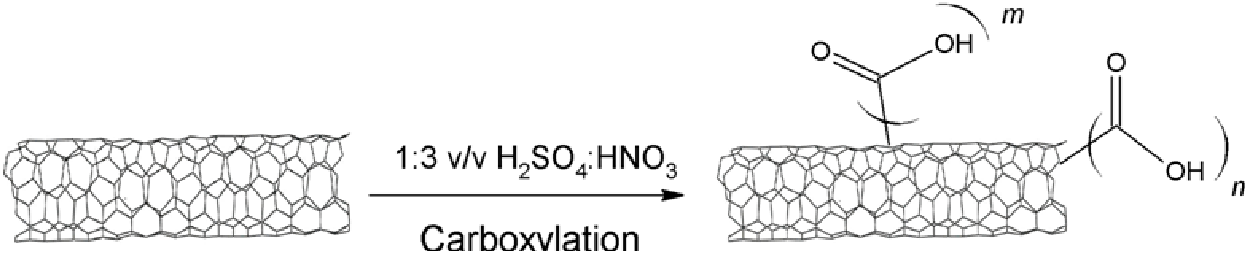

Fig. S11. Preparation of carboxyl MWCNTs

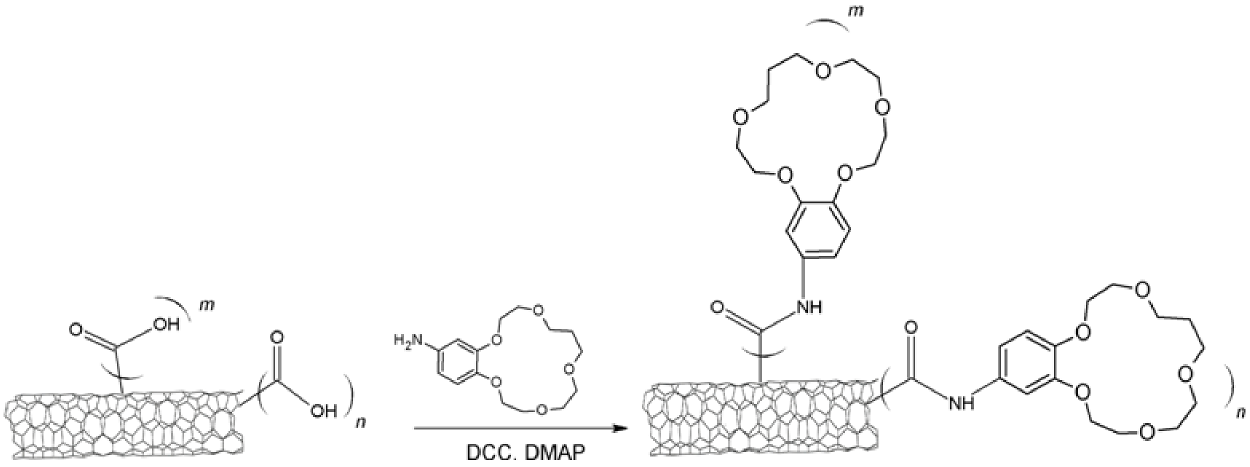

Fig. S12. Preparation of CNT-B15C

Extraction procedures

Solvent extraction of Li^+, Na^+ and K^+ ions by B15C5 in NB

5ml of metal nitrate solution and 5 ml of B15C5 solution in NB were mixed in 20 ml sealed glass bottle. The bottle was kept for stirring with magnetic capsule at 350rpm for 3 hours at room temperature. The mixture was left overnight undisturbed so that the two layers separate. Then upper part of the solution was then centrifuged and the clear supernatant solution was analyzed for alkali metals using Flame Atomic Absorption Spectrometer (FAAS, Make-GBC, Model-Avanta). The distribution coefficient values were calculated from the ratio of concentration of metal ion in organic solution and aqueous phase.

Adsorption of metal ions by CNTs and CNT-B15C5

5ml of metal nitrate solution was placed in a fresh and clean glass bottle. 10mg of adsorbent (CNT or CNT-B15C5) were added into it and sonicated for 10 minutes. Then magnetic stirrer was place in the glass bottle and the mixture was kept for stirring for 3 hours. The mixture was left overnight undisturbed so that the CNTs get settle down. Then clear supernatant solution was analyzed for Li^+, Na^+ and K^+ ionsusing FAAS. The distribution coefficient (K_d) and equilibrium adsorption capacity (q_e) of an adsorbent were determined from the following relations:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \text{ (mL g}^{-1}\text{)} \qquad (1)$$

$$q_e = (C_0 - C_e) \times \frac{V}{m} \text{ (mg g}^{-1}\text{)} \qquad (2)$$

where C_o, and C_e are the initial and equilibrium analyte concentration (ppm) respectively, V is the volume of the solution (mL or L) and m is the mass of adsorbent (g).

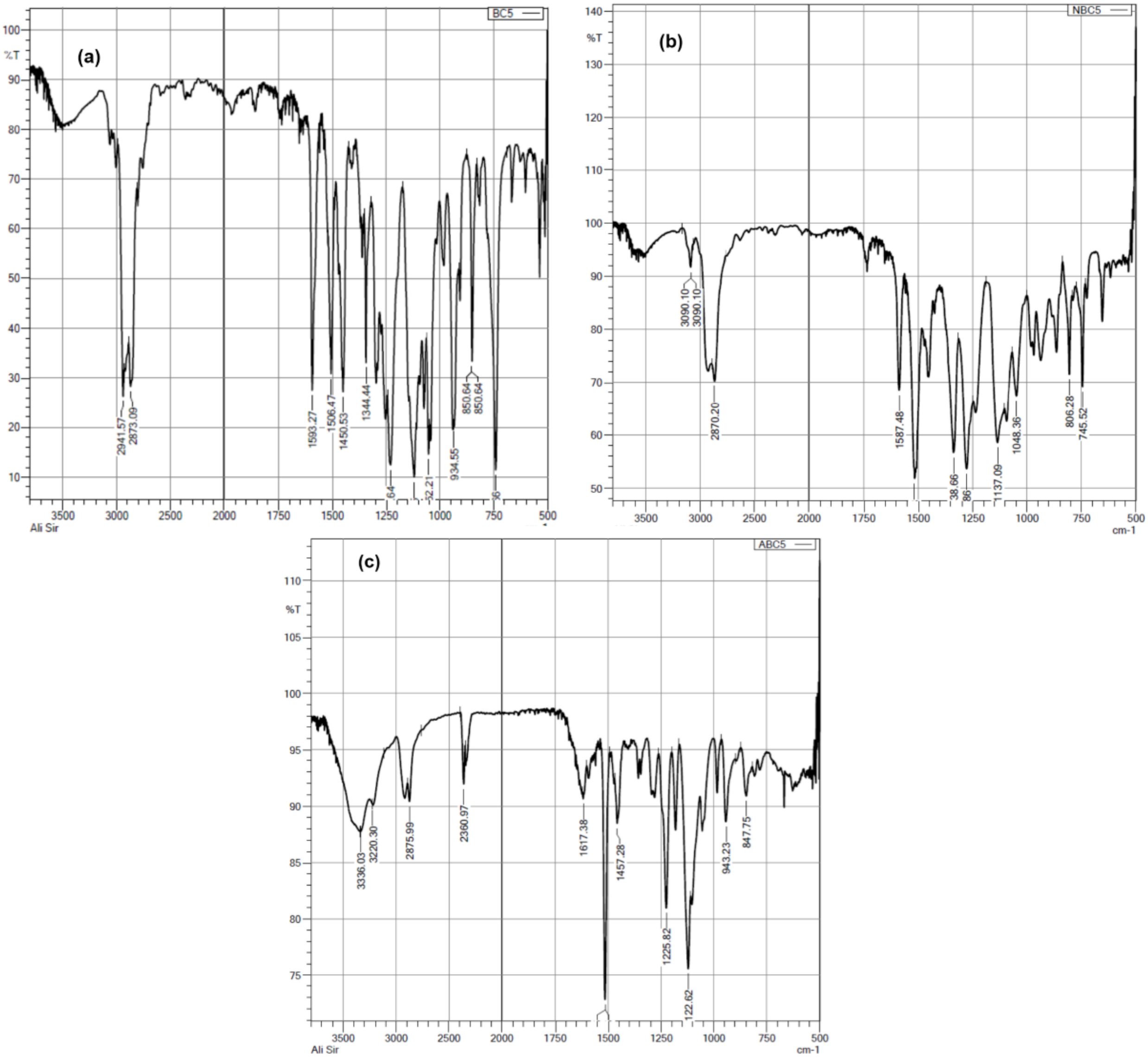

Fig. S13. FTIR spectra of (a) B15C5, (b) NB15C5, and (c) AB15C5

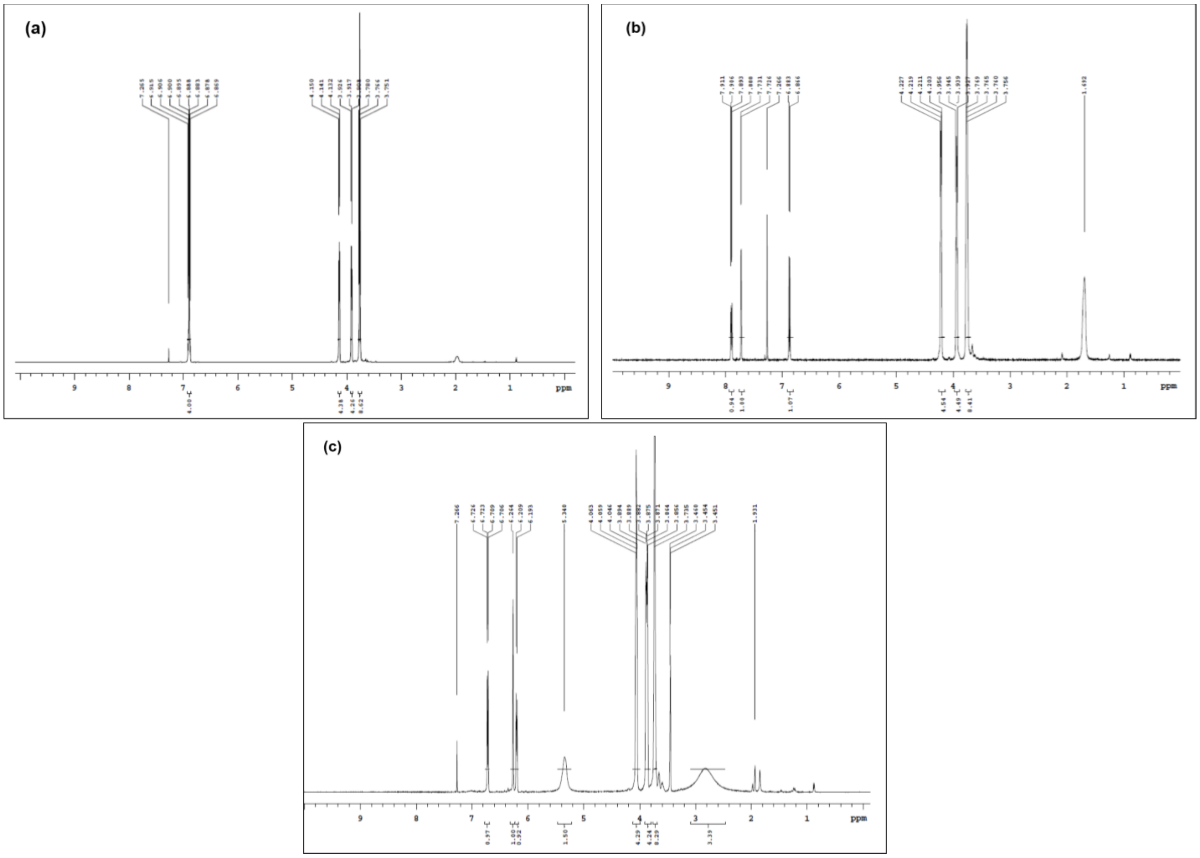

Fig. S14. 1H NMR spectra of (a) B15C5, (b) NB15C5, and (c) AB15C5

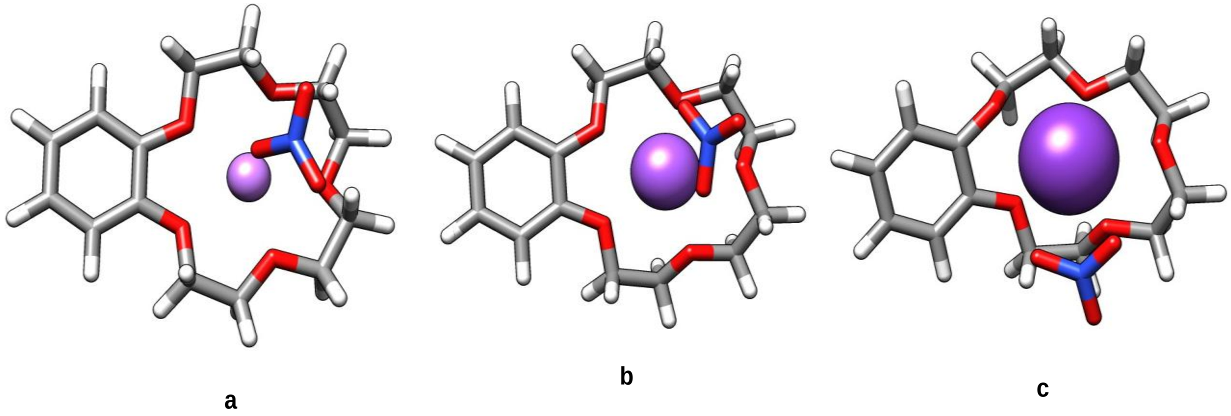

Fig. S15. Optimized structures of the complexes of metal ion with B15C5 in the presence of nitrate anion (a) Li (b) Na and (c) K.

Table S1: Bonded Forcefield Parameters[S5-S8]

Molecules	**Bonds(i-j)**	**K_r (kJmol^{-1}nm^{-1})**	**r_{eq} (nm)**
CNT-B15C5			
	CC-CC	392459.2	0.140
	CC-CA	374049.6	0.149
	CB-CB	392459.2	0.141
	CE-CE	224262.4	0.152
	CC-HC	307105.6	0.108
	CB-HB	307105.6	0.110
	CE-HE	284512.0	0.111
	CA-OA	476976.0	0.122
	CA-NA	410032.0	0.133
	CB-NA	364844.8	0.134
	CB-OE	376560.0	0.136
	CE-OE	267776.0	0.142
	NA-HA	363171.2	0.101

Molecules	**Angles(i-j-k)**	**K_θ (kJmol^{-1}rad^{-2})**	**θ_{eq} (degree)**
CNT-B15C5			
	CC-CC-HC	292.88	120.0
	CC-CC-CC	527.18	120.0
	CC-CC-CA	711.28	120.0
	CC-CA-NA	588.76	115.5
	CC-CA-OA	669.44	120.0
	NA-CA-OA	669.44	122.9
	CA-NA-HA	292.88	119.8
	CA-NA-CB	418.4	121.9
	NA-CB-CB	585.76	120.1
	CB-CB-OE	585.76	120.0
	CB-OE-CE	502.80	114.75
	OE-CE-HE	292.88	109.5
	OE-CE-CE	418.40	109.5
	CE-CE-HE	313.80	110.70
	HE-CE-HE	276.14	107.8

Table S2. Non bonded forcefield parameters

Molecules	**site**	**σ (nm)**	**ε (kJ/mol)**
CNT-B15C5			
	CC	0.355	0.292
	CA	0.375	0.439
	CB	0.355	0.292
	CE	0.350	0.276
	N	0.350	0.2761
	OA	0.325	0.711
	OE	0.290	0.585
	HC	0.242	0.125
	HB	0.242	0.125
	HE	0.250	0.125

Table S3. Non bonded forcefield parameters for ions

Species	**charge**	**σ (nm)**	**ε (kJ/mol)**
Li	1	0.212	0.764
Na	1	0.333	0.115
K	1	0.493	0.147
Cl	-1	0.441	0.492

Table S4. Compositions of MD simulation systems: Box size and number of solvent molecules for pure liquid.

System	**CNT-B15C5**	**Na^+**	**K^+**	**Li^+**	**Cl^-**	**H_2O**	**Boxsize [ÅxÅxÅ]**
P1	1	12			12	2215	45.4 x 45.4 x 45.4
P2	1		12		12	2215	45.4 x 45.4 x 45.4
P3	1			12	12	2215	45.4 x 45.4 x 45.4
P123	1	4	4	4	12	2215	45.4 x 45.4 x 45.4

Table. S5. Molecular descriptors (eV) in aqueous phase.

Complex	E_{HUMO}	E_{LUMO}	$E_{LUMO-HOMO}$	χ	η	ΔN		
						Li	Na	K
$[Li(H_2O)_4]^+$	-11.39	-0.04	11.35	5.71	5.67			
$[Na(H_2O)_6]^+$	-10.84	-0.37	10.46	5.61	5.23			
$[K(H_2O)_6]^+$	-11.04	-0.52	10.52	5.78	5.26			
CNTB15C5	-4.87	-3.23	1.63	4.05	0.81	0.128	0.129	0.142

Table S6: Calculated values of free energy of complexation (kcal/mol) in the solution phase for open and sidewall functionalized CNT.

Chemical reaction	**ΔG**	
	Open	Side
$[Li(H_2O)_4]^+$ + CNTB15C5 = $[CNTB15C5\text{-}Li\text{-}(H_2O)_2]^+$ + $2H_2O$	-7.12	-16.95
$[Na(H_2O)_6]^+$ + CNTB15C5 = $[CNTB15C5\text{-}Na\text{-}(H_2O)_2]^+$ + $4H_2O$	-33.58	-26.5
$[K(H_2O)_6]^+$ + CNTB15C5 = $[CNTB15C5\text{-}K\text{-}(H_2O)_2]^+$ + $4H_2O$	-42.15	-39.7

Table S7. Characteristic IR vibrations of MWCNT-COOH and MWCNT-B15C5.

IR Peaks (cm^{-1})	**Interpretations**
MWCNT-COOH	
3390	O-H stretching of COOH
2360, 2339	C-H stretching of CNT
1740 - 1680	C=O stretching of COOH
1560-1400	Skeletal vibrations, representing C=C stretching
1277, 1170, 1062	C-H bending, in-plane
887, 847	Aromatic C-H bending, out-of-plane
MWCNT-B15C5	
3448, 3420	N-H stretching of amide
2360, 2332	C-H stretching of CNT
1740 - 1680	C=O stretching of amide (C=ONH)
1560-1400	Skeletal vibrations, representing C=C stretching
1284, 1230, 1210	C-H bending
1176, 1140	C-O-C stretching of crown ether
955	C-H bending of –CH2-
890	Aromatic C-H bending

Table S8. Experimental values of K_d for Li^+, Na^+ and K^+ ions with CNT and CNT-B15C5 in aqueous solution.

Type of CNT-ion complex	K_d (L/g)
$Li^+ + CNT = [CNT\text{-}Li]^+$	2.6
$Na^+ + CNT = [CNT\text{-}Na]^+$	1.1
$K^+ + CNT = [CNT\text{-}K]^+$	0.9
$Li^+ + CNT\text{-}B15C5 = [CNT\text{-}B15C5\text{-}Li]^+$	-*
$Na^+ + CNT\text{-}B15C5 = [CNT\text{-}B15C5\text{-}Na]^+$	23
$K^+ + CNT\text{-}B15C5 = [CNT\text{-}B15C5\text{-}K]^+$	68.4

*below detection

Table S9: Calculated values of free energy of complexation (kcal/mol) of metal ion in presence of nitrate ion with B15C5 and CNT-B15C5 in the solution phase (for B15C5, nitrobenzene was taken as solvent phase).

Complexation reaction	**Solution phase**
CNT	
$Li^+(H_2O)_4 + CNT + NO_3^- = CNTLiNO_3 + 4H_2O$	15.7
$Na^+(H_2O)_6 + CNT + NO_3^- = CNTNaNO_3 + 6H_2O$	-24.4
$K^+(H_2O)_6 + CNT + NO_3^- = CNTKNO_3 + 6H_2O$	-28.2
B15C5	
$Li^+(H_2O)_{4(aq)} + B15C5_{(org)} + NO_3^-{}_{(aq)} = B15C5LiNO_{3(org)} + 4H_2O_{(aq)}$	-21.0
$Na^+(H_2O)_{6(aq)} + B15C5_{(org)} + NO_3^-{}_{(aq)} = B15C5NaNO_{3(org)} + 6H_2O_{(aq)}$	-36.5
$K^+(H_2O)_{6(aq)} + B15C5_{(org)} + NO_3^-{}_{(aq)} = B15C5KNO_{3(org)} + 6H_2O_{(aq)}$	-47.1
CNT-B15C5	
$Li^+(H_2O)_4 + CNTB15C5 + NO_3^- = CNTB15C5LiNO_3 + 4H_2O$	-22.5
$Na^+(H_2O)_6 + CNTB15C5 + NO_3^- = CNTB15C5NaNO_3 + 6H_2O$	-35.8
$K^+(H_2O)_6 + CNTB15C5 + NO_3^- = CNTB15C5KNO_3 + 6H_2O$	-38.1

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