Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Designing biomimetic pores based on internally functionalized self-assembling α,γ-peptide nanotubes

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Supporting Information

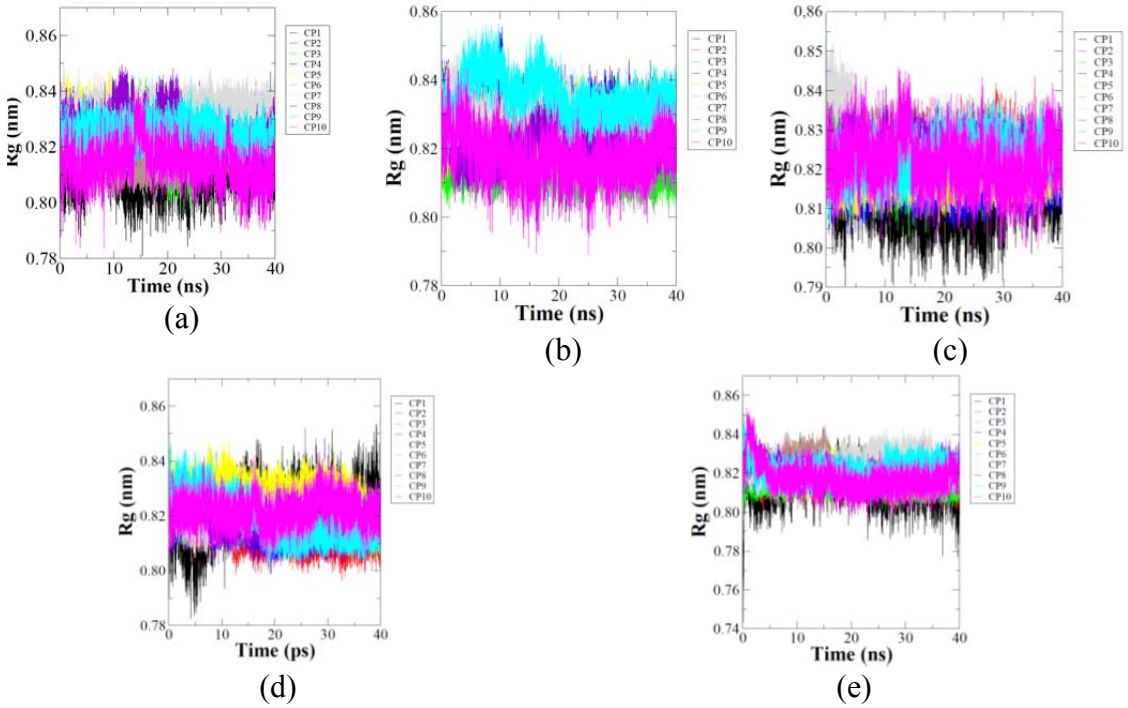


Figure S1: Radius of gyration (Rg) for each one of the cyclic peptides forming **SCPN$_{4OH}$** in different salt solutions (a) LiCl, (b) NaCl, (c) KCl, (d) CsCl and (e) $CaCl_2$ 0.5 M, simulated during 40 ns.

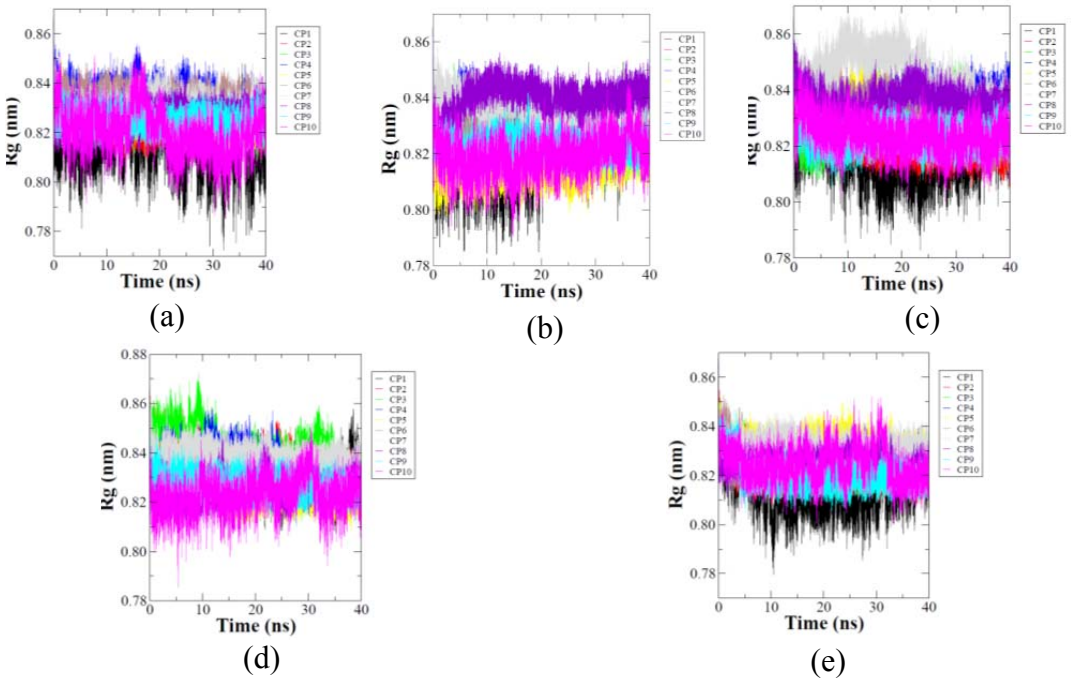


Figure S2: Radius of gyration (Rg) for each one of the cyclic peptides forming **SCPN$_{2OH}$(a)** in different salt solutions (a) LiCl, (b) NaCl, (c) KCl, (d) CsCl and (e) $CaCl_2$ 0.5 M, simulated during 40 ns.

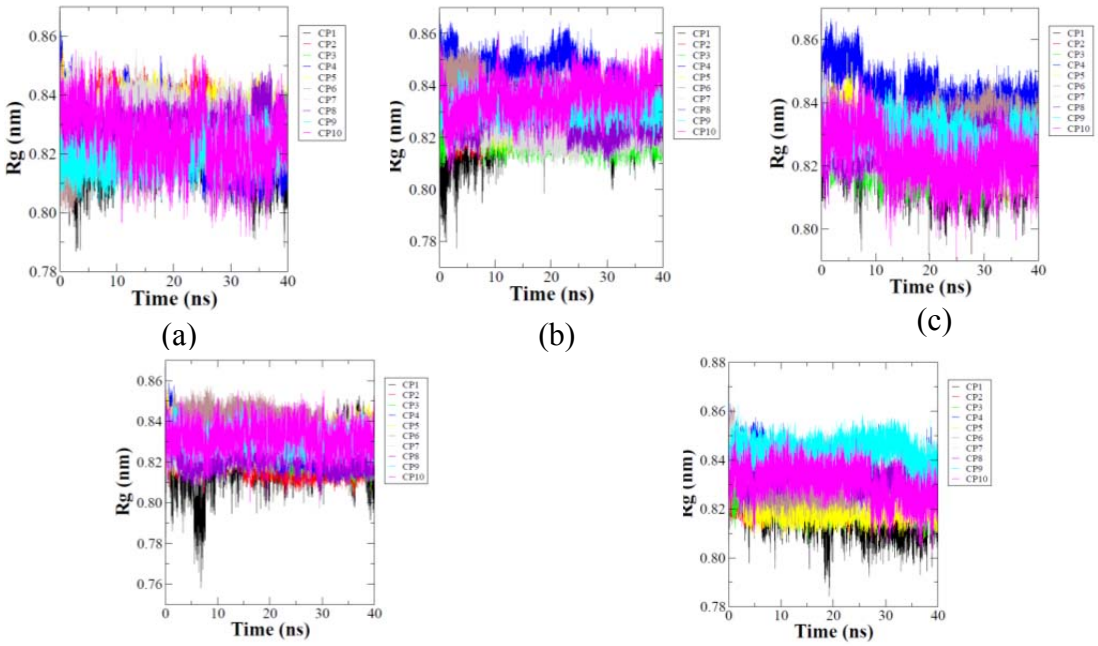


Figure S3: Radius of gyration (Rg) for each one of the cyclic peptides forming **$SCPN_{2OH}$(e)** in different salt solutions (a) LiCl, (b) NaCl, (c) KCl, (d) CsCl and (e) $CaCl_2$ 0.5 M, simulated during 40 ns.

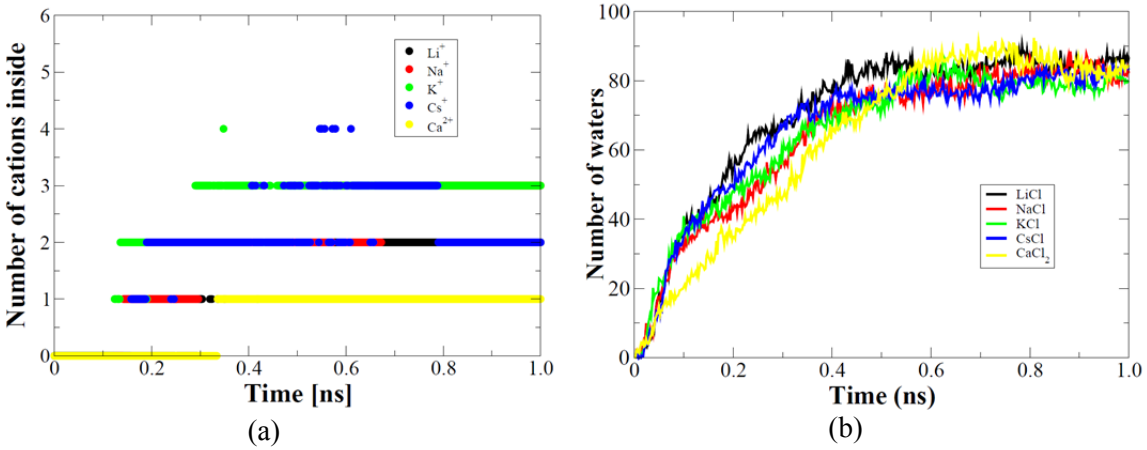


Figure S4: Time filling of the nanotube **$SCPN_{4OH}$** with ions (a) and water (b) at different salt solutions. It can be noticed that the nanotube is filled both of ions and waters after the first ns.

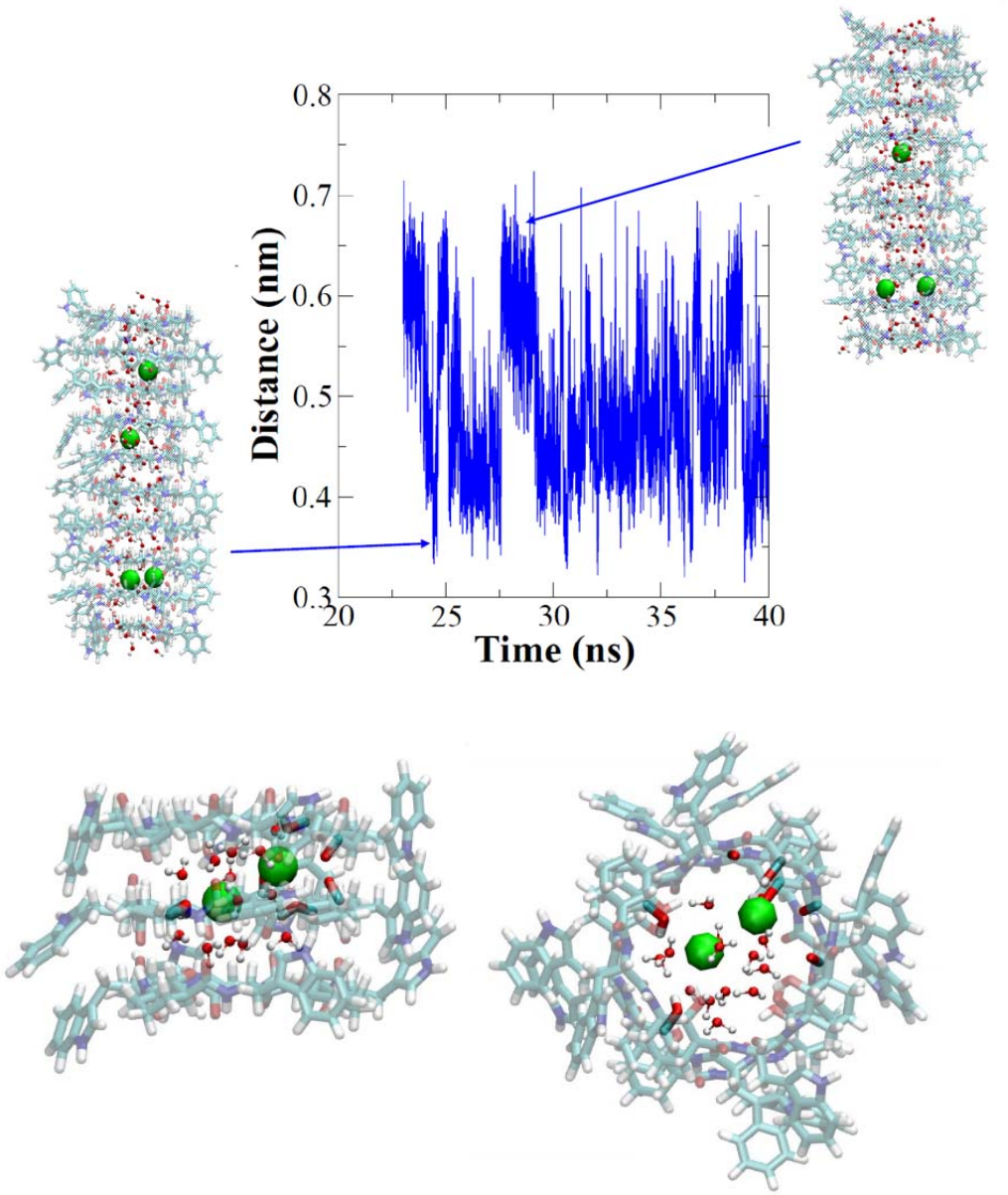
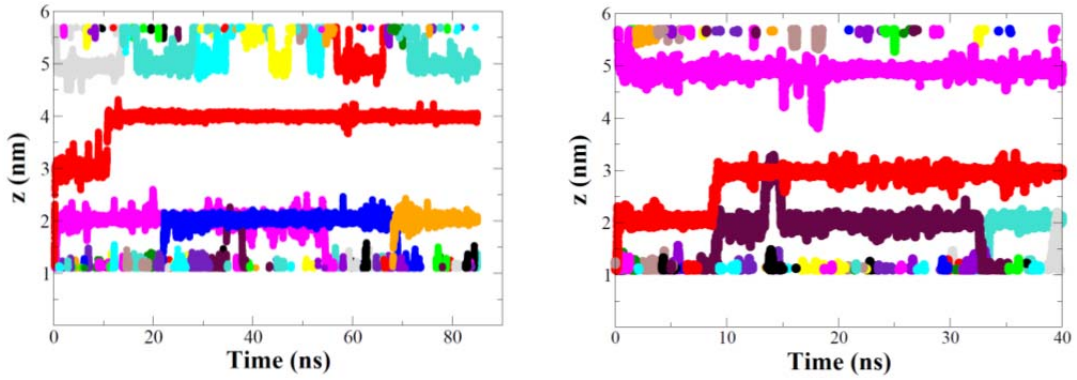


Figure S5: Up: Variation of the distance between cations K^+ along the simulation during the time both of them are inside **SCPN$_{4OH}$**. Down: Detail of the position and coordination of these K^+ cations. By simplicity, the distant CPs and the water molecules not participating actively in the cation coordination have been removed. The first K^+ cation enters the channel during the first nanoseconds and locates in the region between the planes of the CPs establishing a α-α interaction, remaining there during all the simulation time. A second cation enters the channel about 20 ns later and locates very near the former one. Both cations are coordinated to water molecules and the groups OH y C=O from the aminoacids, without any appreciable difference in the coordination numbers with respect to the other K^+ cations inside the channel.



(a) (b)

Figure S6: z-coordinate for each one of the cations inside the simulated peptide nanotube **SCPN$_{4OH}$** along the extended trajectory presented in the main part (a), or for a different replica (b).

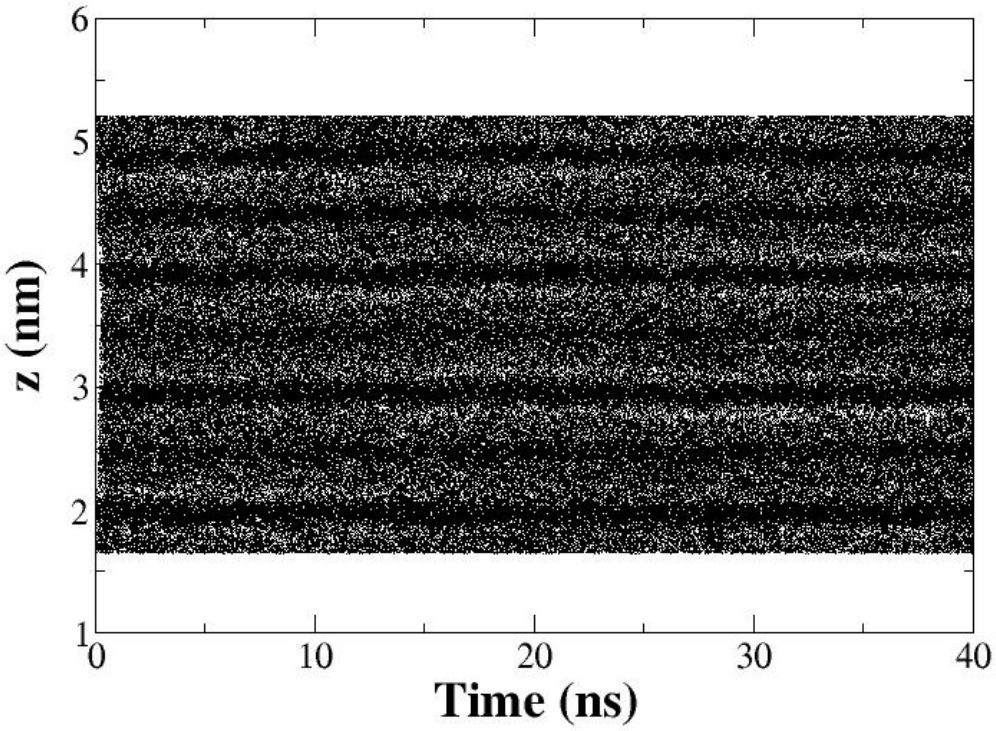
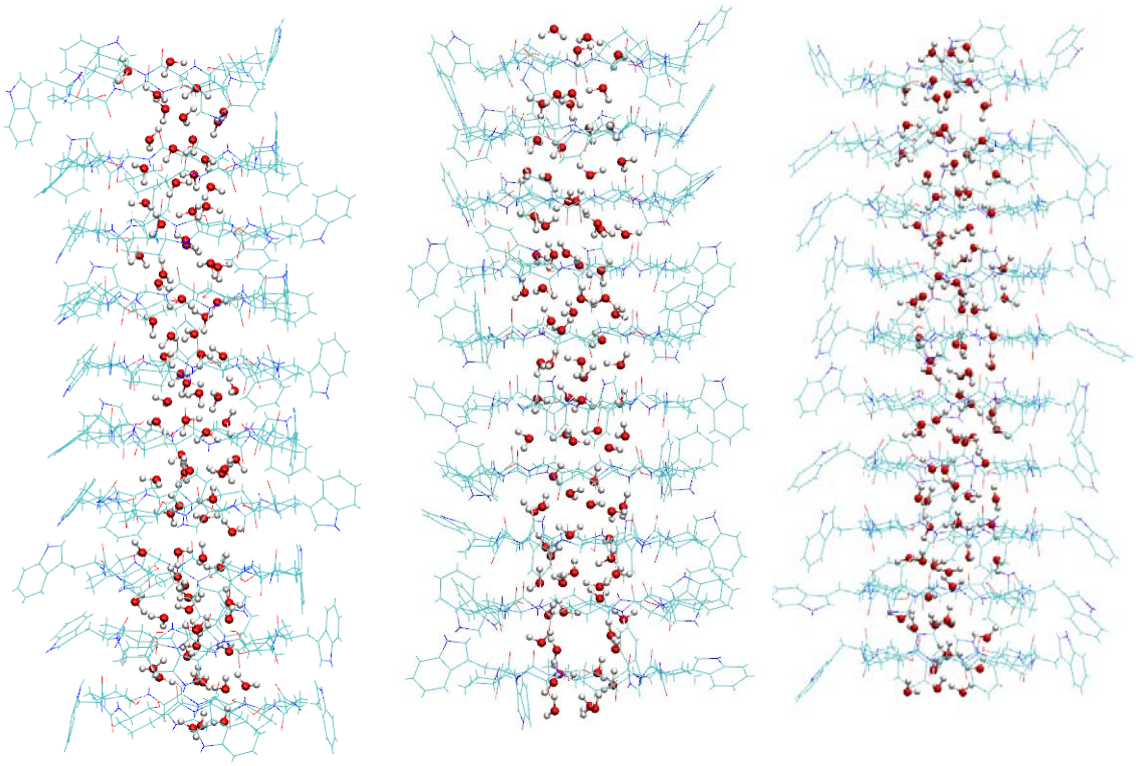


Figure S7: Example of the Z-coordinate of the internal waters populating the inner cavity of a nanotube along the simulation time. This figure corresponds to the results obtained from the simulation of **SCPN$_{4OH}$** in LiCl 0.5 M.



$SCPN_{4OH}$ **$SCPN_{2OHa}$** **$SCPN_{2OHe}$**

Figure S8: Snapshots from the simulation of the peptide nanotubes in pure water, pointing out the structure of the internal water and ions. Lipids and external water and ions were removed for clarity.

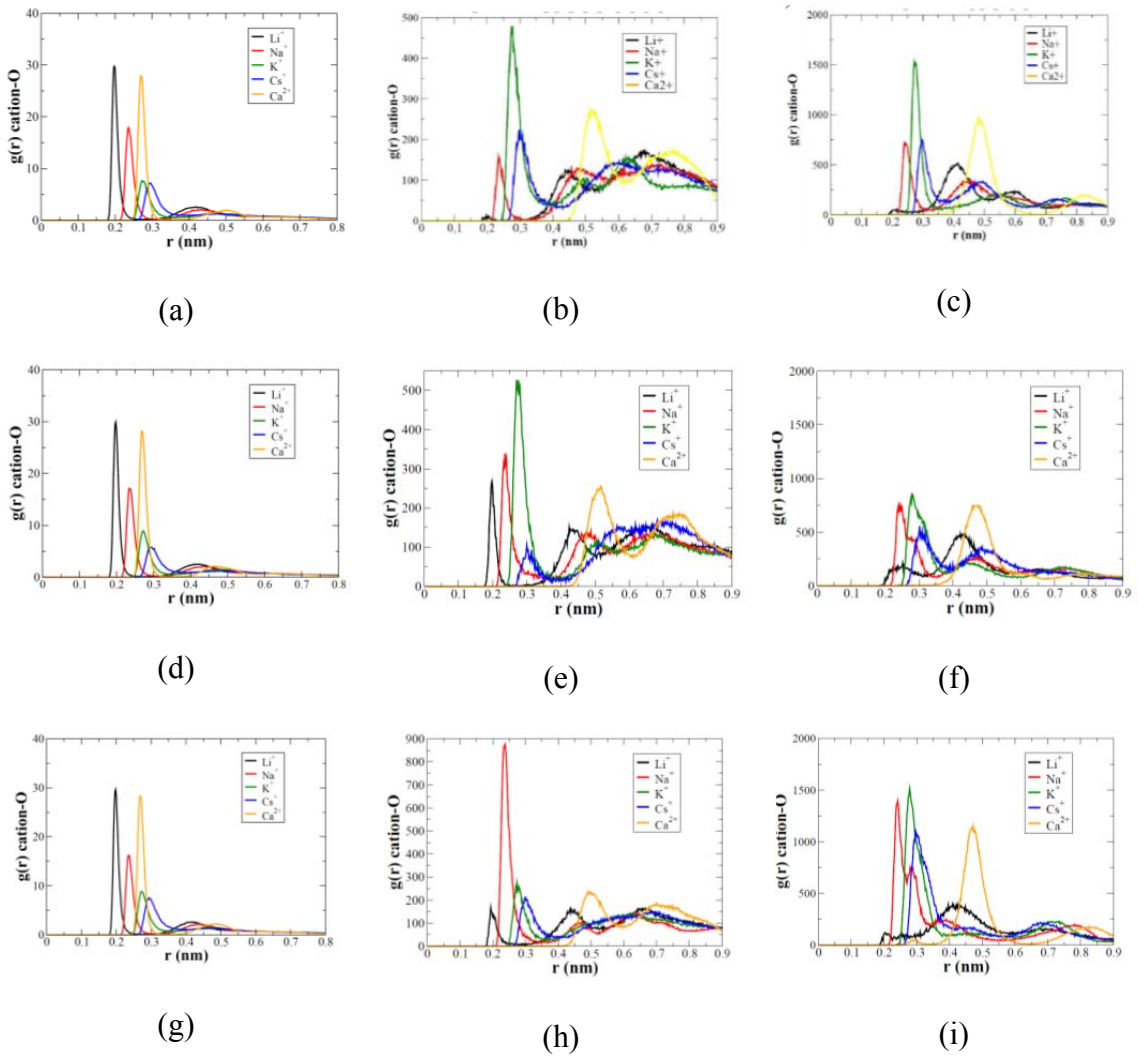
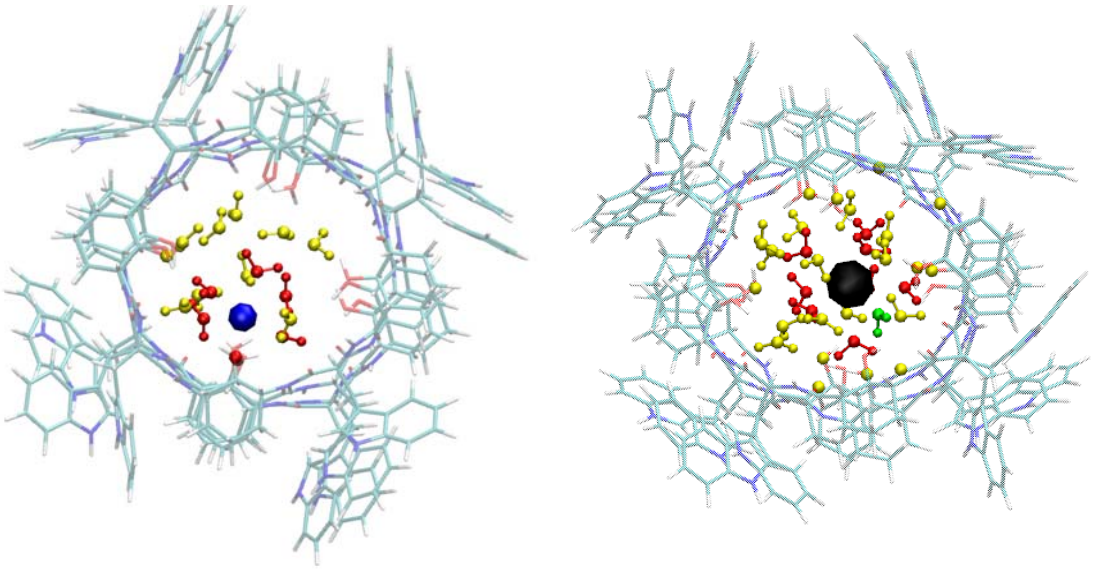


Figure S9: Radial distribution of the distance cation-O inside the nanotube [$\mathbf{g_{ion\text{-}oxygen}(r)}$] (a-c) $\mathbf{SCPN_{4OH}}$, (d-f) $\mathbf{SCPN_{2OHa}}$, (g-i) $\mathbf{SCPN_{2OHe}}$ considering the contribution of the oxygens of water, C=O or OH, separately.



NaCl $CaCl_2$

Figure S10: Detail of the first coordination sphere in two structures from the simulation of **SCPN$_{4OH}$** in NaCl (a) and $CaCl_2$ 0.5 M. Waters in red belong to the first hydration shell and waters in blue are from the second one.

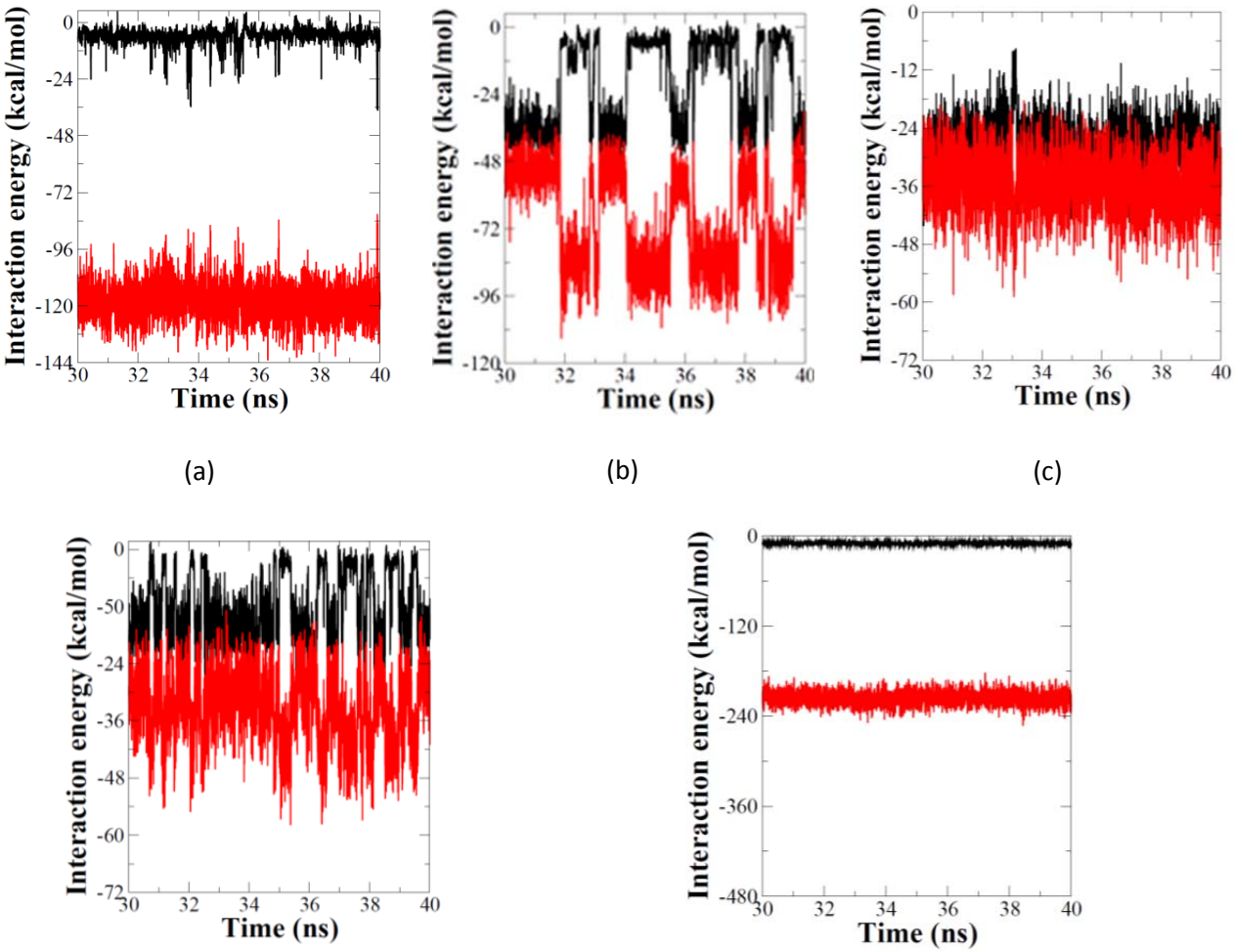
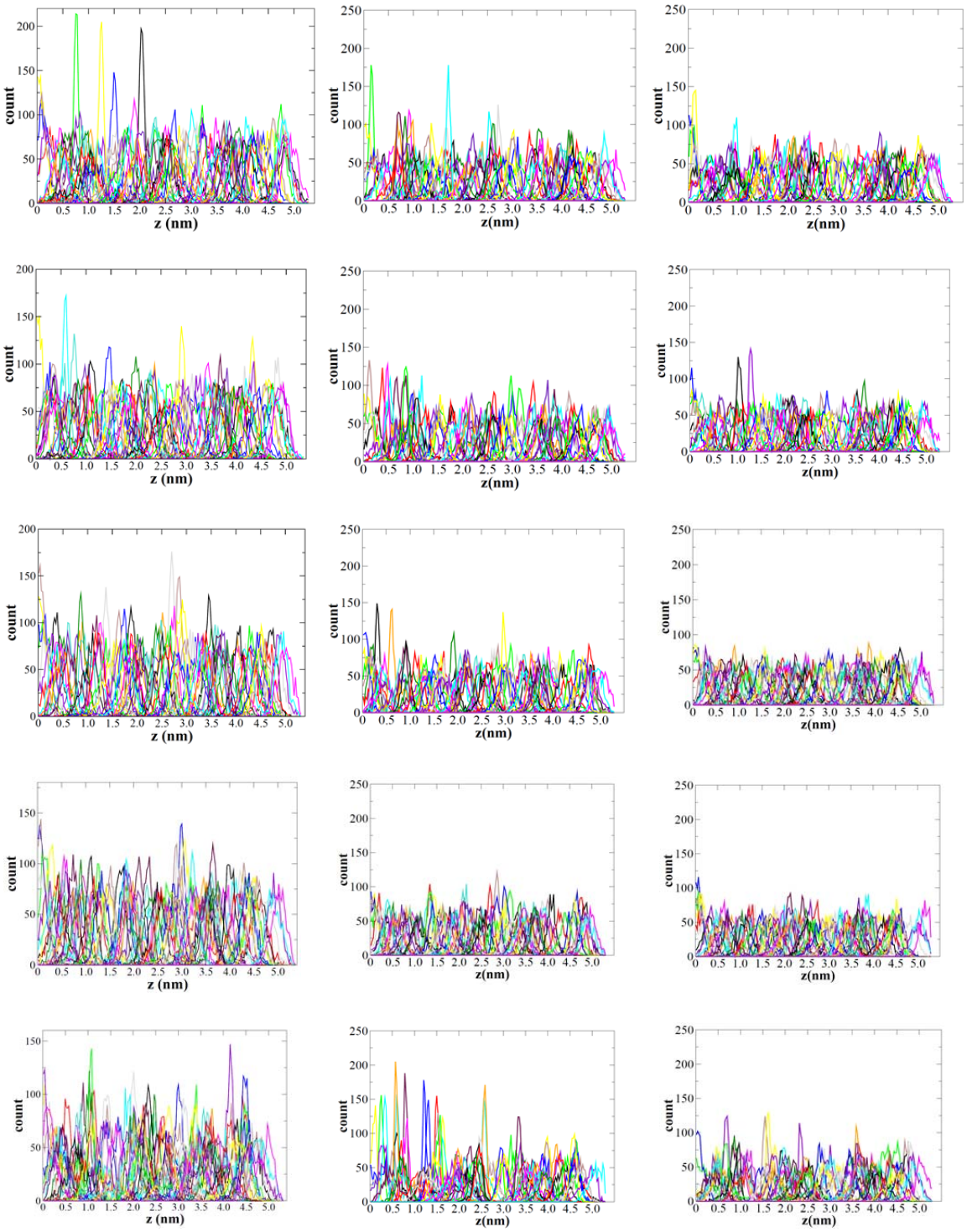


Figure S11: Interaction energy between one of the ions (Li^+, Na^+, K^+, Cs^+, Ca^{2+}) and the nanotube (in black) or the water surrounding it (in red) during 10 ns inside of the nanotube.



$SCPN_{4OH}$ **$SCPN_{2OHa}$** **$SCPN_{2OHe}$**

Figure S12: Histograms for the PMF calculations obtained from the Weighted Histogram Analysis Method (WHAM). Each column shows the results obtained for a different salt solution (LiCl, NaCl, KCl, CsCl and $CaCl_2$ 0.5 M). Histograms give an idea of the convergence of each one of the PMF calculations.

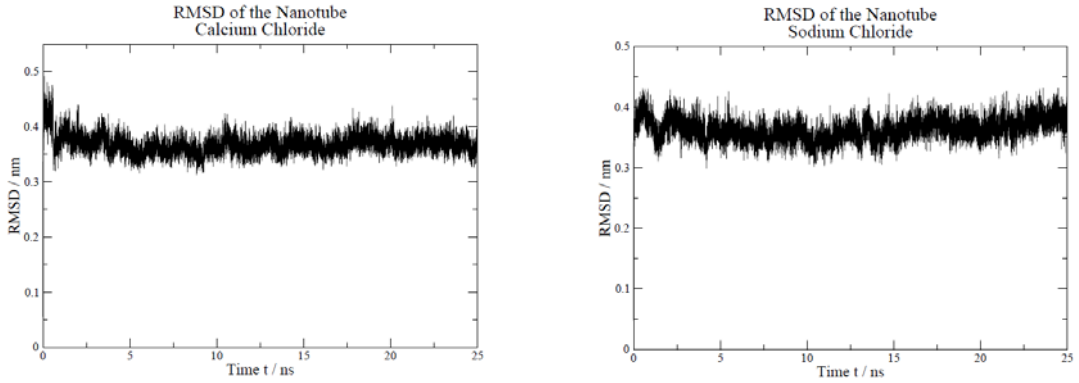
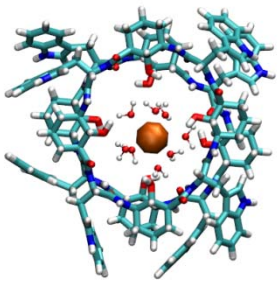


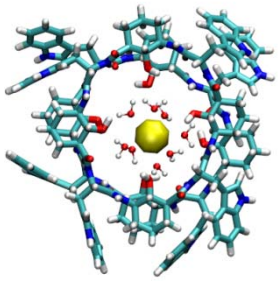
Figure S13: RMSD for the hydroxymethylated nanotube **SCPN$_{4OMe}$** simulated in NaCl and $CaCl_2$ 0.5 M for 25 ns.

Table S1: Diffusion coefficients (mean and standard deviations along 40 ns of simulation) for the different salt solutions studied. Units in 10^{-8} cm^2/s Global coefficients and those given parallel to the nanopore axis. For the sake of comparison, values for the diffusion in bulk solution are Na^+ 1.2, Cl^- 1.8, K^+ 1.8 and Ca^{2+} 0.53 $\times 10^{-5}$ cm^2/s.[1]

		Global	z Only
SCPN	**LiCl**	0.25 ± 1.15	0.80 ± 3.30
	NaCl	6.20 ± 14.10	15.00 ± 43.00
	KCl	9.80 ± 12.90	29.00 ± 40.00
	CsCl	2.30 ± 3.50	7.20 ± 11.50
	$CaCl_2$	2.60 ± 2.90	7.70 ± 8.50
SCPN$_{4OH}$	**LiCl**	4.64 ± 4.42	13.85 ± 12.94
	NaCl	1.26 ± 3.03	0.41 ± 1.23
	KCl	1.65 ± 4.07	2.78 ± 7.97
	CsCl	8.72 ± 15.77	26.66 ± 45.53
	$CaCl_2$	0.19 ± 0.45	0.21 ± 0.29
SCPN$_{2OH}$(a)	**LiCl**	1.57 ± 1.30	4.78 ± 4.02
	NaCl	1.17 ± 4.39	4.26 ± 10.04
	KCl	0.46 ± 9.73	1.25 ± 29.75
	CsCl	20.54 ± 36.16	19.14 ± 55.96
	$CaCl_2$	0.04 ± 0.06	0.01 ± 0.40
SCPN$_{2OH}$(e)	**LiCl**	1.52 ± 28.50	38.10 ± 75.23
	NaCl	0.19 ± 0.71	0.19 ± 0.24
	KCl	2.97 ± 20.42	4.95 ± 59.70
	CsCl	2.08 ± 1.11	5.45 ± 2.16
	$CaCl_2$	0.02 ± 0.09	0.11 ± 0.02

Table S2: Comparison between the interaction energies of different components of the systems obtained with the MD parameters used in this study and those calculated with B3LYP/6-31G(d). All the values are referred to a single structure obtained from the MD simulations in $CaCl_2$, where only 2 CPs and 8 water molecules around the cation were maintained. Ca^{2+} was substituted by Na^+ and both structures were minimized using AMBER/GAFF parameters or quantum calculations using Gaussian 09[2]. Units are in kcal/mol.





		Na^+	**Ca^{2+}**
AMBER /GAFF	cation-water	-98.3	-174.6
	cation&H_2O-dimer	-72.9	-79.4
B3LYP/6 -31G(d)	cation-water	-137.6	-307.1
	cation&H_2O -dimer	-53.3	-128.0

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2. Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.;

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