Electronic Supporting Information (ESI) for Endohedral Filling Effects in Sorted & Polymer-Wrapped Single-Wall Carbon Nanotubes

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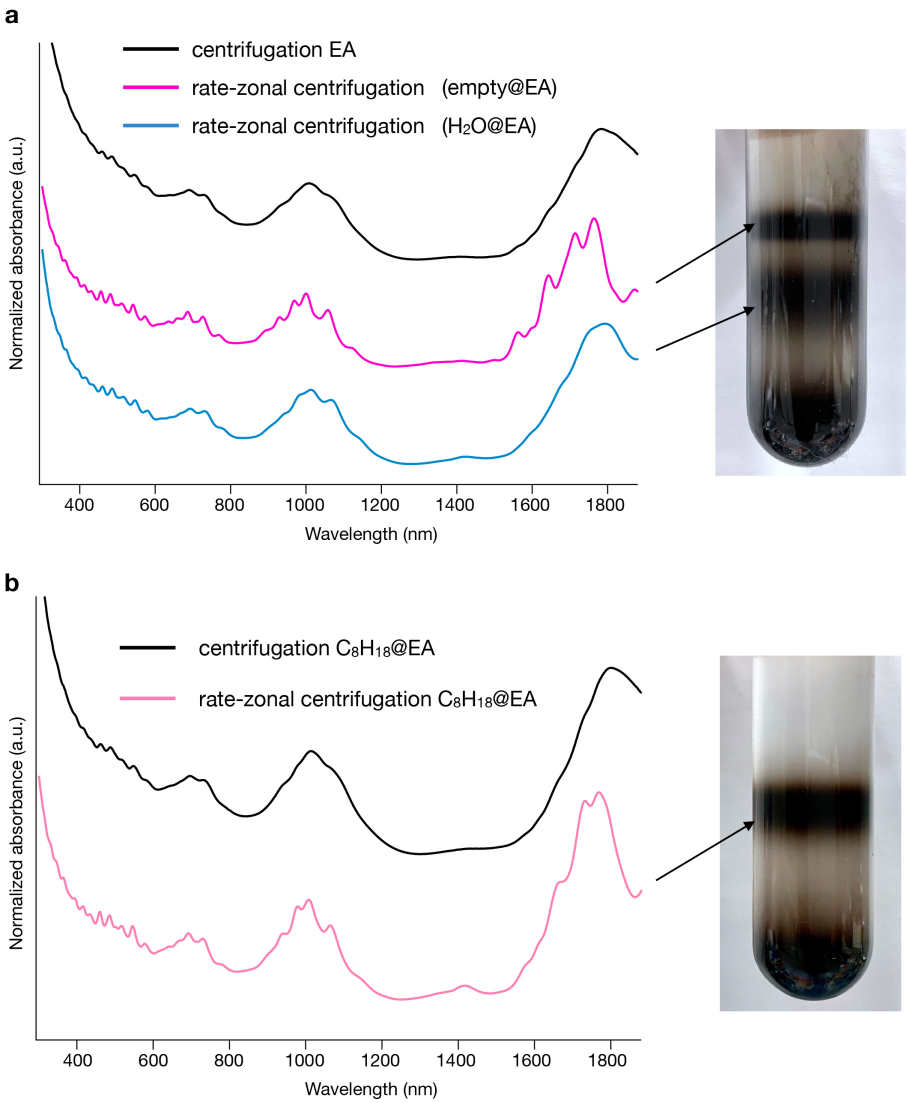

Figure S1. Rate-zonal centrifugation of empty, H_2O and C_8F_{18} filled EA SWCNTs. (a) As shown extensively in previous works,[1-3] the top band in the centrifuge tube (photo) is enriched in closed (empty) EA-SWCNTs due to their density being the lowest. The broad band underneath this belongs to the water filled SWCNTs EA (H_2O@EA). (b) C_8F_{18} filled EA-SWCNTs were prepared from a raw soot absent of closed species and only have one band associated with filled SWCNTs. Corresponding absorption spectra of these bands are shown in a 1% DOC aqueous solution and compared to the parent dispersion (black). All spectra are normalized at 270 nm and offset vertically to aid comparison.

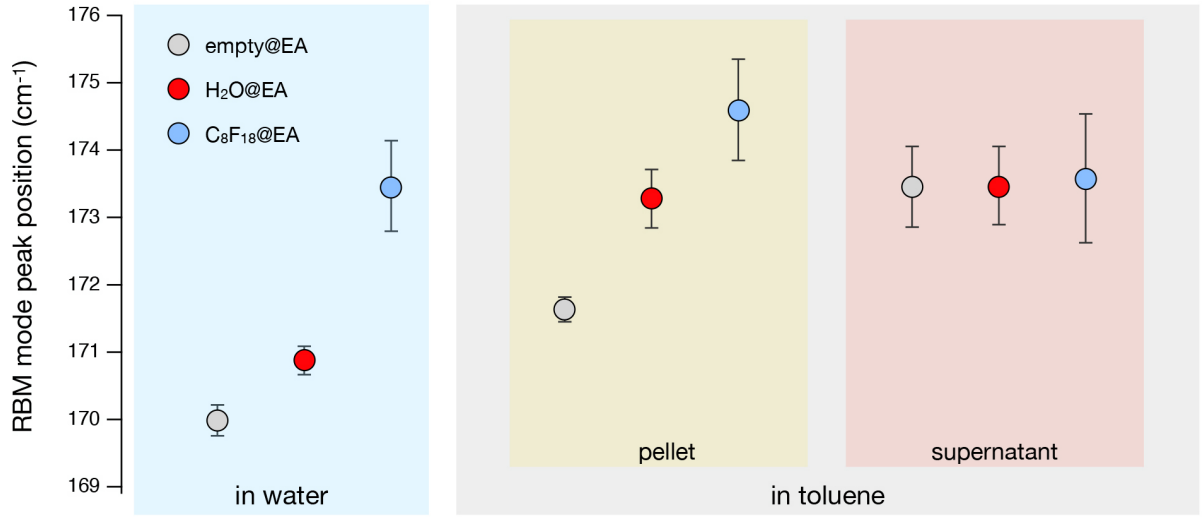

Figure S2. Multiple resonant Raman measurements with 532 nm excitation of the empty EA, H_2O@EA and C_8F_{18}@EA samples dispersed in water along with the pellet and supernatant after transfer to toluene using PFO-BPy.

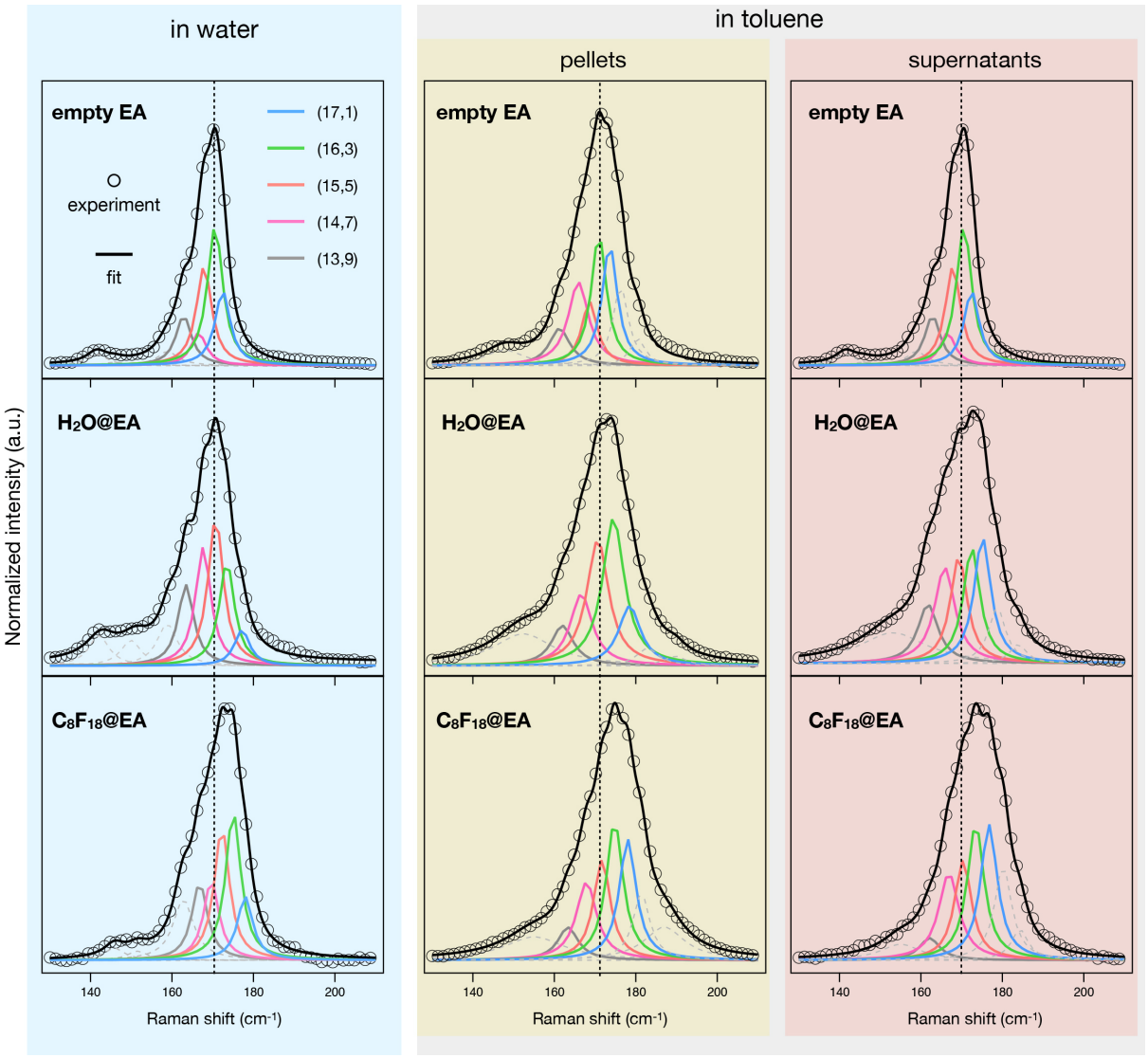

Figure S3. Resonant Raman spectra measured at 532 nm. The radial breathing mode (RBM) region for empty EA, H_2O@EA and C_8F_{18}@EA samples is shown in water along with the pellet and supernatant after transfer to toluene using PFO-BPy. Experimental spectra are shown as empty circles and these are fit with the solid black line and de-convoluted into 5 chiral species: (17,1) blue, (16,3) green, (15,5) orange, (14,7) pink and (13,9) grey.

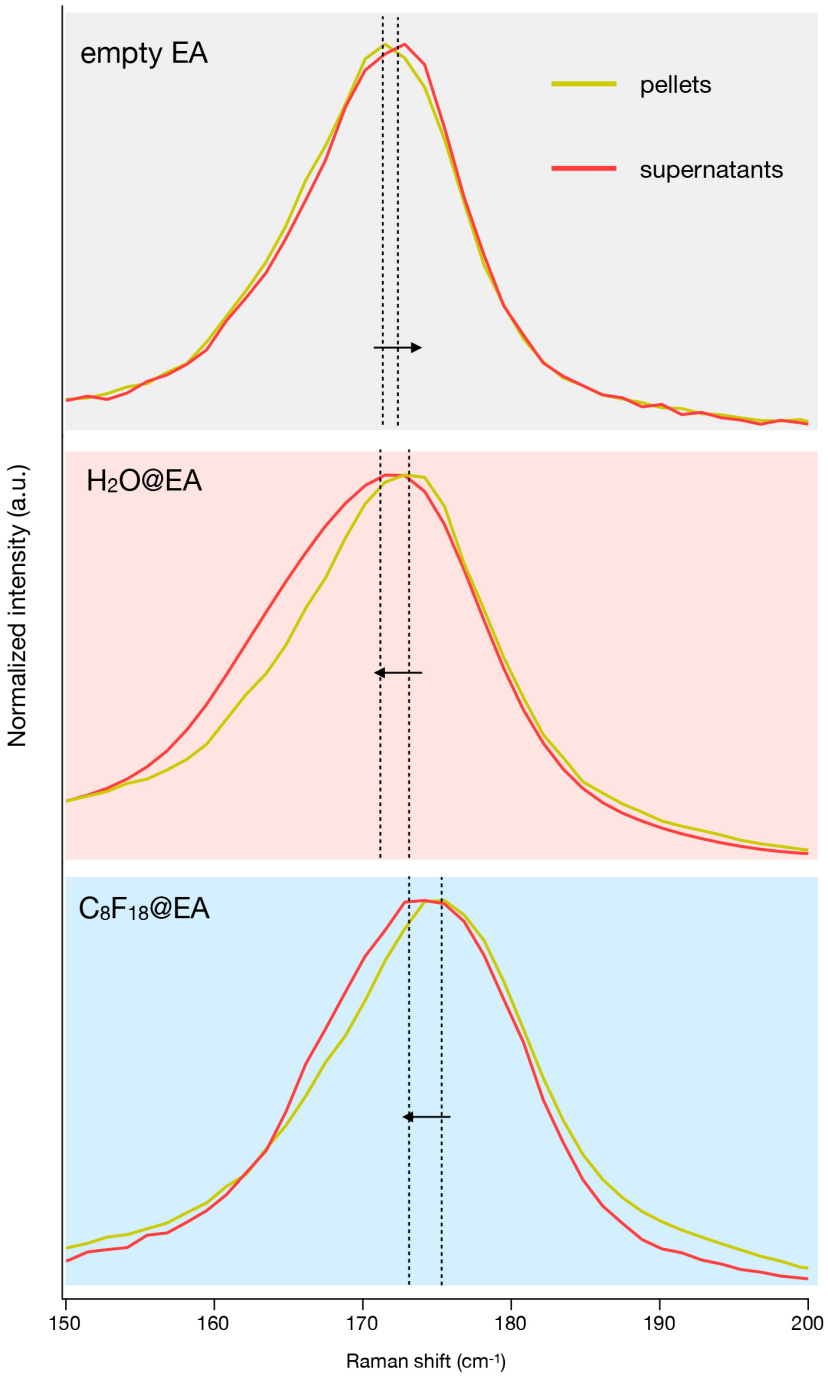

Figure S4. Resonant Raman spectra measured at 532 nm showing the radial breathing mode (RBM) region for empty EA, H_2O@EA and C_8F_{18}@EA in the pellet and supernatant after PFO-BPy wrapping in toluene.

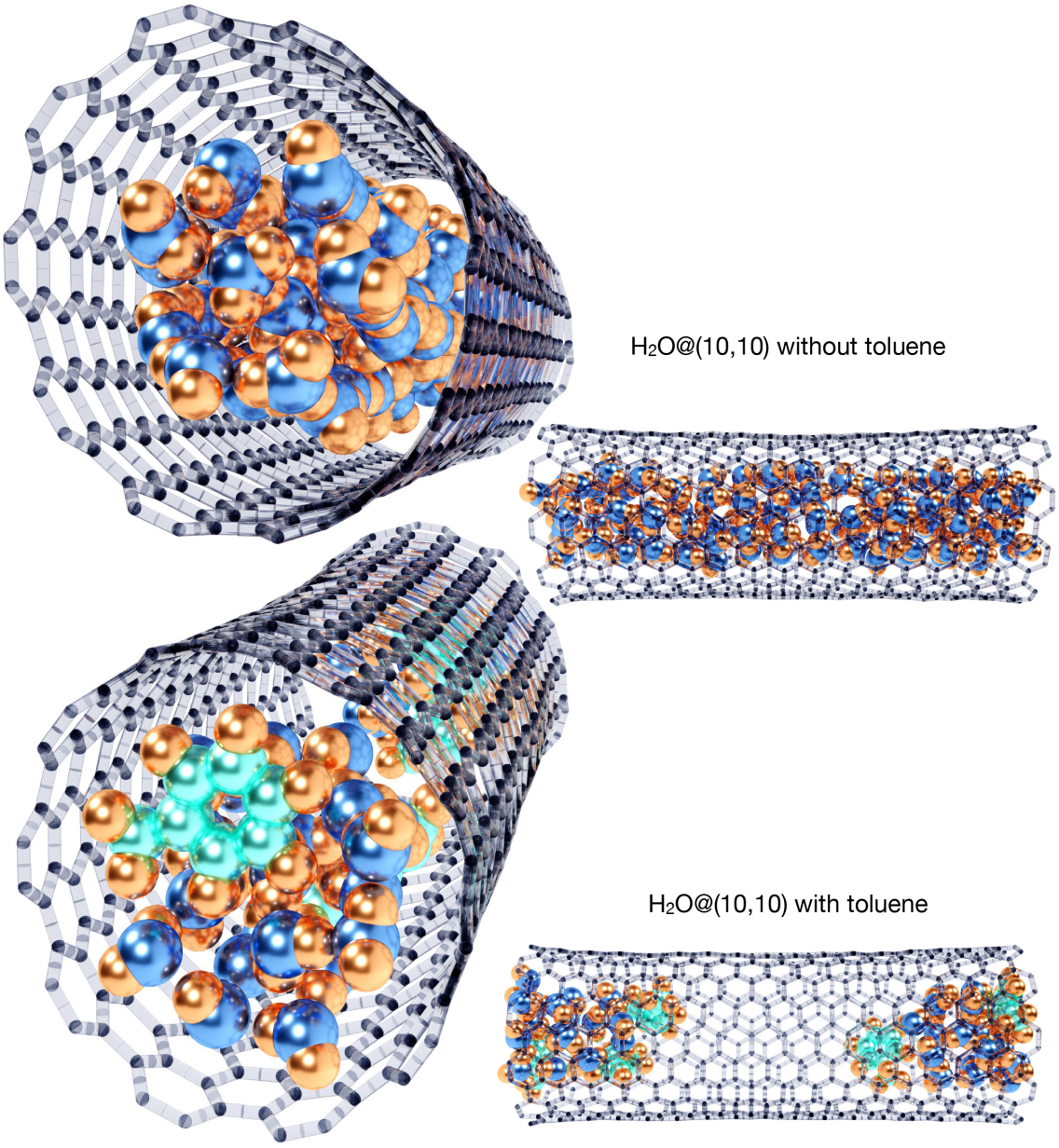

Figure S5. Enlarged view of the simulation of H_2O@(10,10) without and with toluene molecules shown in Figure 4 (c).

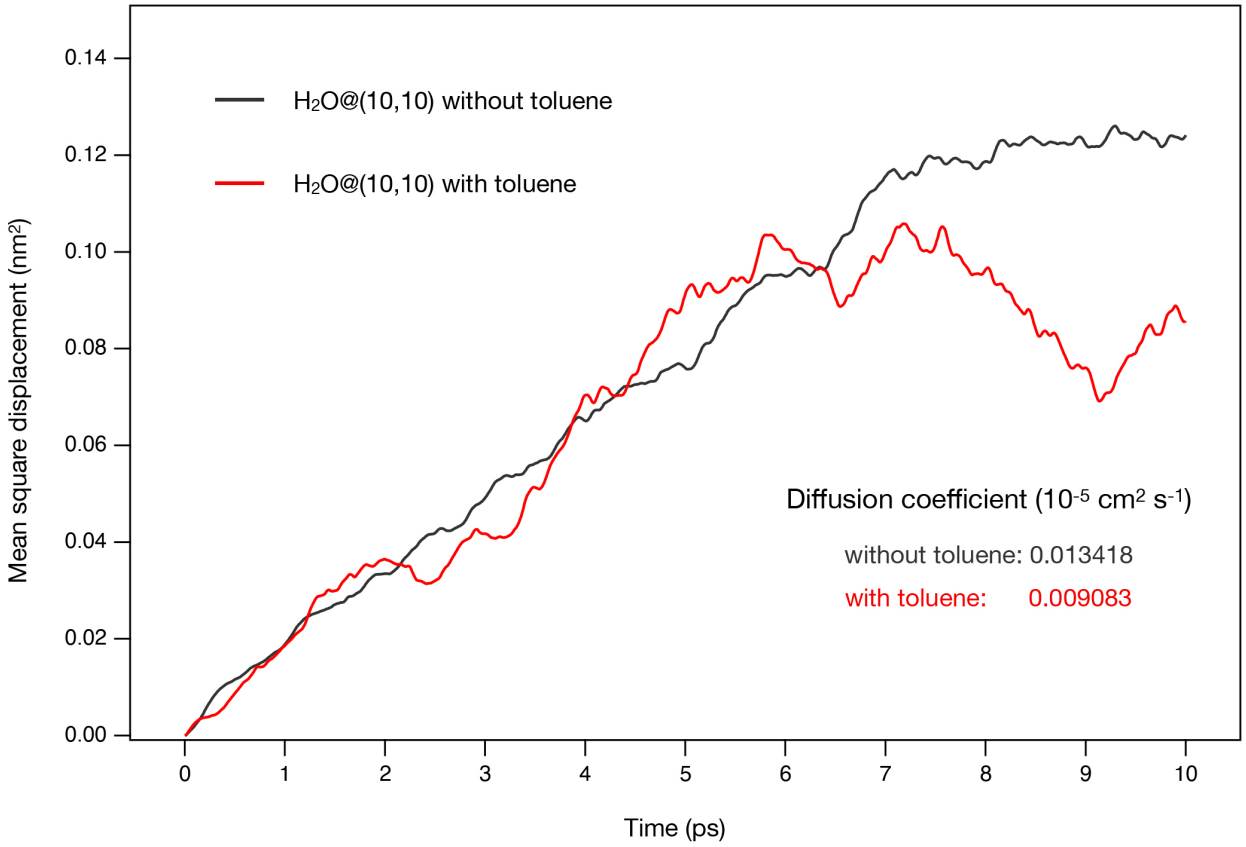

Figure S6. Mean square displacement plots of the water molecules of H_2O@(10,10) without and with toluene molecules.

	RBM peak positions in water (cm^{-1})			RBM peak positions in toluene (cm^{-1})					
				pellets			supernatants		
	empty EA	H_2O@EA	C_8F_{18}@EA	empty EA	H_2O@EA	C_8F_{18}@EA	empty EA	H_2O@EA	C_8F_{18}@EA
(17,1)	172.4	177.2	177.9	173.5	176.7	178.8	174.7	175.1	176.7
(16,3)	170.5	173.4	175.0	170.9	173.8	175.3	172.2	172.5	173.4
(15,5)	167.8	170.7	172.2	168.5	170.5	172.1	169.3	169.3	170.3
(14,7)	166.5	167.6	169.6	165.9	166.8	168.1	165.6	165.8	166.8
(13,9)	162.8	163.4	166.8	161.3	162.0	163.4	161.4	161.7	162.1

Table S1. RBM peak positions of fitted Raman spectra for the different (n,m) species shown in Figure S2.

Chirality	Standard Deviation (cm^{-1})	Systematic Error (cm^{-1})	Total Error (cm^{-1})
(13,9)	0.976355345	0.39539661	1.053379437
(14,7)	0.776857518	0.307003003	0.835319369
(15,5)	0.6995058	0.213941904	0.731491286
(16,3)	0.602864193	0.180465874	0.62929577
(17,1)	0.706158876	0.178847971	0.728455184

Table S2. Summary of the error associated with the RBM fitting procedure. Statistical error represents standard deviation, calculated using multiple different Raman spectra acquired from the same sample. The systematic error is obtained using peak-o-mat software for a given model.

System	n_w	n_{Tol}	n_C	x	y	z
(10,10) without toluene	110	-	680	4.000	4.000	4.000
(10,10) with toluene	40	5	680	4.000	4.000	4.000
H_2O in toluene	216	787	-	7.551	7.551	7.551

Table S3. Details of the simulated systems: number of H_2O molecules (n_w); number of toluene molecules (n_{Tol}); number of carbon atoms constituting the nanotube (n_C); dimensions of the simulation cell along X, Y and Z (in nm).

References

1. Cambré, S.; Wenseleers, W., Separation and Diameter‐Sorting of Empty (End‐Capped) and Water‐Filled (Open) Carbon Nanotubes by Density Gradient Ultracentrifugation. *Angew. Chem. Int. Ed.* **2011**, *50*, 2764-2768.
2. Campo, J.; Piao, Y.; Lam, S.; Stafford, C. M.; Streit, J. K.; Simpson, J. R.; Walker, A. H.; Fagan, J. A., Enhancing Single-Wall Carbon Nanotube Properties through Controlled Endohedral Filling. *Nanoscale Horiz.* **2016**, *1*, 317-324.
3. Li, H.; Gordeev, G.; Garrity, O.; Peyyety, N. A.; Selvasundaram, P. B.; Dehm, S.; Krupke, R.; Cambré, S.; Wenseleers, W.; Reich, S., Separation of Specific Single-Enantiomer Single-Wall Carbon Nanotubes in the Large-Diameter Regime. *ACS Nano* **2019**, *14*, 948-963.