Electronic Supplemental Information

for

Finely tuned water structure and transport in functionalized carbon nanotube membranes during desalination

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In Fig. S1, it was observed that $C_r(t)$ curves of the pristine, as well as $-CH_3$ and -F functionalized (7,7) CNT membranes all display an extremely fast decay, while -OH modification slightly slows the decay of $C_r(t)$. In (8,8) CNT membranes, the methylated membrane demonstrates the largest decay rate of $C_r(t)$, followed by the pristine, -F and then -OH functionalized one. However, the $C_r(t)$ curve decays extremely slowly for pristine (9,9) CNT membrane, while modification with different functional groups all significantly accelerate the decay of $C_r(t)$. In (10,10) CNT membranes, the decline rates of $C_r(t)$ follow the order of -F functionalized > pristine CNT > $-CH_3$ functionalized > -OH functionalized membranes.

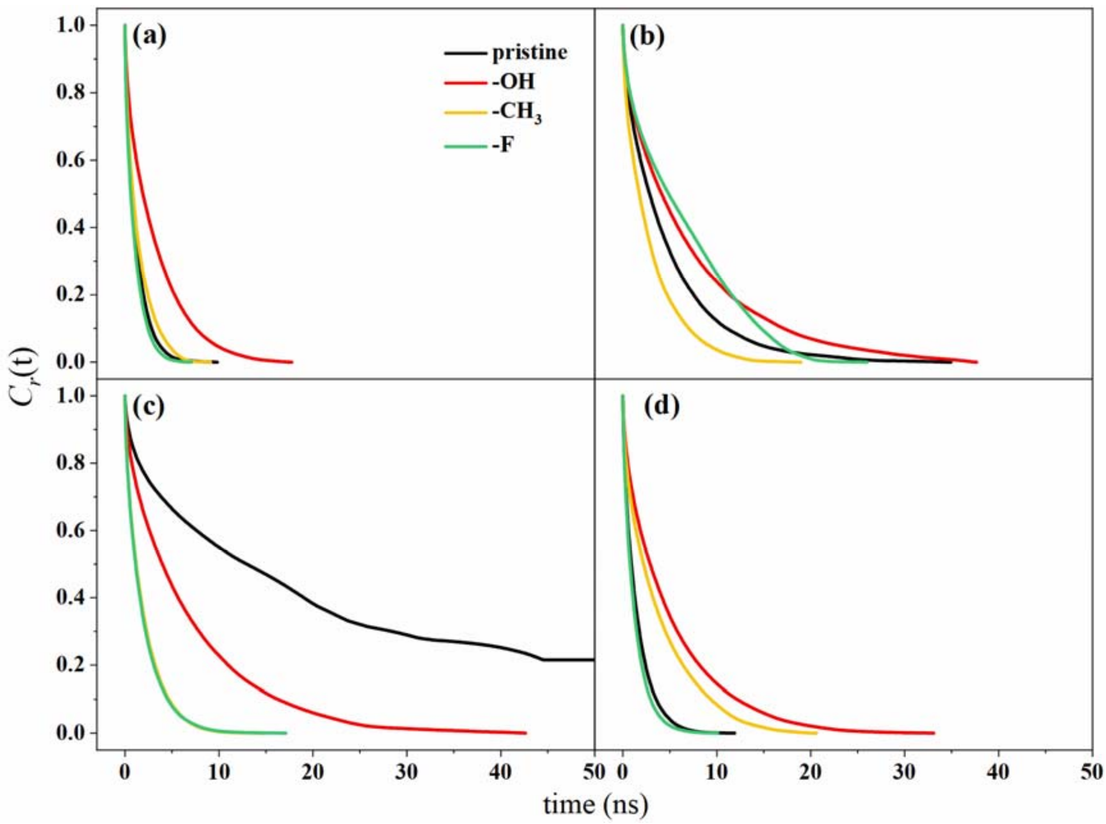

Fig. S1 Residence time autocorrelation functions of water molecules within different CNT membranes: (a) (7,7) CNT; (b) (8,8) CNT; (c) (9,9) CNT; (d) (10,10) CNT.

It can be seen from Fig. S2 that, for almost all pristine and functionalized CNT membranes, N_w increases linearly during the 100 ns of simulation except for the pristine (9,9) CNT that a plateau occurs after 56 ns. The linear-increasing curves indicate the steady-state flows inside CNT membranes. Moreover, we can see from Fig. S2 that both pore diameter and functionalization play an important role in governing water transport. More interestingly, the effects of functional groups on water permeation for different diameter CNT membranes vary significantly.

In pristine (7,7), (8,8) and (9,9) CNT membranes, N_w across the membrane declines with the expansion of CNT diameter. Particularly, no change in the value of N_w was observed for pristine CNT (9,9) after 56 ns, indicating that the water transport rate is almost zero. While N_w is significantly enhanced for a larger diameter (10,10) CNT. For small diameter (7,7) CNT membrane, F-modified CNT possesses a higher N_w compared with the pristine one, but $-CH_3$ and -OH functionalization causes a decrease in N_w. Nevertheless, N_w of methylated membrane is larger than that of the pristine as well as the fluoridated and hydroxylated one for the (8,8) CNT membranes. Both the $-CH_3$ and -F functionalized (9,9) CNT membranes show a significantly higher N_w than the pristine and -OH functionalized membranes. For (10,10) CNT membranes, N_w across the fluorinated membrane is the largest, followed by the pristine, while N_w of the methylated and hydroxylated membranes are much smaller.

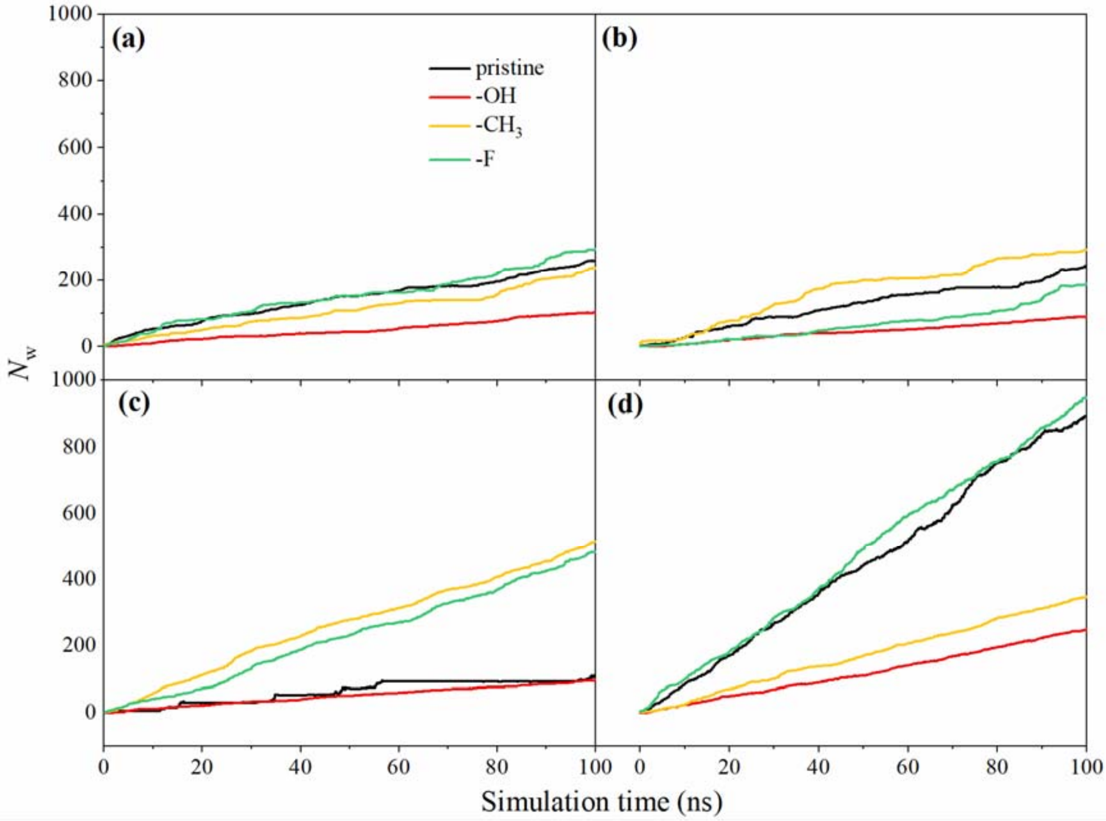

Fig. S2 Number of transferred water molecules N_w through different CNT membranes from saline solution side to pure water side as a function of simulation time: (a) (7,7) CNT; (b) (8,8) CNT; (c) (9,9) CNT; (d) (10,10) CNT.

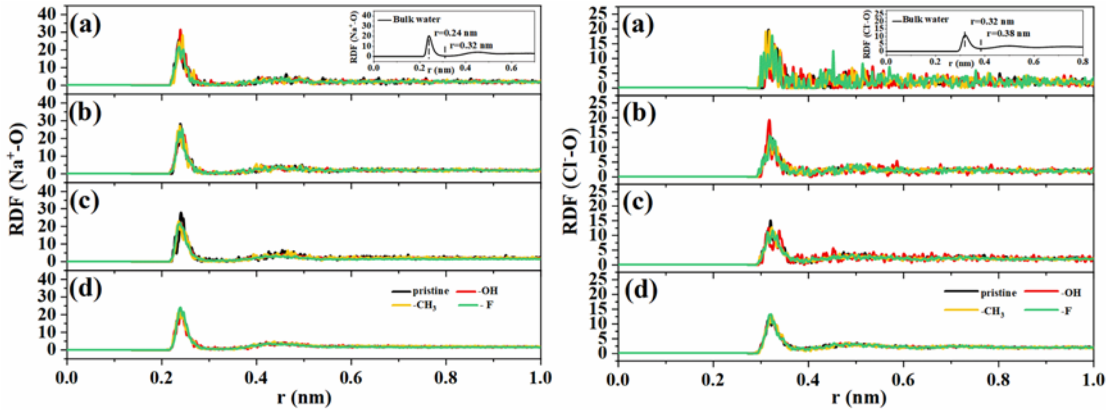

Fig. S3 RDFs of Na^+-O_w (left) and Cl^--O_w (right) for NaCl within a distance of 0.35 nm from the entrance of CNT membranes: (a) (7,7) CNT; (b) (8,8) CNT; (c) (9,9) CNT; (d) (10,10) CNT.

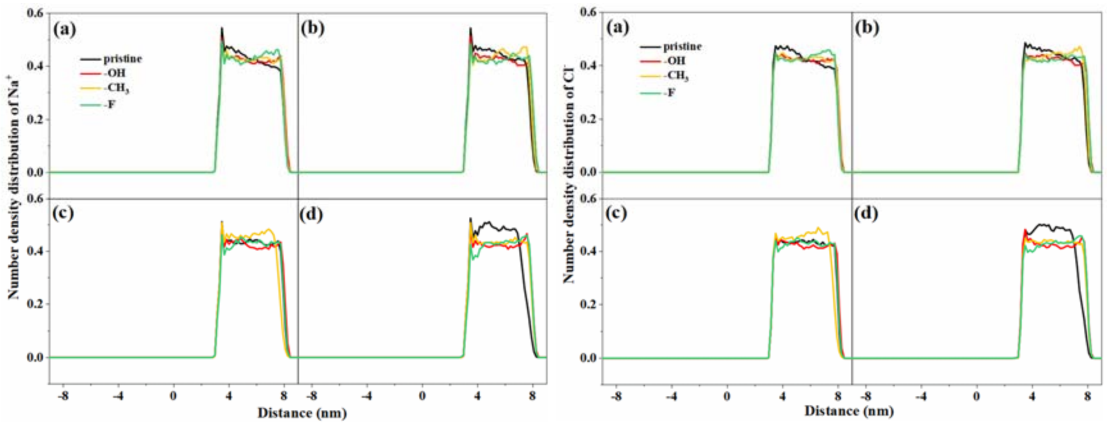

Fig. S4 Number density of Na^+ (left) and Cl^- (right) ions along z coordinate: (a) (7,7) CNT; (b) (8,8) CNT; (c) (9,9) CNT; (d) (10,10) CNT.

Table S1 Coordination numbers of salt ions near entrance of CNT membranes

CNT membranes	Coordination numbers of NaCl	
	Na^+	Cl^-
Bulk water	5.23	6.81
Pristine (7,7) CNT	4.95	6.53
OH-(7,7) CNT	5.37	6.20
CH_3-(7,7) CNT	4.94	6.14
F-(7,7) CNT	4.85	6.40
Pristine (8,8) CNT	4.80	6.65
OH-(8,8) CNT	5.28	6.73
CH_3-(8,8) CNT	5.13	6.69
F-(8,8) CNT	5.16	6.51

Pristine (9,9) CNT	5.48	6.70
OH-(9,9) CNT	5.32	6.52
CH_3-(9,9) CNT	4.79	6.60
F-(9,9) CNT	5.23	6.54
Pristine (10,10) CNT	5.38	6.60
OH-(10,10) CNT	5.17	6.74
CH_3-(10,10) CNT	5.28	6.77
F-(10,10) CNT	5.52	6.74

Table S2 Effective pore diameter (nm) of different CNT membranes

CNT membranes	(7,7) CNT	(8,8) CNT	(9,9) CNT	(10,10) CNT
Pristine CNT	0.350	0.607	0.715	0.815
OH-CNT	0.412	0.574	0.703	0.837
CH_3-CNT	0.331	0.435	0.552	0.662
F-CNT	0.390	0.612	0.645	0.712

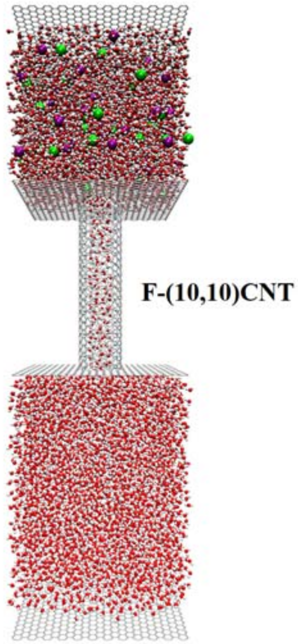

Fig. S5 Snapshot of F-(10,10) CNT membrane system at 100 ns.