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

Ab initio Molecular Dynamics Simulations of Aqueous Triflic Acid Confined in Carbon Nanotubes

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Supplementary Information

Table S1. Hydrogen bond data for the optimized 14N3 system using different methods.

	Avg. O···O Distance (Å)		Avg. H···O Distance (Å)		Avg. $\lvert\delta\rvert$ (Å)[†]	
Functional	H_2O/SO_3H	H_2O/H_2O	H_2O/SO_3H	H_2O/H_2O	H_2O/SO_3H	H_2O/H_2O
PBE	2.65	2.56	1.65	1.53	0.64	0.49
PBE0	2.64	2.55	1.66	1.54	0.67	0.51
HSEsol	2.64	2.55	1.66	1.54	0.67	0.51
PBE-D3	2.65	2.57	1.66	1.53	0.65	0.49
optB86	2.67	2.58	1.67	1.54	0.66	0.50

[†]The value of δ always has water molecules/solvated protons as the hydrogen bond donor.

Table S2. Hydrogen bond data for the optimized 17F3 system using different methods.

	Avg. O···O Distance (Å)		Avg. H···O Distance (Å)		Avg. $\lvert\delta\rvert$ (Å)[†]	
Functional	H_2O/SO_3H	H_2O/H_2O	H_2O/SO_3H	H_2O/H_2O	H_2O/SO_3H	H_2O/H_2O
PBE	2.72	2.51	1.75	1.42	0.75	0.32
PBE-D3	2.73	2.51	1.76	1.42	0.77	0.32
optB86	2.75	2.52	1.77	1.43	0.78	0.33

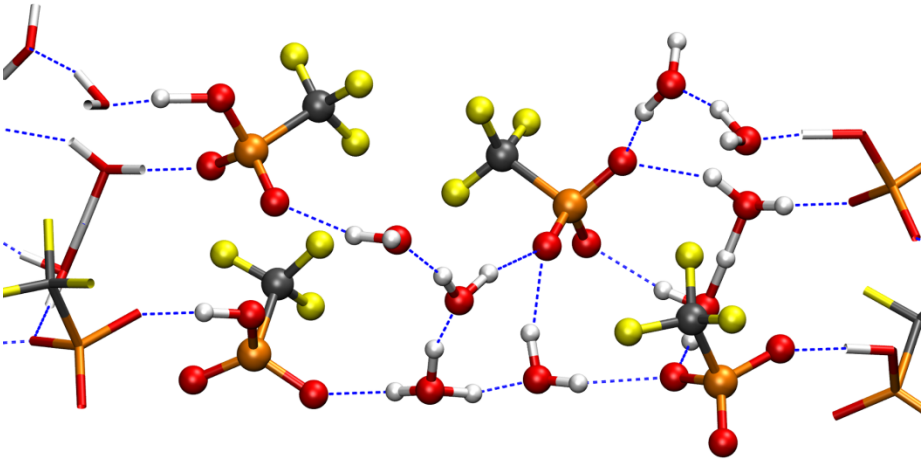
[†]The value of δ always has water molecules/solvated protons as the hydrogen bond donor.

Table S3. 14N3 dissociation data from sample MD runs using PBE and PBE-D2.[†]

Functional	Bound	Shared: SO_3H/SO_3H	Shared: SO_3H/H_2O	Dissociated: Zundel	Dissociated: H_3O^+
PBE	-	-	0.025	0.276	0.699
PBE-D2	-	-	0.026	0.286	0.688

[†] Data represents fraction of time spent in the different states

(a) 17N2



(b) 17F2

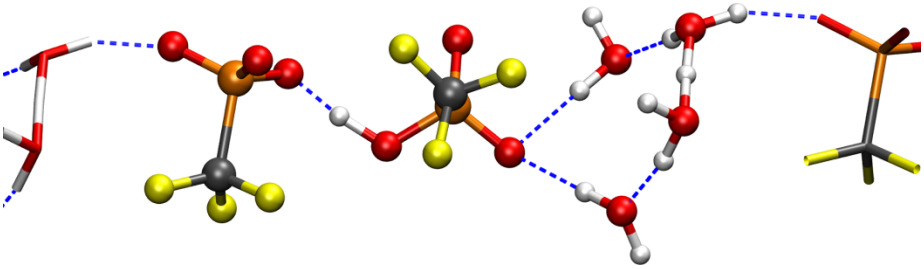
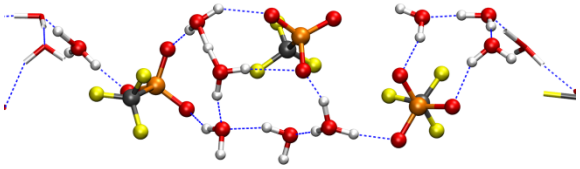
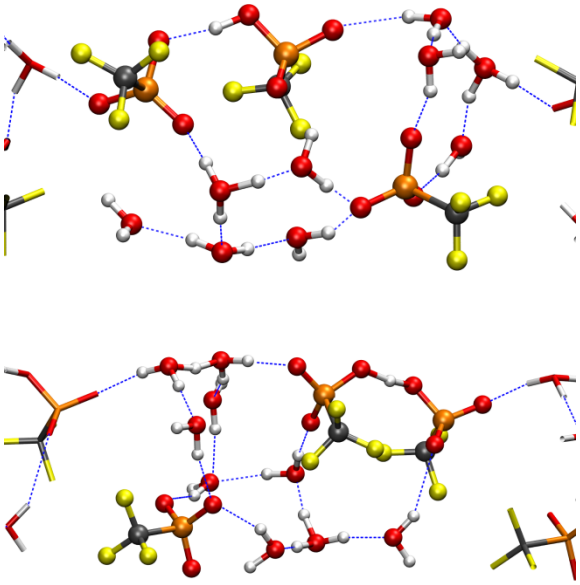


Figure S1. Snapshots showing ring formation in (a) 17N2 and (b) 17F2.

(a) 14N3



(b) 17N3



(c) 17F3

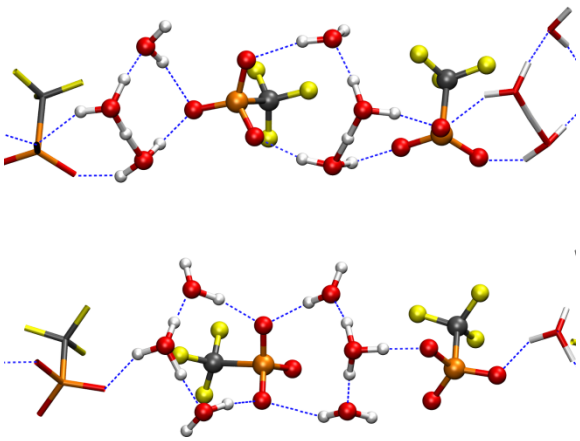


Figure S2. Snapshots showing ring formation in (a) 14N3, (b) 17N3 showing a 5-membered ring (top) and a 9-membered ring, and (c) 17F3 showing a 4-membered ring (top) and an 8-membered ring (bottom).

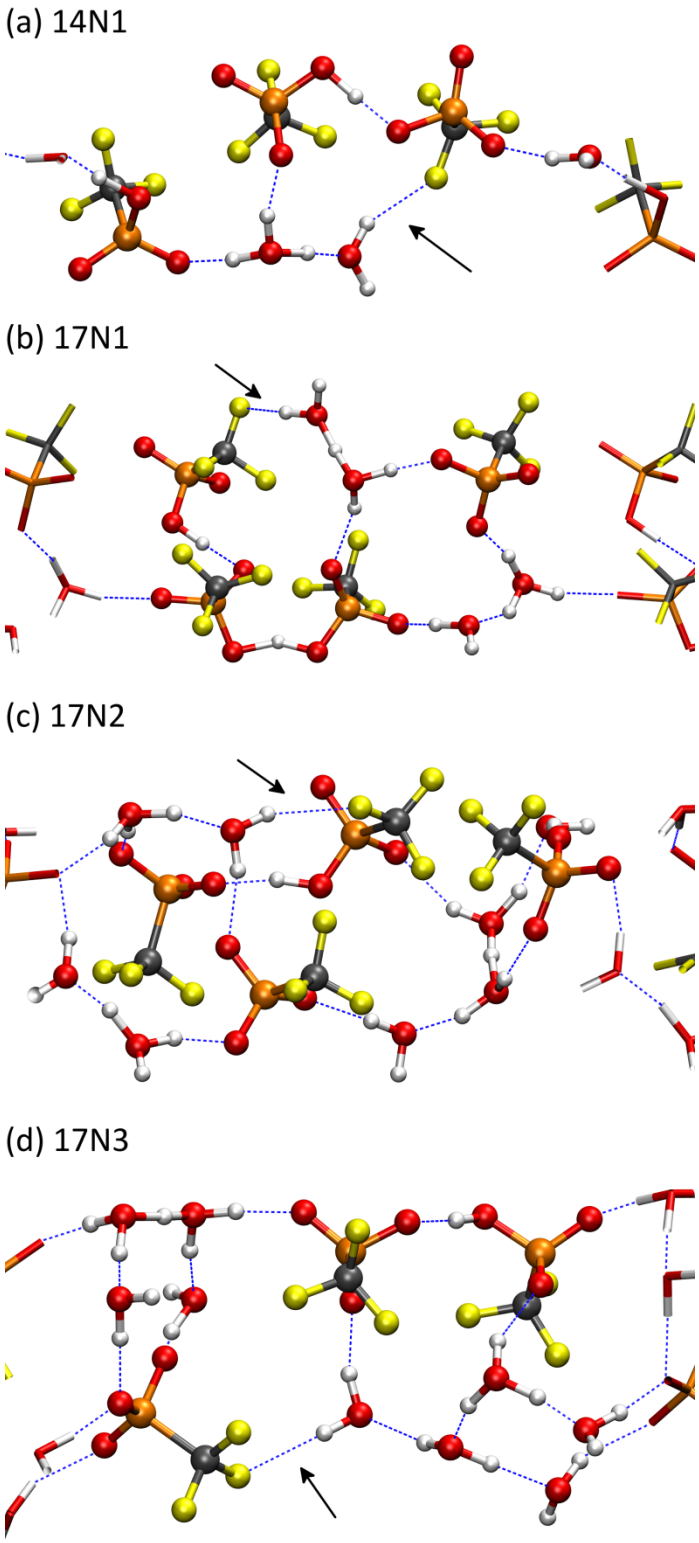


Figure S3. Snapshots of the bare CNT systems that contained OH···F hydrogen bond between water molecules and a fluorine atom of triflic acid over 15% of the time: (a) 14N1, (b) 17N1, (c) 17N2, and (d) 17N3.

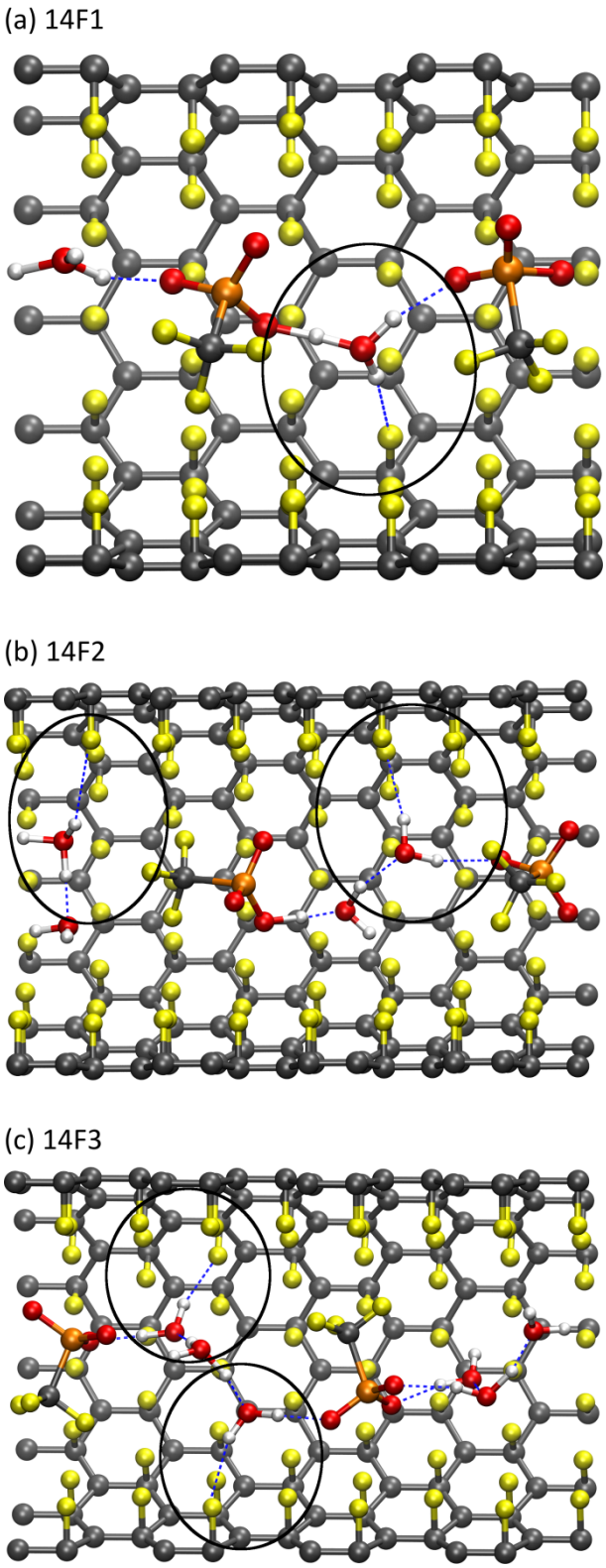


Figure S4. Snapshots of hydrogen bonding to the fluorinated wall in the smaller CNT systems: (a) 14F1, (b) 14F2, and (c) 14F3.

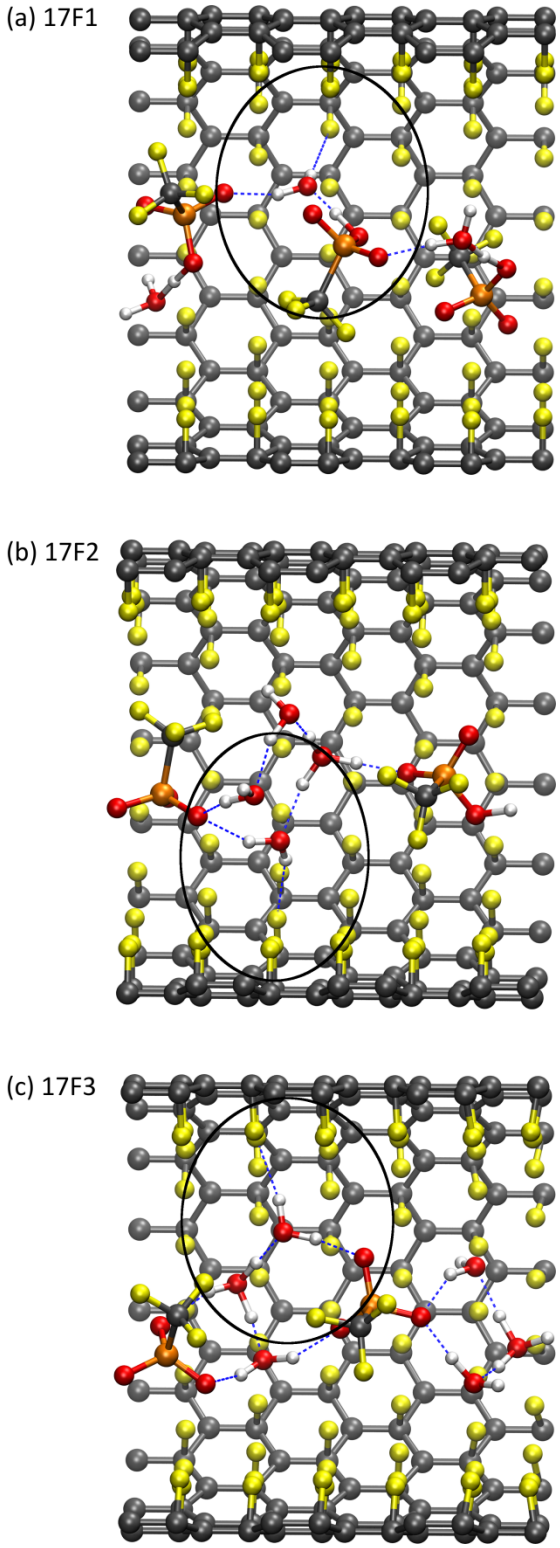


Figure S5. Snapshots of hydrogen bonding to the fluorinated wall in the larger CNT systems: (a) 17F1, (b) 17F2, and (c) 17F3.