Electronic Supplementary Information (ESI)

Unanticipated favoured adsorption affinity of Th(IV) ions towards bidentate carboxylate functionalized carbon nanotubes (CNT-COOH) over tridentate diglycolamic acid functionalized CNT: Density functional theoretical investigation

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Table S1. Calculated structural parameters (in Å) of Th^{4+} ion with HCOOH, DGA and C_{60}-COOH at BP/SVP level of theory.

Species	M-O distance (Å)			
	amide O	carboxy O	ethereal O	alcoholic O
HCOOH		1.994		4.146
DGA	2.182	2.198	2.495	
C_{60}-COOH		2.078		2.357

Table S2. Calculated various molecular descriptors (eV) at B3LYP/TZVP level of theory.

	E_{HOMO}	E_{LUMO}	E_{LUMO}-E_{HOMO}	χ	η	$\Delta N(Th^{4+})$	$\Delta N(Th^{4+}$-$(H_2O)_8)$
Th^{4+}	-56.23	-34.09	22.13	45.16	11.06		
Th^{4+}-$(H_2O)_8$	-25.46	-17.58	7.87	21.52	3.93		
CNT-DGA	-4.32	-3.91	0.41	4.11	0.205	1.820	2.101
CNT-COOH	-4.24	-3.83	0.40	4.03	0.200	1.824	2.111
C_{60}-COOH	-5.85	-4.14	1.70	4.99	0.85	1.684	1.725

Table S3. Calculated values of interaction energies (kcal/mol) at B3LYP/TZVP level of theory.

Various stoichiometric reaction	ΔE
CNT-DGA + Th^{4+} = CNT-DGA-Th^{4+}	-875.61
CNT-COOH + Th^{4+} = CNT-COOH-Th^{4+}	-792.84
C_{60}-COOH +Th^{4+} = C60-COOH-Th^{4+}	-627.06
HCOOH= Th^{4+} = HCCOH-Th^{4+}	-292.65
HDGA + Th^{4+} = HDGA-Th^{4+}	-581.46

Table S4. Comparison of bond distances in Å from Th^{4+} metal centre for complexes/system under consideration without nitrate at BP/SVP level of theory with and without dispersion-corrected DFT of Grimme's D3 scheme.

Bond	DFT-D				Without DFT-D			
	System of Th^{4+} bonded with							
	CNT-Side Surface	CNT-Open End	CNT-COOH	CNT-DGA	CNT-Side Surface	CNT-Open End	CNT-COOH	CNT-DGA
Th-C* (CNT)	2.552	-	-	-	2.542	-	-	-
Th-H(CNTedge)	-	4.013	-	-	-	3.935	-	-
Th-O$^{\#}$(COOH)	-	-	2.265	-	-	-	2.265	-
Th-O$^{\#}_{carbonyl}$(DGA)	-	-	-	2.192	-	-	-	2.205
Th-O_{ether}(DGA)	-	-	-	2.440	-	-	-	2.480

*M-C: distances between metal and nearest six carbon atoms of a hexagon the CNT; # Average of two similar Th-O distances.

Table S5. Comparison of electronic and thermodynamic energies (in kcal/mol) of Th^{4+} ion with non-functionalized and functionalized CNT in absence of nitrate ion at two level of theory: (i)# Geometry optimization at BP with Grimme's D3 dispersion correction/SVP & single point energy at B3LYP/TZVP level and (ii)† Geometry optimization at BP with Grimme's D3 dispersion correction/SVP & single point energy at B3LYP with Grimme's D3 dispersion correction /TZVP level.

Complexation reaction	ΔE (i)#	ΔE (ii)†
$Th^{4+} + CNT_S = CNT_S\text{-}Th^{4+}$	-760.61	-764.28
$Th^{4+} + CNT_O = CNT_O\text{-}Th^{4+}$	-754.62	-765.84
CNT-COOH + Th^{4+} = CNT-COOH-Th^{4+}	-792.83	-793.96
CNT-DGA + Th^{4+} = CNT-DGA-Th^{4+}	-891.37	-884.54
$Th^{4+}(H_2O)_8 + CNT_S = CNT_S\text{-}Th^{4+} + 8H_2O$	22.98	35.14
$Th^{4+}(H_2O)_8 + CNT_O = CNT_O\text{-}Th^{4+} + 8H_2O$	28.97	33.58
CNT-COOH + $Th^{4+}(H_2O)_8$ = CNT-COOH-Th^{4+} +$8H_2O$	–9.23	5.46
CNT-DGA + $Th^{4+}(H_2O)_8$ = CNT-DGA-Th^{4+} +$8H_2O$	–107.77	-85.11

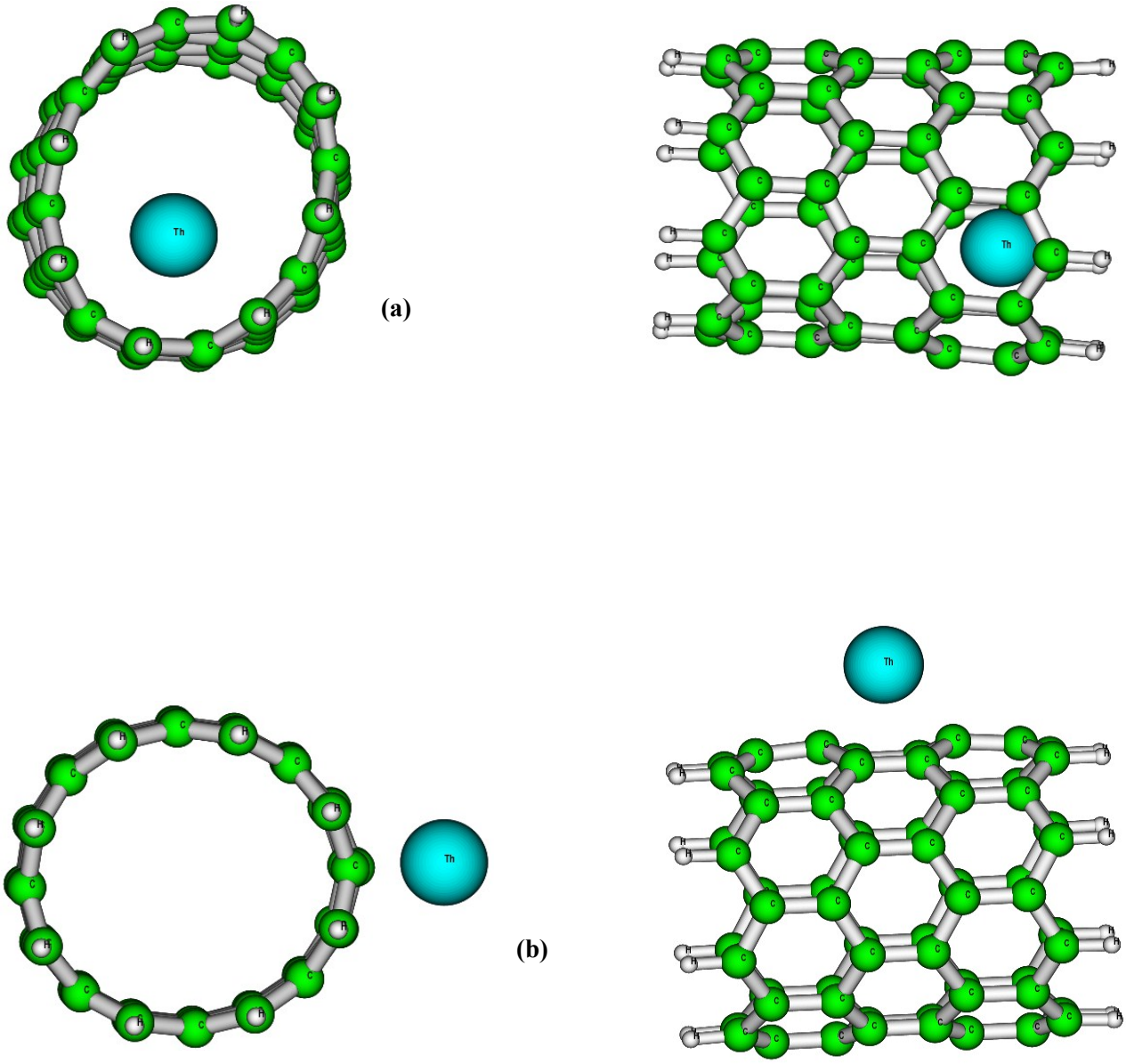


Fig. S1. Optimized structures of complexes of Th^{4+} ion with non-functionalized/pristine CNT: (a) Interaction from sidewall of CNT (CNT_s) and (b) from open edges of CNT (CNT_o) at BP/SVP level of theory.

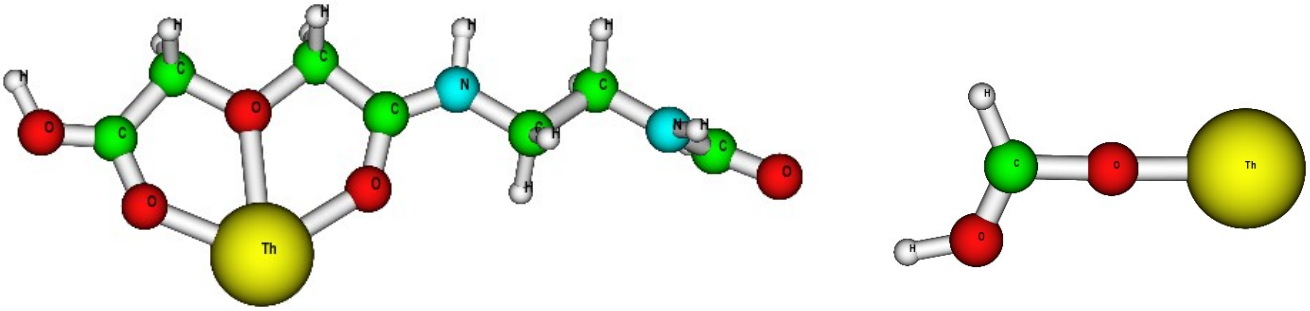


Fig. S2. Optimized structures of Th^{4+} complexes with DGA and COOH unit (connected to CNT in CNT-DGA and CNT-COOH, respectively) at BP/SVP level of theory.

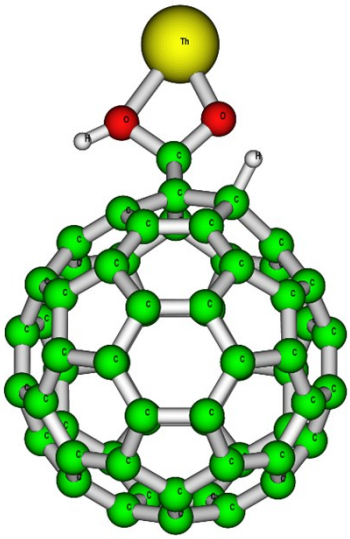


Fig. S3. Optimized structure of Th^{4+} complexes with C_{60}-COOH at BP/SVP level of theory.

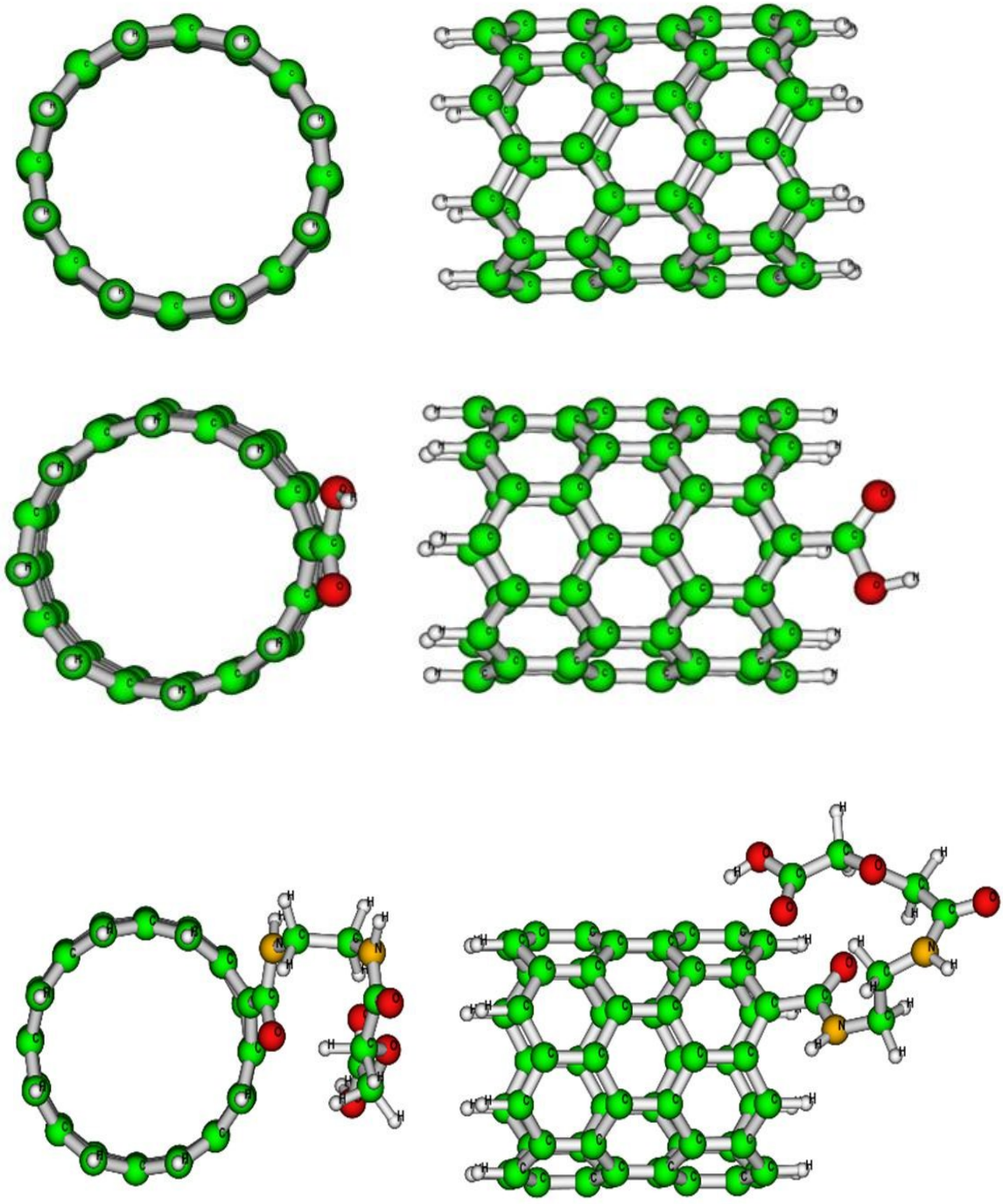


Fig. S4. Optimized geometries of pristine and COOH and DGA functionalized CNT at BP/SVP level of theory with dispersion-corrected DFT of Grimme's D3 scheme.

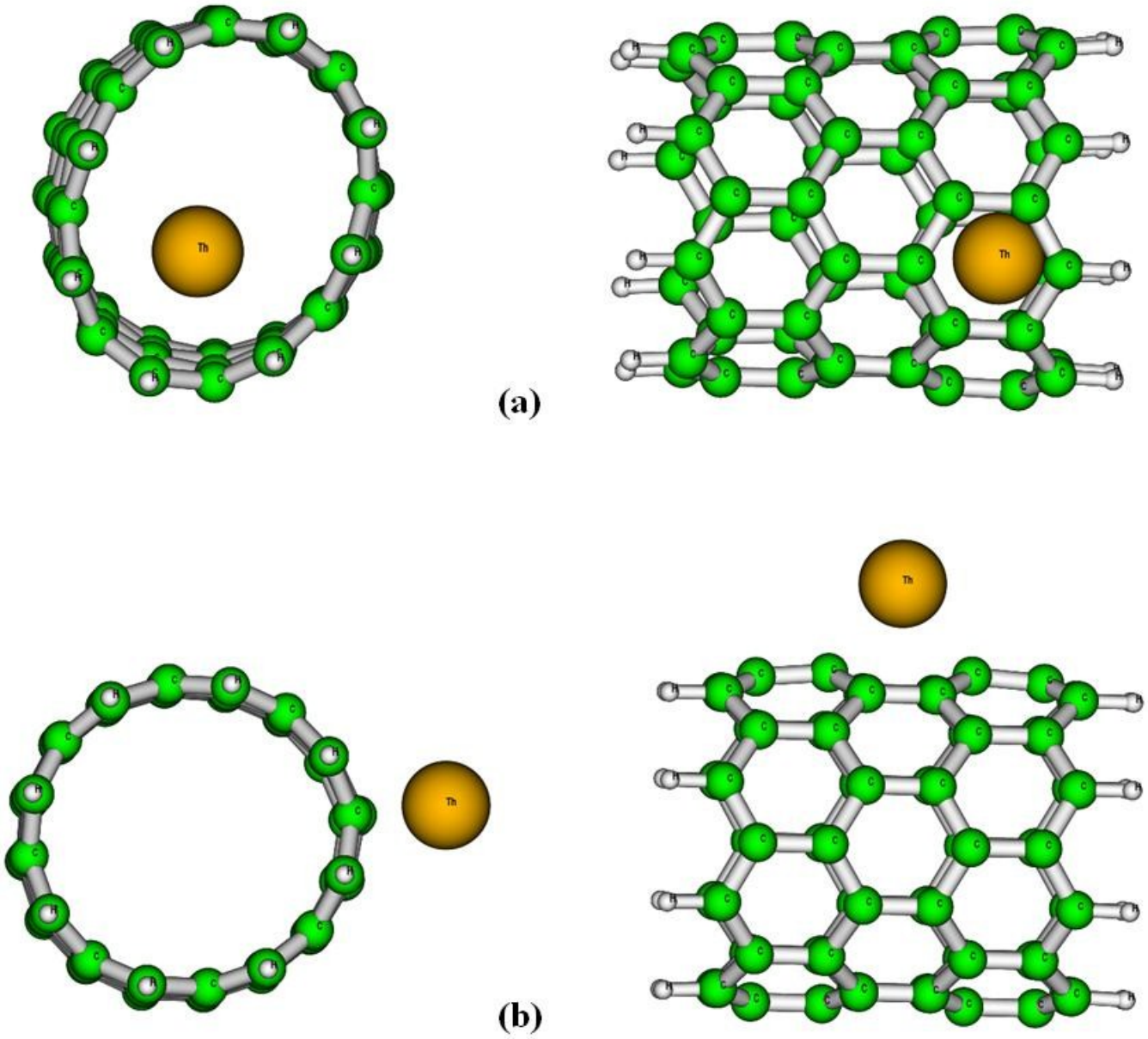


Fig. S5. Optimized structures of complexes of Th^{4+} ion with non-functionalized/pristine CNT at BP/SVP level of theory with dispersion-corrected DFT of Grimme's D3 scheme: (a) Interaction from sidewall of CNT (CNT_s) and (b) from open edges of CNT (CNT_o).

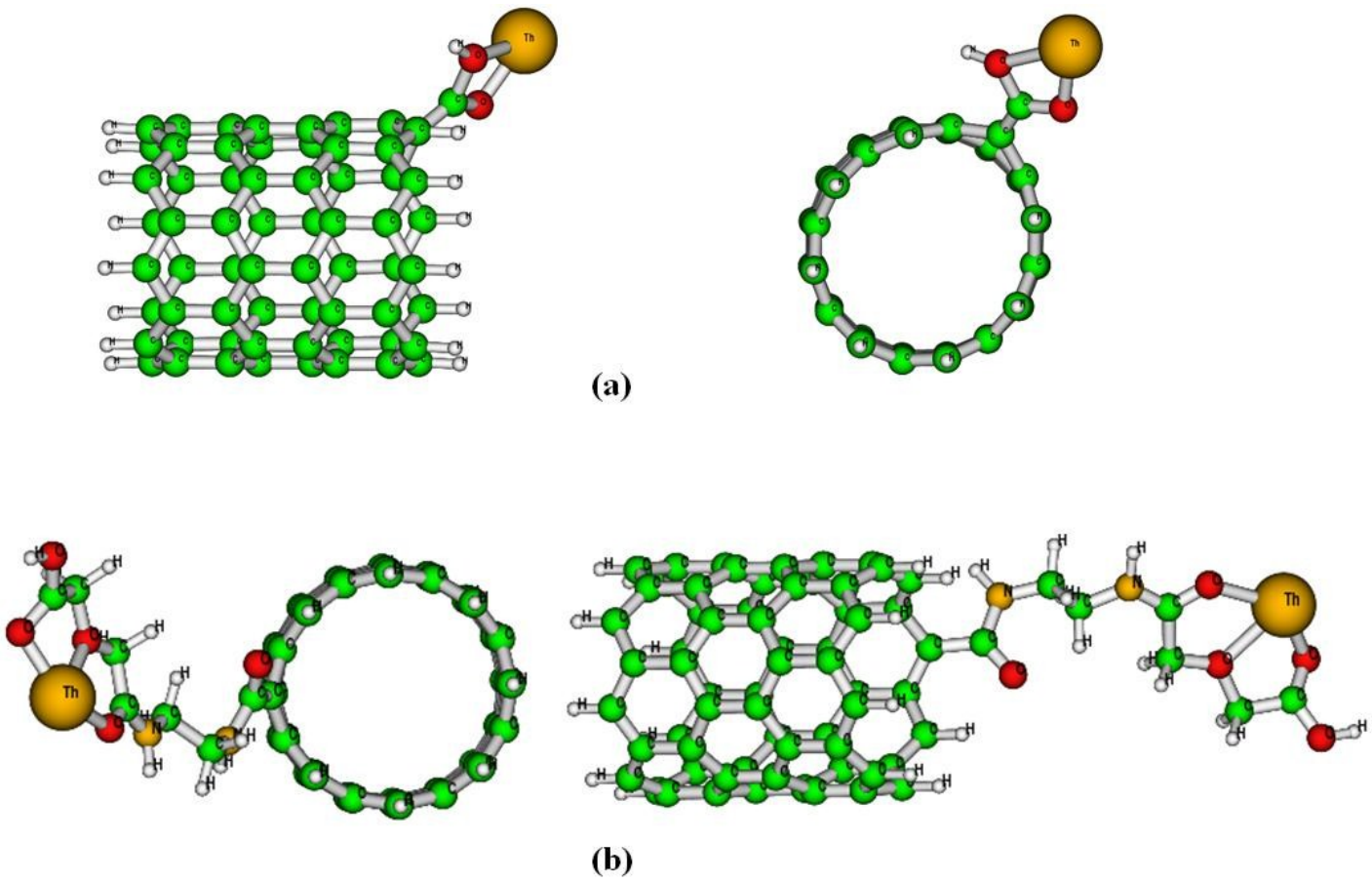
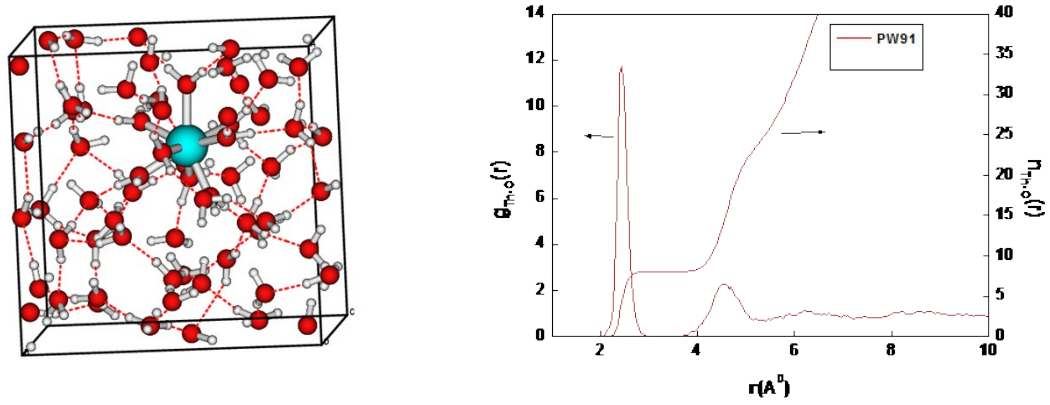


Fig. S6. Optimized structures of Th^{4+} ion complex with (a) CNT-COOH, and (b) CNT-DGA, at BP/SVP level of theory with dispersion-corrected DFT of Grimme's D3 scheme.

AIMD simulation of Th^{4+}-water system

AIMD simulation was carried out using Perdew-Wang 91 (PW91) density functional with projector augmented wave method as implemented in VASP simulation package[S1]. The MD simulation box consists of one Th^{4+} ion and 64 water molecules in a cubic simulation cell of dimension 12.50Å×12.50Å×12.50Å with standard periodic boundary condition resulting into water density of 1g/cc. The cutoff value of 984.83 eV was used for kinetic energy. The final temperature was kept at 440K to maintain the system at liquid state. Nose-Hoover thermostat was employed in the NVT ensemble with time step of 1 fs for total simulation run of 30 ps. The trajectories of last 10ps were used to calculate the radial distribution function of Th^{4+} ion water system and then first solvation shell coordination number. The first sphere coordination number calculated from the integrated RDF was found to be 8.00.



(a) **(b)**

Fig. S7. (a) AIMD snap shot of Th^{4+}-$(H_2O)_{64}$ system and (b) radial distribution function of Th-O ($g_{Th\text{-}O}(r)$) using PW91.

Reference

S1. G. Kresse and J. Hafner, Phys. Rev. B, 1993, 48, 13115–13118.