Supporting Information

Trapping and Sensing Hazardous Insecticides by Chemically Modified Single Walled Carbon Nanotubes

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Computational Details:



Figure S1: Supercell consideration for our calculations. Red, green and blue sides are x, y and z axes, correspondingly. In y axis (shown in green here) also we apply \sim 46 Å cell length to maintain a vacuum of 20 Å in each side of the nanotube. In the z axis, 'a' depicts the length of the nanotube.

Water molecules considered for the calculations:

We have considered 75 and 105 water molecules around the nanotube to consider the effect of water medium in pesticide trapping. This represents a low water concentration but can give rise to a hydration sphere near the metal atom. This type of explicit water medium consideration has been already employed in some previous studies to find the water-substrate interaction pattern.¹⁻³ Firstly, we equilibrate the nanotube and water molecules and find that water molecules create a hydration environment near the metal atom. Next, we adsorb the pesticide molecule and run the simulation again and find that still the molecule adsorbs on the CNT surface. Six water molecules remain near the metal atom, creating a hydration sphere near the TM atom. Other water molecules do not interact directly with the TM atom, thus do not affect the TM-molecule binding directly, though they can affect the molecular configuration on the CNT. Thus, we find that the number of water molecules does not directly affect the hydration environment near the metal atom, thus both our models can capture the type of interaction present in the system.



Figure S2: V@3N-(5, 5) CNT and DDT composite in presence of 105 water molecules.

Structural equilibration:

We find a binding energy of ~-13.1 kcal/mol for DDT adsorbed on pristine CNT at 0K i.e. performing DFT-based optimization. After that we perform MD with the optimized structure.

The following figures indicate the achievement of equilibrium in our systems. The Energy vs. Time plot suggests the energy fluctuates around a mean value after equilibration is reached. This fluctuation comes from the flexible nature of the molecule.



Figure S3: Potential energy vs. time plot for V@3N (5, 5) CNT + DDT, DDD and DDE composites.



Figure S4: Time evolution of distance between pristine CNT + (a) DDT and (b) DDE in 300 K. Note that, distance can be more than 20 Å as the molecules can access the corners of the box as well.



Figure S5: Bond length variation with simulation time, where the Distance calculated is between a C atom from a benzene ring of DDT and the metal atom, V, as indicated in the inset. Note that, this distance is slightly greater than the molecule-TM distance reported in main manuscript, as there we calculate the distance between the TM and the centre of the benzene ring.



Figure S6: Snapshots of the DDT and V@3N-(5, 5)-CNT composite from the last 5 ps of the simulation.

Binding energy and adsorption energy:

We have calculated binding energies using the formula $E_{\text{bind}} = E_{\text{CNT+molecule}} - E_{\text{CNT}} - E_{\text{molecule}}$, where, E_{bind} is the binding energy, $E_{\text{CNT+molecule}}$ is the energy of the CNT-molecule composite, E_{CNT} is the energy of the optimized CNT and E_{molecule} is the energy of the optimized isolated molecule. We have taken 20 snapshots from the last 5 ps of the equilibrated structures and calculated the binding energy. As the total energy of the system fluctuates around a mean value, the mean binding energy is considered. We have defined another parameter,

$$E_{\text{adsorption}} = E_{\text{CNT+molecule}} - E_{\text{CNT (single pt.)}} - E_{\text{molecule (single pt.)}}$$

Where, $E_{adsorption}$ is the adsorption energy, $E_{CNT+molecule}$ is the energy of the CNT-molecule composite, E_{CNT} is the energy of the CNT separately taken from the composite and single point energy calculated and $E_{molecule}$ is the energy of the isolated molecule separately taken from the composite and single point energy calculated. We find that, naturally, $E_{adsorption}$ is slightly greater than E_{bind} . For example, V@3N-(5, 5) CNT and DDT complex shows the biding energy value of -56.5 kcal/mol, whereas, the $E_{adsorption}$ value is -58.4 kcal/mol. Note that, for adsorption energy, we do not have to take a mean value, as both the CNT and molecular structure is obtained from the composite. Thus, it always shows similar adsorption energies.

In case of imidacloprid molecule, binding through the 5-membered ring leads to a less stable complex. The pyridinic ring binding generates a CNT-molecule complex, which is 1.2 eV more stable than the complex formed through 5 membered ring. This happens because of the presence of side chains on both sides of the 5-membered ring. Due to the presence of these bulky side chains, the molecule prefers to interact via the pyridinic ring.





Figure S7: Equilibrated structures of (a) DDT+Fe@3N-(5, 5) CNT, (b) DDD+Fe@3N-(5, 5) CNT, (c) DDE+Fe@3N-(5, 5) CNT, (d) DDT+Cu@3N-(5, 5) CNT, (e) DDD+Cu@3N-(5, 5) CNT and (f) DDE+Cu@3N-(5, 5) CNT

Optical properties:

The optical absorption spectra of the isolated molecules are in UV range, thus, the peaks in the IR range of composite systems do not appear because of the molecular transition, and rather they are the CNT π - π transition peaks or the CNT-molecule charge transfer peaks. Interestingly, DDE shows a stronger absorption than DDT or DDD (see Figure S6). This appears because of the extended π conjugated molecular structure of DDE.



Figure S8: Optical absorption spectra of the isolated molecules (a) DDT, (b) DDD and (c) DDE. (d) Depicts the wavefunction plots corresponding to the transition of DDE.



Figure S9: Optical absorption spectra of Fe@3N-(5, 5)-CNT and their molecular complexes in presence of implicit water medium considered in a quantum mechanical continuum solvation models (PCM).⁴ This suggests the nanotubes are able to sense the molecule even in water medium.

In Presence of water, the peak around 1190 nm for the pure CNT shifts because of molecule-CNT interactions. For DDT, the peak shifts to around 1050 nm, showing clear signatures of molecular adsorption. For DDE, again we observe a very intense peak around 1380 nm, because of the presence of extended conjugation.

Different initial conformations and g(r) Plot:

We have considered different initial conformations and simulate them at ambient condition. However, we find reluctance of adsorbate molecules towards getting adsorption on CNT surfaces within our simulation timescale (see Figure S10). This indicates that the resulting weak interaction between molecules and CNTs is not biased by our chosen initial conformation. From these results, we further speculate, during very long simulation even if the molecules come back in the vicinity of CNTs, these will be repealed by the CNTs and will stay far.



Figure S10: (a)-(c) different initial and (a')-(c') final configuration of DDT on pristine CNT (after 10 ps).

To find the distribution of distances between adsorbate molecules (i.e. DDT, DDD, DDE) and CNT (pristine as well as functionalized) over simulation time, we further plot the g(r) of the composites. The most probable adsorbate-adsorbent distance (r) has been calculated and tabulated in Table S1 from the g(r) peak with highest amplitude.

The distribution of distances (g(r)) between the benzene ring of the molecules and the CNT are plotted considering trajectory of 25 ps simulation-time. From Figure S11(a-c), we find that the most probable distances of the benzene ring of the adsorbates and the pristine CNT are quite large (>10Å, see Table S1) and consequently, adsorbate-adsorbent interaction is negligible. On the other hand, when the adsorbates interact with TM doped CNTs (Figure S12, S13, S14), the g(r) exhibit sharp peaks at smaller distances (<4 Å, see Table S1), indicating efficient adsorption of molecules over CNTs within the time-scale of our simulation.



Figure S11: RDF g(r) for (a) DDT, (b) DDD, (c) DDE with pristine (5, 5) CNT over 25 ps time scale.



Figure S12: RDF g(r) plot for (a) DDT, (b) DDD, (c) DDE with V doped (5, 5) CNT in the 25 ps time scale.



Figure S13: RDF g(r) for (a) DDT, (b) DDD, (c) DDE with Fe doped (5, 5) in the 25 ps time scale.



Figure S14: RDF g(r) for (a) DDT, (b) DDD, (c) DDE with Cu doped (5, 5) in the 25 ps time scale.

Note that, the adsorbate-adsorbent distances for pristine CNT and molecules are not physically meaningful as these depend on the simulation box-size in the non-periodic direction. However, we still have included those numbers in the Table S1 just to show that adsorbate-adsorbent distances for them are quite larger than that of the doped-TM CNT and molecule composites.

Table S1: Most Probable distances from the g(r) plot for the CNT and molecule composites

Molecule	distance (Å) between the molecule benzene ring and the CNT			
	Pristine	V	Fe	Cu
DDT	16.9	2.3	2.2	2.9
DDD	16.4	2.3	2.05	3.4
DDE	15.7	2.25	2.2	2.9

Furthermore, to test the equilibration of the systems with TM-doped CNT and molecules in terms of adsorbate-adsorbent distance, we plot g(r) considering 2ps trajectories

of simulation time, 19-21 ps 21-23 ps and 23-25 ps (see Figure S15). As the sharp g(r) peaks remain almost at the same distance, we can ensure that these simulated systems are in thermal equilibrium in terms of adsorbate-adsorbent interactions.



Figure S15: RDF g(r) for (a) DDT, (b) DDD and (c) DDE with V doped (5, 5) CNT over different timescales.

References:

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