Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information File

Polarization Influences the Evolution of Nucleobase - Graphene Interactions

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Table T1: Parameters transferred from benzene to graphene sheet in Drude FF. The atom descriptors are presented in Figure 1 of manuscript.

Identifier	Parameter	Force Constant	Multiplicity
l_{C-C} (Å)	1.375	305.000	–
l_{C-H} (Å)	1.080	340.000	–
θ_{CCC} (°)	120.00	40.000	–
θ_{CCH} (°)	120.00	30.000	–
ϕ_{CCCC} (°)	180.00	2.800	2
ϕ_{CCCH} (°)	180.00	4.200	2
$q_{C\#}$ (e)	0.0000	–	–
$q_{C\dagger}$ (e)	0.0000	–	–
$q_{C\ddagger}$ (e)	-0.1106	–	–
q_H (e)	0.1106	–	–
k_D (kcal/mol/Å^2)	1000	–	–
ϵ_C (kcal/mol)	-0.0690	–	–
σ_C (Å)	2.0900	–	–

Table T2: Solute-water pair distances and interaction energies for linear coronene-water interaction modes. All distances reported in Å and energies are reported in kcal/mol. QM calculations are performed at MP2/6-31G(d) level of theory.

Interaction	$MM_{Distance}$	$QM_{Distance}$	QM-MM	MM(Drude)	QM	Δ_{QM-MM}
$Center_{Linear}$	2.46	2.29	-0.17	-2.55	-0.99	1.56
$Top^{\#}{}_{Linear}$	2.43	2.35	-0.08	-2.89	-0.88	2.01
$Top^{\dagger}{}_{Linear}$	2.37	2.41	-0.04	-3.15	-1.27	1.88
$Top^{\ddagger}{}_{Linear}$	2.36	2.36	0.00	-2.57	-1.17	0.80
$Average_{Linear}$	2.41	2.35	-0.07	-2.79	-1.08	1.56

Table T3: Binding free energies of nucleobases obtained from Additive, Drude and QM, PMF calculation. All energies are reported in units of kcal/mol. $Add^{\#}$ and $Drude^{\#}$ corresponds to PMF calculations in Additive and Drude polarizable FF on an unconstrained mono-layer graphene sheet. $Add^{\dagger}$ and $Drude^{\dagger}$ corresponds to PMF calculations calculations in Additive and Drude polarizable FF on a fully constrained mono-layer graphene sheet. Binding free energies are calculated as the difference between the energies of equilibrium state and well separated states.

Nucleobase	$Add^{\#}$(c36)	$Add^{\dagger}$(c36)	$\Delta E_{Add^{\#}\text{-}Add^{\dagger}}$	$Drude^{\#}$	$Drude^{\dagger}$	$\Delta E_{Drude^{\#}\text{-}Drude^{\dagger}}$
Adenine	-8.51	-9.06	0.55	-8.35	-8.92	0.57
Guanine	-8.93	-9.41	0.48	-9.85	-9.76	-0.09
Cytosine	-6.86	-6.89	0.03	-5.96	-6.64	0.68
Thymine	-7.73	-8.47	0.74	-7.66	-6.32	-1.34
Uracil	-6.83	-7.03	0.20	-7.03	-6.86	-0.17

Table T4: Average life times of the hydrogen bonded dimers observed in the nucleobases for Additive and Drude polarizable FF simulations. Lifetimes are calculated by fitting to a two term-exponential.

Nucleobase	$\tau_{Additive}$ (ps)	τ_{Drude} (ps)
Adenine	21.73	79.86
Guanine	28.08	49.73
Cytosine	19.39	74.94
Thymine	14.49	71.88
Uracil	34.72	49.17
Average$_\tau$	23.68	65.11

Table T5: Computational Performance of Additive and Drude polarizable FF for a 500 ns simulation. Benchmarks were performed using NAMD Git-2019-03-15 for Linux-x86_64-multicore-CUDA on a cluster computer with Tesla V100 GPU on 32 compute cores.

System	FF Type	Wall clock (h)
Uracil (21 Bases)	Additive	145.44
Uracil (21 Bases)	Drude	337.60

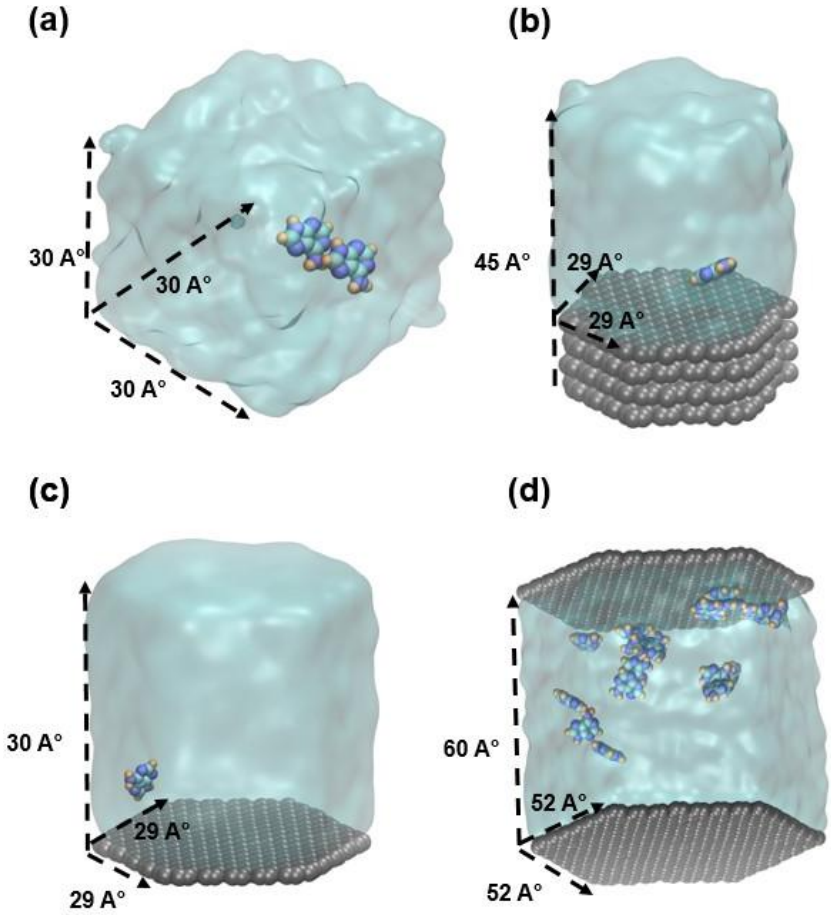


Figure S1: Representative structures for the systems considered in the present study. (a) Free-standing nucleobases (b) Graphene - nucleobase PMF calculations using ABF simulations with multi-layer graphene sheet, (c) Graphene - nucleobase PMF calculations using ABF simulations with mono-layer graphene sheet and (d) Homogeneous nucleobase- graphene system.

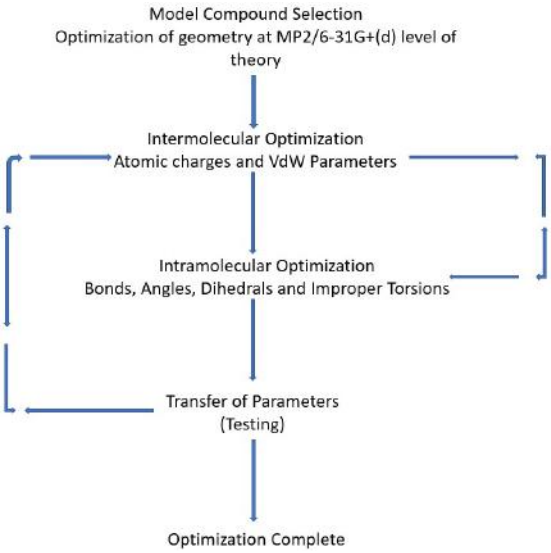
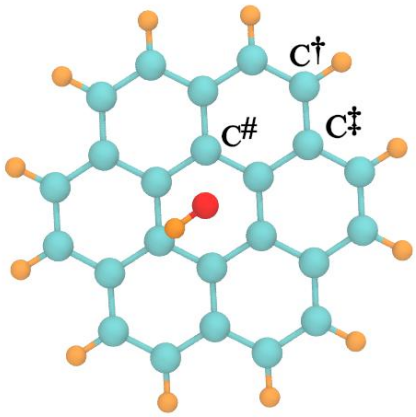
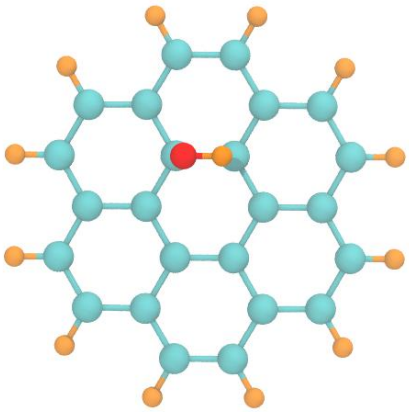


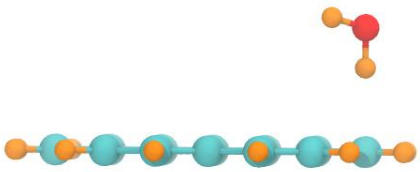
Figure S2: Parameterization strategy followed for parameterization of novel residues in CHARMM FF.



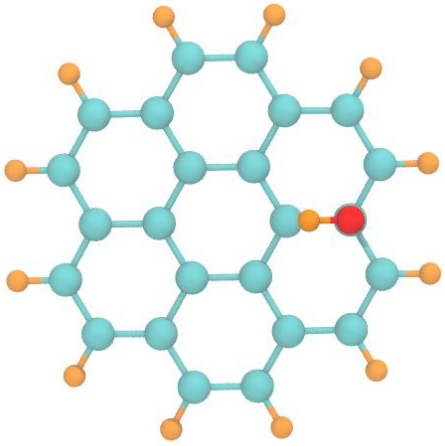
(a) $\text{Center}_{\text{Linear}}$



(b) $\text{Top}^{\#}{}_{\text{Linear}}$



(c) $\text{Top}^{\dagger}{}_{\text{Linear}}$



(d) $\text{Top}^{\ddagger}{}_{\text{Linear}}$

Figure S3: Linear modes of solute-water interactions. Carbon atoms are colored green, Oxygen atoms as red and Hydrogen atoms as orange. $C^{\#}$ forms the central six-membered ring of coronene. $C^{\dagger}$ corresponds to carbon atoms on the peripheral ring, connected to hydrogen atoms. $C^{\ddagger}$ corresponds to carbon atoms on the periphery, not connected to hydrogen atoms. All figures are generated using VMD.[1]

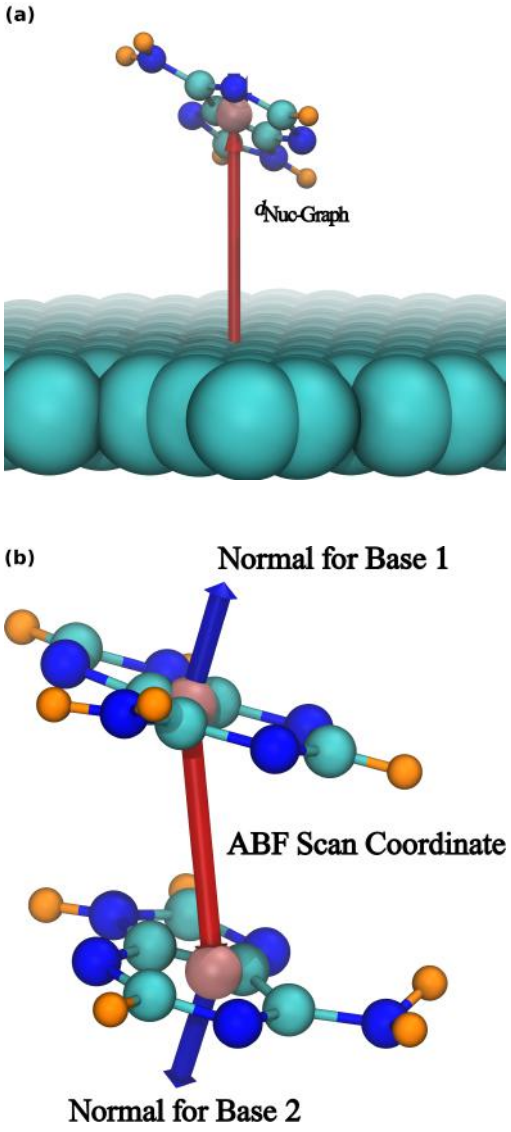
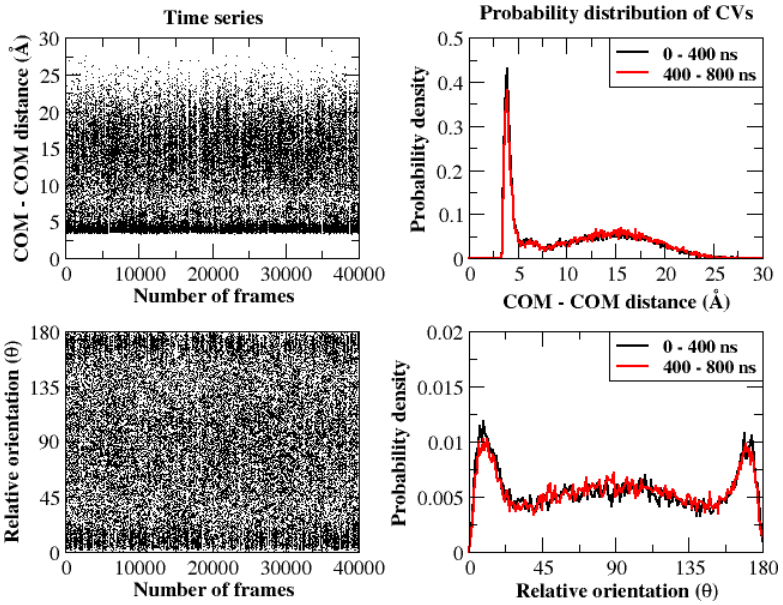
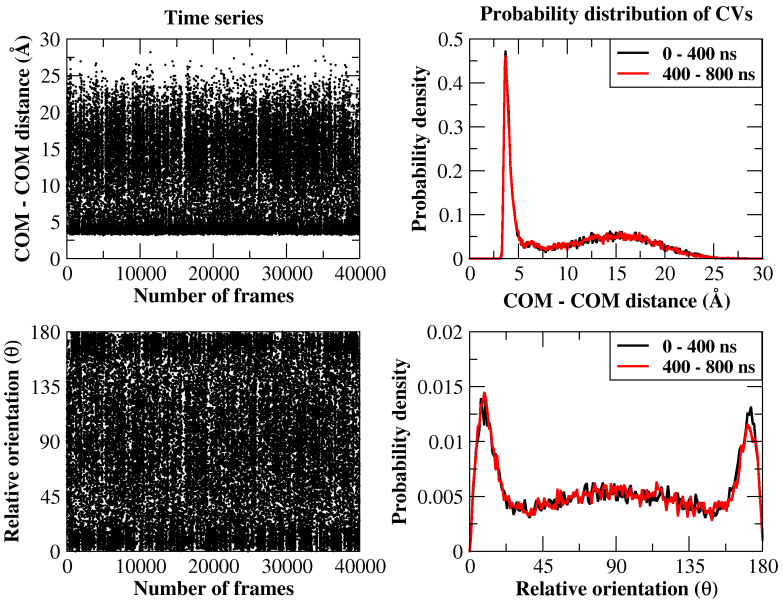


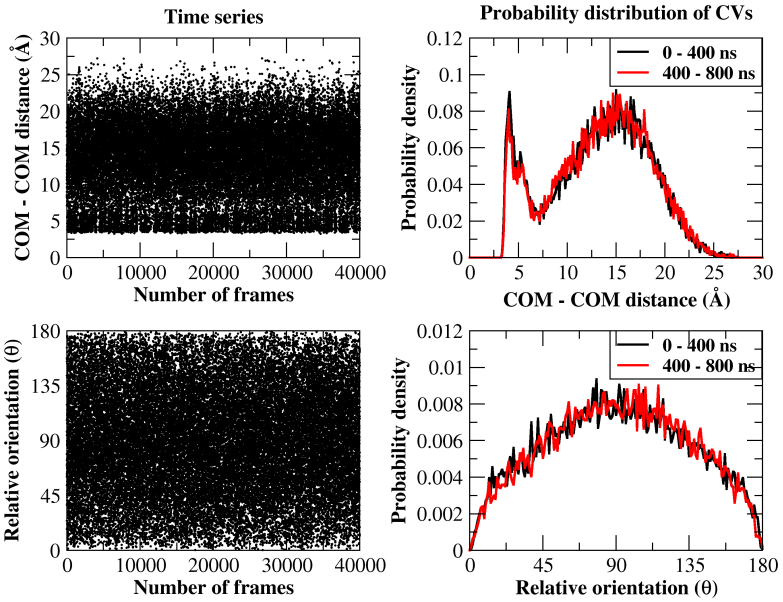
Figure S4: Representative image for scan coordinate in (a) nucleobase-graphene sheet and (b) nucleobase - nucleobase ABF simulations. Orientation of nucleobases in (b) are calculated from the normal vectors of molecular planes, as $\arccos\left(Normal_1 \cdot Normal_2\right)$.



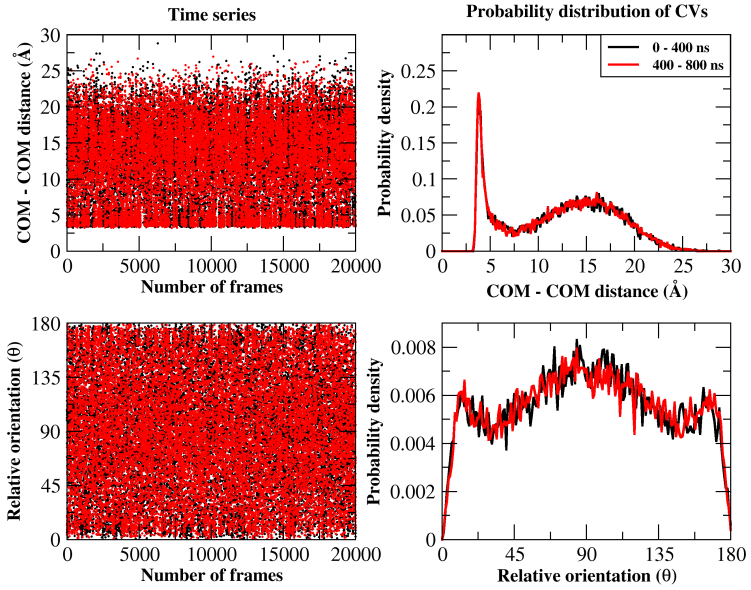
(a) Adenine (Additive)



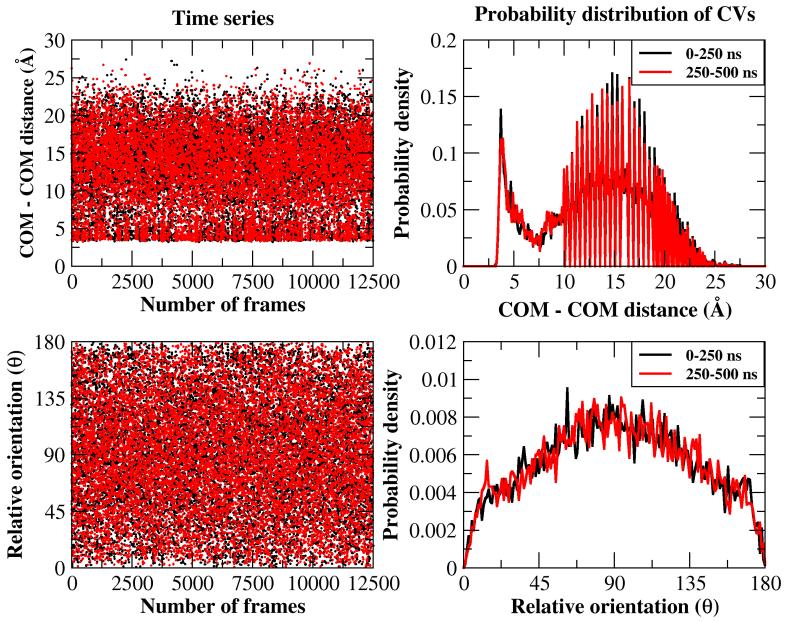
(b) Guanine (Additive)



(c) Cytosine (Additive)

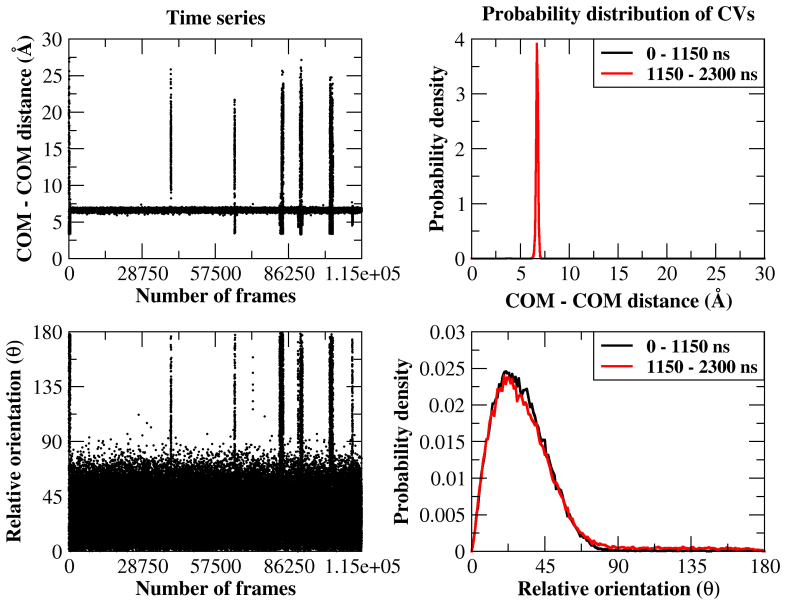


(d) Thymine (Additive)

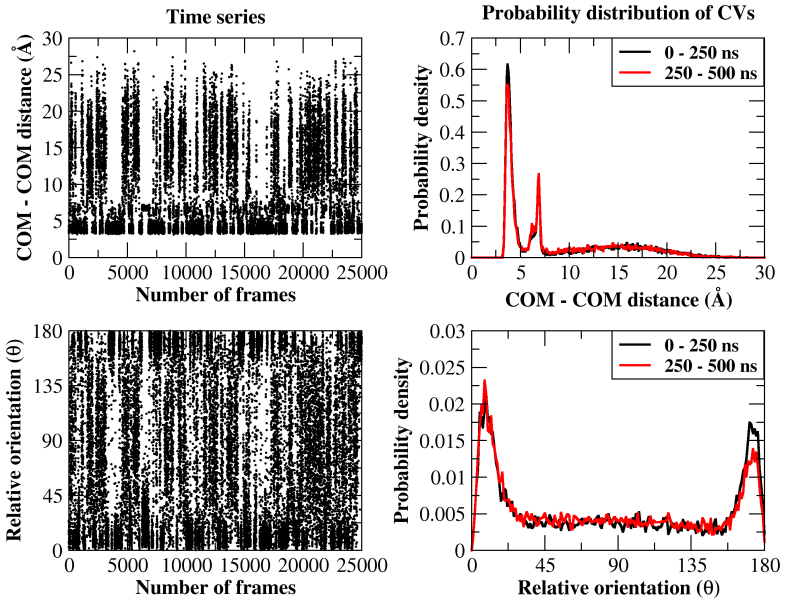


(e) Uracil (Additive)

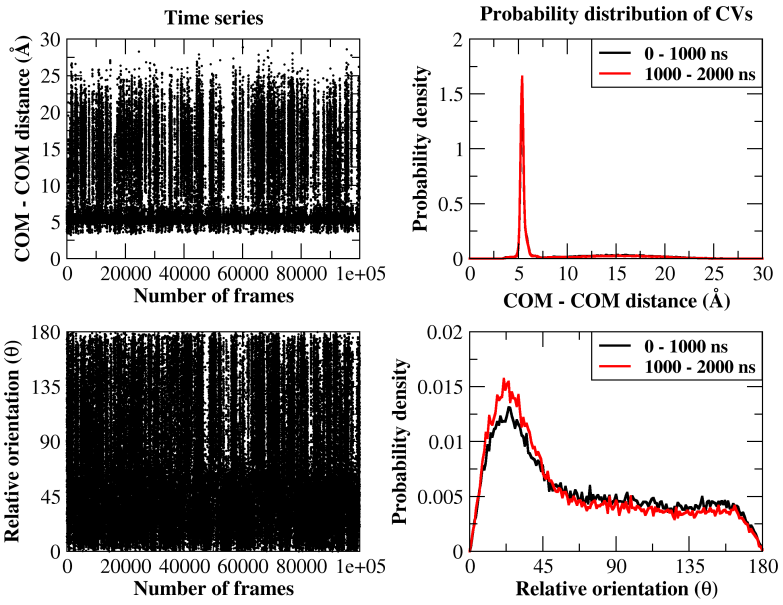
Figure S5: Time series plots for the COM distances and relative orientation of the nucleobases for (a) Adenine, (b) Guanine, (c) Cytosine, (d) Thymine and (e) Uracil obtained from Additive FF simulations. Distances are presented in Å and Orientation in degrees (°).



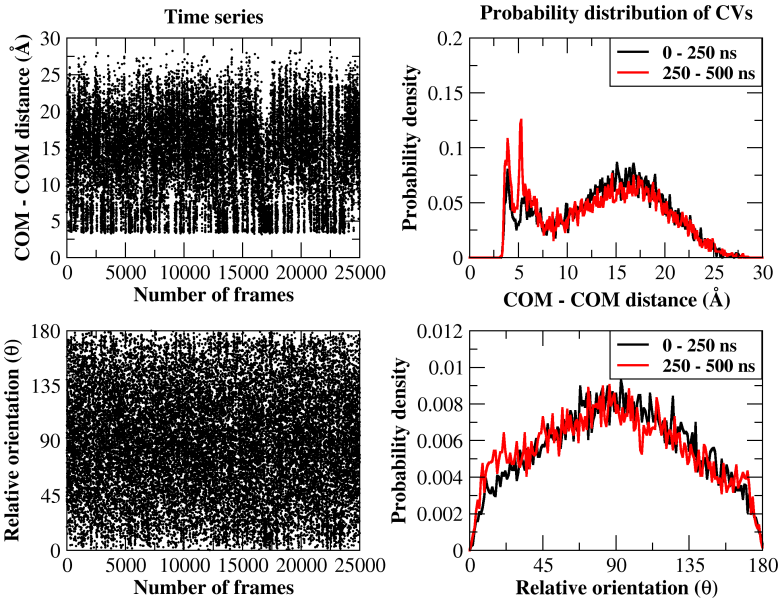
(a) Adenine (Drude)



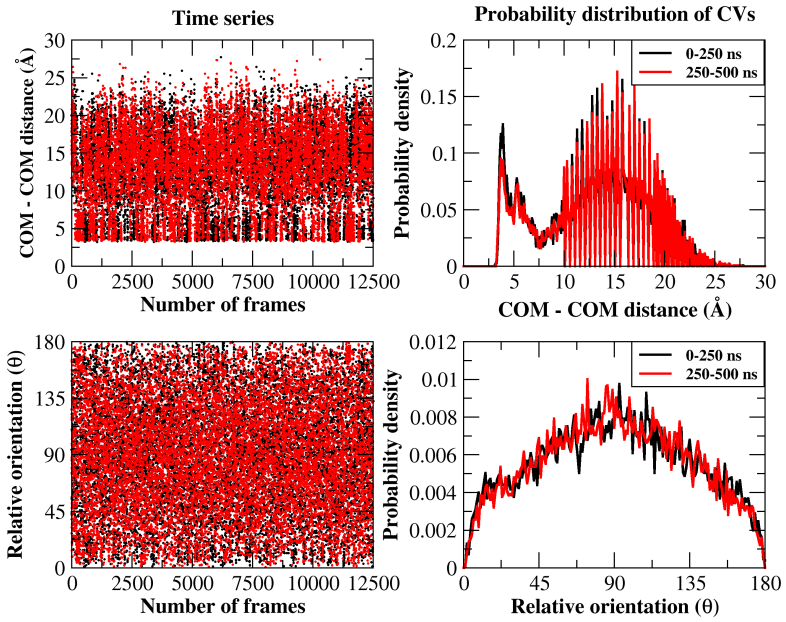
(b) Guanine (Drude)



(c) Cytosine (Drude)

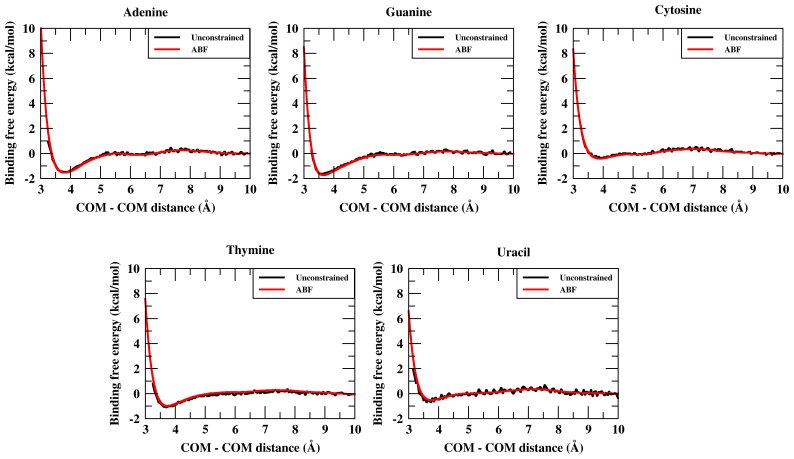


(d) Thymine (Drude)

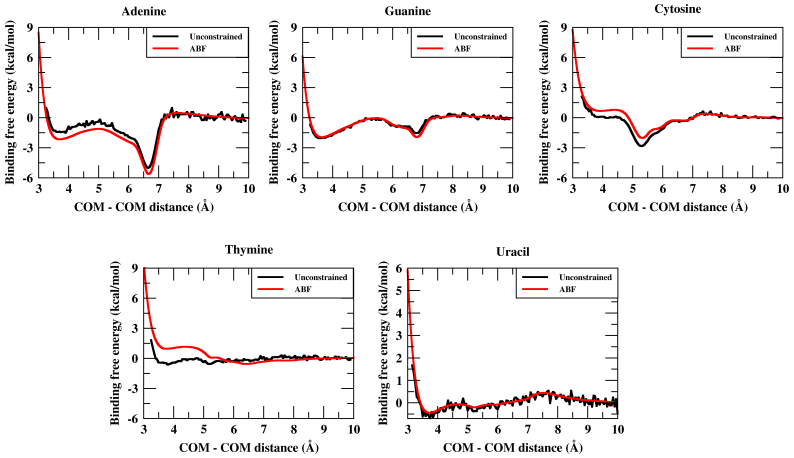


(e) Uracil (Drude)

Figure S6: Time series plots for the COM distances and relative orientation of the nucleobases (a) Adenine, (b) Guanine, (c) Cytosine and (d) Thymine obtained from Drude FF simulations. Distances are presented in Å and Orientation in degrees (°).



(a) Additive



(b) Drude

Figure S7: Potential of Mean Force (PMF) plots for nucleobase-nucleobase interactions obtained from (a) Additve and (b) Drude FF simulations.

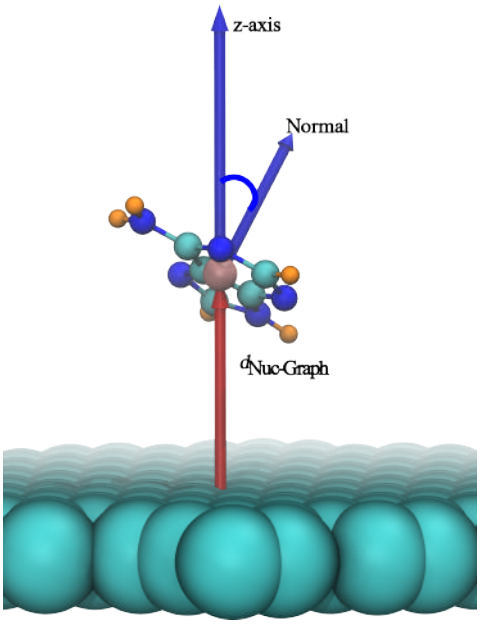
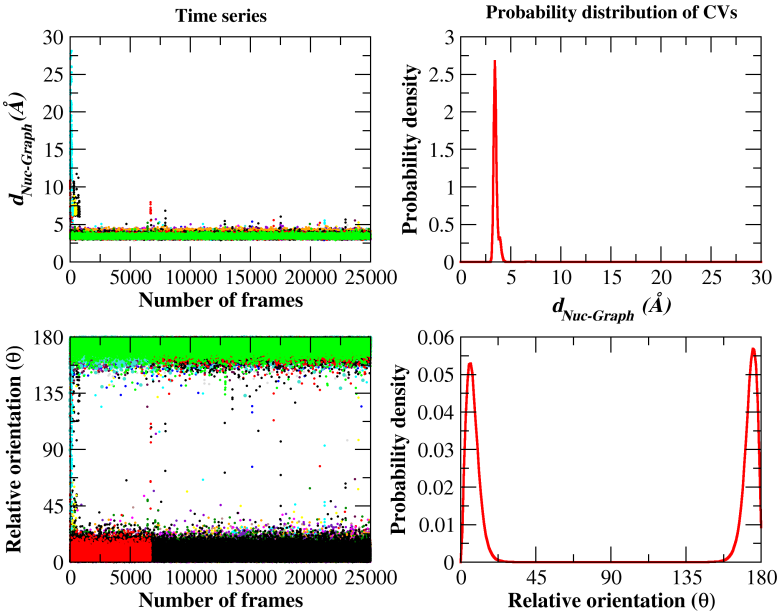
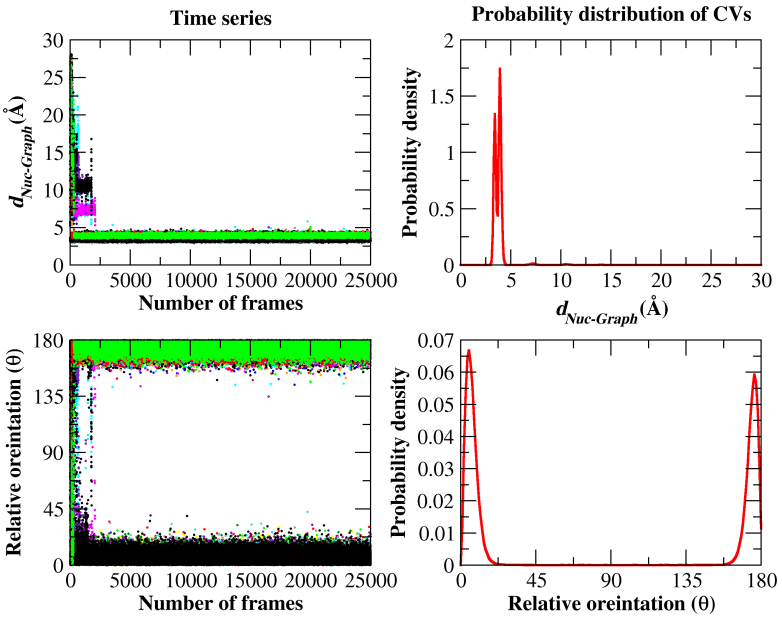


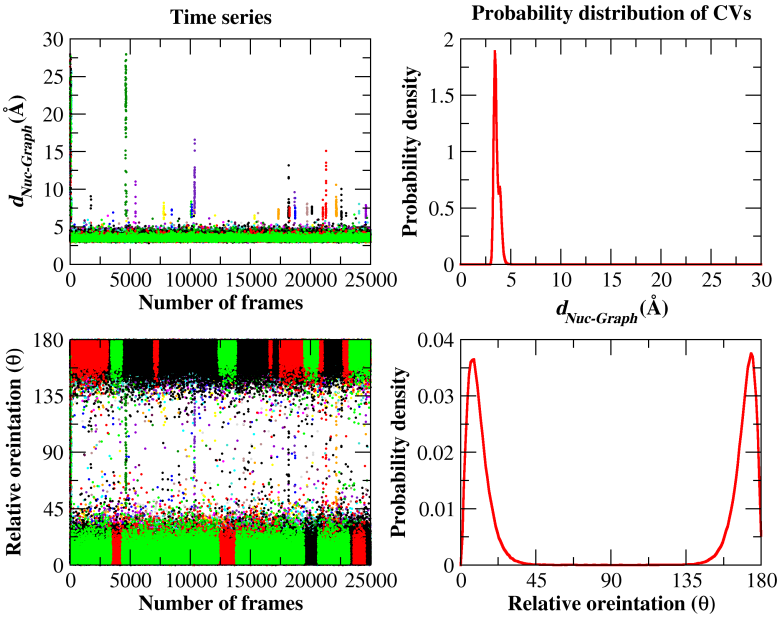
Figure S8: Representative illustration of the CVs used to study the evolution of the interactions between the nucleobases and the underlying graphene sheet. Relative orientations are calculated as $\arccos\left(z - axis \cdot Normal\right)$. $d_{Nuc-Graph}$ is evaluated as the difference between z-coordinates of COM of nucleobase and graphene sheet.



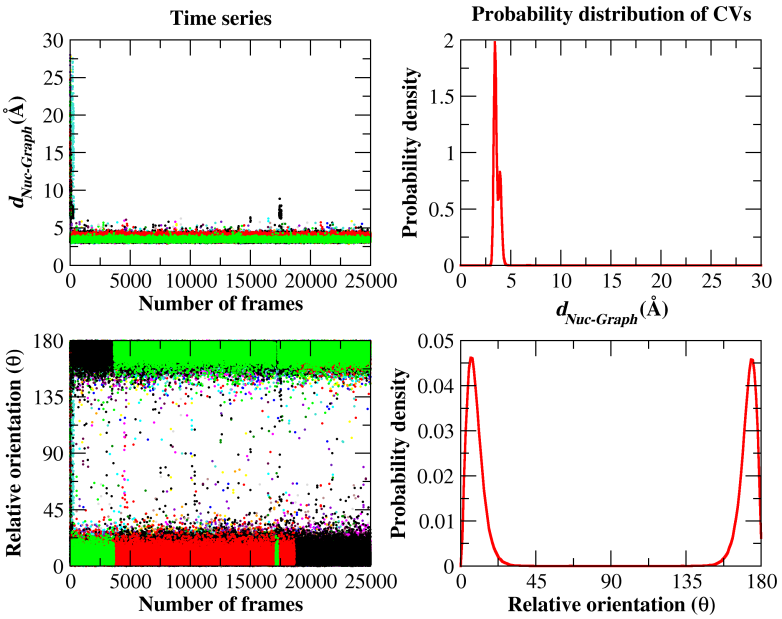
(a) Adenine - 21 Bases (Additive)



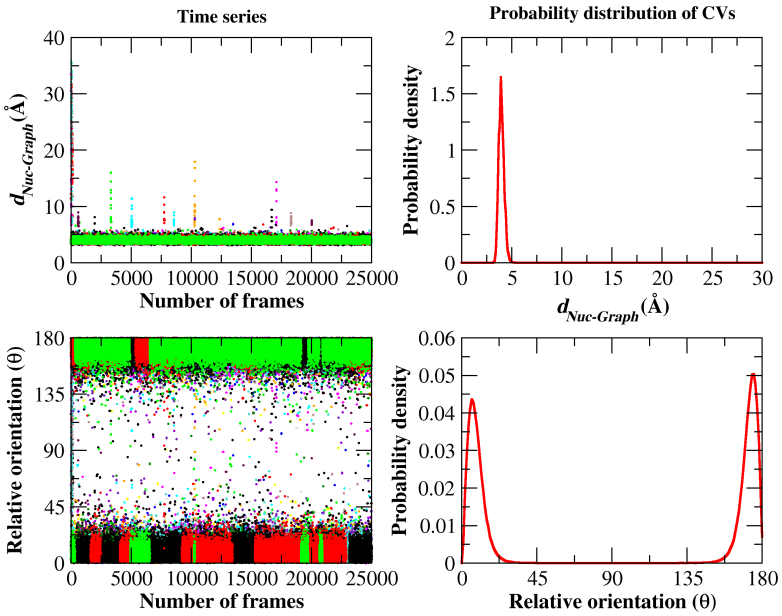
(b) Guanine - 21 Bases (Additive)



(c) Cytosine - 21 Bases (Additive)

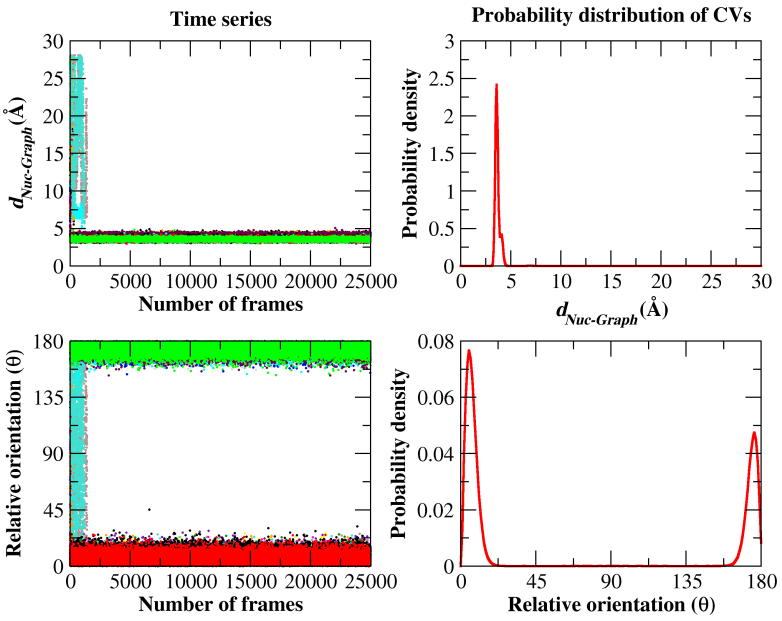


(d) Thymine - 21 Bases (Additive)

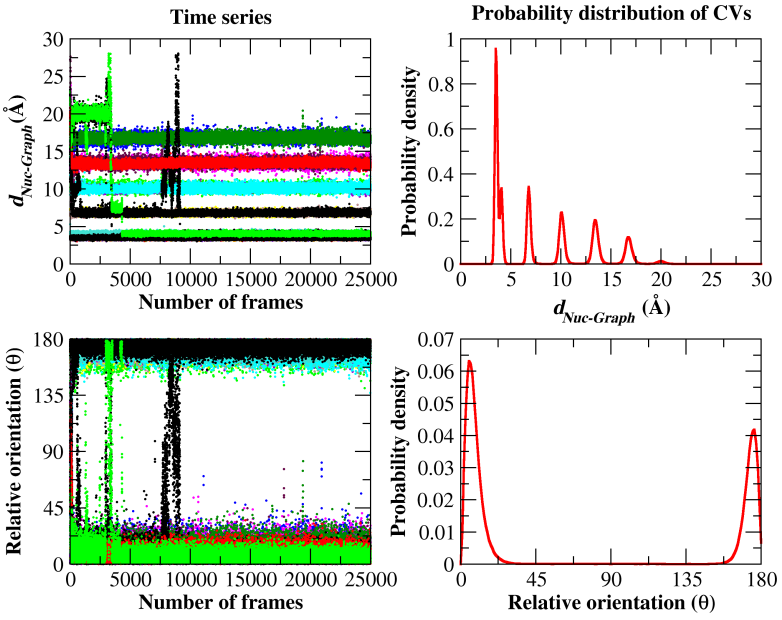


(e) Uracil - 21 Bases (Additive)

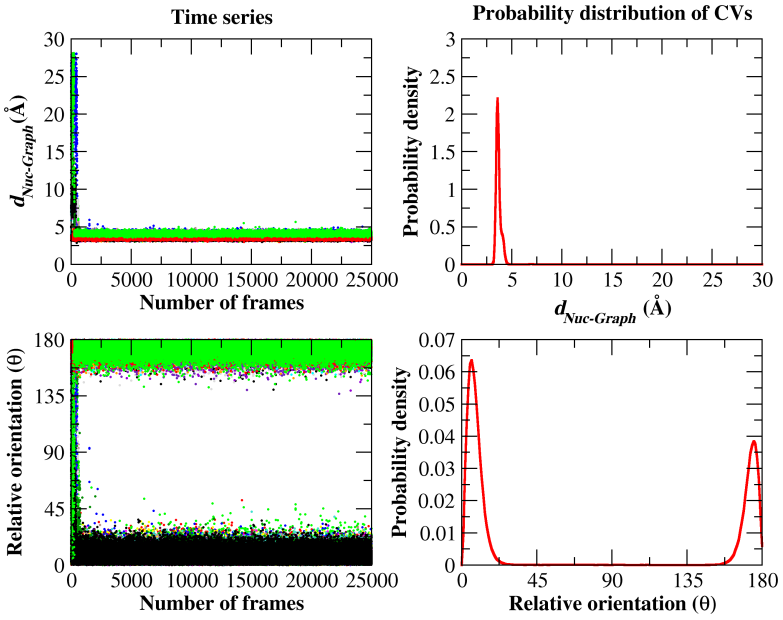
Figure S9: Time series plots for the $d_{Nuc-Graph}$ and relative orientation of the nucleobases (a) Adenine, (b) Guanine, (c) Cytosine, (d) Thymine and (e) Uracil obtained from Additive FF simulations of nucleobase - graphene sheet system. Distances are presented in Å and Orientation in degrees (°).



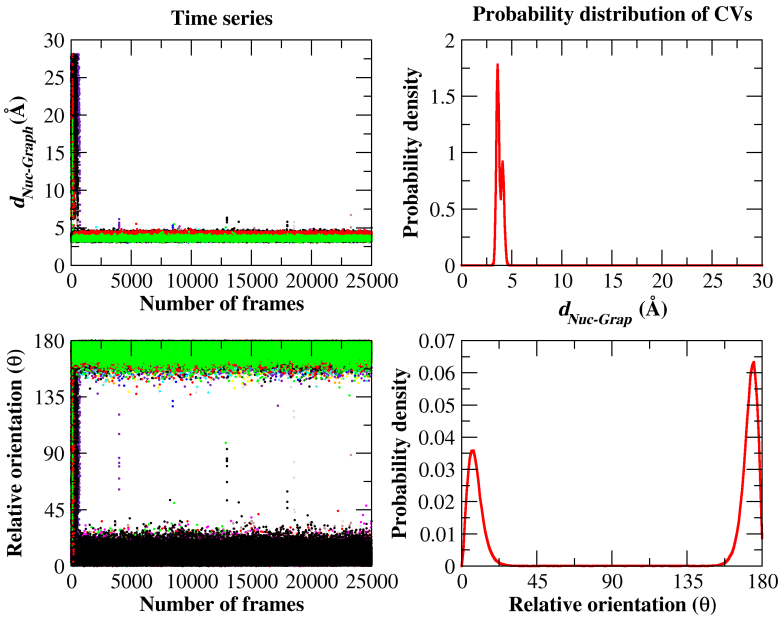
(a) Adenine - 21 Bases (Drude)



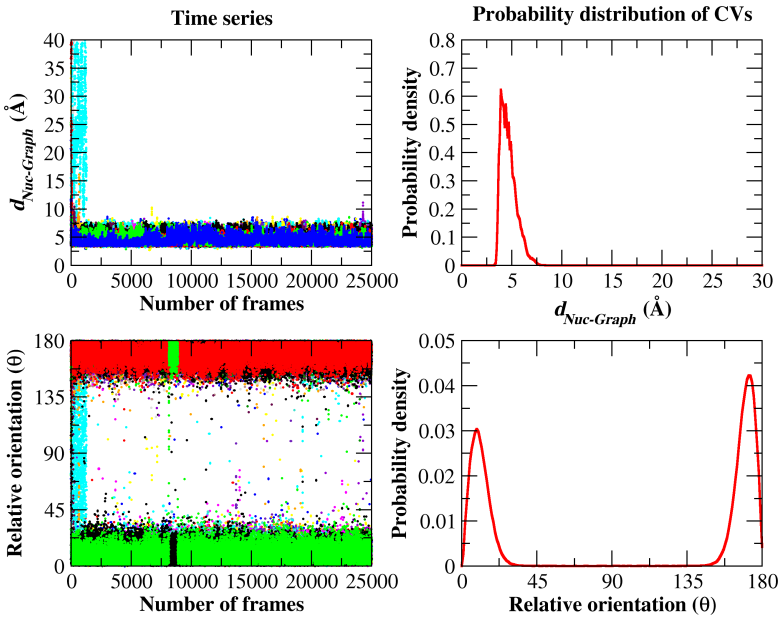
(b) Guanine - 21 Bases (Drude)



(c) Cytosine - 21 Bases (Drude)

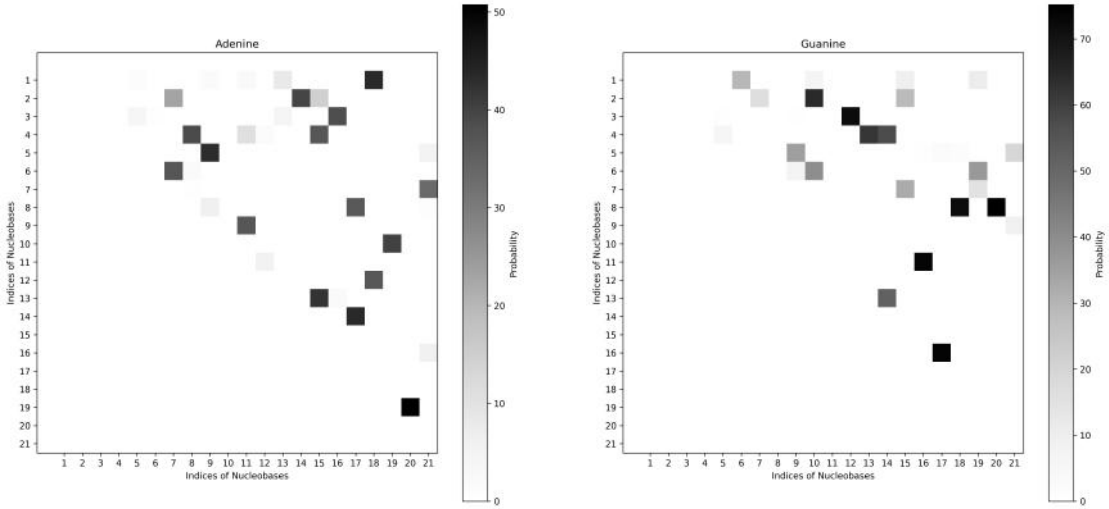


(d) Thymine - 21 Bases (Drude)



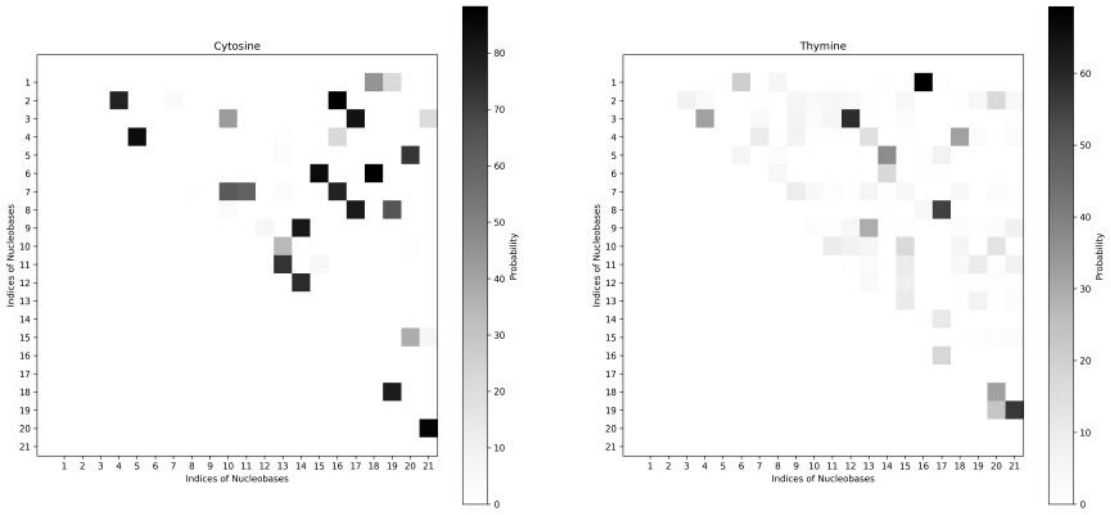
(e) Uracil - 21 Bases (Drude)

Figure S10: Time series plots for the $d_{Nuc-Graph}$ and relative orientation of the nucleobases (a) Adenine, (b) Guanine, (c) Cytosine, (d) Thymine and (e) Uracil obtained from Drude FF simulations of nucleobase - graphene sheet system. Distances are presented in Å and Orientation in degrees (°).



(a) Adenine

(b) Guanine



(c) Cytosine (d) Thymine

Figure S11: Heat-map plots depicting the probabilities of different hydrogen bonded dimers within the simulation box for homogeneous nucleobase - graphene sheet simulations. Probabilities were calculated as number of occurrences of each dimer in the simulation trajectory.

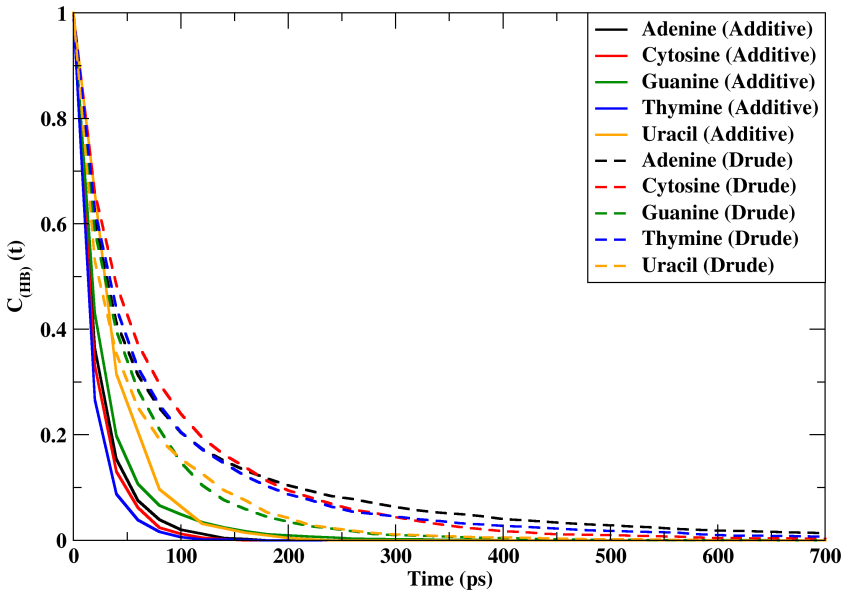


Figure S12: Comparison of continuous H-bond auto-correlation function for the dimer pairs in the simulation systems.

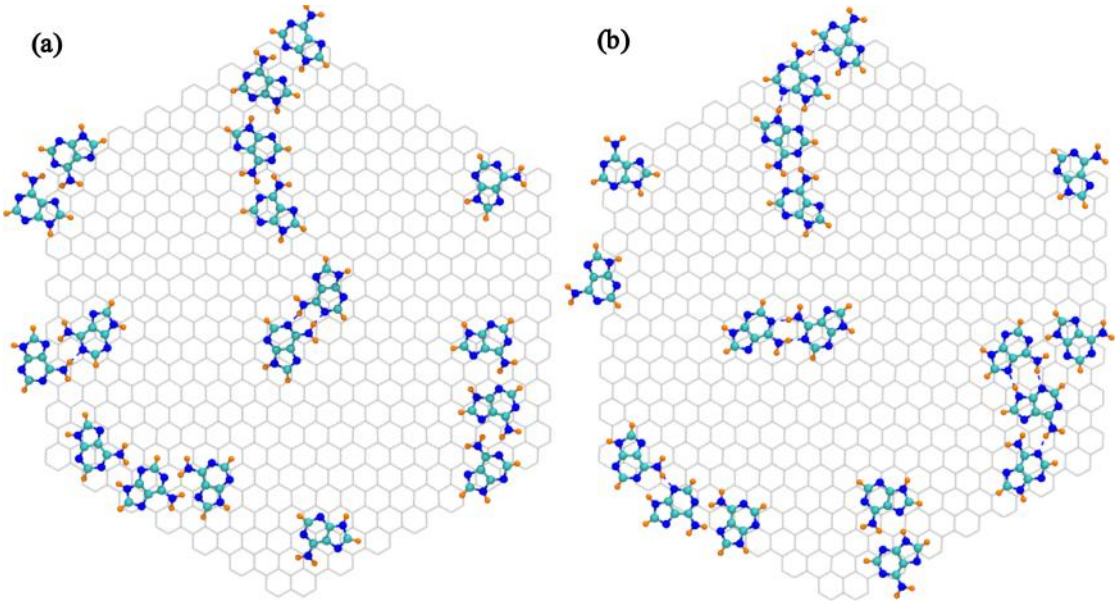


Figure S13: Representative image showing various H-bonded structures formed by Adenine on graphene sheet.

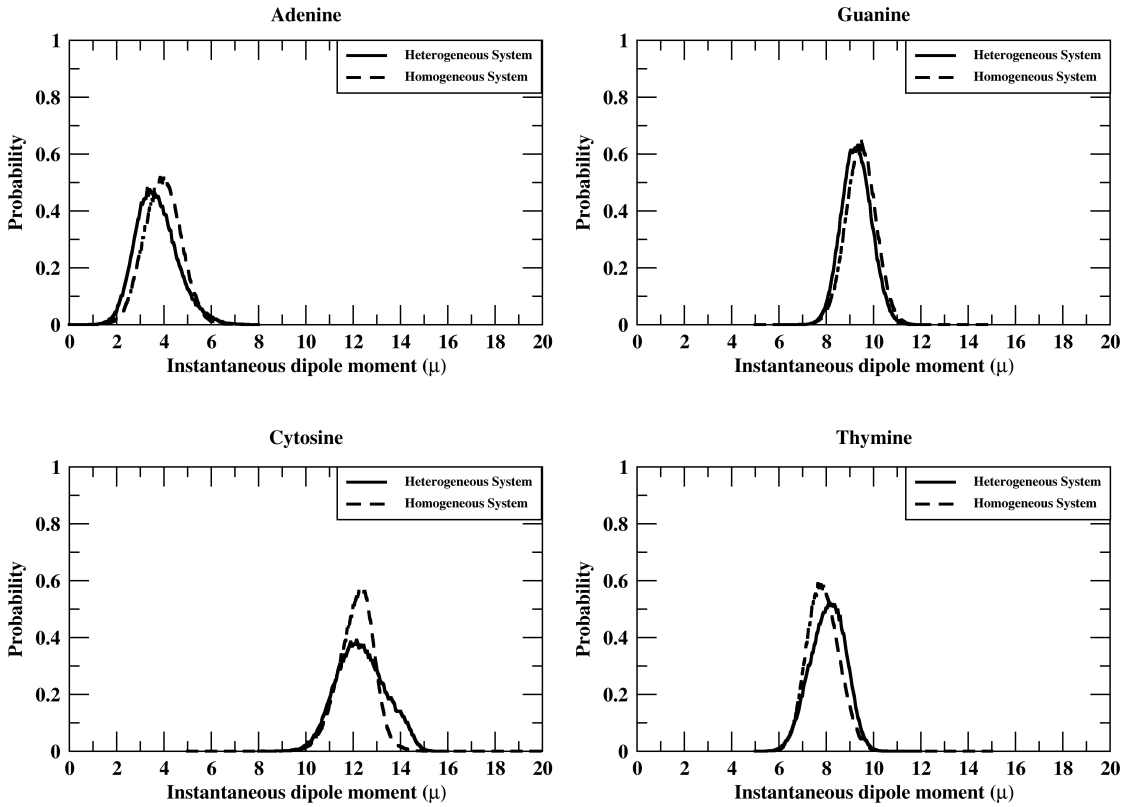
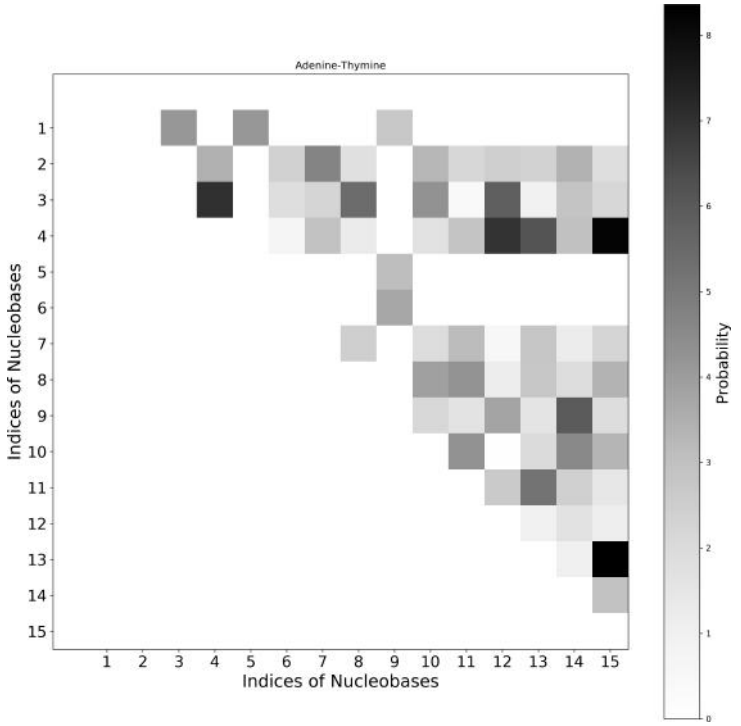
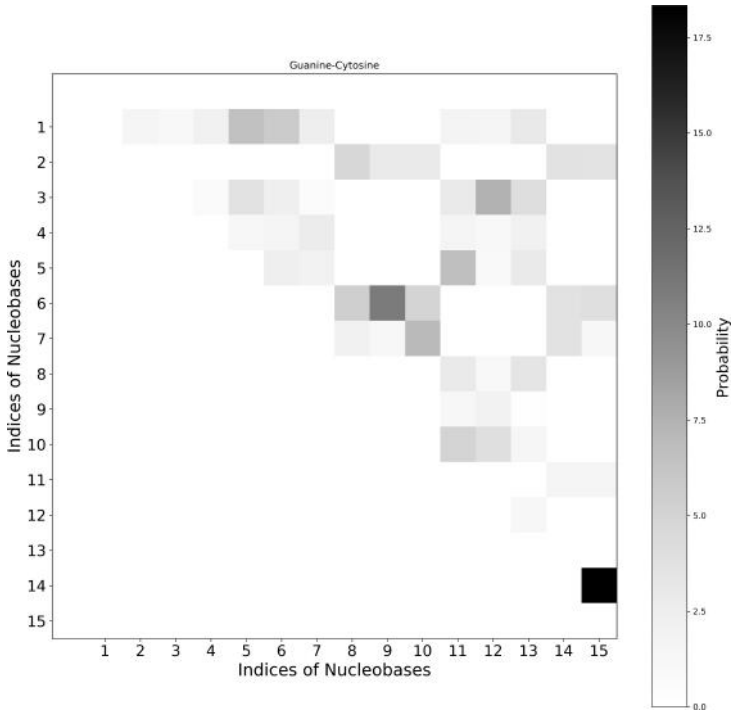


Figure S14: Probability distribution of Instantaneous dipole moments for nucleobases; Adenine, Guanine, Cytosine, Thymine and Uracil respectively. Dipole moments are reported in units of Debye.

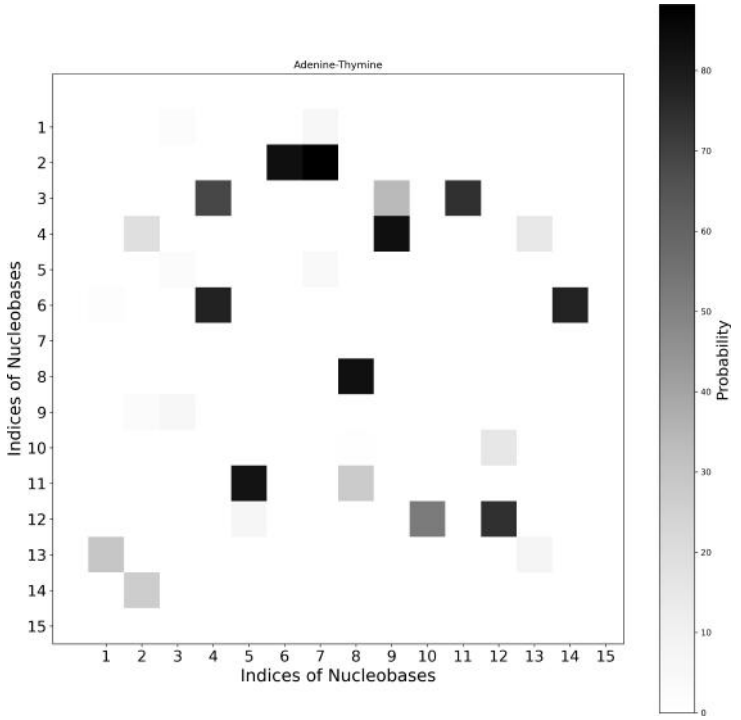


(a) Adenine-Thymine (Additive)

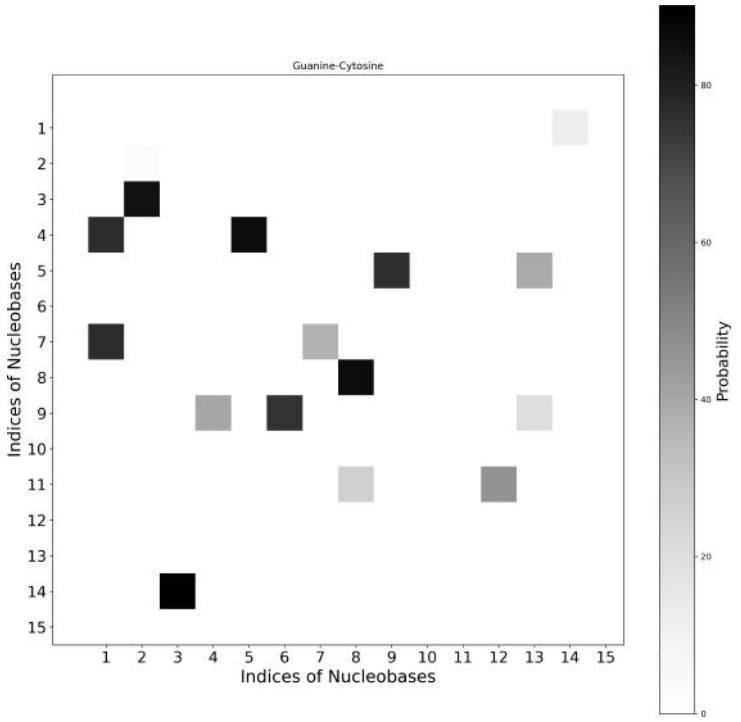


(b) Guanine-Cytosine (Additive)

Figure S15: Heat-map plots depicting the probabilities of different hydrogen bonded dimers within the simulation box for heterogeneous nucleobase - graphene sheet simulations in Additive FF. Probabilities were calculated as number of occurrences of each dimer in the simulation trajectory.



(a) Adenine-Thymine (Drude)



(b) Guanine-Cytosine (Drude)

Figure S16: Heat-map plots depicting the probabilities of different hydrogen bonded dimers within the simulation box for heterogeneous nucleobase - graphene sheet simulations in Drude FF. Probabilities were calculated as number of occurrences of each dimer in the simulation trajectory.

References

[1] W. Humphrey, A. Dalke and K. Schulten, *Journal of Molecular Graphics*, 1996, **14**, 33–38.