Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Load Bearing Study and Interfacial Interactions of Hydroxyapatite Composite Coatings for Bone Tissue Engineering

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A clear picture of the QTAIM molecular graphs of all the three composite models can be seen in Figures **S1** (CNT), **S2** (HAP-hBN), **S3** (HAP-GrO), and **S4** (HAP-CNT) which illustrate all binding features [noncovalent (*via* conventional and NBPs) and covalent interactions] involved therein the species. *For the sake of clarity of the graphical visualization of all the MNIs, NCIs, and weak vdW interactions, all the three dimer complexes can be seen by viewing these through Zoom (Zoom-In Mode).*

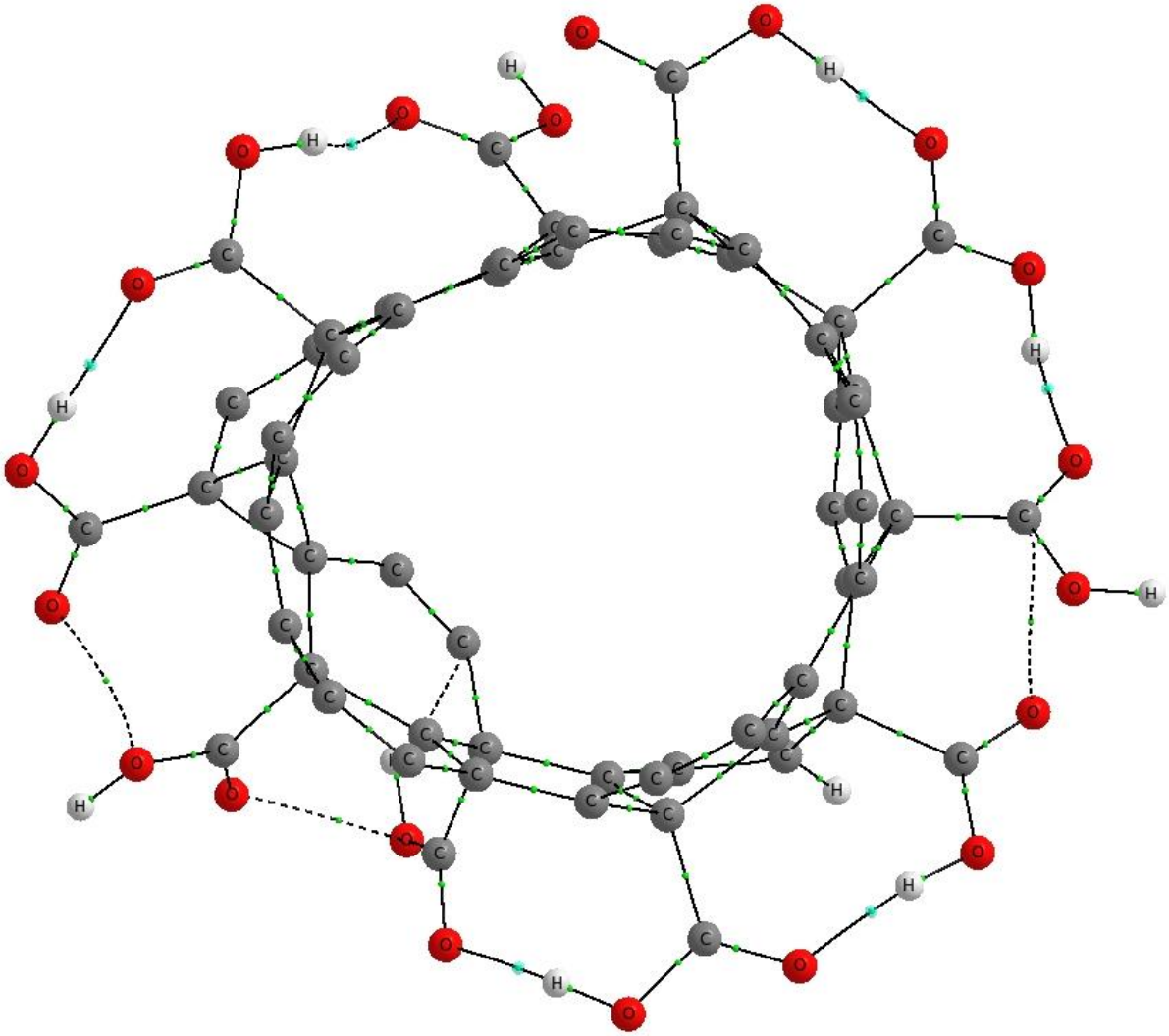

Figure **S1**. QTAIM-based Molecular Graph for the HAP-CNT Composite Model

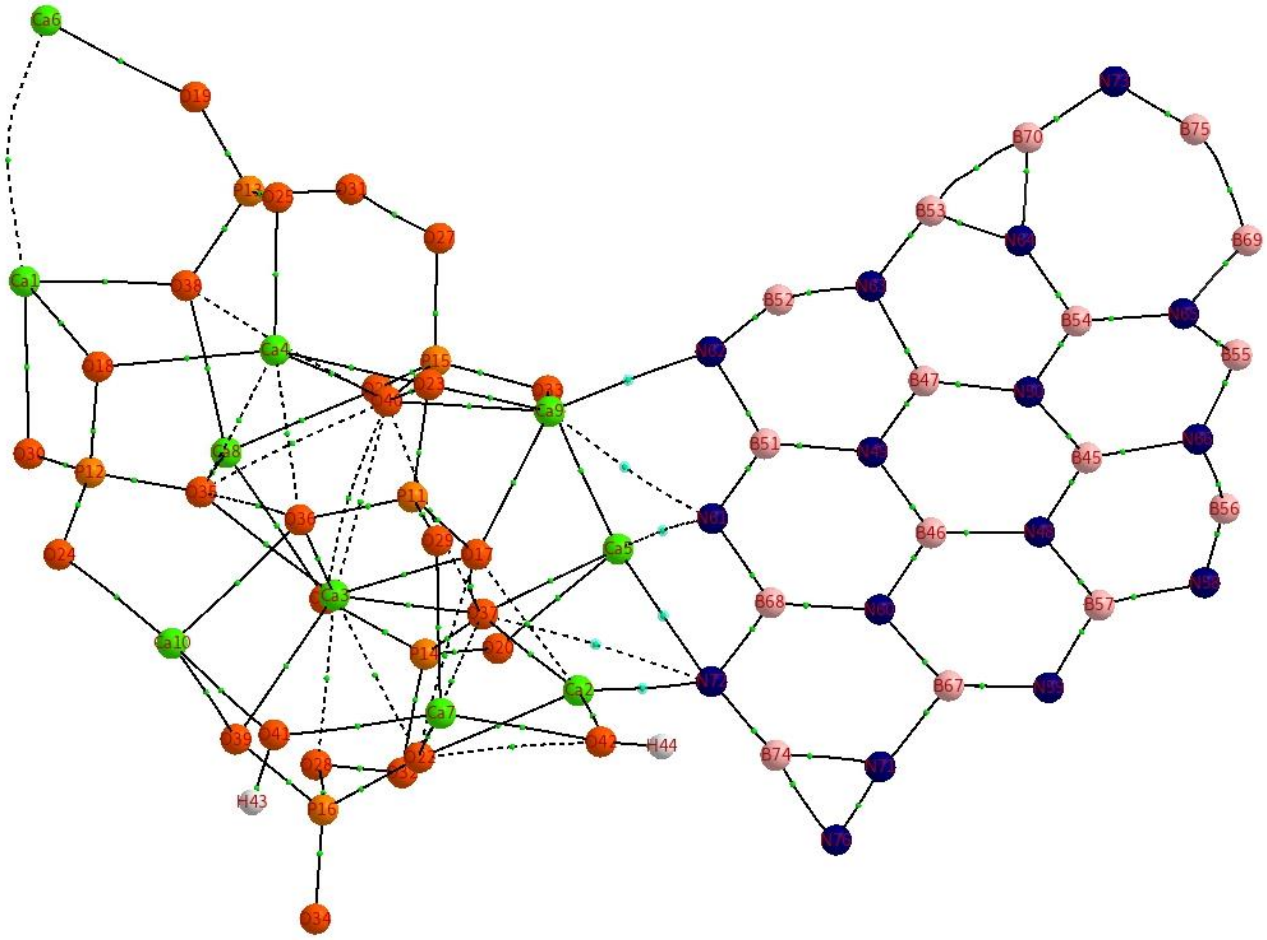

Figure **S2**. QTAIM-based Molecular Graph for the HAP-hBN Composite Model

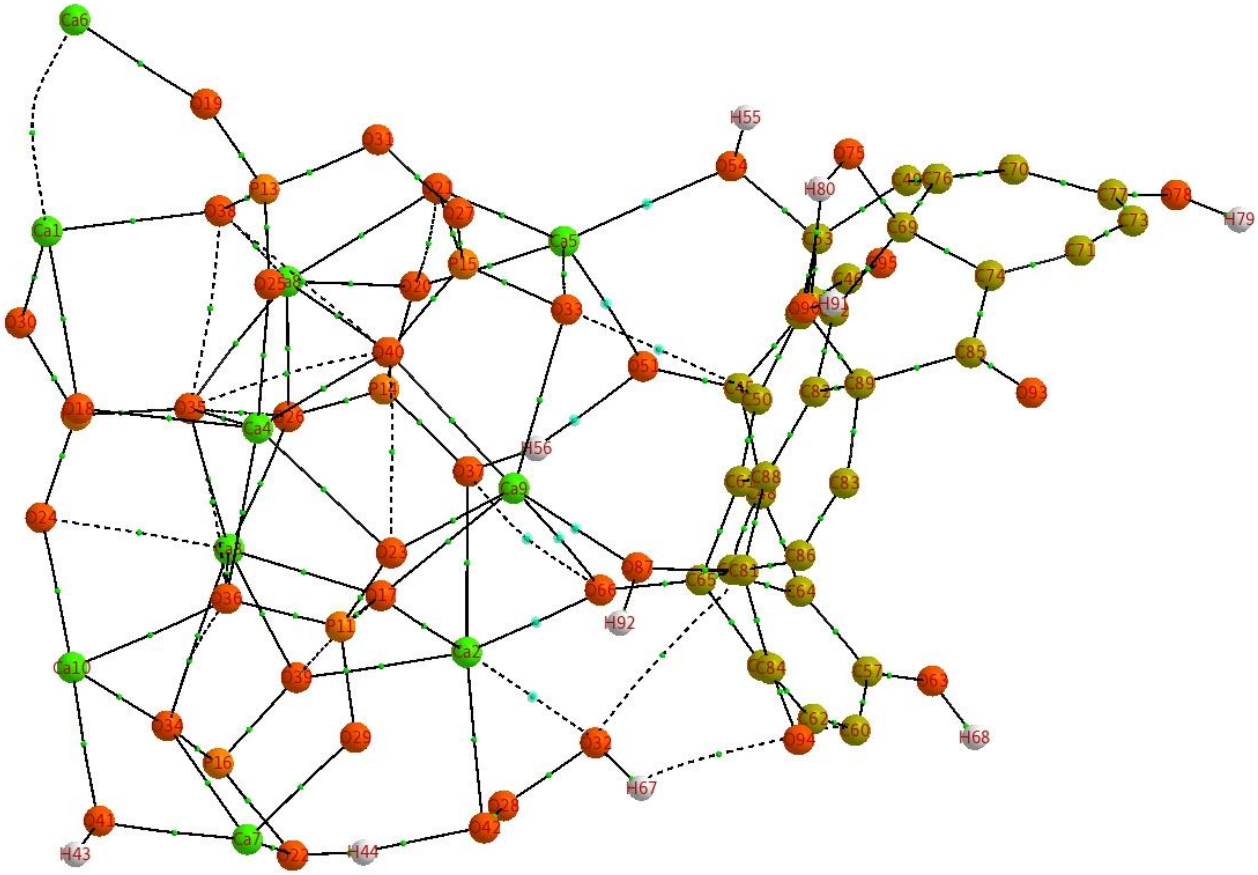

Figure **S3**. QTAIM-based Molecular Graph for the HAP-GrO Composite Model

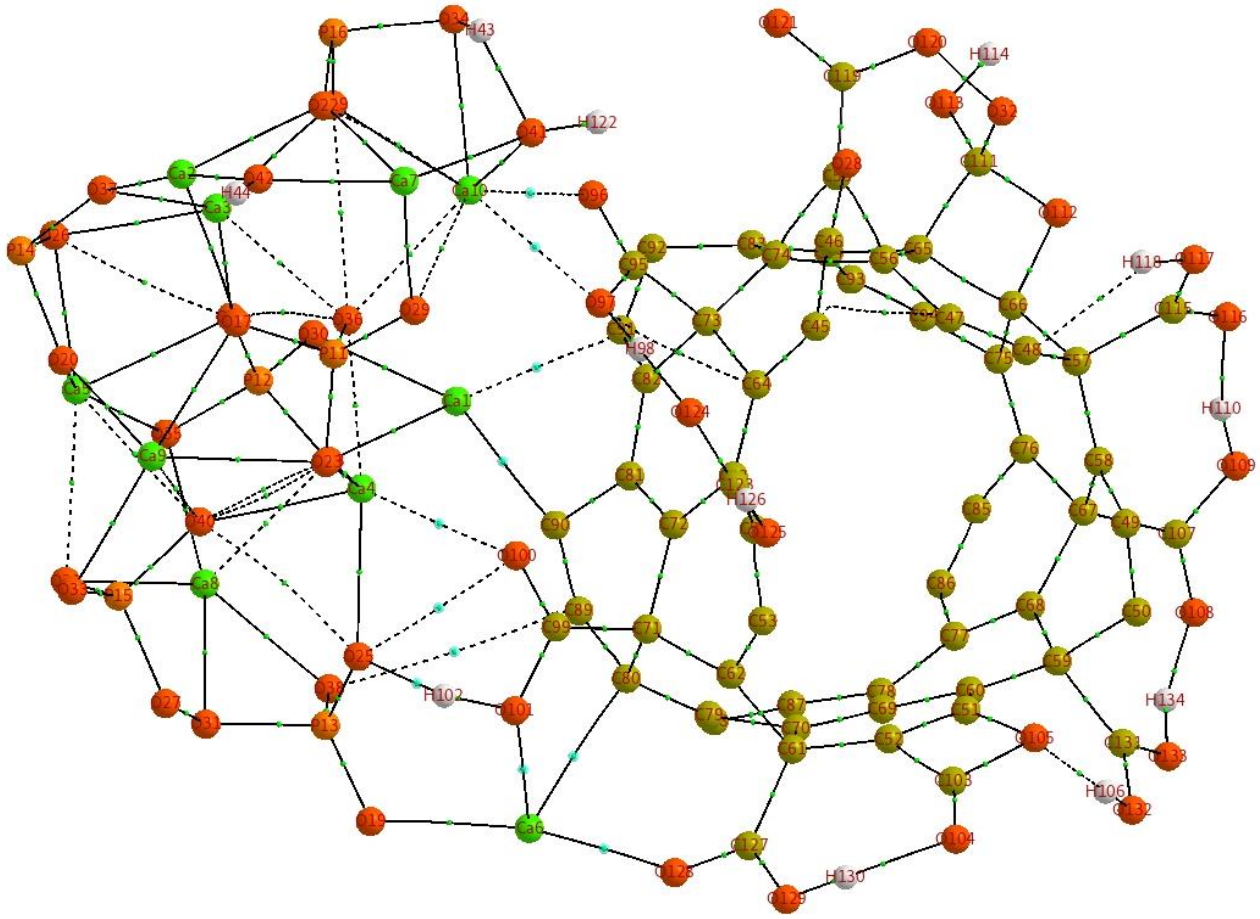

Figure **S4**. QTAIM-based Molecular Graph for the HAP-CNT Composite Model

Table **S1**. Some Important and Selected Optimized Geometrical Parameters (Bond Length and Bond Angle) and QTAIM-based Topological Parameters [ρ, ∇^2 (ρ), and *V*] of the HAP-hBN, HAP-GrO, and HAP-CNT Composite Models

HAP-hBN				
MNIs				
Bonding /Nonbonding Interaction	Bond Length (Å)/Angle (°)	ρ (in au)	∇^2(ρ) (in au)	*V* (in au)
Ca9-N62	2.382	0.0366	+0.1859	-0.0381
Ca5-N72	2.493	0.0303	+0.1365	-0.0288
Ca2-N72	2.541	0.0278	+0.1199	-0.0254
Ca9--N61	2.69	0.0201	+0.081	-0.0164
Ca5--N61	2.693	0.0207	+0.0811	-0.017
Nonconventional bond path (stabilizing interaction)				
O37···N72	3.211	0.0113	+0.0272	-0.0075
HAP-GrO				
MNIs				
Ca5-O51	2.294	0.0419	+0.2277	-0.0482
Ca9-O66	2.352	0.0369	+0.1914	-0.0403
Ca2-O66	2.4	0.0312	+0.121	-0.0324
Ca9-O87	2.469	0.0262	+0.1327	-0.0257
Ca5-O54	2.488	0.0271	+0.1255	-0.0263
Ca2-O32	2.545	0.0223	+0.114	-0.0225
H-bond				
O37-H56···O51	1.831/159.3°	0.0354	+0.1043	-0.0299
Nonconventional bond path (stabilizing interaction)				
O37···O66	3.004	0.0107	+0.0328	-0.0083
O33···C50	3.342	0.0054	+0.0188	-0.0032
HAP-CNT				
Ca6-O128	2.269	0.0402	+0.2424	-0.0467
Ca6-O101	2.449	0.0283	+0.1435	-0.0285
Ca4-O100	2.496	0.0229	+0.1191	-0.0218
Ca10-O97	2.513	0.0236	+0.1160	-0.0227
Ca10-O96	2.63	0.0197	+0.0858	-0.0176
Ca1···C90	2.539	0.0327	+0.1256	-0.0302
Ca1-C91	2.639	0.0248	+0.0894	-0.0202
Ca6-C80	2.64	0.0262	+0.0951	-0.0218
H-bond				
O101-H102···O25	1.559/148.3	0.0658	+0.1805	-0.0594
Nonconventional bond path (stabilizing interaction)				
O25···O100	2.843	0.0123	+0.0478	-0.0111
O38···C89	3.752	0.0023	+0.0079	-0.0009

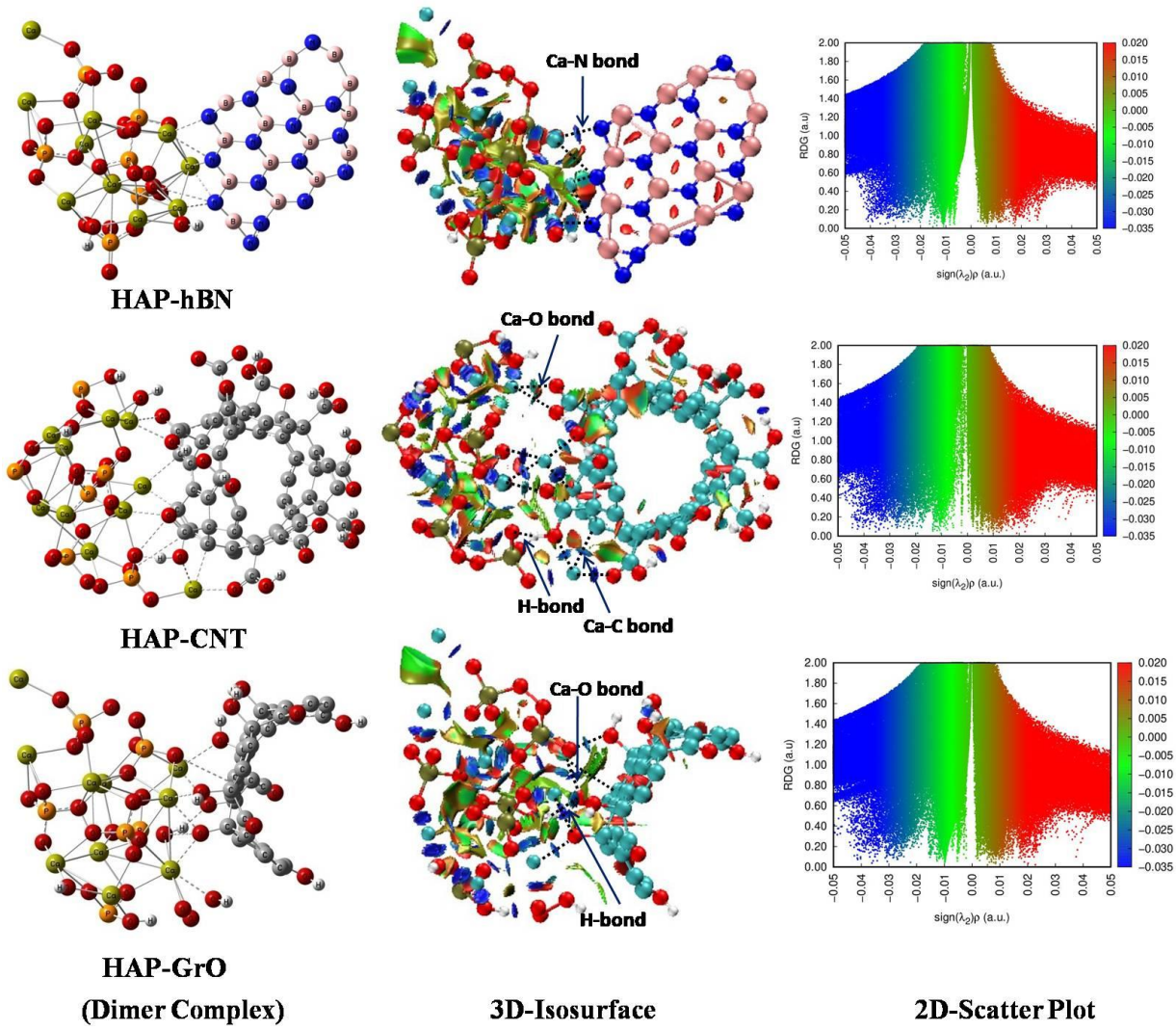

Figure **S5** (*For the sake of clarity of the graphical visualization of all the MNIs, NCIs, and weak vdW interactions, it is Figure **10** taken from the article***)**.** Optimized/Equilibrium Structures (left), 3D-Isosurafces (middle), and 2D-Scatter Plots (right) of the HAP-hBN (top), and HAP-CNT (middle), HAP-GrO (bottom) dimer model complexes at the B3LYP/6-31G level of theory.

Note 1: *All MNIs and NCIs involved in all three dimer composites can be seen by doing (Zoom-In Mode) the structures.*

NCI-Plot (2D scattered plot and 3D isosurface map)

Understanding and plotting of the NCIs in a better way, a detail information can be seem in the literature [Contreras-García, J.; Johnson, E. R.; Keinan, S.; Chaudret, R.; Piquemal, J. P.; Beratan, D.N.; Yang, W. NCIPLOT: A Program for Plotting Noncovalent Interaction Regions. *J. Chem. Theory Comput.* **2011**, *7* (3), 625–632; Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W. Revealing Noncovalent Interactions. *J. Am. Chem. Soc.***2010**, *132* (18), 6498–6506]. Some attention-grabbing insights into the electron density (ED)

and its derivatives-based method can be seen in the literature reported by Yang *et al* [Johnson, E. R.; Keinan, S.; Mori-Sánchez, P.; Contreras-García, J.; Cohen, A. J.; Yang, W. Revealing Noncovalent Interactions. *J. Am. Chem. Soc.***2010**, *132* (18), 6498–6506]. A comprehensive analysis of the NCI-plot on some biocomposites can be seen in literature [S. Awasthi, J. Gaur, S. K. Pandey, M. S. Bobji, and C. Srivastava, High Strength, Strongly Bonded Nanocomposite Hydrogels for Cartilage Repair ***ACS App. Mat. Int.*** *13,* (**2021**), 24505-24523] and references therein.

Hints: The RDG isosurface displayed on horizontal axis is 0.5 (ranging from -0.05 to +0.05). The Ω(r) values ranging from -0.035 atomic unit (au) to +0.02 au on vertical axis (Figure **10**, right) show the color surfaces of the species on a blue-green-red scale. The detailed description of the NCI tool clarifies that the higher density values ($\Omega(r) < 0$) show the stronger attractive interactions while the very low-density values ($\Omega(r) > 0$) indicate the repulsive interactions. Moreover, blue color spike in the scatter map two-dimensional (2D) plot and blue color disc-shaped NCI isosurface three-dimensional (3D) representation showing the attractive (stabilizing) interaction. The green color spikes in the 2D scatter plot and green color disc-shaped NCI 3D isosurface demonstrating a variety of vdW interactions. The presence of steric effect is evidently shown by the low-gradient spikes appearing at positive side. This effect as shown by the red ellipsoid depicts the electron density depletion which is because of the electrostatic repulsion.